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Siderophile Elements in Tracing Planetary Formation and Evolution

Geochemical Perspectives

Each issue of ***Geochemical Perspectives*** presents a single article with an in-depth view on the past, present and future of a field of geochemistry, seen through the eyes of highly respected members of our community. The articles combine research and history of the field's development and the scientist's opinions about future directions. We welcome personal glimpses into the author's scientific life, how ideas were generated and pitfalls along the way. *Perspectives* articles are intended to appeal to the entire geochemical community, not only to experts. They are not reviews or monographs; they go beyond the current state of the art, providing opinions about future directions and impact in the field.

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ABOUT THE COVER

Upper mantle peridotite xenolith present in basalt from the Yangyuan locale, China. Two stages of Earth's accretional history are recorded in mantle peridotites like this one. The moderately siderophile elements are present in abundances consistent with high pressure and temperature partitioning between metal and silicate, such as may have occurred at the bases of magma oceans over the course of the final 10-20% of Earth's accretion. The highly siderophile elements are in chondritic relative abundance and were likely emplaced in the mantle by a final approximately 0.5% of Earth's accretion.

Photo credit: Richard J. Walker

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I accomplished most of the writing of this article while on sabbatical. I thank the University of Maryland for providing sabbatical support, as well as the Carnegie Institution of Science's Department of Terrestrial Magnetism, the Lunar and Planetary Institute, the University of Vienna, and the Tokyo Institute of Technology's Earth-Life Science Institute for hosting me during the sabbatical. The work described below by the UMd group has been supported by numerous NSF and NASA grants over the years, most recently by NASA grants NNX13AF83G and NNA14AB07A, and NSF-CSEDI grants EAR1160728 and EAR1265169. These sources of funding are gratefully acknowledged. *Mary Horan* and *Igor Puchtel* provided reviews of the first draft and are thanked for bravely wading into a manuscript containing so many words! I am especially grateful for the heroic editing by *Tim Elliott* and the equally heroic reviewing done by *Laurie Reisberg* and *Graham Pearson*. They all provided many great comments for improvements. I also wish to acknowledge *Marie-Aude Hulshoff* for her important assistance in assembling and proofing the manuscript.

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SIDEROPHILE ELEMENTS IN TRACING PLANETARY FORMATION AND EVOLUTION

ABSTRACT

The siderophile, or iron-loving elements have many applications in the Earth and planetary sciences. In primitive meteorites, differences in the relative abundances of these elements are likely due to both nebular and parent body processes. In addition, some siderophile elements are also characterised by isotopically distinctive nucleosynthetic signatures. Thus, the relative abundances and isotopic compositions of these elements can be used to trace the genetics of primary planetary building blocks. Although these elements are largely concentrated in the metallic cores of differentiated planetary bodies, their absolute and relative abundances, as well as their isotopic compositions can also reveal important information regarding conditions of core formation and the chemical evolution of the silicate portions of the planetary bodies. The lithophile-siderophile nature of the radiogenic ^{182}Hf-^{182}W system allow it to be used to place chronologic constraints on planetary core formation. The differing incompatibilities of the two elements in silicate systems further mean that the system can also be used to study early differentiation processes and subsequent efficiency of mixing in the silicate portions of differentiated bodies, including Earth.

The abundances of siderophile elements in the terrestrial mantle are used to assess primary and secondary melting processes, and resulting metasomatic interactions. In addition, the Re-Os isotope system can, in some instances, be used to place chronologic constraints on when these processes occurred. The abundances of siderophile elements, and ^{187}Os/^{188}Os and ^{186}Os/^{188}Os ratios in the mantle sources of ocean island basalts can be used to place constraints on the age of recycled materials, and in some instances, the types of recycled materials present in these mantle domains.

1. INTRODUCTION

The *siderophile*, or Fe-loving elements, were defined by Goldschmidt as those elements with a tendency to partition into metallic iron relative to the silicate Earth, the hydrosphere, or the atmosphere (Goldschmidt, 1937). Some of the siderophile elements are also chalcophile, and tend to strongly partition into sulphide melts and some sulphide minerals. Here, I provide an overview of siderophile elements in geochemical and cosmochemical systems, focusing on what I consider to be some of the more important and interesting applications of these elements to Earth and planetary science. There is, of course, no hope of covering all applications related to this extensive group of elements, or of even discussing all of these elements. Most of the focus will be on so-called highly siderophile elements (to be defined later), with some forays to moderately siderophile elements. Although slightly siderophile elements, such as Mn, V and Cr, are not unloved, they will largely be ignored here, due to space limitations, as well as my lack of expertise regarding them. Siderophile elements have been used to learn some important details about the origin of the Earth and Moon, and how our planet ended up the way it did. However, ambiguities in how siderophile element data are interpreted have also provided us with some "mysteries" that we will likely debate for years to come.

As has become a tradition in *Geochemical Perspectives*, I begin by explaining how I managed to wind up in a career focused on geochemical research that has been largely centred on the generation and interpretation of siderophile element data. At the outset, I must admit that my entry into the world of siderophile elements did not occur as a result of a geochemical epiphany, or careful planning. I simply blundered into this suite of elements as an unlikely outcome of the transition from my dissertation project to a postdoctoral project.

My doctoral dissertation project at the State University of New York at Stony Brook involved the study of strictly lithophile trace elements, including Sr, Nd and O isotopes, in granites and granitic pegmatites of the Black Hills, South Dakota. My advisor, *Jim Papike*, who had moved to the Black Hills at the beginning of my Ph.D. project, was directing much of his research energies towards these granitic rocks at the time. The original research plan for my Ph.D. project was to determine rare earth element (REE) and some other trace element concentrations in minerals and bulk samples (whatever that means when working with pegmatites) of these rocks. To do this, I was to utilise the instrumental neutron activation analysis (INAA) technique at a distant facility. For this work, I drove off to the northwestern portion of the U.S. to work with *J.C. Laul* at the Battelle Northwest Laboratory in Richland, Washington, and spent 6 months generating data. The ultimate goal of the project was to model mineral-melt and mineral-fluid evolution in a complexly-zoned, granitic pegmatite. This seemed like a good idea at the time, yet, despite the popularity of leucogranites in kitchen countertop culture, they can have a dark side. Although they are composed of alluring minerals and textures, some of the granites and granitic pegmatites I worked on proved to be surprisingly challenging with respect to determining the concentrations of REE. To make a long story short, the quite low REE abundances in many of the rocks and minerals of interest, coupled with very high abundances of some elements that can swamp the signals of the REE when conducting INAA (like Ta and U), led to problems obtaining accurate data. I eventually returned to Stony Brook without the primary data needed for my dissertation. After discussing the analytical problems I had with Stony Brook professor *Gil Hanson*, he suggested that I could gather the data I needed by the more painful isotope dilution method, using his thermal ionisation mass spectrometry (TIMS) lab. Isotope dilution of these elements involves quite a bit of chemistry, as it requires dissolution of the rock or mineral, adding precisely determined amounts of enriched isotopes to the solution, and separating the REE through a series of cation exchange columns. I accepted the challenge, and over the next few years became inculcated in the joys and frustrations of chemistry labs and TIMS. The project eventually wended its way to completion in late 1984.

As the defense date of my dissertation neared, I began to look for gainful employment to follow my graduate career. Like many soon to be freshly minted Ph.D.'s, I was naturally looking to extend this same line of research of granites into a sixty year research career. This seemed like a good idea at the time. The rocks I was working on proved to be very interesting, and there was much left to learn from them about crustal evolution, and even about processes that can create economically viable mineral deposits (Walker *et al*., 1986). But how and where to find a follow-on research home that would allow me to continue this work?

Sometimes jobs can be found where you least expect them. As a result of working in *Gil Hanson*'s lab, I became particularly well versed in the care and feeding of mass spectrometers built by the U.S. National Bureau of Standards (NBS), which has subsequently been renamed the National Institute of Standards and Technology (NIST). We had two such mass spectrometers at Stony Brook. These were not commercial mass spectrometers. The NBS would build and sell you a mass spectrometer…, but only if you were nice to them and convinced them the mass spectrometer would be put to good use. Younger readers are reminded that, at that time in the early 1980's, commercially made thermal ionisation mass spectrometers were still relatively rare, and most labs that did TIMS work (*e.g.*, Caltech, MIT, Carnegie) utilised custom-built mass spectrometers, or commercial concoctions that operated with mixed success. The mere mention of the word *Nuclide* may still bring smiles to some faces, and looks of abject horror to others.

Towards the end of my graduate career it was decided that the smaller of the two Stony Brook mass spectrometers should have a beam valve installed. This would permit preservation of the vacuum in the flight tube while changing samples. Only one sample could be put into these instruments at a time, so maintaining the flight tube and collector can at vacuum, while changing a sample, would lead to much shorter pump down times, greater efficiency, and more data! The machining and welding for this was to be done at the NBS, so the necessary parts were hoisted into a van, and fellow graduate student *Jay Banner* (now a professor at the University of Texas) and I drove them down to the NBS in Gaithersburg, Maryland for the modifications. While there we received a tour that was akin to a James Bond briefing by Q. We got to see some of the newer versions of their mass spectrometers. One that was particularly intriguing was introduced as a *resonance ionisation mass spectrometer* (RIMS). It consisted of a relatively small TIMS combined with a tunable dye laser, which was, in turn, pumped by a Nd-YAG laser (pulsed at a very slow 10 Hz!). This was not laser ablation. The idea was to chemically separate and purify the element or elements of interest from matrix, just like with normal TIMS. The separated material was loaded onto a filament as with TIMS, however, for this measurement technique, the heat of the filament was used to atomise, rather than ionise the element. The laser light could be used to selectively photo-ionise atomic species of certain elements from the gas cloud in the source region of the mass spectrometer. The element-selective photo-ionisation would then take you from the atomised ground state to an excited state, then on to ionisation, whereby the mass spectrometer could do the rest with high voltage acceleration, focusing, and magnetic separation. The specificity of resonance ionisation would either allow you to do a bit less chemistry on the samples, *e.g.*, to selectively photo-ionise elements in order to eliminate isobaric interferences from other elements present in the separate, or to ionise elements that were not amenable to efficient thermal ionisation. It was pointed out to me that there was currently no one at the NBS working full time on the experimental instrument, and that I might want to apply for a National Research Council postdoctoral fellowship to do this. Although this didn't sound much like a follow up to a degree in geochemistry, the mass spectrometer was shiny, had flashing lights and looked really neat, so I applied and the proposal was selected for funding.

As I recall, my proposal primarily promised to use the new instrument to make more REE measurements on granites using simplified chemical separation methods, but also included a short section on measuring the siderophile elements Re and Os. I had included these two elements because they were on the list of elements that allegedly could be photo-ionised and analysed by RIMS. This was potentially handy because the very high first ionisation potentials of both elements made them unsuitable for standard TIMS measurements, using a hot filament for ionisation. I had read the pioneering applications of the ^{187}Re-^{187}Os isotopic system in several seminal papers published by *Jean-Marc Luck* and *Claude Allègre*, of the University of Paris, a few years earlier (*e.g.*, Allègre and Luck, 1980; Luck *et al.*, 1980; Luck and Allègre, 1983). This radiogenic isotope system seemed very exciting, with promising applications in cosmochemistry and geochemistry. Luck and Allègre accomplished their remarkable measurements by chemically separating Re and Os from a geological or cosmochemical matrix, highly purifying the elements in a chemistry laboratory, then using a secondary ion mass spectrometer (SIMS) to sputter the purified fractions in the mass spectrometer, which led to ionisation of a small fraction of each element. The methodology for doing this was exacting, suffered from very low ion yields in the mass spectrometer, and achieved relatively poor precision (ca. ±0.5 %). Maybe I could do better with RIMS.

I moved to Gaithersburg in January 1985 and began work on the new instrument. It was decided that I would first tackle the Re-Os isotope system, because Re and Os were perfect targets for photo-ionisation, and this might make a splash in the mass spectrometry world. I planned to conquer the system after maybe a few months of work. I then expected to get back to the more important measurements of the REE.

Development of the mass spectrometry was surprisingly straightforward. With help from my NBS mentor, *Jack Fassett*, I was able to make nearly state-of-the-art isotope ratio measurements of these two elements after just a few months of methods development, using the six inch radius of curvature RIMS mass spectrometer (Fig. 1.1). State-of-the-art, of course, was still only about ±0.5 to 1 % precision, and I never did top the precision of the Paris group's technique using RIMS. Fortunately, such low precision is not a problem for some applications of this isotope system. Unlike for Nd isotope applications, for example, where the ability to make measurements at the parts per 10,000 level is critical, the atomic abundance of ^{187}Os present in different rocks and minerals vary by more than 1000 %. Consequently, measurement precision of ±1 % was not necessarily a major handicap. Due to the selectivity of the photo-ionisation schemes used,

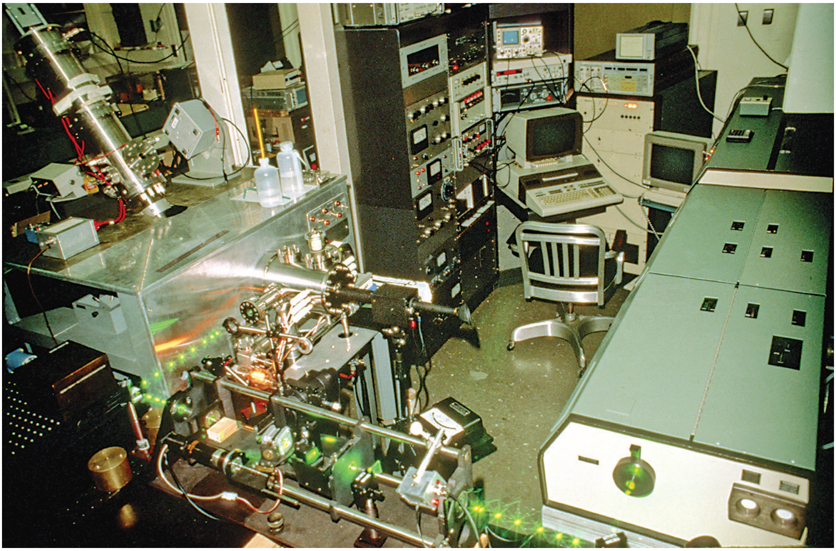


Figure 1.1 Resonance ionsation mass spectrometer, *circa* 1986, used for initial Re and Os measurements by the author at the U.S. National Bureau of Standards (now NIST). Note the trace of the pulsing laser light.

I could alternately measure the isotopic compositions of Re and Os loaded onto the same filament, simply by turning a dial on the side of the dye laser! The technique was far from perfect, but it worked. Among the requirements was that tiny, custom Ta filaments had to be hand-crafted for each analysis. Eventually we even learned to pulse the temperature of the filament to crudely coincide with the pulse rate of the laser, gaining us a modicum of improved efficiency. Refinement of equipment and methods led to the publication of a paper in *Analytical Chemistry* (Walker and Fassett, 1986), partially fulfilling my contractual obligation to the project. This meant I could move on to geologic applications!

Unfortunately, getting a viable chemistry to work for the Re-Os system proved to be much more elusive than development of the mass spectrometry. At that time I didn't understand that Os was easily volatilised from oxidising solutions, so the initial spikes I made (in nitric acid!) suffered rapid Os loss. Before I knew it, most of my two year postdoc had evaporated, along with the Os. I became sufficiently frustrated with the limited progress that I ultimately humbly contacted *Jean-Marc Luck*, who at the time was working on Os at Yale with *Karl Turekian*. He generously provided me with a manuscript that detailed his chemical procedures. I ended up copying some parts of his methods, and adapted others for the RIMS method (Walker, 1988), and was beginning to obtain some reasonable numbers on USGS standard rock powders by the time my first postdoc ended.

By this time, I had applied for a number of assistant professor positions. Mapping out many failures with a virtually unknown isotope system and no geologically relevant results, however, was not a good strategy for acquiring a faculty position in the geosciences. I even have some humorous interview stories from this period. For example, one institution sent me a nice letter (yes, it was paper back then) that stated their department was very interested in my work and would soon be inviting me for an interview. I was told that I should prepare a talk for the interview. About a week later I received another letter that said the instrumentation I was using was very expensive, so they had changed their minds and decided not to invite me for an interview after all. I ultimately did interview for a number of faculty jobs, but selling myself based on the (theoretical) promise of good things to come did not get me a job. Fortunately, during my final few months as an NBS postdoc I was invited to give a talk at the nearby Carnegie Institution of Washington's Department of Terrestrial Magnetism (DTM). I spoke about the RIMS technique and reviewed what I thought were some potentially exciting future applications of the Re-Os system. The talk interested staff scientists *Rick Carlson* and *Steve Shirey* to a sufficient degree that they convinced DTM's then Director, *George Wetherill*, to hire me for a follow-on two year postdoc. This turned out well for all of us. Both *Rick* and *Steve* had great ideas for initial applications of the system, while I had the means to make the measurements. While continuing to use the mass spectrometer at NBS, I was able to produce the first Re-Os isochron for a terrestrial igneous system, the 2.7 Ga Pyke Hill komatiites, in collaboration with *Steve* and *Ole Stecher* (Walker *et al*., 1988). I also generated the first Re-Os isotopic data for mantle xenoliths, in this case from the Kaapvaal Craton, South Africa, in collaboration with *Rick*, *Steve* and *Joe Boyd*.

For this study we found that the Os isotopic compositions of the xenoliths were quite variable and were able to correlate Os isotopic compositions with proxies for melt depletion. This led to the conclusion that some of the xenoliths had been depleted in Re, along with melt, more than 3 Ga ago (Walker *et al*., 1989). This in turn demonstrated that portions of the subcontinental lithospheric mantle (SCLM) underlying the Kaapvaal Craton formed at about the same time as the overlying Archean crust, strengthening the then nascent concept of long-lived lithospheric keels to continents. It also means that SCLM is commonly isolated from the convecting upper mantle for long periods of time. This study has led to considerable efforts by numerous labs around the world to date melt depletion in SCLM using Os isotopes. I'll come back to this topic in a later section.

At around the same time, I received a phone call from a guy with a British accent (with maybe a bit of Australian mixed in) who introduced himself as *John Morgan* (Fig. 1.2). He worked at the U.S. Geological Survey in Reston, Virginia, about 40 km away, and invited himself to visit the RIMS lab at the NBS. When he arrived, he made me aware that he had been working on Re, Os and some other siderophile elements in terrestrial and extraterrestrial rocks for "donkey's years" (one of his favourite terms). He had been making these measurements by neutron activation analysis (both instrumental and radiochemical), since the early 1960's, when he completed his Ph.D. dissertation at the Australian National University. During the early stages of his career, he carefully documented the trace element behaviours of Re and Os in terrestrial rocks and meteorites (Morgan and Lovering, 1967a,b), and subsequently was heavily involved in the analyses of Apollo samples (*e.g*., Morgan *et al*., 1972, 1974).

Photo provided by Richard Markey.

Figure 1.2 John Morgan was an innovator and major player in the development of the Re-Os isotope system, and the study of siderophile elements in general. He is shown here in laboratory attire at the U.S.G.S in Reston, VA in the early 1990's.

As later became obvious to me, *John* had been planning a range of important applications of the Re-Os isotope system to geological and cosmochemical problems since the time of his dissertation, and was waiting for an analytical method to come along that would allow him to make the isotopic measurements he knew should be made. He proposed that we collaborate and begin work on meteorites to build on the published results of *Luck* and *Allègre*. We also agreed to do some work on one or two platinum group element (PGE)-rich systems that might be viewed as practical applications by his U.S.G.S. management, given that I was still looking for long-term employment. The deal was that he would do the chemical separations and I would do the mass spectrometry. He used a different chemical processing method from mine. Instead of acid digestion, he used an alkaline fusion method, which had somewhat higher blanks, but completely dissolved a wider range of materials than my method (Morgan and Walker, 1989).

At the time *John* introduced himself to me, I thought iron meteorites were possibly the least interesting topic one could think of, and that chondrites were not far behind on the list of sleeper topics. Nevertheless, I agreed to this arrangement. Together with my wife *Mary Horan* (also a U.S.G.S. employee at the time) we were able to quickly produce some papers that seem primitive by today's standards, but nonetheless laid the groundwork for future applications of the Re-Os system and other siderophile elements to issues of planetary differentiation and late stages of planetary accretion (*e.g.*, Walker and Morgan, 1989; Horan *et al*., 1992).

Collaborating with *John Morgan* was highly beneficial for me, as my career research targets have forever after closely followed those promoted by him. It even turned out that his constant mantra, that lunar breccias are the key to understanding practically everything, really was true. Over the next few years we also turned out papers examining the Re-Os isotopic systematics of rocks from the Stillwater Complex, Montana, in collaboration with *David Lambert* (Lambert *et al*., 1989), and the Sudbury Igneous Complex, Ontario, in collaboration with *Tony Naldrett* (Walker *et al*., 1991). The Stillwater Complex turns out to have had a heterogeneous, but mantle-dominated Os isotopic composition when it formed. By contrast, in our study of Sudbury ores, we discovered that the initial Os isotopic composition of the complex was highly radiogenic, indicating that probably all of the PGE, as well as the Cu and Ni mined from the complex were concentrated from a crustal melt, rather than extracted from the mantle, or the meteoritic impactor that generated the complex.

After my Carnegie postdoc, I spent an additional two years working at the U.S.G.S., where I continued to collaborate with *John* and *Mary* on the Re-Os isotope system. Just before my temporary position at the U.S.G.S. ended in 1990, I saw an advertisement for an assistant professor job at the nearby University of Maryland (UMd), and applied. Although UMd was only about 10 km from where I lived, it was a place I had never previously visited. I was soon invited over for an interview, presumably because I was such a cheap date. I must not have done too poorly in the interview, because I was eventually hired by the Department of Geology, and still work there.

In order to dislodge me from their lab at NBS, where, after 5 years I was still conducting my mass spectrometric measurements, the Mass Spectrometry group there gave me the guts of their oldest, 12 inch radius of curvature, 68° sector TIMS. As part of my university start-up, I had the instrument upgraded with relatively modern electronics and some laser ports. The instrument was shipped the short distance to the UMd in the summer of 1990. Plans were made to turn it into a RIMS capable instrument via the acquisition of a laser system. My new UMd colleague *Erik Krogstad* and I also planned to do Nd, Sr and Pb isotopic measurements, and maybe some REE isotope dilution measurements with this instrument in a non-RIMS mode. We decided to name this mass spectrometer Bobcat I for reasons that centre on the near theft of a stuffed bobcat during a geological field trip (Fig. 1.3a). We also submitted an instrumentation request to the National Science Foundation (NSF) for a laser system, as well as a new-generation, multi-collector TIMS.

Soon after the move to UMd, rumours began to circulate that Re and Os could be analysed as negatively-charged oxide species, eliminating the need for an expensive set of lasers. In 1991, *Rob Creaser* published his now famous paper detailing the negative thermal ionisation mass spectrometric (NTIMS) method for high sensitivity and high precision measurement of Re, Os and Ir (Creaser *et al.*, 1991). A few more papers on this topic from *Klaus Heumann*'s group in Germany quickly followed (*e.g.*, Völkening *et al.*, 1991; Walczyk *et al.*, 1991). At this point, my plans for building a RIMS instrument were terminated. The NTIMS technique was clearly superior with respect to both sensitivity and absolute precision, although it required a higher level of chemical purification of Os. I sent a letter to the NSF and asked them to forget about my request for a laser system, although we asked that the request for the multi-collector TIMS remain active. Fortunately, the TIMS proposal was subsequently funded. I quickly learned that my old NBS mass spectrometer had a "Frankenstein" switch (Fig. 1.3b), which when flipped, converted the instrument from positive to negative ion usage. We were almost immediately off and running with a far better mass spectrometric

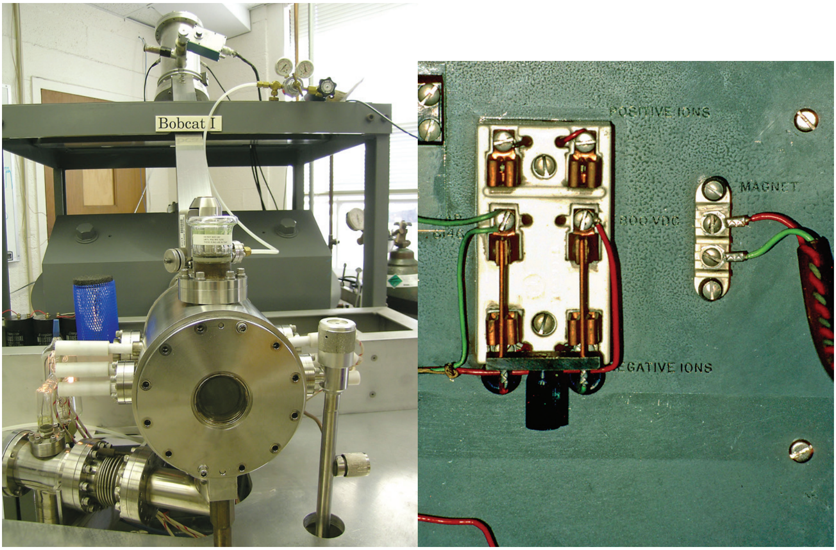


Figure 1.3 **(a)** The Bobcat 1 *NBS* mass spectrometer at the University of Maryland was turned into a negative thermal ionisation mass spectrometer by flipping two switches and adding an oxygen leak valve. **(b)** "Frankenstein" switch used to reverse magnet polarity on NBS mass spectrometers.

technique than either RIMS or SIMS. In 1992, with NSF and UMd combined funding, we added a *VG Sector 54* TIMS to the lab. I have lived in a largely negative ion world ever since. The Bobcat I mass spectrometer lived long and prospered at UMd. In 24 years of action, this 1966 vintage mass spectrometer churned out nearly 15,000 Re, Os, Sr, Pb, Ru and Mo isotopic measurements. In 22 years of action, the *VG* produced an equivalent number of analyses. Both were donated to other institutions in 2014.

I need to add a few additional words about chemical digestions and separations for siderophile elements. As with many scientific advances, chemical separation methods for siderophile elements can be traced back many decades. As noted above, my initial Re-Os chemistry was based mainly on the chemical separation methods handed down to me from *Jean-Marc Luck*. This consisted of a more or less standard acid dissolution of a rock using hydrofluoric, and hydrochloric acids, but with a reductant added to maintain Os in a reduced form. Once the rock matrix was broken down, presumably leading to the equilibration of sample with isotopic spikes, we then added strong oxidants to the solution and distilled the Os out of the pot solution in large glass stills (Fig. 1.4). Most practitioners of Os distillation at the time used chromic acid as the oxidant, but all the chromic acid I could get my hands on had rather high background concentrations of Re that I could not purify from the solution. This one problem cost me several months. Ultimately, my main contribution to this technique was finding that ceric sulphate could also be used as an oxidant for Os, and that it could be purified of Re and Os by boiling it in concentrated sulphuric acid at about 270 °C. This is a rather exciting process that is not for the faint of heart.

My hybrid chemical method for Re-Os ultimately worked well for some rocks, such as the Pyke Hill komatiites, but appeared not to achieve sample-spike equilibration for other types of rocks. This was very troubling, especially after the advent of the NTIMS method for isotopic measurement. For the chemical separation method I was pursuing, I now had a much better mass spectrometric method than chemistry. The alkaline fusion method of *John Morgan*'s worked well, and enabled us to produce a number of papers, but it had blanks that were too high for some samples.

After going through the literature on the dissolution of noble metals, it became apparent that a high temperature oxidative digestion might be necessary to drive the Os of the sample and spike to the same valence (+8 is most desirable). This led to an analytical paradox. Osmium tetroxide is very volatile, so any oxidative, open-system digestion done at high temperatures would lead to the loss of the Os I wanted to capture and analyse. I conducted experiments with radioactive ^{191}Os during my NBS postdoc that convinced me early on that Os tetroxide can pass through Teflon, so even closed Teflon bombs would not work if the Os was oxidised. Fortunately, I recalled that my colleague at the NBS, *Bob Kelly*, had been conducting oxidative digestion of fuel oils using *aqua regia* in sealed *Pyrex* vessels called *Carius tubes*. We discussed the application of the Carius tube to Os measurements and he thought digestion with *aqua regia* would be just the thing.

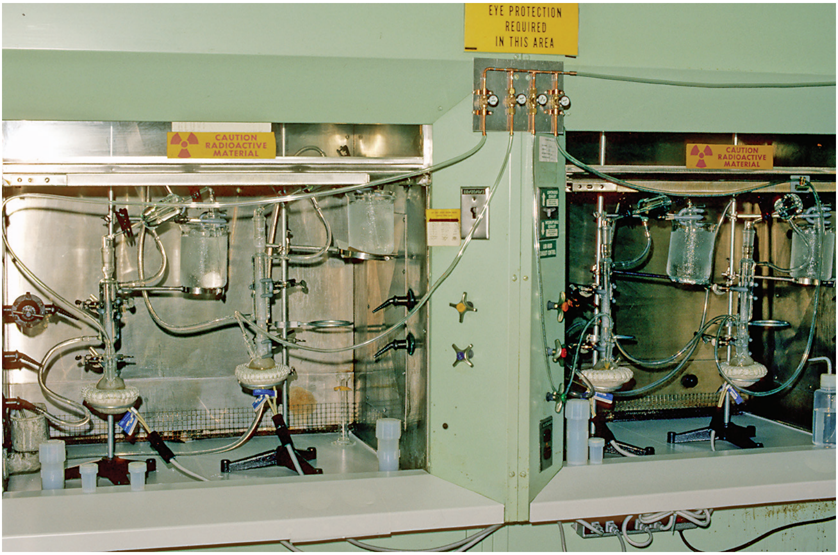


Figure 1.4 Osmium purifications were originally accomplished by the author using a glass distillation apparatus. The volatile Os tetroxide was generated by mixing dissolved rock with ceric sulphate, then distilling through a water-cooled condenser. Osmium gas was trapped and reduced in an ethanol-hydrochloric acid mixture, chilled by ice. Photo shows mass production set-up in two hoods at the NBS, with 4 stills operating at one time, *circa* 1987.

In 1860 Georg Ludwig Carius invented a sealable tube to dissolve all sorts of stuff in acids, including noble metals. The technique had been updated specifically for noble metals at the NBS by Gordon *et al*. (1944) and Wichers *et al*. (1944). So, in collaboration with *Steve Shirey* at DTM, in 1993 I had some tubes fabricated and added sample powder to them. We also added spikes and *aqua regia* to the tubes. We wanted to retain osmium tetroxide that might quickly form with the addition of the *aqua regia*, so we naively added the acids and spikes to the tubes with the tubes sitting in a liquid nitrogen bath, thinking this would keep the Os really cold and stable. Although details are hazy, we then probably went off and had some coffee and doughnuts to congratulate ourselves on a job well done. We eventually took the tubes to the glass shop at UMd where the glass blower, *Mike Trembly*, sealed the tubes at their narrow end. It turns out that while we were enjoying coffee and doughnuts, the liquid nitrogen was trying its utmost to freeze all the oxygen from the atmosphere above the state of Maryland into the tubes. Upon removal of the tubes from the liquid nitrogen and sealing the tubes, the oxygen quickly thawed, expanded, and caused the tubes to explode. *Mike* expressed his extreme displeasure with our project, as the glass and *aqua regia* flew around in his lab, and decided to train us to seal the tubes in our own laboratories. Thereafter, we wisely switched to a higher temperature, ethanol-dry ice slurry for cooling the tubes. *Steve* and I published a short paper on the method (Shirey and Walker, 1995), and since then, this digestion method has been used by many labs around the world. The ease of our technique was greatly improved via the adaptation of liquid-liquid extraction methods to quickly and efficiently separate Os from the other rock components (Cohen and Waters, 1996; Birck *et al*., 1997), as well as the brilliant micro-distillation final clean-up step reported by Birck *et al*. (1997). Rehkämper and Halliday (1997) subsequently developed a nice column chemistry to separate the PGE and Re from one another, which could be added to the back end of our Re-Os chemistry.

Since the early 1990's, my laboratory group at the UMd has focused most of its efforts on the measurement of the Re-Os and Pt-Os systems, and the measurement of abundances of other HSE in geological and cosmochemical materials. More recently, we have added W, Ru and Mo isotopes to the measurements we make using NTIMS.

2. OVERVIEW OF SIDEROPHILE ELEMENTS

Most siderophile elements that accompany us here on top of the silicate Earth are in very low abundance. This is both bad and good, although mainly good. On the negative side, although the Earth is relatively rich in Au, ~98 % of it resides in the core. Thus, if you like objects made of Au, its highly siderophile nature is bad because the paucity of Au that is accessible to humans makes it relatively precious. Also, from an analytical standpoint, the low abundances of many of the siderophile elements, in common rocks, have made them challenging to measure. Further, in addition to low abundance, some are just downright ornery to measure by standard techniques. As discussed above, Os played a minimal early role in the application of isotope geochemistry to geological and cosmochemical problems, because it could not be measured by the conventional positive thermal ionisation mass spectrometric techniques employed in the 1950's through 1980's by isotope geochemists.

On the positive side, the preferential sequestration of siderophile elements into planetary cores makes them wonderful elements for examining a variety of global-scale issues, including primary planetary accretion, planetary differentiation, late stage planetary accretion, and mantle geodynamics. They are also valuable for examining smaller scale processes, such as melt depletion and melt-rock interactions in the mantle. Of course some siderophile elements, such as Au, W, Pt and Pd, are also considered to be valuable commodities by humans, so their abundances, and the potentially diagnostic relative abundances and isotopic compositions of fellow siderophile elements, can even serve as useful prospecting tools (*e.g.*, Walker *et al.*, 2007).

The siderophile elements comprise a geochemically complex group of elements. There are several aspects of these elements that need to be recognised (Table 2.1). First, they are not all equally siderophile. Quoting from Morgan *et al.* (1981), *"the siderophile elements are somewhat analogous to the occupants of Animal Farm (Orwell, 1954) in that some are more siderophile than others…"*. I was never quite sure which siderophile elements *John* considered to be the oppressor-class elements, equivalent to the pigs of Orwell's Animal Farm, but I suspect the vaunted Os was one. At any rate, siderophile elements are often divided into subgroups commonly termed slightly siderophile (SSE: Mn, V, Cr), moderately siderophile (MSE: Ga, P, W, Co, Ag, Ni, Sb, As, Ge, Mo), and highly siderophile (HSE: Re, Os, Ir, Ru, Pt, Rh, Au, Pd) (Fig. 2.1). As the terms suggest, an element is classified as a SSE, MSE or HSE, depending on how strongly it preferentially partitions into metal relative to silicate melt, under 1 bar experimental conditions. The $D^{metal/silicate}$ values (concentration ratios of the element between the two phases at equilibrium) for HSE are typically ≥10,000, whereas MSE D values range from ~3 to 1000, and D values for SSE hover just above 1. These D values cannot be uniquely defined, even for 1 bar conditions, because in addition to their sensitivity to pressure and temperature conditions, they are also strongly controlled by fO_2, and in some cases fS_2. In Table 2.1, I provide a range of D values appropriate for 1 bar systems that have been experimentally examined.

Table 2.1 Relevant data for moderately and highly siderophile elements. 50 % condensation temperatures (T_C) in K, at 10^{-4} bar total pressure from Lodders (2003); abundances in Bulk Silicate Earth (BSE), estimated uncertainties, and C1 chondrite (in ppb) from Anders and Grevesse (1989) (MSE for C1), McDonough and Sun (1995) (MSE for BSE), Arevalo and McDonough (2008) (W for BSE), Fischer-Gödde *et al.* (2010) (HSE for C1) and Fischer-Gödde *et al.* (2011) (HSE for BSE); metal-silicate D values for 1 atm. conditions at fO_2 between IW-1 and IW-2 from cited references.

	50 % T_c (K)	BSE	±	C1	BSE/C1	±	$^{Metal/Silicate}D$	fO_2	ref.
MSE									
W	1789	13	10	93	0.14	1.00	2-600	IW1-IW2	a
Mo	1590	50	20	900	0.056	0.022	35-65	IW1-IW2	b
Ni	1353	1960	196	10500	0.19	0.02	16-27	IW1-IW2	b
Co	1352	105	11	500	0.21	0.02	15-23	IW1-IW2	b
Ag	996	8.0	2.4	200	0.040	0.01	4-110	IW1	c
Ga	968	4.0	0.4	9.2	0.43	0.05	3-30	IW1-IW2	a
Ge	883	1.1	0.2	31	0.035	0.005	400-800	IW1-IW2	d
HSE									
Re	1821	0.35	0.06	37.3	0.0094	0.0016	>8 x 10^6	IW-1	e
Os	1812	3.9	0.5	450	0.0087	0.0011	6 x 10^{10}	IW-1	e
Ir	1603	3.5	0.4	424	0.0083	0.0009	>1 x 10^{12}	IW-2	e
Ru	1551	7.0	0.9	631	0.0111	0.0014	2 x 10^{12}	IW-2	e
Pt	1408	7.6	1.3	864	0.0088	0.0015	7 x 10^{15}	IW-2	e
Rh	1392	1.2	0.5	130	0.0092	0.0037	5 x 10^{12}	IW-2	e
Pd	1324	7.1	1.3	563	0.0126	0.0023	2 x 10^7	IW-2	e
Au	1060	1.7	0.7	149	0.0114	0.0047	3 x 10^7	IW-2	e

a Schmitt *et al.* (1989)
b Righter (2011)
c Wheeler *et al.* (2011)
d Capobianco *et al.* (1999)
e Walter *et al.* (2000)

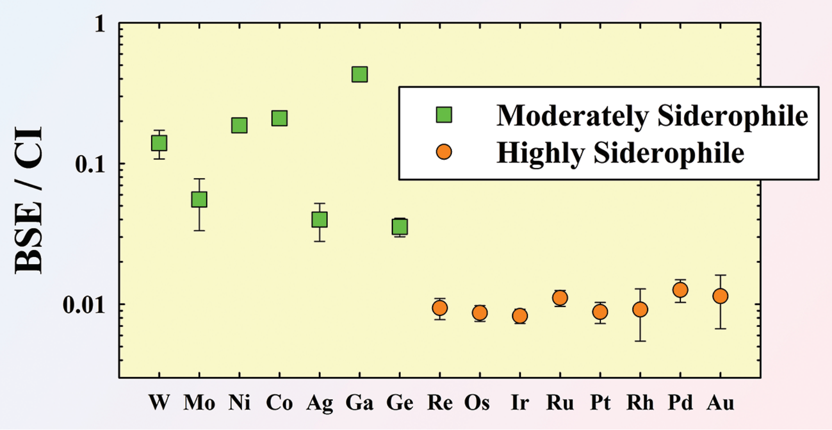


Figure 2.1 Abundances of moderately and highly siderophile elements in the bulk silicate Earth (BSE) normalised to CI chondrite abundances. Concentrations and uncertainties are from Table 2.1. For each category of siderophile nature, the elements are arranged from left to right from most to least refractory, based on their 50 % condensation temperatures (Lodders, 2003) (Table 2.1).

Second, the MSE and HSE range from moderately volatile to highly refractory, with 50 % condensation temperatures as low as ~883 K (Ge), to >1800 K (Re and Os) (Lodders and Fegley, 1998; Lodders, 2003). This means that the elements can be significantly fractionated from one another in cosmochemical settings as a result of condensation and/or evaporation processes (Grossman, 1972).

Third, like most minor and trace elements, the partitioning behaviours of the siderophile elements vary as functions of the composition of the system, as well as pressure and temperature conditions. For most siderophile elements, increasing temperatures and pressures leads to decreases in $D^{metal/silicate}$ values. As will be discussed below, these changes have been well studied for most MSE (*e.g.*, Li and Agee, 1996), but because of analytical and experimental issues, the partitioning characteristics of the HSE are much more difficult to determine and are, therefore, more highly debated (*e.g.*, Cottrell and Walker, 2006; Mann *et al.*, 2012; Bennett *et al.*, 2014; MÉdard *et al.*, 2015; Brenan *et al.*, 2016).

Finally, most of the siderophile elements occur in nature as multivalent species with, in some instances, wildly different geochemical characteristics. For example, although a highly refractory element under reducing conditions, Re in the form of ReO_4 under highly oxidising conditions (boiling point of ~260 °C), can be lost from subaerial volcanic systems as a gaseous phase (*e.g.*, Krähenbühl *et al.*, 1992; Bennett *et al.*, 2000; Lassiter, 2003). Valence can also be important with regard to solubility in low temperature aqueous systems. For example, Mo can range from highly soluble, to relatively insoluble, depending on the oxidation state of the system. In sum, despite the general tendency towards siderophile behaviour, this group of elements spans a broad range of geochemical characteristics, over a large spectrum of conditions.

In addition to serving as a very useful set of elements whose absolute and relative abundances can be used to study cosmochemical- and geochemical problems, some of the MSE and HSE are also actors in several radiogenic isotope systems. These include the long-lived ^{187}Re-^{187}Os ($t_{½}$ = 42 Ga) and ^{190}Pt-^{186}Os ($t_{½}$ = 450 Ga) systems, as well as several short-lived ^{99}Tc-^{99}Ru ($t_{½}$ = 0.21 Ma), ^{98}Tc-^{98}Ru ($t_{½}$ = 4.1 Ma), ^{97}Tc-^{97}Mo ($t_{½}$ = 2.6 Ma), ^{107}Pd-^{107}Ag ($t_{½}$ = 9 Ma), ^{60}Fe-^{60}Ni ($t_{½}$ = 3.5 Ma) and ^{182}Hf-^{182}W ($t_{½}$ = 8.9 Ma) systems (Table 2.2). Some relevant parameters and definitions of terms for the Re-Os, Pt-Os and Hf-W systems (with applications discussed below) are provided in Table 2.3. For the Hf-W system, the parent isotope Hf is a lithophile, not siderophile element. The systems with Tc as the parent isotope are currently not utilised. This stems from the fact that Tc is an element with no stable isotopes, and there is currently only limited evidence that the short-lived isotopes of Tc were extant in our earliest solar system. In order to discern possible effects in the isotopic compositions of the daughter elements, we need to know which early solar system materials may have been characterised by high Tc/Ru and Tc/Mo ratios. Our predictive abilities, however, are not very good with regard to Tc. Most prior workers have assumed that Tc behaves in a manner that is very similar to Re, which it sits directly above in the periodic table. Consequently, we and others originally assumed solid metal-liquid metal fractionation would lead to sizable fractionations between Tc and Ru or Mo (Dauphas *et al.*, 2002; Becker and Walker, 2003), as it does with respect to Re/Ru and Re/Mo. In Lazar *et al.* (2004), however, we experimentally discovered that Tc has a $D^{\text{solid metal/liquid metal}}$ value that is similar to the D values for Ru and Mo. Thus, even if Tc were present in early-formed metal systems, it would not have been strongly fractionated from its daughter elements. It seems likely that very high precision measurements of Mo and Ru will be required if we are ever to observe the effects of Tc decay in early solar system materials.

There is considerable history relating to the analysis and application of siderophile elements. High quality concentration measurements for some of these elements go back at least as far as the 1960's, so there is a long history of applications to geological and cosmochemical systems (Bate and Huizenga, 1963; Hirt *et al.*, 1963a,b; Fouché and Smales, 1967a,b; Morgan and Lovering, 1967a,b). This is especially true for Re and Os, and to a limited degree, even with respect to application of the ^{187}Re-^{187}Os isotope system (*e.g.*, Hirt *et al.*, 1963a,b; Herr *et al.*, 1967; Riley and Delong, 1970). Note too that some of the HSE, most notably Au and Ir, can be measured to high precision with great sensitivity by neutron activation analysis (*e.g.*, Vincent and Crocket, 1960; DEGRAZIA and Haskins, 1964). Consequently, the basics of the geochemical behaviours of some of the siderophile elements were largely worked out using these methods by the time I entered the field (*e.g.*, Morgan and Lovering, 1967a; Barnes *et al.*, 1985).

Table 2.2 Decay schemes, decay constants and associated half-lives for radiogenic isotope systems involving a siderophile element.

	λ (a)	$t_{1/2}$
$^{187}Re \rightarrow {}^{187}Os + \beta^-$	1.67E-11	41.6 Ga
$^{190}Pt \rightarrow {}^{186}Os + \alpha$	1.54E-12	450 Ga
$^{182}Hf \rightarrow {}^{182}W + 2\beta^-$	7.79E-08	8.9 Ma
$^{107}Pd \rightarrow {}^{107}Ag + \beta^-$	7.70E-08	9 Ma
$^{60}Fe \rightarrow {}^{60}Ni + \beta^-$	1.98E-07	3.5 Ma
$^{99}Tc \rightarrow {}^{99}Ru + \beta^-$	3.30E-06	0.21 Ma
$^{98}Tc \rightarrow {}^{98}Ru + \beta^-$	1.69E-07	4.1 Ma
$^{97}Tc \rightarrow {}^{97}Mo + \beta^-$	2.67E-07	2.6 Ma

Although INAA is still used for analysis of siderophile and other elements (*e.g.*, Korotev *et al.*, 2009; Wasson *et al.*, 2013), the advent of inductively-coupled plasma mass spectrometry (ICP-MS) in the 1980's has led to massive growth in the number of siderophile element data available for terrestrial and planetary materials. The capability of the plasma to ionise all of the siderophile elements with great efficiency has made analysis of most siderophile elements practical. This can be achieved through sample dissolution, followed by chemical purification and injection of elements of interest into the mass spectrometer (*e.g.*, Lee and Halliday, 1995a; Plessen and Erzinger, 1998; Pearson and Woodland, 2000; Schoenberg *et al.*, 2000), or by using laser beams to directly ablate material from solids for injection into the mass spectrometer. The latter method of laser ablation allows *in situ* chemical and isotopic analysis of materials with sufficiently high concentrations of siderophile elements (*e.g.*, Campbell and Humayun, 1999; Alard *et al.*, 2000). In addition, because of the ability of ICP-MS to precisely measure isotopic ratios, the isotope dilution method is now commonly applied to most non-monoisotopic siderophile elements. Alas, nature failed us when creating the monoisotopic Au and Rh, but even these elements can be measured well by ICP-MS techniques through comparisons with other siderophile elements (*e.g.*, Fischer-Gödde *et al.*, 2010).

Given that some of the discussion that is to follow involves Os isotopes, and includes references to some early Os isotope applications, this is a good place to note that all studies before 1994 reported Os isotopic compositions in terms of $^{187}Os/^{186}Os$ ratios. This was convenient for those of us who like simplicity because the modern chondritic (and mantle) ratio is ~1. However, in Walker *et al.* (1994) we began to conduct isotopic analyses of materials with very high Pt/Os ratios from Noril'sk, Russia. Some of these samples were enriched in both ^{187}Os and ^{186}Os, relative to mantle-derived rocks with chondritic ratios. The enrichments

Table 2.3 Isotopic information relating to ^{187}Re-^{187}Os, ^{190}Pt-^{186}Os and ^{182}Hf-^{182}W isotope systems. Isotopic data for Os, Pt and Re are from Walker (2012), Morgan *et al.* (2002), and Gramlich *et al.* (1973), respectively. Ratios used for fractionation corrections for Os and Pt measurements are shown in italics. * ^{187}Os and ^{186}Os are produced by radioactive decay of ^{187}Re and ^{190}Pt, respectively, so their relative abundances, as well as the atomic weight of Os vary in nature. Variation in $^{187}Re/^{188}Os$ among bulk chondrites is large (Fischer-Gödde *et al.*, 2010). The ratio listed is used by convention to facilitate comparison between different studies when calculating model ages and γ values.

Isotopic Ratio	Measured Ratio	2σ uncertainty	Isotope	Percentage composition	Atomic Weight
$^{184}Os/^{188}Os$	0.0013037	4	^{184}Os	0.0173 %	190.240
$^{186}Os/^{188}Os$	0.119850	4	^{186}Os	1.5935 %	
$^{187}Os/^{188}Os$	0.113787	9	^{187}Os	1.5129 %	
$^{189}Os/^{188}Os$	1.219710	20	^{188}Os	13.296 %	
$^{190}Os/^{188}Os$	1.983736	30	^{189}Os	16.217 %	
$^{192}Os/^{188}Os$	*3.08271*		^{190}Os	26.376 %	
			^{192}Os	40.988 %	
$^{190}Pt/^{195}Pt$	0.0003821	10	^{190}Pt	0.01292 %	195.080
$^{192}Pt/^{195}Pt$	0.023719	21	^{192}Pt	0.80168 %	
$^{194}Pt/^{195}Pt$	*0.9744*		^{194}Pt	32.934 %	
$^{196}Pt/^{195}Pt$	0.746024	38	^{195}Pt	33.799 %	
$^{198}Pt/^{195}Pt$	0.214149	4	^{196}Pt	25.215 %	
			^{198}Pt	7.240 %	
$^{185}Re/^{187}Re$	0.59738	39	^{185}Re	37.398 %	186.207
			^{187}Re	62.602 %	
Solar System Initial $^{187}Os/^{189}Os_i$ (from Archer *et al.*, 2014) 0.09517					
Average Chondritic $^{187}Re/^{188}Os$ (from Shirey and Walker, 1998) 0.40186					
Chondritic Evolution: $^{187}Os/^{188}Os_t = {}^{187}Os/^{188}Os_i + {}^{187}Re/^{188}Os_{chon} (e^{\lambda(4.568 \times 10E9)} - e^{\lambda t})$ $\gamma_{Os(t)} = \{[({}^{187}Os/^{188}Os_{sample(t)})/({}^{187}Os/^{188}Os_{chon(t)})] - 1\} \times 100$ $T_{MA} = 1/\lambda \times \ln\{[({}^{187}Os/^{188}Os_{chon} - {}^{187}Os/^{188}Os_{sample})/({}^{187}Re/^{188}Os_{chon} - {}^{187}Re/^{188}Os_{sample})] + 1\}$ $^{187}Os/^{188}Os_{sample(EA)} = {}^{187}Os/^{188}Os_{sample} - {}^{187}Re/^{188}Os_{sample} (e^{\lambda t} - 1)$ $T_{RD} = 1/\lambda \times \ln\{[({}^{187}Os/^{188}Os_{chon} - {}^{187}Os/^{188}Os_{sample(EA)})/{}^{187}Re/^{188}Os_{chon}] + 1\}$ where: $^{187}Os/^{188}Os_{sample(EA)}$ is ratio calculated for eruption age $\mu^{182}W = \{[({}^{182}W/^{184}W_{sample})/({}^{182}W/^{184}W_{standard})] - 1\} \times 1\,000\,000$					

in ^{186}Os were the result of the decay of ^{190}Pt. Consequently, we made the switch to reporting ^{187}Os/^{188}Os, a ratio in which the denominator is not modified by radioactive decay. Although this change met with some opposition, most other labs soon followed. This was not a big deal because most labs, like ours, had previously been measuring ^{187}Os/^{188}Os, then converting to ^{187}Os/^{186}Os by multiplying the measured ^{187}Os/^{188}Os ratio by an assumed ^{186}Os/^{188}Os ratio of ~0.12.

3. SIDEROPHILE ELEMENTS IN CHONDRITES AND IRON METEORITES

3.1 Chondrites

It is nearly impossible to discuss siderophile elements in major planetary bodies like the Earth, Moon and Mars without first discussing the general behaviour of these elements in meteoritic systems. A good place to start is with chondritic meteorites. Chondrites are often described as cosmic aggregates. This is because they consist of a variety of distinct components that may not have been made in the same place (Shu *et al.*, 1997), were probably not all made at the same time (Amelin *et al.*, 2002), and in some cases were not even made from the same starting materials (Dauphas *et al.*, 2002; Brandon *et al.*, 2005). These components can include chondrules, after which chondrites are named, refractory inclusions, metal, organics, and silicate-rich matrix. Chondrites are divided into three major classes, ordinary, enstatite and carbonaceous, plus some rare suites such as the Rumeruti, or R chondrites. The major classes are subdivided into different groups. These classes and groups are discriminated based on major element compositions (*e.g.*, Krot *et al.*, 2003). Introductory meteoritics teaches us that the carbonaceous chondrites, in particular the CI group, have chemical compositions most similar to the composition of the Sun's photosphere (Anders and Grevesse, 1989).

When discussing siderophile elements in chondrites, it is important to recognise that no chondrites are pristine examples of their parent bodies on the day they formed. All chondrites have experienced the effects of thermal metamorphism and/or aqueous alteration that occurred at some point(s) in the history of their respective parent bodies. Most studies assume these modifications occurred very early in solar system history, soon after parent body formation. In addition, many chondrites show the effects of shock resulting from impacts. Shock effects include heating and recrystallisation, and can occur at any time in solar system history. Finally, most chondrites, including falls, have been subtly or not so subtly modified by alteration processes that occur in space, or on the surface of the Earth. The effects of parent body modification, including shock, and terrestrial alteration on siderophile elements are still only partially understood. This means that before certain siderophile element characteristics can be attributed to nebular processes, they must first be considered within the context of modifications that may postdate the formation of their parent bodies (*e.g.*, Brearley, 2003).

Siderophile element data for chondrites began to proliferate during the 1960's (*e.g.*, Bate and Huizenga, 1963; Fouché and Smales, 1967a,b; Morgan and Lovering, 1967b; Tandon and Wasson, 1968). Siderophile elements for which data were commonly reported at that time included Re, Os, Ir, Au, Pd, Ni, Ga, Ge. The data for these elements showed that absolute and relative siderophile element abundances varied moderately for bulk meteorites among the major chondrite classes, and even among some of the groups (Takahashi *et al.*, 1978;

Wolf *et al.*, 1980; Hertogen *et al.*, 1983; Morgan, 1985). Thus, there is no one "chondritic" composition for siderophile elements. The differences are particularly well established when considering the ^{187}Re-^{187}Os isotopic system.

Allègre and Luck (1980) and Morgan (1985) were among the first to note the utility of constraining the long-term Re/Os ratio of planetary materials through the use of Os isotopes. The Re/Os ratio of a specific chondrite over 4.57 Ga of solar system history can be precisely defined by its ^{187}Os/^{188}Os isotopic ratio today, in most instances, even for conditions in which the Re/Os ratio has been modified by recent processes. A compilation of published data for bulk samples of chondrites shows an approximately 10 % range in ^{187}Os/^{188}Os ratios (Fig. 3.1a). Some of this variation likely reflects chemical and isotopic heterogeneity among chondrite components, coupled with the heterogeneous distribution of these components within the meteorite. Most measurements of Os isotopic compositions, as well as siderophile element abundances, are for relatively small pieces of chondrite that are typically of only a few hundred milligrams, at most. The bulk sample data reported by many studies are, therefore, probably not very representative of true bulk compositions, due to the inherent petrologic heterogeneity that is common in primitive meteorites. In support of this claim, elemental abundances, and to a lesser extent, isotopic heterogeneity of siderophile elements among multiple pieces of the same meteorite is well documented (*e.g.*, Horan *et al.*, 2003; Fischer-Gödde *et al.*, 2010).

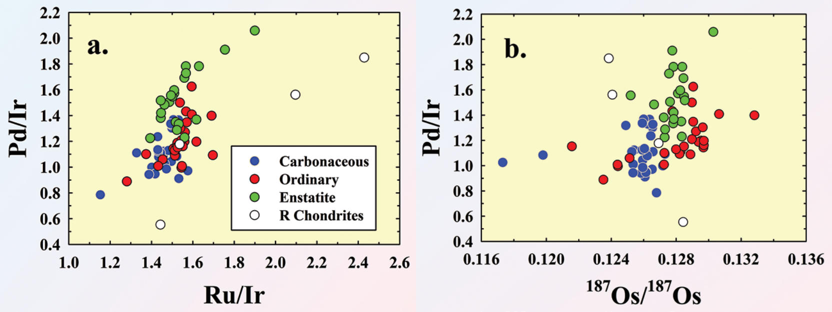


Figure 3.1 **(a)** Ru/Ir *versus* Pd/Ir of bulk samples of chondrites. **(b)** ^{187}Os/^{188}Os *versus* Pd/Ir. Note that there is considerable overlap of data between the chondrite classes, but on average, carbonaceous chondrites are offset to lower Pd/Ir, Ru/Ir and ^{187}Os/^{188}Os ratios, compared with ordinary and enstatite chondrites. Enstatite chondrites are characterised by generally higher Pd/Ir than ordinary chondrites. The few R chondrites for which there are data range to much higher Ru/Ir ratios than other chondrites. Data are from Walker *et al.* (2002a), Horan *et al.* (2003), Brandon *et al.* (2005), Fischer-Gödde *et al.* (2010) and Van Acken *et al.* (2011).

Despite issues with representative sampling, there are broad differences in ^{187}Os/^{188}Os ratios among the chondrite classes (Fig. 3.1a). For example, carbonaceous chondrites have, on average, ^{187}Os/^{188}Os ratios ~2 % lower than ordinary and enstatite chondrites (Walker *et al.*, 2002a; Fischer-Gödde *et al.*, 2010). The lower Re/Os ratios implied by the isotopic data are also evident in the measured Re/Os ratios of chondrites, although evidence for open-system behaviour of Re or Os long after formation makes the elemental ratio less diagnostic than the isotopic ratio (Walker *et al*., 2002a). As with Re/Os, there are some broad differences in the ratios of other HSE among chondrite classes and groups (Fig. 3.1a,b). For example, enstatite chondrites average higher Pd/Ir, and range to higher Ru/Ir, compared to ordinary and carbonaceous chondrites (Horan *et al*., 2003; Fischer-Gödde *et al*., 2010; Van Acken *et al*., 2011). When the HSE Rh and Au are added to the array considered, differences between groups can potentially be better discriminated (Tagle and Berlin 2008; Fischer-Gödde *et al*., 2010), but these elements cannot be measured by isotope dilution, and one must be careful when blending data obtained by different methods.

If these variations in the relative abundances of the HSE are the result of nebular processes, such as condensation or evaporation, they may provide important information regarding the thermal regime and the stability of different presolar phases present in the protosolar nebula, as recorded in primitive meteorites that formed at diverse distances from the proto-Sun. Alternately, if they were generated on a parent body, they may record more localised processes, such as selective aqueous transport and deposition of certain HSE. In order to examine this further, it is necessary to consider chondritic components. Progress has been made identifying the carriers of HSE and their fractionations in primitive meteorites. The origins of some of the fractionations are, however, still poorly understood. For example, Horan *et al*. (2009) reported that non-magnetic fractions of relatively low thermal metamorphic grade H-chondrites (ordinary chondrites that are rich in metal) are characterised by bulk chondrite-normalised hump-shaped HSE patterns, when the HSE are plotted from left to right, in order of decreasing 50 % condensation temperatures (Fig. 3.2a). The metal and non-magnetic fractions evidently incorporated distinct HSE-rich components that formed separately, and remained out of equilibrium with each other. Metal in these meteorites contains ~80 % of the HSE present in the bulk meteortie, but even the metal grains are characterised by moderate variations in HSE concentrations. The metal grains likely formed under conditions at which Pd behaved like the more refractory HSE. Non-magnetic (metal free) fractions, by contrast, have fractionated HSE patterns and abundances that are too high to be in equilibrium with metal, suggesting the presence of highly refractory carrier phases that are well-dispersed in chondrules and matrix. These carrier phases may represent residues of high degrees of melting of metal or high temperature condensates. The cause of the fractionations among the HSE is unknown. Evaporation or condensation effects alone could not produce the pattern shape of the non-magnetic fractions, although they could potentially lead to depletion of the comparatively volatile Pd, relative to the other HSE. Aqueous alteration on the parent body of these meteorites appears to have been minimal, and Re-Os isotopic systematics indicates that the fractionations occurred very early in Solar System history. Consequently, fluid-rock interaction is probably not the causal process either.

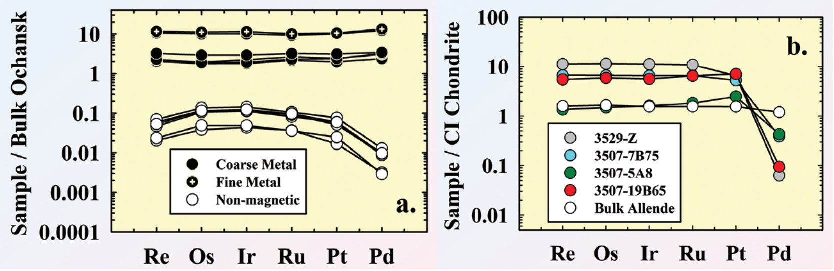


Figure 3.2 **(a)** Highly siderophile element patterns for coarse metal, fine metal and non-magnetic fractions of the separated components from the H 3.8 chondrite Ochansk, normalised to the composition of the bulk sample of Ochansk (modified from Horan *et al*., 2009). HSE are plotted from left to right in order of decreasing 50 % condensation temperature. **(b)** Highly siderophile element patterns for Group 1 calcium aluminum-rich inclusions separated from the Allende CV3 carbonaceous chondrite normalised to the CI chondrite Orgueil (data from Horan *et al*., 2003). Bulk Allende is shown for comparison. Note the major depletion in Pd. Data are from Archer *et al*. (2014).

The HSE in the bulk H chondrites studied are largely sited in metal grains, and so it is the metal phases with relatively unfractionated HSE abundances that primarily define the HSE characteristics of bulk samples. Nevertheless, it is easy to imagine that by sorting of distinct HSE carrier phases, prior to chondrite accretion, modest differences in HSE ratios could be produced in bulk samples. In this case, Re/Os and Pd/Ir would be most affected, consistent with variations in these ratios observed among bulk chondrites (*e.g.*, Fig. 3.1a,b). The observations for the H chondrite components cannot, however, account for variations in Ru/Ir among bulk chondrites.

As part of an M.S. degree thesis, my student *Greg Archer* examined the HSE characteristics of chondrules, matrix and calcium aluminum-rich inclusions (CAI) from the CV3 carbonaceous chondrite Allende (Archer *et al.*, 2014). This meteorite contains essentially no metal. In contrast to the H-chondrites, the only components examined that are characterised by strongly-fractionated HSE abundances (compared to CI chondrites in this case), are the CAIs, which show substantial depletions in Pd, the most volatile of the HSE examined (Fig. 3.2b). The Pd depletions most likely reflect condensation or evaporation processes that fractionated the more volatile HSE from the others. This interpretation is consistent with prior studies of HSE in CAIs (*e.g.*, Mason and Taylor, 1982) which showed that Au, an even more volatile HSE than Pd, is also strongly depleted relative to the more refractory HSE. Despite the comparatively fractionated and high HSE abundances in the CAIs, the relative abundances of HSE in Allende matrix and chondrules, with only a few exceptions, are essentially unfractionated. The study by Archer *et al*. (2014) was unable to identify the Pd-rich phase or phases that must be present to counter the deficiencies in Pd present in the CAIs.

Both Horan *et al*. (2009) and Archer *et al*. (2014) also examined the Re-Os isotopic systematics of the chondrite components studied. In the case of the H-chondrites, some of the non-magnetic fractions appear to have gained modest amounts of Re (or lost Os), long after initial formation of the component. The open system behaviour may reflect a process that occurred on the parent body, or even on the Earth, although all of the meteorites examined by both studies were observed falls. In the case of Allende CAIs, Archer *et al*. (2014), as with Becker *et al*. (2001a), reported what appears to be a resetting of the Re-Os isotopic systematics of some Allende CAIs at ~1.6 Ga. This may be due to the aqueous mobilisation of Re as a result of impact heating in the parent body at about that time. This putative event, however, does not seem to have affected the isotopic systematics of bulk samples of Allende. They are generally well-behaved, plotting on or very near primordial Re-Os reference isochrons (Becker *et al*., 2001a; Walker *et al*., 2002a; Fischer-Gödde *et al*., 2010; Archer *et al*., 2014). Despite this evidence for minor late stage mobility of HSE, it is important to recognise that these effects were dwarfed by the much larger primordial fractionations that occurred between HSE components in metal and non-magnetic fractions.

The study of MSE in chondrites has commonly focused on the distributions of these elements between metals and silicate matrix, and what this can reveal about thermal conditions in the parent bodies. For example, Kong and Ebihara (1996) studied the concentrations of the MSE W and Mo in metals present in equilibrated and non-equilibrated ordinary chondrites. They found that meteorites that are considered to be unequilibrated, based on petrological considerations, tend to have less W and Mo concentrated in the metal phases, compared to equilibrated meteorites in which metals contain a substantially greater share of the W and Mo. Further, they observed that W/Mo ratios remained constant in metals present in equilibrated chondrites. Based on this Kong and Ebihara (1996) concluded that the Mo and W concentrations of at least some ordinary chondrite metals were initially established during melting and reduction of precursor materials that were eventually accreted to the parent bodies. Once the parent bodies formed, subsequent metamorphism led to the diffusive transport of Mo and W from the non-metal phases (mostly pyroxenes) into the surrounding the metals. Similarly, Humayun and Campbell (2002) also noted the extraction of W into metal with increasing metamorphic grade in H chondrites. Studies by both Humayun and Campbell (2002) and Kong and Ebihara (1996), concluded that equilibration of W was complete at a relatively low metamorphic grade (H4).

Other components in ordinary chondrites also show multistage histories for siderophile elements. For example, Grossman and Wasson (1985) examined both HSE and MSE in metal extracted from chondrules, and observed that they were strongly fractionated in a manner consistent with volatility control. Consequently, that study concluded that most metal in the chondrules examined formed in the solar nebula before chondrule formation.

Temperature-time evolution paths for chondritic meteorites of different thermal metamorphic grade from the same parent body can potentially be used to constrain the thermal structure, and possibly the source of heat present in that parent body, yet the thermal structures and cooling histories of chondritic parent bodies are still debated (*e.g.*, Rubin, 2004; Amelin *et al*., 2005; Harrison and Grimm, 2010; Henke *et al*., 2012; Ganguly *et al*., 2013; Scott *et al*., 2014). For instance, the H chondrites experienced a large range of thermal-metamorphic conditions with isotopic closure ages obtained from different chronologic systems (*e.g.*, Rb-Sr, K-Ar, U-Pb) recording diverse temperature *versus* time paths for individual meteorites (Wasserburg *et al*., 1969; Göpel *et al*., 1994; Trieloff *et al*., 2003; Bouvier *et al*., 2007). An "onion-shell" structure of increasing temperature with depth (heated by ^{26}Al decay) has been proposed by some to account for variable metamorphic grades and cooling rates of ordinary chondrites (*e.g.*, Pellas and Storzer, 1981). Impact-induced heating has also been proposed to have been responsible for thermal metamorphism and even minor partial melting in at least some ordinary chondrites (*e.g.*, Rubin, 2004; Hutson *et al*., 2007). Hybrid models that may include cooling in an onion-shell body, but that also require impact mixing and variable cooling within a rubble pile, have also been proposed (*e.g.*, Davison *et al*., 2012; Scott *et al*., 2014).

The ^{182}Hf-^{182}W isotopic compositions of metals present in chondrites can be used to obtain model closure ages. Closure ages following peak metamorphic conditions can also be obtained from internal isochrons generated by plotting ^{182}W/^{184}W *versus* ^{180}Hf/^{184}W for separates of phases with different magnetic susceptibilities (Lee and Halliday, 2000; Kleine *et al*., 2008). In such cases, the slopes of the resulting trends can provide the ^{182}Hf/^{180}Hf at the time of system closure, and by inferring the ^{182}Hf/^{180}Hf at the time of solar system formation, an absolute closure age can be determined by comparison to decay models for ^{182}Hf (see Kleine *et al*., 2008 for a detailed overview of the application).

The H chondrites are particularly appropriate for ^{182}Hf-^{182}W isotopic study of thermal chronology as it relates to metal-silicate equilibration. Several prior studies have investigated this system in H chondrites in order to advance constraints on the thermal history of the parent body (*e.g.*, Lee and Halliday, 2000; Kleine *et al*., 2008). For example, Kleine *et al*. (2008) reported what were interpreted to be isochrons when plotting ^{182}W/^{184}W *versus* ^{180}Hf/^{184}W for metal and non-magnetic fractions separated from individual H chondrites. The slope-derived ages ranged from 4566.0 ± 0.5 Ma for St. Marguerite (H4), to 4562.8 ± 1.0 Ma for Richardton (H5), to 4559.2 ± 1.0 Ma for Kernouvé (H6). The decrease in age with increasing metamorphic grade was interpreted to indicate an inverse correlation between petrologic type and cooling rates. Kleine *et al*. (2008), and later Henke *et al*. (2012) fit their data to calculated temperature *versus* time cooling rate curves that included data for ^{207}Pb-^{206}Pb, ^{40}Ar-^{39}Ar and ^{244}Pu systems reported by other studies. They concluded that the collective results were most consistent with an onion-shell structure of a parent body heated by ^{26}Al decay.

Many questions remain regarding siderophile elements in chondritic meteorites. Although siderophile elements are strongly fractionated from solar relative abundances in some chondrite components, variations between bulk samples of different classes are comparatively minor. Evidently, the accretion of chondritic parent bodies did a pretty good job of blending materials that were quite different in terms of absolute and relative abundances of siderophile elements to achieve roughly common compositions. Nevertheless, whether the differences in siderophile element characteristics between chondrites from different classes reflect differences in the materials from which they were built, or the process involved during the construction of their constituent parts remains poorly understood.

3.2 Iron Meteorites

Iron meteorites, not surprisingly, are fabulous repositories of siderophile elements, and were among the first materials to be studied for the relative and absolute abundances of their siderophile elements. Some iron meteorites represent metal derived from asteroidal cores. Other iron meteorites likely represent something else, although just what, remains debated. The samples of an individual asteroidal core are pretty easy to spot, because when grouped with meteorites with similar chemical and textural characteristics, they form compositional trends that can usually be well described by simple solid metal-liquid metal fractionation processes (*e.g.*, Pernicka and Wasson, 1987). These meteorites are termed "magmatic irons". Traditionally, magmatic irons have been placed into different groups, connoted by Roman numerals and a letter or two, such as IIAB, IIIAB, IVA and IVB, based mainly on the abundances of siderophile elements Ga, Ir and Ni. There is some logic in the arcane terminology. The higher the Roman numeral, the more volatile depleted (*e.g.*, lower Ga and Ge) the system is interpreted to have been when it formed (*e.g.*, Schaudy *et al.*, 1972).

Iron meteorites were also among the first materials interrogated for Re-Os isotopic systematics (*e.g.*, Hirt *et al.*, 1963b; Luck *et al.*, 1980). This is because both elements are in comparatively high abundance in many, although not all, iron meteorites. It is also because the system is one of the few radiogenic systems that can be directly applied to determine the ages of asteroidal core crystallisation. When *John Morgan*, *Mary Horan* and I produced early iron isochrons (*e.g.*, Walker and Morgan, 1989; Horan *et al.*, 1992; Morgan *et al.*, 1992), we imagined that we would ultimately be able to discern differences in crystallisation ages that spanned tens, to possibly hundreds of Ma. Our early work did not have the resolution to do this, but it led us to keep trying to improve our methods.

For his Ph.D. dissertation, my student *Michael Smoliar* conducted a very careful study of the Re-Os isotopic systematics of iron meteorites from the IIAB, IIIAB, IVA and IVB groups, for which he generated the most precise isochrons yet achieved. For this work, he was able to get higher precision isotopic data using our new multi-collector *Sector 54* mass spectrometer. He also developed a mixed Re-Os spike which led to some analytical improvements. In order to convert the slopes of the isochrons to meaningful crystallisation ages for each group, *Michael* needed a more precisely defined decay constant for ^{187}Re than existed at the time. To generate this, he assumed that the Re-Os age of group IIIAB magmatic irons was the same as that of angrite meteorites, which was already well determined by the Pb-Pb method by Lugmair and Galer (1992). He made this assumption based on the observation that the systematics of the short-lived ^{53}Mn-^{53}Cr system for both IIIAB irons (Hutcheon *et al.*, 1992) and angrites (Nyquist *et al.*, 1994) were very similar. Using this bootstrapping method, *Michael* precisely defined the decay constant of ^{187}Re to be 1.666×10^{-11} yr^{-1}, a value that still appears to be accurate to this day! In Smoliar *et al.* (1996), we reported an isochron age for group IIAB irons of 4537 ± 8 Ma, with a precision of better than ±0.2 %! This is pretty good for a long lived radiogenic isotope system that a few years before couldn't be used to generate isochron ages with uncertainties of less than a few percent.

Most subsequent Re-Os isochron studies of iron meteorites have reported crystallisation within the first ~50 Ma of solar system history (*e.g.*, Shen *et al.*, 1996; Horan *et al.*, 1998; Cook *et al.*, 2004; Walker *et al.*, 2008; McCoy *et al.*, 2011). Unfortunately, we now know that crystallisation ages with uncertainties of ±8-20 Ma are of limited utility with regard to understanding the chronological sequence of planetesimal formation, melting, differentiation and crystallisation, given that many such bodies evidently underwent some or all of these processes well within the first 10 Ma of solar system history (*e.g.*, Lugmair and Galer, 1992; Lugmair and Shukolyukov, 1998; Srinivasan *et al.*, 1999; Misawa *et al.*, 2005; Baker *et al.*, 2012).

One semi-alternative to Re-Os chronology of iron meteorites is the application of the ^{182}Hf-^{182}W system (Lee and Halliday, 1995b; Harper and Jacobsen, 1996; Horan *et al.*, 1998). This system is very useful for determining the ages of metal-silicate segregation because the parent element Hf is strongly lithophile, while the daughter element W is moderately siderophile. As with chondritic metals discussed above, this means that as W is removed to metal, a result of metal-silicate equilibration, the metal records the isotopic composition of W at the time when continued diffusive exchange of W from silicates to metal ceases. At this point, the ^{182}W isotopic composition of the metal is frozen in.

A major problem applying the ^{182}Hf-^{182}W system to the chronology of early solar system metals has been post-formation changes in the isotopic composition of W resulting from cosmic ray exposure (CRE) induced burnout and production of isotopes of W and associated elements (*e.g.*, Ta). To circumvent this problem one must either work with metals that were minimally exposed to cosmic rays, or utilise a neutron fluence monitor that can be applied to correct for exposure effects (*e.g.*, Markowski *et al.*, 2006). Recently, it has been shown that isotopes of the HSE Pt and Os can serve as sensitive neutron dosimeters (Walker, 2012; Kruijer *et al.*, 2013; Wittig *et al.*, 2013; Qin *et al.*, 2015). These elements are easily extracted and purified for measurement in tandem with W isotopic measurement. In the case of Os and W, both elements can be measured by negative thermal ionisation mass spectrometry (N-TIMS) using similar protocols. Kruijer *et al.* (2013) showed that the CRE effect-free isotopic composition of W can be obtained for iron meteorite groups by plotting $^{182}W/^{184}W$ *versus* $^{196}Pt/^{195}Pt$ (or $^{189}Os/^{188}Os$) for samples from a group that were variably affected by CRE, then using the intersection of the resulting linear trend with the terrestrial $^{196}Pt/^{195}Pt$ to define the CRE-free $^{182}W/^{184}W$ for the group.

By combining data from the University of Muenster and ETH Zurich, together with data that my postdoc *Mathieu Touboul* produced at UMd, Kruijer *et al*. (2014a) reported the CRE corrected W isotope results for five groups of magmatic iron meteorites (Fig. 3.3). These are the most precise Hf-W model ages yet produced for iron meteorites. When coupled with the most recent determination of the initial $^{182}W/^{184}W$ for the solar system (determined from CAIs; Kruijer *et al*., 2014b), the magmatic iron groups give model ages of 0.7 to 3 Ma, following CAI formation. These young ages and the differences between the ages of the different groups are similar to earlier Hf-W results for magmatic irons (*e.g.*, Horan *et al*., 1998; Kleine *et al*., 2005; Markowski *et al*., 2006; Scherstén *et al*., 2006; Qin *et al*., 2008), but more accurate and precise. The model age uncertainties for this study are ≤±0.9 Ma.

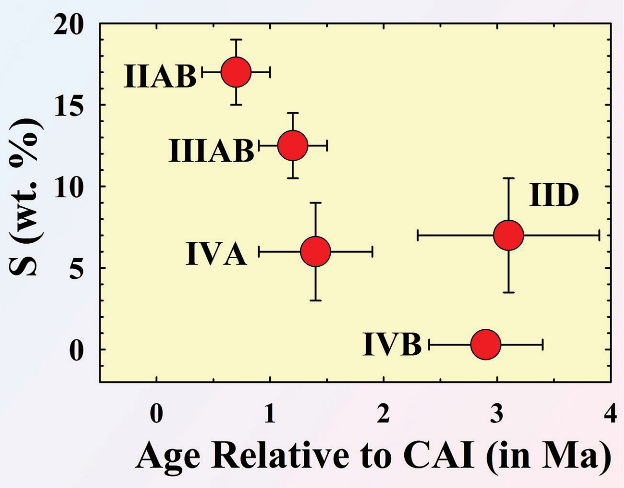


Figure 3.3 Model ^{182}W metal segregation ages relative to calcium aluminum rich inclusions (in Ma) for the major magmatic iron meteorite groups plotted *versus* estimated S (in wt. %) of parental melts to each group. All ages are calculated based on two stage evolution models, and cosmic ray exposure-corrected isotopic compositions. Data are from Kruijer *et al*. (2014a).

The Hf-W results show that the parent bodies of the magmatic irons accreted, heated, partially or wholly melted, and differentiated into cores and mantles within a period of ≤3 Ma of solar system formation. Because of the brevity of this time interval, Kruijer *et al*. (2014a) concluded that the most likely heating mechanism was ^{26}Al. Further, based on thermal modelling, the study also proposed that the parent bodies of these iron meteorite groups all formed within only ~0.5 Ma of CAI formation. This means the magmatic iron meteorites likely provide the earliest record of chemical and isotopic characteristics of differentiated bulk planetesimals.

Noting an apparent negative correlation between model segregation ages and estimated initial S content for four of the five groups (Fig. 3.3), Kruijer *et al*. (2014a) concluded that the timing of core segregation was strongly affected by the volatile content, especially S, of the parent body. Further, the study speculated that the W model ages reflect a mixture of W initially isolated as a result of relatively low temperature melting and segregation of FeS (non-radiogenic), and nearly pure Fe melt later produced at higher temperatures from the now high Hf/W (and more radiogenic) mantle of the body. The IID group does not fit the correlation (Fig. 3.3). Kruijer *et al*. (2014a) called on the sequential core formation model of Wasson and Huber (2006) to explain the offset from the trend. Wasson and Huber (2006) suggested that, although relatively S-poor, the meteorites from this group formed on a comparatively volatile-rich IID parent body. Consistent with this, Kruijer *et al*. (2014a) proposed that segregation of an initial FeS-rich core removed most S and W from the system, which led to a residual body characterised by high Hf/W. A second, P-rich metal melt (immiscible with the FeS-rich core) subsequently segregated to form a denser, chemically separate inner core that was enriched in ^{182}W, due to the period of growth in the high Hf/W mantle. By this account, the IID group irons sample only the P-rich inner core.

The sharp-eyed reader will note that the “well-defined” Re-Os isochron age for the group IIAB irons we reported in Smoliar *et al*. (1996), and mentioned above was 4537 ± 8 Ma, whereas the ^{182}W model age is within 1 Ma of CAI formation, say ~4.567 Ma. This means the Re-Os and ^{182}W ages differ by about 30 Ma. This could reflect slow cooling of the sampled core, given that the Re-Os age should reflect when crystallisation occurred, while the ^{182}W model age presumably dates the age of metal-silicate segregation. The 30 Ma difference seems a bit long for the core of a small body to cool, but this remains an unknown. The result may also suggest the Re-Os system remained open to elemental migration for a few tens of millions of years after crystallisation.

So called “non-magmatic” irons have their own stories to tell. Non-magmatic irons differ from magmatic irons in that within-group concentration variations of elements that do not strongly partition between liquid and solid metal, such as Ni and Ga, are much larger than can be explained by crystal-liquid fractionation process. Instead, some studies (*e.g.*, Wasson and Kallemeyn, 2002) attribute the formation of these irons to sizable impacts onto a chondritic body, resulting in metal segregation and accumulation in the base of a large crater. The large variations in the abundances of these elements can result from the variable mixing of solids and liquids produced by the impact. Some of these meteorites also have younger Hf-W model ages than the magmatic irons (*e.g.*, Scherstén *et al*., 2006; Schulz *et al*., 2012). For example, Schulz *et al*. (2012) concluded that the non-magmatic IAB irons segregated from silicate approximately 5 Ma after CAI. This is a bit later than the magmatic irons, and may mean that their source of heat was impacts rather than ^{26}Al.

Dating metal-silicate segregation using siderophile elements is not the only important application of these elements in metal-hosting systems. Modelling the solid metal-liquid metal crystallisation of magmatic iron meteorite systems using siderophile elements is among the most satisfying of trace element modelling tasks! The chief hindrance to successful modelling of these elements is the lack of knowledge of appropriate solid metal-liquid metal distribution coefficients to apply. Towards this end, much experimental work has been directed towards understanding siderophile element partitioning between solid and liquid metal (*e.g.*, Jones and Drake, 1986; Jones, 1994; Chabot, 2004). Yet, it turns out there are some interesting complexities that make modelling the elements deliciously complex. Probably the most important complexity is the concentrations of the elements S, P and C in the systems to be modelled. These elements are important because they exert a considerable effect on siderophile element partitioning (*e.g.*, Malvin *et al*., 1986; Chabot and Jones, 2003; Chabot, 2004). Thus, their changing abundances in a chemically evolving system must be modelled along with the siderophile element abundances. But it's even better than that! Although S has a major effect on siderophile element partitioning, and was present in significant abundance in most iron meteorite systems, it is difficult to determine the S contents of the initial states of the systems. This is because S is highly incompatible in crystallising solid metal, and may leave little trace of its presence in the meteorites one may wish to model. So how do we know the initial S contents of the iron meteorite systems we wish to study? Paradoxically, the S contents of magmatic iron systems have been estimated in some studies by examining the behaviour of siderophile elements compared to expectations derived from experiments (*e.g.*, Chabot, 2004; Walker *et al*., 2008).

Despite limitations in the modelling, the siderophile elements of some iron meteorite groups can be well modelled by making educated guesses about S contents and appropriate distribution coefficients (*e.g.*, Wasson and Richardson, 2001). Perhaps the least problematic group to model is the IVB system. Meteorites from this group show little evidence for significant initial S, P or C. Despite the apparent chemical simplicity, the chondrite normalised HSE patterns for iron meteorites from this group are are strongly depleted in the most volatile HSE, Pd and Au, and look like no other major iron meteorite groups that we know (Fig. 3.4a). In our study of this group (Walker *et al*., 2008) we showed that most HSE abundances can be accounted for through trace element modelling with only modest increases in S and P contents throughout the crystallisation sequence. Perhaps of greatest note resulting from this study was the conclusion that the starting metal liquid had relative abundances of HSE that were significantly fractionated from chondritic abundances (Fig. 3.4b).

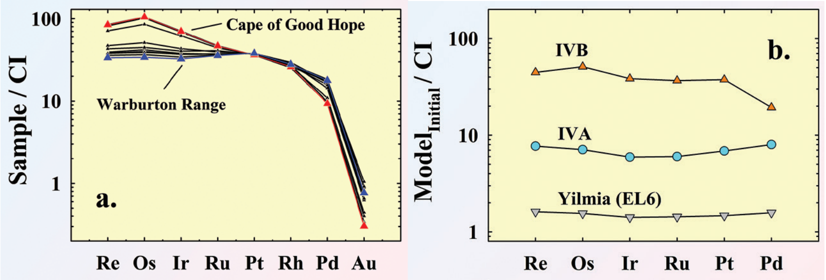


Figure 3.4 **(a)** CI chondrite normalised concentrations of HSE for IVB iron meteorites reported by Walker *et al.* (2008). Meteorites Cape of Good Hope and Warburton Range are highlighted as the least and most fractionated (lowest and highest Ni contents) IVB irons, respectively. Note the major depletions in volatile HSE Pd and especially Au. **(b)** CI chondrite normalised concentrations of HSE calculated for the initial melts in the IVA and IVB iron meteorite groups. Data are from McCoy *et al.* (2011) and Walker *et al.* (2008). For comparison, the HSE pattern for the EL6 chondrite Yilmia is shown (Horan *et al.*, 2003). Note that the relative abundances of the HSE for the IVA initial melt are only modestly fractionated compared with the EL6 chondrite Yilmia, which is the chondrite with the most similar pattern shape. By contrast, the calculated initial melt concentrations of HSE for the group IVB irons are much more highly fractionated and much higher than for any bulk chondrite.

The fractionated parental melt concentrations of HSE in the group IVB iron meteorites are difficult to explain. If it is assumed the parent body was characterised by chondritic overall relative abundances of HSE, a core segregating in this body should also be characterised by chondritic relative abundances, as it presumably concentrates >99 % of the HSE present in the bulk parent body. One possible way to achieve non-chondritic relative abundances of HSE in the initial melt is by a hit and run impact of a body into the primary parent body of the system (*e.g.*, Asphaug *et al.*, 2006; Yang *et al.*, 2007). This could lead to separation of liquid metal, with fractionated HSE, from a partially crystallised core, as well as the mixing of metal from the impactor with the impacted body. This could also lead to some of the observed depletions in the more volatile HSE Pd, and especially Au. Consistent with this interpretation, a subsequent study of the metallographic cooling history of IVB irons concluded that this group originated in a disrupted parent body that was stripped of its silicate mantle, most likely by a hit and run impact (Yang *et al.*, 2010).

In contrast to the IVB iron meteorite system, the IVA system was somewhat more S rich when it began to crystallise (Chabot, 2004). In McCoy *et al.* (2011), we were able to successfully model most HSE and some MSE for this group by assuming a modest initial S content (3 wt. %). The results of the model are difficult to tell from the actual measurements (Fig. 3.5a,b). The most fractionated, highest Ni meteorites in the group, such as Chinautla, are characterised by major depletions in Re, Os and Ru. The least fractionated, lowest Ni meteorites from the group, such as Jamestown, are characterised by generally flat, chondrite normalised HSE patterns (Fig. 3.5b). As a consequence, the calculated initial relative abundances of HSE for the parental melt to this group are much more chondrite-like compared to the group IVB irons (Fig. 3.4b). Nevertheless, metallographic cooling rates for iron meteorites from this group also suggest cooling in a body that was stripped of its silicate mantle (Yang *et al.*, 2008). This conclusion was based on the observation that the least evolved iron meteorites of this group (lowest Ni) show very rapid metallographic cooling rates, whereas the most highly evolved have relatively slow metallographic cooling rates. Yang *et al.* (2008) suggested that this can only be explained as a result of a disrupted body stripped of its insulating silicate mantle. The first solids to form in this system, therefore, cooled very rapidly. This would be unexpected in a core that was well insulated by an overlying mantle. In a well-insulated closed-system core, essentially uniform cooling rates would be expected for the entire crystallisation sequence.

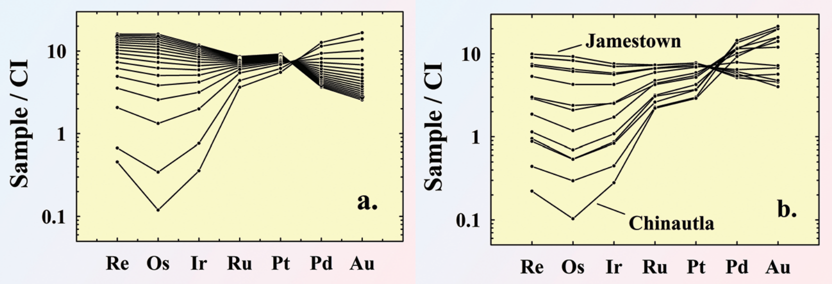


Figure 3.5 **(a)** Model of CI chondrite normalised solid compositions generated by fractional crystallisation for every 5 wt. % of crystallisation from an initial melt composition (from Fig. 9b). **(b)** CI chondrite normalised data for IVA iron meteorites. Model and meteorite data are from McCoy *et al.* (2011).

3.3 Additional Observations Regarding Siderophile Elements in Meteorites

There is another important aspect of siderophile element applications to chondrites and irons that bears review. This aspect pertains to planetary genetics. By *genetics*, here, I refer to the origin of the matter that makes up the building blocks of planetesimals and planets, as identified by their isotopic compositions. It is now well known that the matter from which our solar system formed was isotopically heterogeneous. The atoms of our precursor materials were made by a variety of nucleosynthetic processes. Nucleosynthetic processes include the slow addition of neutrons, or the *s*-process, rapid addition of neutrons, or the *r*-process, and by proton enrichment, or the *p*-process, such as by photodisintegration of heavy elements or neutrino interactions (Burbidge *et al.*, 1957).

These nucleosynthetic processes have been confirmed through the presence of large-scale isotopic enrichments and depletions in diverse presolar grains, extracted from low metamorphic-grade primitive meteorites (*e.g.*, Zinner, 1998; Nittler, 2003). Most of the isotopic compositions observed in presolar grains conform to predictions based on nucleosynthetic models.

Although the mixing of presolar grains in the solar nebula greatly attenuated the nucleosynthetic isotopic variability observed among presolar components, some elements continued to remain isotopically heterogeneous through the formation of planetesimals and larger bodies. For example, Trinquier *et al.* (2007) reported a small deficit in ^{54}Cr in meteorites believed to come from Mars. Yin *et al.* (2002a) and Dauphas *et al.* (2002) reported mass independent isotopic variations in the MSE Mo in bulk samples of chondrites and iron meteorites. *Mass independent* here means variations in isotopic compositions that do not scale in proportion to differences in nuclidic mass. They are typically the result of nuclear rather than physico-chemical processes. They concluded that these variations were nucleosynthetic in origin and reflect either a deficit in *s*-process isotope contributions, or an *r*- or *p*-process enrichment. Some of these heterogeneities are on the order of several parts per ten thousand. More recently, Burkhardt *et al.* (2011) reported a similar range of mass independent Mo isotopic composition variability among chondrites and iron meteorites. Burkhardt *et al.* (2011) argued that the pattern of Mo isotope enrichments and depletions for the carbonaceous chondrites, as well as most iron meteorites reflect a deficit in *s*-process isotope contributions to these materials, rather than an *r*- or *p*-process enrichment, and consistent with the earlier conclusions of Dauphas *et al.* (2002). Further, Chen *et al.* (2010) and Fischer-Gödde *et al.* (2015) reported comparably large ^{100}Ru isotopic heterogeneities among chondrite and iron meteorite groups.

The causes for the creation and retention of such large-scale isotopic heterogeneity in sizable bodies remain debated (*e.g.*, Andreasen and Sharma, 2007; Carlson *et al.*, 2007; Trinquier *et al.*, 2007; Regelous *et al.*, 2008; Yokoyama and Walker, 2016). Regardless of the true cause, the evidence for nucleosynthetic isotopic heterogeneity in components incorporated into diverse planetesimals is strong. Like mass independent isotopic differences in O or Cr, the isotopic variations in Mo and Ru can potentially serve as fingerprints of unique sources of siderophile elements within the nascent solar system.

By combining data reported in different studies, Dauphas *et al.* (2004, 2014) made the important observation that, when plotting the range of nucleosynthetic heterogeneities for Mo and Ru in bulk planetary materials, most of these materials plot along a generally linear trend with Earth, IAB iron meteorites, and enstatite chondrites at one end of the trend, and some carbonaceous chondrites at the other end of the trend (Fig. 3.6). As such, coupled Ru-Mo isotopic variability may serve as a sensitive genetic tracer of siderophile elements, much like mass independent variations in ^{17}O are used for genetic tracing of oxide-rich materials (*e.g.*, Clayton, 2003). As the isotopic database for these siderophile elements expands, knowledge of the genetics of siderophile elements present in diverse planetary bodies will undoubtedly grow and provide exciting new insights to the chemical structure and evolution of the early solar system. Dauphas *et al.* (2004) noted that if the Mo and Ru added to the silicate portion of the Earth came from genetically, hence, isotopically distinct reservoirs, then it might not be expected that the Earth plot on this trend. This is a really interesting observation, and one I'll come back to in the next section.

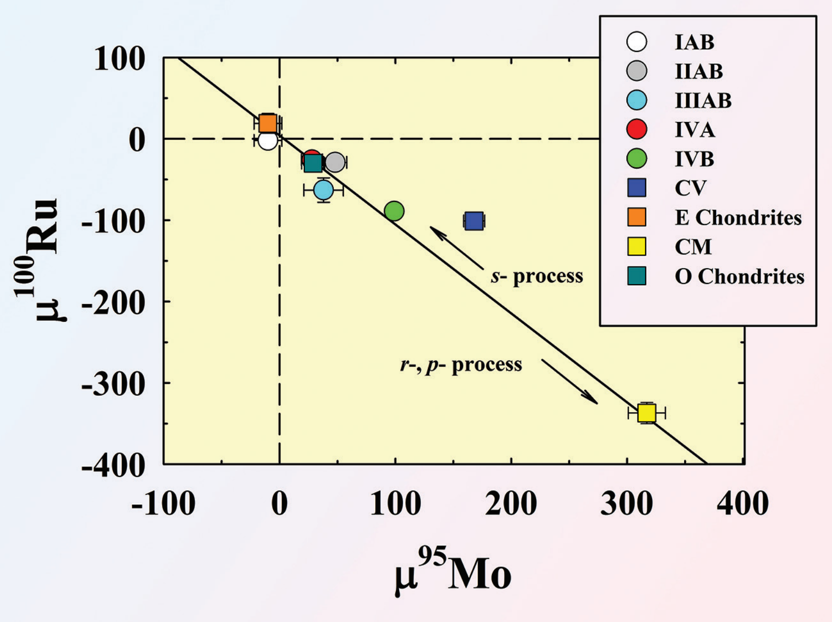


Figure 3.6 Plot of μ^{95}Mo *versus* μ^{100}Ru for bulk irons and chondrites. μ^{95}Mo and μ^{100}Ru are the deviation in parts per million of the ^{95}Mo/^{96}Mo and ^{100}Ru/^{101}Ru ratios of the samples compared to terrestrial standards. Data are combined from Burkhardt *et al.* (2011) and Fischer-Gödde *et al.* (2015). The Earth's mantle, presumably represented by the standards used for analysis, plots at μ values of zero. Here μ^{100}Ru is plotted against μ^{95}Mo, rather than μ^{92}Mo, as in the original study by Dauphas *et al.* (2004).

4. ORIGIN OF SIDEROPHILE ELEMENTS IN THE SILICATE PORTIONS OF DIFFERENTIATED PLANETARY BODIES

Siderophile element concentrations in the silicate portions of the Earth, Mars and Moon range from very well to rather poorly constrained. In this section I'll provide an overview of what we know of siderophile element abundances in the silicate portions of these planetary bodies, as well as two asteroids, and what these abundances may mean with regard to the origin of these bodies, their differentiation histories, and their chemical evolution since primary differentiation.

4.1 Origin of Siderophile Elements in the Bulk Silicate Earth

In order to consider the origin of the siderophile elements in the bulk silicate Earth (BSE) we must first try to define their absolute and relative abundances in this conceptual domain. To do this we must deconstruct all of the chemical heterogeneity that the silicate portion of the Earth has worked hard to generate through time. This is a tricky business, as core formation and subsequent processes have strongly modified MSE and HSE abundances in the silicate Earth, so that their absolute, and in some cases relative abundances, are far from the CI chondritic reference that is commonly applied. Fortunately, on Earth we can directly measure siderophile element abundances in upper mantle materials through the analysis of mantle xenoliths and tectonically exposed mantle rocks, such as some peridotite massifs, as well as abyssal and ophiolite peridotites. We can also measure siderophile element abundances in crustal rocks, although for some elements this can be analytically challenging because differentiation has resulted in very low abundances in some rocks. Collectively, these materials provide us with strong constraints on the concentrations of siderophile elements in the upper mantle, and by extrapolation, the BSE. None of these materials, however, provides a simple, one stop shop characterisation of the BSE.

Considerable research has been directed at the siderophile elements present in mantle xenoliths (*e.g.*, Morgan, 1986; Walker *et al.*, 1989; Griffin *et al.*, 2004; Pearson *et al.*, 2004), with recent reviews by Aulbach *et al.* (2016) and Luguet and Reisberg (2016). In most such studies, the xenoliths have been peridotitic rocks derived from the sub-continental lithospheric mantle (SCLM). Although very interesting for understanding the relationship between lithospheric mantle and overlying continental crust, these rocks can provide only a hazy look at siderophile element abundances in the BSE, because three dimensional relationships cannot be observed. The much more voluminous oceanic mantle may be a better reference frame from which to assess the compositions of siderophile elements in the BSE, however, by the time these rocks get to us, they are often highly modified by secondary processes, including seafloor alteration. Note that the oceanic mantle is also referred to as the depleted mid-ocean ridge basalt source mantle (DMM), as it is the mantle from which mid-ocean ridge basalts (MORB) originate.

It is also commonly referred to as the convecting upper mantle, given that it is believed to be continually stirred by convection. Because it is shortest, hereafter, I'll stick with the term DMM. Numerous siderophile element measurements have been made on peridotites that definitively come from the DMM, although it remains unknown how representative these materials are of the bulk DMM (*e.g.*, Snow and Reisberg, 1995; Standish *et al.*, 2002; Harvey *et al.*, 2006; Liu *et al.*, 2009; Schulte *et al.*, 2009). For example, abyssal peridotites may be exposed at the surface because they experienced prior melt removal and are less dense than average DMM (Warren, 2016). There are also considerable data for peridotites that *likely* originated in the DMM (*e.g.*, Luguet *et al.*, 2001; Büchl *et al.*, 2002; Bizimis *et al.*, 2007). Characterisation of peridotitic rocks from SCLM and DMM domains has been critical for defining siderophile element abundances in the BSE.

Before we proceed, it is important to review some additional terminology. The term BSE has been used as a reference to a uniform composite composition for the entire silicate portion of the Earth. Thus, it incorporates SCLM and the DMM, oceanic and continental crust, as well as any other potentially chemically distinct mantle domains, such as the seismically distinct D″ layer, as well as large low shear velocity provinces (LLSVPs) that may also be chemically distinct. The term BSE is often used synonymously with the term Primitive Mantle (PM). Siderophile element abundances have also commonly been referred to with respect to the term Primitive Upper Mantle (PUM). This term has utility if you believe the upper and lower mantles are not chemically well mixed. In this case, for reasons that will be discussed below, it is conceivable that the lower mantle has lower HSE concentrations than the upper mantle. I think that the considerable tomographic evidence for mass exchange between the upper and lower mantle (*e.g.*, Montelli *et al.*, 2004; French and Romanowicz, 2015) argues for a reasonably well mixed mantle, so I will continue to use the term BSE, despite the fact that many of the prior studies have used PM or PUM.

It is also important to realise that the HSE and MSE abundances in the BSE may have arisen by different processes. As a consequence, I'll first discuss the MSE, and then move on to the HSE. The MSE are characterised by highly-diverse geochemical behaviours in the silicate portion of the Earth. Some MSE, such as W, are highly incompatible during mantle melting, and thus, are strongly concentrated in the crust. Nearly half of the W present in the BSE resides in the continental crust. By contrast, Co and Ni are compatible during mantle melting, and their crustal abundances have little impact on their mass balance in the BSE. Because of the geochemical diversity of this group of elements, the abundance of each of the MSE in the BSE must be estimated individually.

A good overview of how the abundances of the MSE have been estimated for the BSE is given in McDonough and Sun (1995). Perhaps the greatest surprise that comes from reading this paper is that the abundance estimates are not always directly based on their measured abundances in mantle and crustal rocks. Instead, the BSE abundances of MSE are mainly obtained through comparisons with similarly compatible or incompatible lithophile trace elements. If the elemental ratio of the siderophile element to the lithophile trace element is relatively constant for different types of rocks, then the estimated abundance of the lithophile element in the BSE, coupled with that ratio can be converted to a BSE concentration for the siderophile element (Newsom *et al*., 1986). Absolute abundances of lithophile trace elements in the BSE are typically much more accurately estimated than those of siderophile elements, because the latter were preferentially incorporated in the inaccessible core, and are present in comparatively low concentrations in the BSE. For example, in most igneous systems, Mo behaves with an incompatibility that is similar to the lithophile REE Ce. Consistent with this, Sims *et al*. (1990) examined Mo/Ce ratios in a variety of Archean and post-Archean rocks and found relatively little variance. McDonough and Sun (1995) utilised this observation to couple Mo with their estimate for Ce in the BSE and derived a Mo BSE concentration of 50 ± 20 ppm (Table 2.1).

The abundance of W in the BSE was determined in a similar manner, this time in comparison to the similarly incompatible lithophile trace element U. Arevalo and McDonough (2008) measured W in a large number of basalts and found comparatively little variability in the W/U ratio. The ratio of 0.65 ± 0.45 (2σ) for MORB was also found to be the same, within uncertainties, for ocean island basalts (OIB) and rocks of the continental crust. Based on assumptions about the U content of the BSE, they used this ratio to estimate a W concentration for the BSE of 13 ± 10 ppb. König *et al*. (2011) estimated a similar BSE concentration of 12 ppb, based on similar constraints. Using the concentration of U estimated for the DMM, Arevalo and McDonough (2008) also estimated a W concentration for the DMM of 3.0 ± 2.3 ng/g that is consistent with long term melt (and W) depletion in the DMM.

Although the estimates for most MSE abundances in the BSE lack precision, from Figure 2.1 it is easily seen that the MSE are all depleted relative to CI chondrites, as should be expected for siderophile elements. They have BSE/CI ratios ranging from 0.035 to 0.21 (Table 2.2). This may be surprising because we earlier defined MSE as having $D^{metal/silicate}$ values ranging from about 5 to 1000. None of the refractory MSE, however, are depleted relative to CI by anything approaching a factor of 1000! How can this be explained?

The observation that some MSE in the BSE are not as depleted as would be predicted from experimental studies of metal-silicate partitioning has been known for more than forty years (*e.g.*, Ringwood, 1966; Ringwood and Kesson, 1977). One way around this problem was recognised by some early studies that predicted that at high pressures and temperatures, $D^{metal/silicate}$ values would drop to much lower values than those determined for the relatively low temperature, 1 atmosphere experimental systems explored at that time (*e.g.*, Ringwood, 1966; Murthy, 1991). Thus, in these studies it was speculated that the higher than expected abundances of many of the MSE in the mantle resulted from metal-silicate equilibration under high pressure and temperature conditions. Subsequent experimental studies confirmed that the abundances of most MSE can indeed be accounted for by metal-silicate partitioning at pressures of between

30 and 60 GPa (Li and Agee, 1996; Righter and Drake, 1997; Seibert *et al.*, 2011; Wade *et al.*, 2012), as might be found at the base of a global magma ocean. Given the likelihood that the last stage of major accretionary growth of the Earth was dominated by giant impacts (*e.g.*, Raymond *et al.*, 2006; Morbidelli *et al.*, 2012), it is difficult to envision how the MSE abundances in the BSE could have been established by a single magma ocean event. Hence, the relative and absolute abundances of these elements most likely reflect the integrated effects of metal-silicate equilibration at increasingly higher temperatures and pressures, as planet Earth grew (Wade and Wood, 2005; Rubie *et al.*, 2015).

Now we'll move on to the HSE. To begin characterisation of the HSE in the BSE, let's start with the crust. The good news, unless you seek to discover a Pt mine through a random search of the crust, is that none of the HSE are strongly incompatible during common mantle melting scenarios. Of the HSE, Os, Ir and Ru, are strongly compatible under most conditions of mantle melting, and Pt, Rh, Pd, Au and Re range from moderately compatible to moderately incompatible. This means that, unlike many lithophile incompatible trace elements, the HSE are not strongly concentrated in the crust, relative to the mantle. The primary exception to this has been for mantle melting to produce komatiitic melts. In most such cases, the sulphide hosts of HSE in the mantle are totally consumed by melting, leading to incompatible behaviour for all of the HSE (*e.g.*, Puchtel and Humayun, 2005; Puchtel *et al.*, 2005). Komatiites are comparatively rare, however, and mostly limited to the first half of Earth history (Arndt *et al.*, 2008). Further, because most komatiites formed as a result of extensive degrees of partial melting of their mantle sources, the HSE are typically not significantly enriched, even in komatiitic melts, compared to their mantle sources (*e.g.*, Puchtel *et al.*, 2014).

Given the limited volume of the crust compared to the mantle, especially long-lived continental crust, the importance of the crust is minor when considering the mass balance of HSE in the BSE. With the exception of recycled oceanic crust, discussed in a later section, we will, henceforth, ignore the HSE sited in the crust in the characterisation of the BSE. Although HSE abundances in mantle rocks, such as peridotites, are modified by melt removal and melt-rock reactions (*e.g.*, Lorand *et al.*, 2009; Luguet *et al.*, 2015), their abundances in what appear to be relatively fertile upper mantle materials are generally uniform to a first order (*e.g.*, Morgan *et al.*, 2001). Converting observed abundances to abundances representative of the BSE, however, requires some manipulation of the data, and the assumption that the upper and lower mantles are well mixed with regard to these elements. Somewhat more sophisticated estimates of BSE abundances of HSE are usually made by projection. Projections of the concentrations of the HSE from measured concentrations in mantle peridotites to BSE concentrations usually rely on the analysis of variably melt depleted peridotites, and plotting concentration, or isotopic data in the case of ^{187}Os/^{188}Os, *versus* reliable indicators of mantle melt depletion in peridotites, such as Mg#, Al_2O_3, Yb or Lu. The idea is to project the (sometimes) linear trends upward to a fertile mantle composition, based on the melt depletion indicator used (Morgan, 1986; Meisel *et al.*, 1996; Becker *et al.*, 2006). For example, an Al_2O_3 content of 4.4 wt. % has commonly been proposed as appropriate for the BSE (McDonough and Sun, 1995).

A good place to start when considering projections to BSE is with trends of Al_2O_3 *versus* $^{187}Os/^{188}Os$ for mantle peridotites. In orogenic peridotite massifs and in off-cratonic xenoliths, $^{187}Os/^{188}Os$ is often correlated with indices of melt extraction, notably Al_2O_3 (*e.g.*, Reisberg and Lorand, 1995). Why is this? Mantle melting and subsequent removal of the melt tends to remove some Re from the mantle residue, given the moderately incompatible nature of Re. By contrast, Os is highly compatible and becomes somewhat more concentrated in the mantle residue as melt is removed. From a radiogenic isotope standpoint, progressive melt removal increasingly leads to lower Re/Os, and accompanying retardation in the growth of ^{187}Os (Walker *et al.*, 1989). With time, a suite of variably melt depleted mantle peridotites, that all began with the same initial $^{187}Os/^{188}Os$ at the time of primary melting, will evolve to have a range of more radiogenic isotopic compositions, proportional to their Re/Os (Fig. 4.1a). Handler *et al.* (1997) suggested that by the point at which melt removal has reduced the Al_2O_3 content of the mantle residue to ~0.7 wt. %, Re is nearly entirely removed from the residue. In an ideal scenario, on a plot of $^{187}Os/^{188}Os$ *versus* Al_2O_3, these variably melt (and Re) depleted samples will fall on an initially horizontal linear trend that gradually rotates upward with time, pivoting from the point defined by 0.7 wt. % Al_2O_3 and the initial $^{187}Os/^{188}Os$ of the system (Fig. 4.1a).

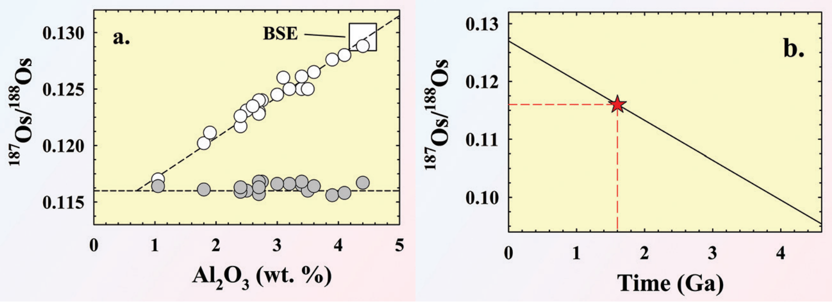


Figure 4.1 **(a)** Plot of Al_2O_3 *versus* $^{187}Os/^{188}Os$ for a hypothetical suite of mantle peridotites that were part of the DMM at 1.6 Ga. At this time, they all had $^{187}Os/^{188}Os$ ratios of ~0.116. At 1.6 Ga this mantle was variably melt depleted. Because increasing degrees of melt depletion results in progressively decreasing Re/Os each of the samples grows to a different $^{187}Os/^{188}Os$ to the present time. Upward projection of these data today to an Al_2O_3 of 4.4 wt. % can potentially reveal the Os isotopic ratio for the BSE today. Downward projection of the trend to 0.7 wt. % Al_2O_3 gives the initial ratio of the system (0.116) at the time of partial melting. Using a chondritic evolution model for the convecting mantle, gives a model depletion age of 1.6 Ga, in this example. **(b)** Possible evolution trajectory for bulk silicate Earth. The initial ratio of 0.116 extends horizontally to the evolution trend, consistent with a model age of 1.6 Ga.

Projecting the trend upward to an Al_2O_3 concentration of 4.4 wt. % gives $^{187}Os/^{188}Os$ for the BSE, if the mantle from which the suite was isolated had never previously had Re removed from or added to it (Meisel *et al.*, 2001). Further, projecting the trend downward to an Al_2O_3 concentration of 0.7 wt. %, and comparing the $^{187}Os/^{188}Os$ at the intersection point with an evolution model for Os in the mantle provides a model age for the putative melt depletion event (Reisberg and Lorand, 1995; Handler *et al.*, 1997; Fig. 4.1b). Because of the similarities to an isochron, this trend has been informally called an *aluminochron* by some. It is not a great term, but many people seem to like it. It can be asked why, if Re depletion follows depletion in Al_2O_3, we don't simply plot $^{187}Re/^{188}Os$ *versus* $^{187}Os/^{188}Os$ and generate a *bona fide* isochron and be done with it. The reason is that Re concentrations can be easily modified in peridotitic rocks by mechanisms related directly or indirectly to their tectonic and magmatic emplacement processes. For example, most peridotite xenoliths are brought to the surface in comparatively Re-rich basaltic or kimberlitic melts, thus, leading to possible direct contamination. Rhenium is also more easily removed from peridotites, compared to Os, when exposed to surface weathering. This means that peridotite suites that define good linear trends on plots of Al_2O_3 *versus* $^{187}Os/^{188}Os$ are rarely also characterised by good Re-Os isochrons, although there are some exceptions (*e.g.*, Gao *et al.*, 2002).

Projected BSE isotopic compositions and concentrations must be interpreted with care. For example, Meisel *et al.* (2001) obtained the $^{187}Os/^{188}Os$ ratio of the BSE (they termed it primitive upper mantle, PUM) by separately plotting the Os isotopic compositions of 8 suites of peridotites of diverse age, taken from around the world, *versus* Al_2O_3. Most of these peridotites were samples of SCLM. As noted above, SCLM is mantle that has been isolated from the convecting upper mantle for anywhere from short to long periods of time. In most cases, its formation is coupled with the formation of the overlying continental crust. Thus, the projections most likely reveal the Os isotopic compositions of the DMM at the times these materials became isolated, not the true BSE. Remarkably, the eight different suites examined by Meisel *et al.* (2001) projected to very similar $^{187}Os/^{188}Os$ ratios at the intersection point with Al_2O_3 of 4.4 wt. %. From this convergence of ratios, that study concluded that the BSE has a *minimum* $^{187}Os/^{188}Os$ of 0.1296 ± 0.0008 (level of confidence 95 %). Data for many additional suites of variably melt-depleted peridotites have been published since then. Surprisingly, data from about 80 % of these studies still project to a BSE ratio within uncertainties of the 2001 study.

Why is this ratio a minimum estimate for the BSE? Some still poorly-defined proportion of Re has been removed from the convecting mantle over Earth history, through the melting of the mantle to form basaltic crust. This almost certainly occurred prior to the isolation of these suites in lithospheric mantle. Thus, the true Os isotopic composition of the BSE must be somewhat higher. Nevertheless, the convergence of projected ratios to ~0.13, for sample suites extracted from lithospheric mantle of widely differing ages, suggests that progressive Re removal from the mantle, by formation and removal of crust, did not have a major impact on the isotopic evolution of this system. This may be because Re from the oceanic crust is quickly mixed back into the DMM, although some evidence contrary to this interpretation is presented below in Section 5. Nevertheless, if this approach is valid, and if the Al_2O_3 for the BSE really averages 4.4 wt. %, then the true BSE ratio is probably no more than 1-2 % more radiogenic than the projected ratio.

The ^{190}Pt-^{186}Os isotope system in most bulk geological materials generates very little variation in ^{186}Os/^{188}Os. This is because ^{190}Pt is a minor isotope of Pt (0.0129 %; Table 2.3), and it has a very long half-life of about 450 Ga. I'll return to a discussion of this system below in Section 6, but it is important to briefly mention here that, based on high precision measurements of bulk samples of the mantle (*e.g.*, Brandon *et al.*, 2000a; Luguet *et al.*, 2008a), as well as analyses of Os-Ir-Ru alloy grains and other materials that likely formed in the DMM (*e.g.*, Walker *et al.*, 1997; Brandon *et al.*, 1998; Walker *et al.*, 2005; Coggon *et al.*, 2013), it appears that the upper mantle has evolved along a chondritic trajectory (*e.g.*, Brandon *et al.*, 2006). As with the ^{187}Os/^{188}Os ratio estimate of the BSE, this constraint on the Pt/Os ratio of the mantle indicates that the long-term Pt/Os ratio of the BSE was chondritic within a range of about ±30 %.

What about the other HSE? In an early attempt to define the concentrations of HSE in the BSE (he used the term primitive mantle, PM), Morgan (1986) utilised a plot of Re concentration *versus* Mg# for a suite of peridotite xenoliths from seven global locations in order to constrain the Re concentration of the BSE. As with the ^{187}Os/^{188}Os *versus* Al_2O_3 projections, he projected the resulting linear trend to an appropriate Mg# for fertile mantle. From this, he reported a concentration of 0.26 ppb for the BSE. Remarkably, this estimate is consistent with later studies, based on many more data (*e.g.*, Becker *et al.*, 2006). In the early 2000's we had the powders of samples used in the original study by *John Morgan*, as well as a sizable collection of peridotites from other locations. By that time we also had developed the means to make high precison isotope dilution measurements of Ir, Ru, Pt and Pd, in addition to Re and Os. Consequently, *Harry Becker* decided to redo the study of Morgan (1986) with a larger suite of samples and a greater array of HSE. *Harry* approached the abundances of the HSE in the BSE by projecting linear trends to the BSE value for Al_2O_3. In addition to obtaining new data for many of the same samples analysed by the earlier Morgan (1986) and Meisel *et al*. (2001) studies, that study also added abyssal peridotites and samples from peridotite massifs into the mix of samples included in the projections. In Becker *et al*. (2006), we reported that, as with ^{187}Os/^{188}Os, projected HSE abundances are generally similar, whatever the age or prior melt depletion/enrichment history of a peridotitic locale. At the Freie University, Berlin, *Harry Becker*'s Ph.D. student, *Mario Fischer-Gödde* subsequently updated the results to include some new samples, and also added Rh and Au data (Fischer-Gödde *et al.*, 2011). The most recent estimates of the HSE concentrations in the BSE are provided in Table 2.1. When the HSE data are normalised to CI chondrite abundances and adjusted to a common Ir content, it can be quickly ascertained that most HSE occur in chondritic relative abundance (Fig. 4.2). However, the BSE estimates also indicate somewhat suprachondritic Ru/Ir and possibly suprachondritic Pd/Ir. Enrichments in these ratios were also noted in bulk mantle samples by prior studies (*e.g.*, Pattou *et al.*, 1996; Schmidt *et al.*, 2000).

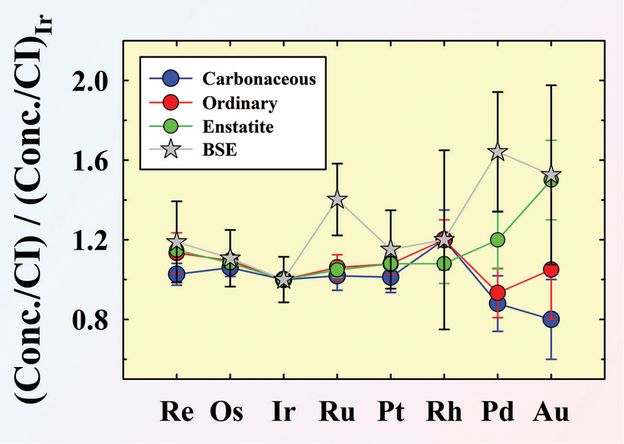


Figure 4.2 Plot of projected concentrations of HSE in the bulk silicate Earth (BSE) normalised to abundances in both CI chondrites and Ir. The range of normalised concentrations for carbonaceous, ordinary and enstatite chondrites are shown for comparison. Note that BSE estimates for Ru/Ir and Pd/Ir are suprachondritic. The error bars for the BSE data reflect uncertainties in the estimates. The error bars for the chondrite data represent the ranges of 95 % of the data for each group. The BSE estimate is from Becker *et al.* (2006) and Fischer-Gödde *et al.* (2011). Chondrite data are from Walker *et al.* (2002a), Horan *et al.* (2003), Brandon *et al.* (2005) and Fischer-Gödde *et al.* (2010).

It is important to recognise that there are some limitations in applying the projection approach towards the characterisation of HSE abundances in the BSE. Of greatest concern is whether or not the utility of the peridotites used in the projections have been compromised by repeated prior depletion and enrichment events (*e.g.*, Lorand *et al.*, 2009). It is likely that the absolute and relative concentrations of some of the most fertile peridotites in some of the suites used in generating the estimates for the BSE have been affected by refertilisation processes (Pattou *et al.*, 1996; Alard *et al.*, 2000; Schmidt *et al.*, 2000; Le Roux *et al.*, 2007). This could have a significant effect on the HSE, particularly Pd, Re and Au, that range from moderately compatible to moderately incompatible. The factors that govern these behaviours remain poorly understood. Thus, although the broadly chondritic nature of the BSE is in little doubt, the details in the relative abundances claimed by the authors of the studies utilising the projection methods have been called into question (*e.g.*, Lorand *et al.*, 2009). The primary question is whether large numbers of data for mantle peridotites from around the globe can provide sufficient fidelity by averaging out all of the process noise in the suites.

The typically strongly compatible natures of Os, Ir and Ru, make them less susceptible to modification by partial melting and metasomatic processes, compared to Pt, and especially the incompatible Pd, Au and Re. Consequently, Os/Ir and Ru/Ir ratios provide the strongest constraints on the HSE composition of the BSE, and the suprachondritic nature of Ru/Ir in the BSE appears in little doubt. Further, the similarity of HSE characteristics of large numbers of variably "fertile" mantle peridotites, ranging from abyssal peridotites, to peridotites from the mantle sections of ophiolites, to oceanic mantle xenoliths, supports the contention that the BSE is characterised by suprachondritic Ru/Ir, and possibly Pd/Ir (Becker *et al.*, 2006; Fischer-Gödde *et al.*, 2011). However, compilation of an even larger number of data from all types of mantle lithologies, combined with an improved understanding of how HSE from oceanic crust have been recycled back into the oceanic mantle, will ultimately be required to assemble a high-confidence understanding of HSE in the BSE.

The bottom line regarding HSE in the BSE is that they are in approximately, but not necessarily exactly, chondritic relative abundances. Further, the absolute abundances of HSE in the BSE are only about 200 times lower than average chondritic. How can we explain this? Much has been written about the ultimate origin of HSE in the terrestrial mantle. Most models invoke one of two or three scenarios that are not mutually exclusive. These scenarios were reviewed by Jones and Drake (1986), and, although we have considerably more data today, the strengths and weaknesses of each of the options haven't changed much since then. As noted above, it has long been known that the siderophile natures of at least some siderophile elements become greatly reduced at elevated temperatures and pressures. Thus, one option is that the abundances of the HSE in Earth's mantle were established under conditions at which they were all less strongly siderophile, just as has been argued for the MSE. A second option is that core segregation was incomplete and that a small portion of the metal destined for the core became trapped in the mantle, and subsequently oxidised. This is sometimes referred to as incomplete core segregation model. Finally, it is possible that the Earth continued to accrete moderate sized bits of mass subsequent to cessation of core formation. Any delivery of material with bulk chondritic abundances of HSE to the silicate Earth would tend to partially replenish HSE that had been stripped by prior core formation. This process would also be expected to impart chondritic relative abundances of the HSE to the mantle, and has been termed by some to be a "*late veneer*" (Kimura *et al.*, 1974; Chou, 1978; Morgan *et al.*, 2001). I prefer the term *late accretion* for reasons discussed below. If all of late accreted matter contained bulk chondritic abundances of HSE, in the form of differentiated or undifferentiated planetesimals, and all of it remained in the silicate Earth following accretion, a mass equivalent to approximately 0.5 wt. % of the total Earth would be required to account for the HSE present in the BSE.

So, if high temperature and pressure partitioning of MSE works to explain their abundances in the mantle, why shouldn't this work for HSE? Although the jury remains out on whether or not this can ultimately account for HSE abundances in the BSE, in my view, the accumulated evidence does not favour this scenario. On the plus side, a number of studies have shown that the siderophilic nature of some HSE, as with MSE, can be reduced sufficiently under some conditions to meet the requirements for metal-silicate equilibration (Righter *et al.*, 1997; Walter *et al.*, 2000; Cottrell and Walker, 2006; Mann *et al.*, 2012; Brenan *et al.*, 2016). Explaining the HSE by this process, however, requires that it account for the abundances of all of the HSE, not just one or two. More importantly, it must account for their nearly chondritic relative abundances. This is important because it means the partition coeffieicents for all of these elements would have to change by exactly the same factor over 3 or 4 orders of magnitude. The few experimental studies that have simultaneously examined multiple HSE in metal-silicate partitioning studies at different pressures and temperatures do not appear to explain well the high absolute and generally chondritic relative abundances of all HSE in the mantle (*e.g.*, Holzheid *et al.*, 2000; Brenan and McDonough, 2009; Mann *et al.*, 2012).

The cautionary note that must be injected into this discussion is that experiments relevant to this issue are devilishly difficult to conduct and interpret. The chief problem is that most of the HSE tend to form tiny nuggets that reside in the silicate portions of the metal-silicate experimental run products. This has resulted in debate about whether or not the nuggets form as part of the quench process from the silicate liquid. If not, they may be bits of metal derived from the main mass of metal, floating in the silicate. In the former case, the HSE should be counted as part of the silicate, leading to lower calculated $D^{metal/silicate}$ values. In the latter case, the nuggets do not belong to the silicate portion of the run charge, and the HSE present in the nuggets should not be counted as part of the silicate budget. In this case, if the nuggets are avoided in analysis, much higher D values result. Various studies have addressed this problem in different ways, and come to different conclusions (Cottrell and Walker, 2006; Brenan and McDonough, 2009; Médard *et al.*, 2015).

Thus far, it has been impossible simultaneously and precisely to assess the metal-silicate partitioning characteristics of the two most relevant HSE to this issue, Re and Os. These are the key elements because, as noted above, we have a very strong constraint on the Re/Os of the BSE as determined from $^{187}Os/^{188}Os$. For high temperature and pressure partitioning to be accepted as the process that established HSE abundances in the mantle, it will have to be experimentally shown that some set of conditions exist where the D values for these two elements converge to be almost exactly the same, such that the BSE retains a chondritic $^{187}Os/^{188}Os$ ratio after more than 4 Ga of growth. Given that in non-metal systems, Re and Os partition very differently, this will be a tall order to fill. A limited number of experiments suggest that metal-silicate partitioning cannot account for both HSE abundances and chondritic Re/Os in the mantle (Bennett and Brenan, 2013). If high temperature and pressure partitioning can ultimately be shown to be the primary origin of the HSE in the BSE, then it means that nature worked really hard to confuse us on this issue, by generating a chondritic Os isotopic composition through a happenstance process. As noted above, happenstance also must be argued for Pt/Os, due to the chondritic ^{186}Os/^{188}Os of the mantle.

The idea of incomplete core segregation also sounds like it could be a winner; just leave some metal behind in the mantle during planetary differentiation. This metal will eventually get oxidised so that the contained HSE can be evenly mixed throughout the mantle. The flaw with this hypothesis, as noted by Jones and Drake (1986), is that crystallisation of metal, and drainage of the residual, probably S-rich liquid metal to the core would likely result in the residual metal having fractionated HSE. The fractionations expected would mimic the fractionations discussed above that are relevant to iron meteorite systems. This can be observed in the fractionated HSE patterns present in primitive achondrites, such as brachinites and brachinite-like achondrites (*e.g.*, Day *et al.*, 2012). In these instances, although the overall composition of the meteorite is broadly chondritic, some amount of FeS has evidently been removed from the system, leaving fractionated HSE abundances in the resulting residue. If, on the other hand, one envisions that metal from impactors is not processed by crystal-liquid fractionation, then this metal will allow retention of chondritic relative abundances of HSE. However, every major planetary melting event during the giant impact stage of growth of the Earth, would likely have led to drainage of the stored metal to the core. Thus, residual metal present in the mantle would be dominated by metal added during the later stages of planetary accretion. At this point, the incomplete core segregation hypothesis merges with the late accretion hypothesis.

The late accretion hypothesis has two major factors in its favour. First, it predicts the imposition of chondritic relative abundances of HSE onto the mantle. As we have seen, this is close to being true, and is certainly consistent with the chondritic ^{187}Os/^{188}Os (and ^{186}Os/^{188}Os) projected for the BSE (Morgan, 1986; Walker *et al.*, 1997; Brandon *et al.*, 2000a; Meisel *et al.*, 2001). These ratios require precisely chondritic Re/Os (and Pt/Os), over the 4.5 Ga history of the Earth, albeit at the upper range of chondrites (Fig. 4.3). Second, I'll present evidence below that the Moon formed by a giant impact, and that this event was a clearinghouse event for HSE in the Earth's mantle. This means that soon after the impact, the mantles of the nascent Moon and the newly reconstituted mantle of the Earth were highly depleted in HSE. Models for planetary dynamics normally have modest accretion to the Earth and Moon continuing beyond the time of the giant impact (*e.g.*, Marchi *et al.*, 2014). Thus, there is no way to avoid some degree of late accretion, witness the basins and craters on the Moon.

As with the MSE and magma ocean hypothesis, some issues remain with the late accretion hypothesis. As we have seen, current estimates of HSE abundances in the BSE suggest modest enrichments in Ru/Ir, and possibly Pd/Ir, above chondritic values (*e.g.*, Pattou *et al.*, 1996; Schmidt *et al.*, 2000; Becker *et al.*, 2006; Fischer-Gödde *et al.*, 2010), yet the delivery of HSE with chondritic relative abundances to the mantle is a major prediction of the late accretion hypothesis.

This is a good place to remind the reader that it is extremely unlikely that our meteorite collections sample all chemical and isotopic variants of primitive objects that existed in the early solar system. Thus, it is possible that some primitive materials which existed at that time, or that may even exist today but have not been sampled, match the HSE characteristics of the BSE estimate. Indeed, the Ru/Ir and Pd/Ir of some lunar impact melt rocks appear to record the HSE signatures of impactors with HSE ratios somewhat outside of the range of ratios observed in bulk chondrites currently falling to Earth (*e.g.*, Fischer-Gödde and Becker, 2012; Liu *et al.*, 2015).

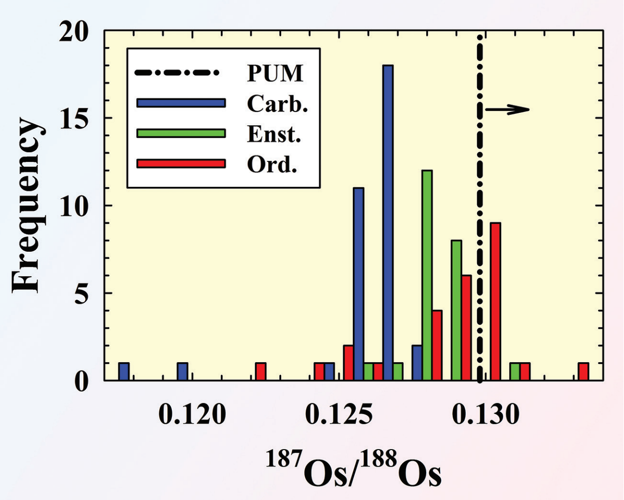


Figure 4.3 Histogram plot of ^{187}Os/^{188}Os data for bulk chondrites compared to the minimum BSE value estimated by Meisel *et al*. (2001). The arrow implies the true BSE may be 1-2 % higher than shown. Chondrite data are from Walker *et al*. (2002a), Brandon *et al*. (2005) and Fischer-Gödde *et al*. (2010).

A second issue with late accretion is the mismatch in estimated mantle abundances between the Earth and Moon (see below). The Earth appears to have a much higher fraction of HSE incorporated in its mantle than in the lunar mantle. Despite the effects of gravitational focusing and impactor retention (*e.g.*, Morgan *et al*., 2001), the magnitude of the mismatch of late accretionary additions is, on first blush, unexpected. Finally, there is the issue of timing. As we will see, the dominant stage of late accretion is most propitious for the hypothesis if it occurs soon (0-20 Ma) after formation of the Moon. If later, then the thick permanent lunar crust would likely have prevented late accreted materials from reaching the lunar mantle. There is, however, no strong theoretical basis for a surge in a late accretionary flux in this seemingly random period of solar system evolution. There is also no evidence for a large proportion of HSE trapped in the lunar crust.

Is it possible that the MSE abundances present in the mantle were primarily established by magma ocean processes and HSE abundances were established by late accretion? At this time there is no prohibition against this. Appealing to a mixed model for origin of the MSE and HSE, however, is accompanied by some potential pitfalls. Although $D^{metal/silicate}$ values for some HSE, such as Ir, do not sufficiently decrease to values necessary to account for mantle abundances, even at very high pressures and temperatures (Mann *et al*., 2012), the $D^{metal/silicate}$ values of some other HSE, such as Pt and Pd evidently decrease to values that when combined with late accretion could result in excess abundances of these elements in the mantle, and lead to some non-chondritic HSE ratios following late accretion (Cottrell and Walker, 2006; Mann *et al*., 2012). This may be consistent with the apparent, slightly suprachondritic Pd/Ir of the BSE. Current partitioning data at highest pressures and temperatures, however, appear to be inconsistent with the slightly suprachondritic Ru/Ir, and chondritic Pt/Ir estimates for the BSE.

4.2 Origin of Siderophile Elements in the Moon and Mars, and Some Lesser Bodies

The Moon and Mars and the parent bodies of the angrite and diogenite meteorites present some major challenges when it comes to understanding their siderophile element budgets. Angrites and diogenites for non-meteoriticists are mafic and ultramafic rocks derived from at least two differentiated parent bodies. Both of the larger planetary bodies have jealously guarded the secrets of their mantles. As far as we know, we have no macroscopic samples of mantle materials from either the Moon or Mars, although there has been occasional discussion that some tiny inclusions in lunar rocks and regolith may constitute bits of lunar mantle (*e.g.*, Ryder *et al*., 1997). Consequently, unlike for Earth, we have no direct measurements of siderophile elements for the most volumetrically significant portions of these bodies. The angrites are basaltic and, therefore, represent derivative melts from the mantle of their parent body. Although diogenites are mainly ultramafic rocks, and it has been proposed that some of them may represent pieces of the mantle of the asteroid Vesta (Warren *et al*., 2009b), other studies have interpreted their compositions as crustal cumulates from mafic magmas (*e.g.*, Barrat *et al*., 2010). Collectively, the paucity or absence of mantle materials from all of these bodies means we must constrain siderophile element abundances using somewhat more convoluted means than we used to estimate concentrations in the BSE. The focus here will be mainly on the HSE.

Given that we mainly have only mafic and ultramafic rocks from the crusts of these bodies to work with, the most common way to estimate mantle abundances of siderophile elements has been to compare concentrations of the elements of interest in extraterrestrial igneous rocks with terrestrial rocks showing similar extents of petrologic evolution (*e.g.*, Warren, 2004). In order for this comparison to be meaningful, the siderophile elements must behave in a manner similar to how they behave on the Earth during partial melting processes.

4.2.1 The Moon

Before considering the origin of the siderophile elements in the lunar mantle, we must first settle on the concentrations of siderophile elements in the mafic rocks and picritic glasses returned from the surface. This has proven challenging from both the analytical and interpretive points of view. For the HSE, perhaps the most important materials to characterise are Apollo 15 green, and Apollo 17 orange picritic glass spherules. These relatively high MgO glasses (15-17 wt. %) originated from deep mantle sources and were deposited on the surface through fire fountaining, between 3.4 to 3.5 Ga ago (Podosek and Huneke, 1973; Shearer and Papike, 1993). When the tiny spherules fell to the surface they formed glass rich layers, becoming a part of the regolith. Because they are more primitive than the more common, crystalline lunar basalts, they are the lunar materials with HSE abundances that may most closely resemble abundances in the lunar mantle. However, deciphering data for the picritic glasses is complicated. Initial studies of glass spherules by neutron activation reported relatively high concentrations of HSE in bulk samples, broadly comparable to what might be found in similarly primitive terrestrial picrites (Ganapathy *et al.*, 1973; Morgan and Wandless, 1979, 1984). It was also found that the abundances of a number of elements, including the HSE Au and Ir, were correlated with the surface area to volume ratios of sieved size fractions of the spherules (Chou *et al.*, 1975; Krähenbühl, 1980). The finer fractions had higher concentrations of these elements. This led to the conclusion that some elements are concentrated on the surfaces of the spherules as coatings or micrometeoritic contaminants. Some of the more volatile elements, characterised by such correlations, evidently condensed onto the surfaces of the spherules during the fire fountaining process by which they were erupted. Other elements, such as Au and Ir, were likely added to the regolith by micrometeorite bombardment. This means that the apparent bulk abundances may not well represent the compositions of the original melts from which the spherules quenched.

Knowing of all these complexities, in 2004 we nevertheless set off to measure ^{187}Os/^{188}Os and HSE abundances in bulk samples of the green and orange glasses, as well as in lunar dunite 72415, a cumulate from a mafic melt. What we found is that much of the budget of HSE in sieved but unground fractions of the spherules could be removed by aggressive leaching using *aqua regia* (Walker *et al.*, 2004). The powdered glass beads, following the leaching step, were characterised by very low and moderately-fractionated abundances of HSE, characterised by radiogenic ^{187}Os/^{188}Os of ≥0.2. Rhenium was so low in comparison to our chemical blank, that we were unable to measure it in most samples. We concluded that the radiogenic Os in the leached samples likely reflected suprachondritic Re/Os in the spherules, and the effects of radiogenic ingrowth following eruption. To complement the work on the glass beads, we found that the concentrations of HSE in the dunite 72415 were also very low and fractionated.

Of all the HSE, Pt is commonly the least fractionated between the mantle and crust on Earth. Thus, it may be the best candidate HSE with which to compare abundances in the lunar and terrestrial mantles, while only crustal rocks are available from the Moon. Our data for the lunar picritic glasses and the dunite, plot well below typical concentrations for terrestrial rocks with comparable MgO (Fig. 4.4). We interpreted the concentration data to mean that the mantle sources of the parental melts were strongly depleted in HSE, compared to the terrestrial mantle. Overall, we estimated the concentrations of the HSE in the lunar mantle to be at least 20 times lower than in the terrestrial mantle (<0.0004 x CI chondrites). This raised an important question. If the HSE were added to the lunar mantle by late accretion, as claimed above for the Earth's mantle, why were the abundances proportionally so much lower than in the terrestrial mantle?

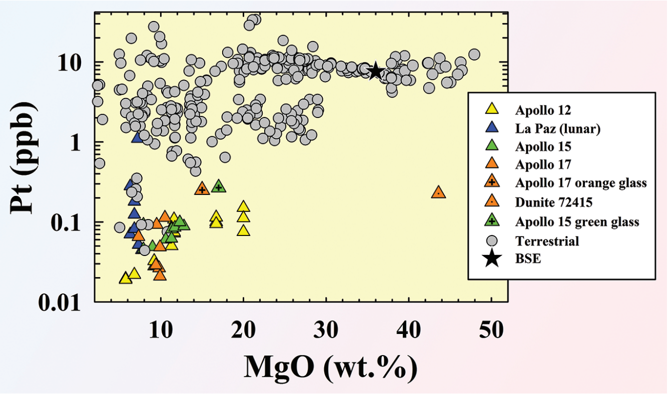


Figure 4.4 Plot of MgO *versus* Pt concentrations for lunar basalts, picritic glasses and dunite 72415. Data for terrestrial rocks and the BSE are shown for comparison. Note that the lunar samples are strongly offset to lower concentrations for a given MgO, compared with most terrestrial samples. Lunar data are from Walker *et al*. (1994), Day *et al*. (2007) and Day and Walker (2015). BSE Pt and MgO are from Becker *et al*. (2006) and McDonough and Sun (1995), respectively. Data for terrestrial rocks are from Woodland *et al*. (2002), Puchtel and Humayun (2005), Puchtel *et al*. (2005, 2007, 2009), Ireland *et al*. (2009b), Day *et al*. (2010b, 2016) and Day (2013).

The next obvious thing to do was to measure HSE in lunar basalts. Numerous prior studies analysed elements such as Ir, Re, Os and Au in lunar basalts (*e.g.*, Anders *et al*., 1971; Ganapathy *et al*., 1974; Wolf *et al*., 1979; Birck and Allègre, 1994) and all reported concentrations at the low ppt level. As a student at Durham University, *James Day*, working with *Graham Pearson* and *Larry Taylor*, measured ^{187}Os/^{188}Os and all HSE that can be determined by isotope dilution in La Paz 02226, a lunar basaltic meteorite, as well as some Apollo 15 and 17 basalts. As with the glass spherules, Day *et al*. (2007) found very low concentrations for all of the HSE measured, and as with the glasses and the dunite, have Pt concentrations that are very low in comparison to most terrestrial rocks with comparable MgO (Fig. 4.4). That study came to a similar conclusion to that reached by Walker *et al*. (2004), that the lunar mantle is highly depleted in HSE compared to the BSE.

If the HSE behave similarly on the Earth and Moon, then their low abundances in lunar basalts and picritic glasses must almost certainly mean the mantle sources of these materials are severely depleted in HSE, compared to the Earth's mantle. Consistent with these findings, Day *et al*. (2007) also projected the trends formed by plots of individual HSE *versus* MgO to an assumed fertile mantle MgO composition for the Moon, in a similar manner to the approach taken to estimate the BSE concentrations of HSE. From this they concluded that, not only does the lunar mantle have HSE abundances of ~0.0002 × C1 chondrite, but that the inferred chondrite normalised HSE pattern for the lunar mantle is broadly similar to that of the BSE. After *James* began to work with me at UMd in 2008, he also analysed HSE abundances in pristine lunar crustal highland rocks (Day *et al*., 2010a), and more recently, in Apollo 12 basalts (Day and Walker, 2015). Apollo 12 basalts are similarly depleted compared with the Apollo 15 and 17 basalts (Fig. 4.4), but extend to higher MgO. Consequently, they provide a more robust comparison to terrestrial rocks. Although the data for the highland rocks are much more difficult to extrapolate to HSE abundances in the mantle, the conclusion was the same, that the lunar magma ocean at the time of crust flotation was much more strongly depleted in HSE than the BSE (Day *et al*., 2010a).

This is a seemingly self-consistent story, and perhaps I should stop here. But there are some additional issues with these interpretations that need to be mentioned. Perhaps the most critical unknown in the reasoning presented above is whether or not the HSE behaved the same way during mantle melting of both the lunar and terrestrial mantles. The answer to this question remains uncertain. At this point, none of us would bet our lives that our interpretations are correct. One of the complexities is the possible presence of metal in the lunar mantle. It is more reduced than the terrestrial mantle, and metal is present in some lunar igneous rocks. Thus, the issue of whether or not metal is a residual phase in the mantle following melting to form lunar basalts, has long been debated. This issue is very important for understanding the HSE budget of the Moon. If there was residual metal following partial melting of the mantle to form the basaltic and picritic melts, then the metal would strongly retain HSE in the lunar mantle. In this case, all HSE would be extremely compatible with the mantle residue, much more so than for terrestrial mantle melting scenarios. Consequently, the very low HSE abundances in the lunar basalts and picritic glasses could mean that the abundances of HSE in the mantle are much higher than estimated by either Walker *et al*. (2004) or Day *et al*. (2007). Abundances could be even higher than in the terrestrial mantle!

Despite the cautionary note, there are three hints in the siderophile element data for the Moon that there was no metal in the mantle residues of at least some lunar basalt sources, and that mantle-basaltic melt partitioning of most HSE was similar for terrestrial and lunar systems. First, ignoring Re, some CI normalised HSE patterns for lunar basalts look strikingly similar to terrestrial basalts, albeit with lower HSE abundances. For example, CI chondrite normalised HSE patterns for both the La Paz lunar basalt 02226,13 (Day *et al*., 2007) and basalt KS-624 from the Parana flood basalts, Brazil (Rocha-Júnior *et al*., 2012) are very similar in terms of relative abundances of HSE (Fig. 4.5a). [Note that for normalised HSE plots for rocks produced as a result of planetary mantle melting and subsequent crystal-liquid fraction processes, I plot the elements from left to right in the order of increasing incompatibility, as observed for terrestrial systems (*e.g.*, Barnes *et al*., 1985; Pearson *et al*., 2004)]. The similarities in pattern shape make a convincing argument that the HSE pattern shapes of the terrestrial and lunar mantles are broadly similar, and therefore, that HSE partitioning between mantle and basaltic melt, in at least some melting scenarios of both bodies are roughly equivalent. Osmium, Ir and Ru are evidently strongly compatible on both bodies, and Pt and Pd may bracket compatibility-incompatibility. However, there are also lunar basalts with patterns that don't look as much like terrestrial analogues (Fig. 4.5b). Regardless of pattern shapes, lunar basalts, on average, plot systematically lower than terrestrial basalts by more than a factor of 20. What about Re? Unlike in terrestrial basalts, Re appears to behave compatibly with respect to mantle melting and lunar basalt production. This has previously been attributed to the more reduced nature of the lunar mantle compared to the terrestrial mantle (Birck and Allègre, 1994).

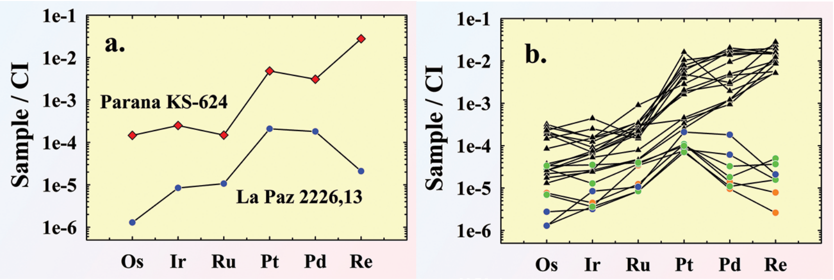


Figure 4.5 **(a)** CI chondrite normalised HSE data for the lunar basalt La Paz 02225,13 (Day *et al*., 2007) compared with data for Parana basalt KS624 from Brazil (Rocha-Júnior *et al*., 2012). With the exception of Re, the patterns for these two basalts are quite similar for such low HSE abundance rocks, suggesting similar partitioning of HSE between mantle and basaltic melt for both the Earth and Moon. **(b)** Data for additional lunar (coloured symbols) and terrestrial basalts (black symbols) show both similarities and differences. Lunar basalts plot systematically lower than terrestrial basalts by more than a factor of 20. Green, orange and blue symbols are from Apollo 15 and 17 landing sites, and the La Paz meteorites, respectively. Lunar basalt data are from Day *et al*. (2007). Terrestrial basalt data are from Rocha-Júnior *et al*. (2012).

Second, in Day and Walker (2015) we studied a suite of Apollo 12 basalts with MgO ranging from 5.8 to 20 wt. %. As part of this study directed primarily at HSE, the rocks were also analysed for other siderophile elements, as well as some lithophile trace elements. With one exception, the data show a strong linear correlation between the MSE W and the strongly incompatible lithophile trace elements U and Th (Fig. 4.6a). As noted above, in Earth's mantle, W is similarly incompatible to U and Th (Arevalo and McDonough, 2008; König *et al*., 2011).

If the production of Apollo 12 lunar basalts involved variable degrees of partial melting of the lunar mantle, as seems likely from major element compositions, the linearity of the trend suggests that metal was not present in the source of these basalts. This is because residual metal would have strongly retained W in the mantle, while U and Th would have behaved strongly incompatibly, regardless of the presence or absence of metal. Thus, it is difficult to envision a scenario in which metal was present in the residue, yet W remained strongly correlated with U and Th. Nevertheless, the number of data is limited, the slope is not 1:1 (which may indicate that W is less highly incompatible than U in the mantle sources of these rocks), and one sample (12022) does not fit the trend. Acquiring similar data for additional lunar basalts is clearly needed to confirm or reject this inference.

Third, Day and Walker (2015) also showed that the highest MgO Apollo 12 lunar basalts have HSE in nearly chondritic relative abundances, as is seen in some high-MgO terrestrial komatiites (Fig. 4.6b). Again, this is a very unlikely outcome if metal were present in the mantle residue, as strong fractionations among the HSE would likely be present in the newly generated melt (*e.g.*, Mann *et al.*, 2012).

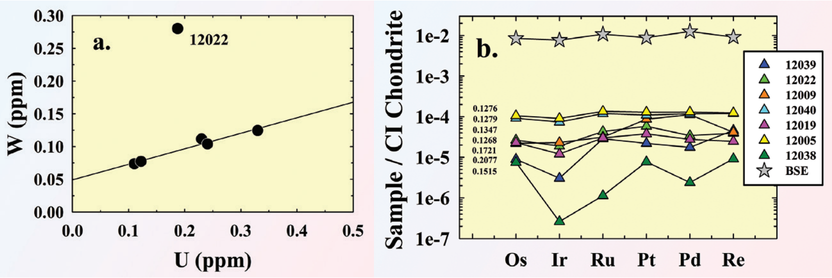


Figure 4.6 **(a)** Plot of U *versus* W concentrations for seven Apollo 12 basalts. Six of the seven basalts form a linear trend, the regression of which is shown as the solid line. Basalt 12022 has much higher W relative to U (or Th), compared with the other basalts. **(b)** CI chondrite normalised HSE patterns for the same Apollo 12 basalts. Present day $^{187}Os/^{188}Os$ is shown to the left of the patterns in the order from top to bottom of decreasing Os concentrations. Note the two highest Os (and MgO) samples, 12005 and 12040 are characterised by relatively flat patterns and chondritic $^{187}Os/^{188}Os$. Apollo data for both plots are from Day and Walker (2015). BSE values are from Becker *et al.* (2006).

In summary, although data remain limited, most of the evidence currently suggests a lunar mantle with strong depletions in HSE, and approximately chondritic relative abundances. Some recent studies have sought to constrain siderophile element abundances in the lunar magma ocean by determining distribution coefficients that are relevant to reverse modelling the abundances present in presumed products of magma ocean crystallisation, in particular anorthositic crust (*e.g.*, Sharp *et al.*, 2015). However, many questions remain and much further work will be required to advance this issue sufficiently. For example, is the lunar mantle relatively homogeneous with regard to HSE, or did lunar magma ocean processes, or late accretionary additions result in a compositionally heterogeneous mantle with respect to HSE? Needless to say, it would be *very* informative if we could one day obtain some *bona fide* samples of the lunar mantle to analyse for HSE. Prime candidates for sampling lunar mantle include olivine-rich surfaces (Yamamoto *et al.*, 2010). If you find this issue interesting, you should be supportive of future sample return missions to the Moon.

4.2.2 Mars

The evidence regarding HSE in the mantle of Mars comes entirely from the analysis of shergottite, nakhlite and chassignite (SNC) meteorites. Based on a number of observations, including age and similarities between the compositions of gases extracted from SNC meteorites and the atmosphere of Mars, measured *in situ* by Viking landers, most accept that this suite of meteorites comes from Mars (McSween, 2003). If so, by considering data for SNC meteorites the case can be made that we know more about HSE abundances in the mantle of Mars than we do for the Moon. This is because some shergottites have highly Mg-rich compositions, and are likely quite young, compared to lunar basalts. This means their Os isotopic compositions can, in some cases, be used to precisely assess the long-term Re/Os ratio of the mantle source.

Most early studies that examined the HSE abundances in SNC meteorites reported highly variable concentrations (Birck and Allègre, 1994; Warren and Kallemeyn, 1996; Kong *et al.*, 1999). Adding to the mix, I hired *Al Brandon* as a postdoc in 1996 and encouraged him to broaden his already thick research portfolio by doing some cosmochemical research, in addition to continuing his work on terrestrial mantle and volcanic mantle rocks (more on that later). One of the types of materials we agreed he should work on was the SNC meteorite suite. The first stage of this work resulted in our publishing ^{187}Re-^{187}Os isotopic data for several shergottites and nakhlites, as well as the Chassigny meteorite (Brandon *et al.*, 2000b). Collectively, these papers showed that HSE abundances in SNC meteorites are typically negatively correlated with degree of magmatic evolution, just as with terrestrial igneous rocks. High MgO ultramafic rocks have the highest HSE abundances, whereas the most highly-evolved basalts with lowest MgO also have the lowest abundances of typically compatible HSE, such as Os and Ir. More recent papers by Riches *et al*. (2011), Brandon *et al*. (2012), Dale *et al*. (2012) and Yang *et al*. (2015) confirm the earlier results with many additional HSE data (Fig. 4.7). Most of these studies have also reported accompanying ^{187}Os/^{188}Os data.

Several of the characteristics of the HSE in shergottites are reminiscent of terrestrial basalts. The range of absolute abundances and variations in pattern shape corresponding to variations in MgO are similar to terrestrial rocks (Fig. 4.7, 4.8a,b). For example, Pt/Ir ratios regularly increase with decreasing MgO. Probably the strongest constraint on HSE concentrations in the martian mantle comes from the ultramafic shergottites. Most prior studies of these high MgO rocks have concluded that they are cumulate rocks from mafic lavas (McSween, 2003). Nevertheless, terrestrial ultramafic rocks formed by similar cumulate processes, have HSE concentrations that broadly mimic mantle abundances (*e.g.*, O'Driscoll *et al.*, 2009). The high MgO shergottites, such as LEW 88516, are characterised by moderately fractionated chondrite-normalised HSE patterns that have average HSE concentrations that are similar to the estimate for BSE (Fig. 4.8b). Collectively, these observations led Brandon *et al.* (2012) to conclude that the HSE abundances in the martian mantle are within a factor of 2 of terrestrial mantle abundances. Using a different set of data, Yang *et al.* (2015) came to a similar conclusion.

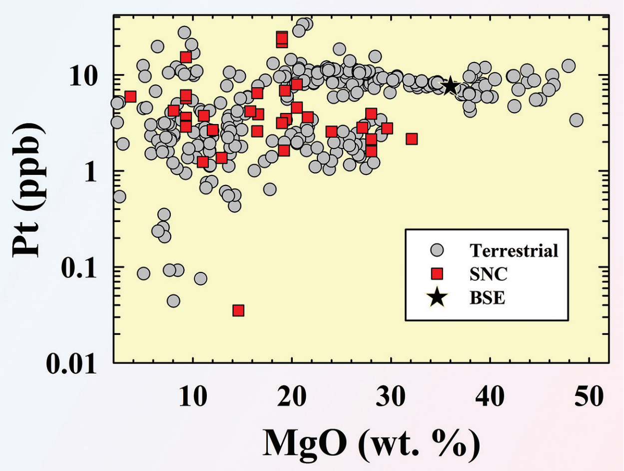


Figure 4.7 Plot of MgO *versus* Pt concentrations for martian SNC meteorites. Data for terrestrial rocks and the BSE are shown for comparison. Note that, unlike the lunar samples (Fig. 4.4), the Pt abundances of martian samples overlap with terrestrial average abundances, suggesting similar HSE abundances in the martian and terrestrial mantles. SNC data are from Riches *et al.* (2011), Brandon *et al.* (2012) and Dale *et al.* (2012). BSE Pt and MgO are from Becker *et al.* (2006) and McDonough and Sun (1995), respectively. Data for terrestrial rocks are from Woodland *et al.* (2002), Puchtel and Humayun (2005), Puchtel *et al.* (2005, 2007, 2009), Ireland *et al.* (2009b), Day *et al.* (2010b, 2016) and Day (2013).

In Brandon *et al.* (2012) we also concluded that the HSE occur in approximately chondritic relative abundances. This latter point is most strongly made by considering the initial γ_{Os} values of relatively young shergottites. Remember that γ_{Os} is the percent deviation in the calculated initial $^{187}Os/^{188}Os$ ratio of a rock, compared to a chondritic reference; Table 2.3). All of the ultramafic shergottites plot well within the range of chondritic meteorites (Fig. 4.8c). Some of the basaltic (and olivine phyric) shergottites also plot within the range of chondritic meteorites, although some extend to γ_{Os} values that plot significantly above the chondritic range (Fig. 4.8c).

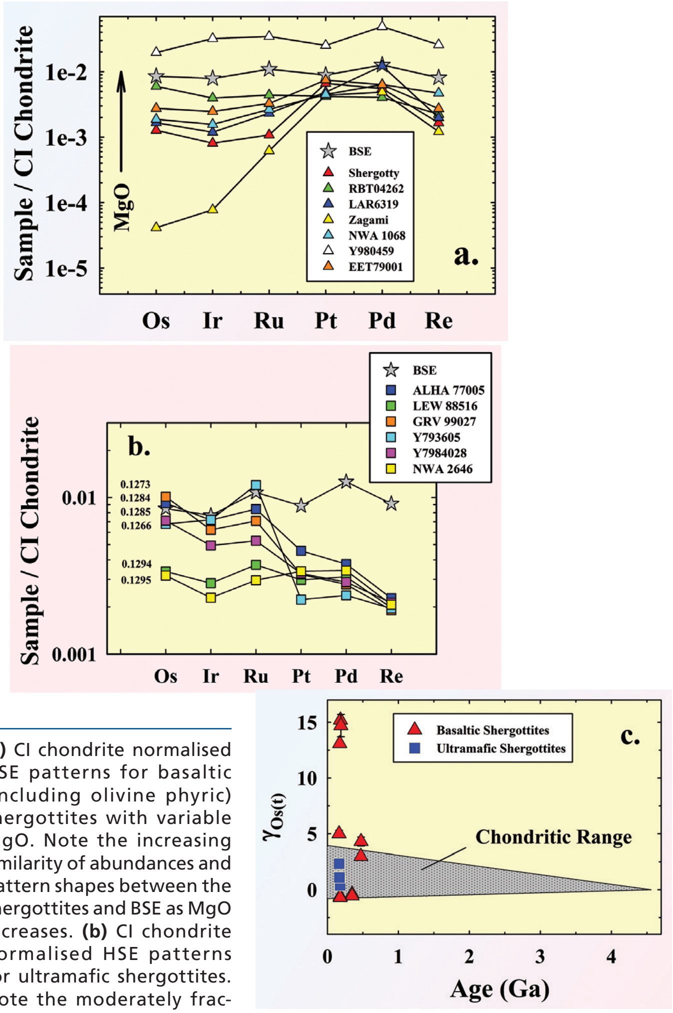


Figure 4.8 **(a)** CI chondrite normalised HSE patterns for basaltic (including olivine phyric) shergottites with variable MgO. Note the increasing similarity of abundances and pattern shapes between the shergottites and BSE as MgO increases. **(b)** CI chondrite normalised HSE patterns for ultramafic shergottites. Note the moderately fractionated nature of the shergottite patterns compared to BSE. Present day $^{187}Os/^{188}Os$ are shown to the left of the patterns in order of increasing Os upward. All are within the range of projected evolutionary trajectories of 95 % of chondrites (grey field). **(c)** Calculated initial γ_{Os} values for basaltic and ultramafic shergottites. Data are from Riches *et al*. (2011), Dale *et al*. (2012) and Brandon *et al*. (2012). BSE values are from Becker *et al*. (2006).

It has long been known that, if ages determined by Rb-Sr and Sm-Nd isochrons are magmatic crystallisation ages, there is a correlation between initial $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios among shergottite meteorites (*e.g.*, Borg *et al.*, 2002). Shergottites with low ε^{143}Nd values (to as low as ~-7), termed *enriched shergottites*, are typically characterised by comparatively higher initial ^{87}Sr/^{86}Sr, and *vice versa*. Conversely, *depleted shergotiites* have ε^{143}Nd values that range to as high as ~+40, and generally low initial ^{87}Sr/^{86}Sr. The correlated variations in Nd and Sr isotopic compositions may result from either a primordial mantle differentiation event, or the more recent assimilation of ancient martian crust (*e.g.*, Borg *et al.*, 1997, 2003). The ^{143}Nd and Sr isotopic compositions for the mantle sources of the shergottites also broadly correlate with the short-lived ^{182}W and ^{142}Nd isotopic compositions (Foley *et al.*, 2005; Debaille *et al.*, 2008), which is more consistent with an ancient differentiation event. In Brandon *et al.* (2012) we also noted a strong correlation between initial γ_{Os} and ε^{143}Nd values for shergottites (where γ and ε notations are the percent, and parts per 10,000 deviations, respectively, in the Os or Nd isotopic compositions of a sample at the time of formation, relative to a chondritic reference; Table 2.3). Given the <500 Ma ages of these rocks, coupled with their broadly chondritic Sm/Nd and Re/Os ratios, means that the differences in age have little impact on calculated initial ε_{Nd} and γ_{Os} values. The depleted shergottites, showing evidence of long-term melt depletion in their Nd isotopic compositions, as well as those with intermediate Nd isotopic compositions (ε values of +8 to +17), are characterised by generally chondritic γ_{Os} values ranging modestly from -1 to +5 (Fig. 4.9). By contrast, enriched shergottites with ε_{Nd} values <0, evidence of long term melt enrichment, are characterised by higher initial γ_{Os} values of +5 to +15. Our mixing calculations utilising Os isotopes suggested that the broadly correlated Nd-Os isotopic variations are present in the martian mantle, not a result of mixing of mantle materials with crust (Brandon *et al.*, 2012). A ^{142}Nd-^{143}Nd isochron that includes both enriched and depleted shergottites suggests a large scale fractionation event, perhaps in the form of magma ocean crystallisation that occurred at 4.535 Ga (Debaille *et al.*, 2008). Thus, it is possible that Mars underwent a fundamental, early differentiation event that led to the formation of chemically enriched and depleted domains, that also led to a modest fractionation of the HSE.

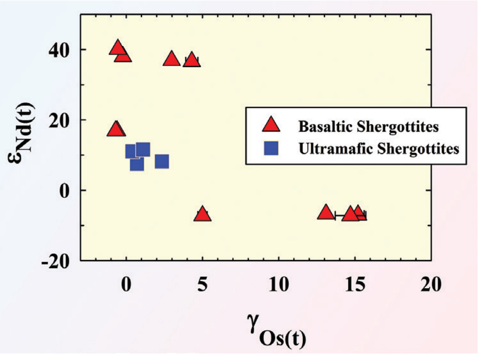


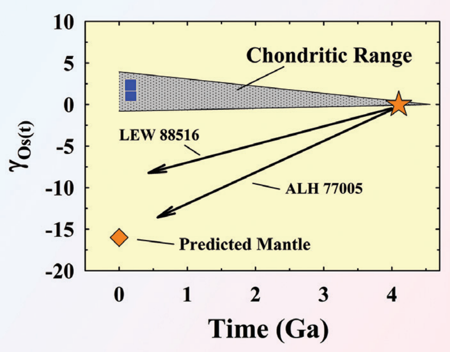
Figure 4.9 Plot of γ_{Os}(t) *versus* ε_{Nd}(t) for basaltic (including olivine phyric) and ultramafic shergottite meteorites. Data are from Riches *et al.* (2011) and Brandon *et al.* (2012).

I haven't mentioned nakhlites or chassignites much yet. There are very few HSE data coupled with Os isotopic compositions for these chemically distinct types of martian meteorites. Brandon *et al*. (2000a) and Dale *et al*. (2012) reported data for the meteorites Nakhla and Chassigny. Both studies found broadly chondritic initial ^{187}Os/^{188}Os ratios for them. ^{182}W isotopic data suggest that these rocks may come from a fundamentally different mantle domain from the shergottites (Foley *et al*., 2005), so these meteorites need additional study with regard to siderophile elements.

Before leaving the subject of martian meteorites, I note that there has been some longstanding debate about the true age of shergottites. Most prior studies have utilised Sm-Nd and Rb-Sr isochrons generated from carefully selected mineral separates of individual meteorites to determine ages between 165 Ma and 4.1 Ga (*e.g.*, Borg *et al*., 2002, 2003). A majority of the shergottites have isochron ages <500 Ma. There is always some ambiguity in the meaning of these ages as they require the authors to include data from "good" phases and reject data from "bad" phases that are presumed not to represent a closed system since crystallisation. Some studies utilising Pb isotopes, however, have argued that the Sm-Nd and Rb-Sr isotopic systematics of shergottites have been reset, and that the true ages of crystallisation, based on Pb-Pb isochrons are approximately 4.1 Ga (*e.g.*, Bouvier *et al*., 2009). Everyone agrees that martian meteorites are geochemically complex, so both sides in the age debate have made some good points. Osmium isotopes provide an alternate perspective to the lithophile geochronologic systems. First, the one Re-Os isochron generated for a shergottite (EETA 79001) gives the same age (164 ± 12 Ma) as the lithophile Sm-Nd and Rb-Sr radiogenic isotope systems (Brandon *et al*., 2012). It can be argued, however, that this system was reset by impact in the same way as the lithophile systems. More convincing for comparatively young ages are the Os isotopic data, coupled with HSE concentration data, for the ultramafic shergottites. This is because, despite the fact that these rocks have moderately fractionated HSE abundances relative to chondrites (Fig. 4.8b), they all have similar, present day chondritic ^{187}Os/^{188}Os. This is true despite the fact that most of the ultramafic rocks have subchondritic Re/Os. If these meteorites formed as igneous rocks at 4.1 Ga, when the martian mantle was likely considerably less radiogenic than modern chondrites, how did they ultimately end up with precisely chondritic ^{187}Os/^{188}Os today (Fig. 4.10)?

It could be argued that they were contaminated with chondritic impactors, but if so, why do they retain fractionated HSE patterns? On the other hand, it could be argued that the martian mantle had a ^{187}Os/^{188}Os of ~0.127 at 4.1 Ga, and that these rocks were generated with very low Re/Os at that time and retained the same isotopic composition to the present because of the lack of Re. However, other less MgO-rich shergottites with relatively high Re/Os (*e.g.*, EETA 79001) give calculated initial ^{187}Os/^{188}Os ratios of approximately the same isotopic composition as the ultramafic shergottites. I think the evidence from the Os isotopes, at least for the ultramafic shergottites, is that these are relatively young (<300 Ma), not ancient rocks.

Figure 4.10 Schematic plot of Time *versus* γ_{Os} trajectories for ultramafic shergottite samples LEW 88516 and ALH 77005, assuming they were extracted from the martian mantle at 4.1 Ga (orange star) and that their measured Re/Os ratio was established at that time. Over time, both meteorites would have evolved to appreciably subchondritic isotopic compositions, yet both have measured, present day γ_{Os} values of +1 to +2, shown as the blue squares, arguing against an ancient crystallisation age. Data are from Brandon *et al*. (2012). The orange diamond shows the predicted γ_{Os} value for the martian mantle today based on the experiments of Righter *et al*. (2014). According to that study, the high projected S content of the martian core would lead to a $D^{metal/silicate}$ value for Re that is higher than that for Os. This in turn leads to the prediction that the martian mantle would be substantially subchondritic with respect to Re/Os, and with time, grow to the low γ_{Os} value shown. Instead, the shergottites are characterised by chondritic or suprachondritic γ_{Os} values, as shown in Figure 4.8c.



4.2.3 Other differentiated bodies

In the past few years, a large number of HSE data, including $^{187}Os/^{188}Os$, for meteorites from the angrite parent body and the parent body of the howardite, eucrite, diogenite (HED) suite of meteorites that presumably sample the asteroid Vesta, have been published (Riches *et al.*, 2011; Dale *et al.*, 2012; Day *et al.*, 2012). These meteorites sample basaltic crust (angrites, eucrites), cumulates from mafic melts, and possibly even mantle materials (some diogenites), present on their parent bodies. These rocks are important points of comparisons to the Earth, Moon and Mars. They sample much smaller bodies that differentiated much earlier in solar system history. Some angrite and eucrite ages indicate their formation, and therefore, primary differentiation of their parent bodies, within the first 10 Ma of solar system history (*e.g.*, Lugmair and Galer, 1992; Misawa *et al.*, 2005). Thermal models of their interiors suggest that, although magma ocean crystallisation and overturn may have occurred, the resulting mantles would likely have been poorly mixed (Elkins-Tanton, 2012). Thus, in comparison to the much larger Earth, Moon and Mars, it can easily be envisioned that the mantles of the parent bodies of these meteorite groups might be much more heterogeneous with respect to HSE. Rapid post-overturn solidification of these mantles may have resulted in the preservation of mantle domains with HSE abundances that reflect low pressure metal-silicate fractionation. Grainy late accretion to the mantles may have resulted in proportionally more or less HSE than in the mantles of the Earth, Moon and Mars. Extrapolating from the Moon, if the size of the body dominates the mass additions of late accreted materials, it might be expected that most diogenites and angrites would have lower absolute abundances of HSE than estimated for the lunar mantle. If formation age or residence time of a magma ocean is more important, abundances might be expected to be higher than in the BSE.

It turns out that diogenites are characterised by highly variable HSE concentrations. The higher the concentrations, the flatter the chondrite-normalised patterns and the more chondritic the $^{187}Os/^{188}Os$ becomes (Fig. 4.11). Some of this undoubtedly represents direct contamination of the rocks with the chondritic or iron meteorite impactors that caused the brecciation observed in some of these rocks. However, many of the rocks are un-brecciated and show no other signs of direct chondritic or iron meteorite contamination. The authors of these papers have speculated that the parent bodies experienced late accretion soon after formation of the parent bodies (Dale *et al.*, 2012; Day *et al.*, 2012). Thus, the samples with the higher and more chondritic HSE abundances really were contaminated by chondrites, but in this case it was their mantle source regions that were contaminated, not direct contamination. These meteorites may, therefore, document continued (late) accretion to their parent bodies, even after primary differentiation and the formation of crust (Day *et al.*, 2012). Diogenites with very low abundances of HSE are characterised by highly fractionated HSE patterns. Most also have non-chondritic present day $^{187}Os/^{188}Os$. These HSE characteristics may reflect derivation from mantle that was stripped of HSE by core formation, followed by little or no replenishment by late accretion.

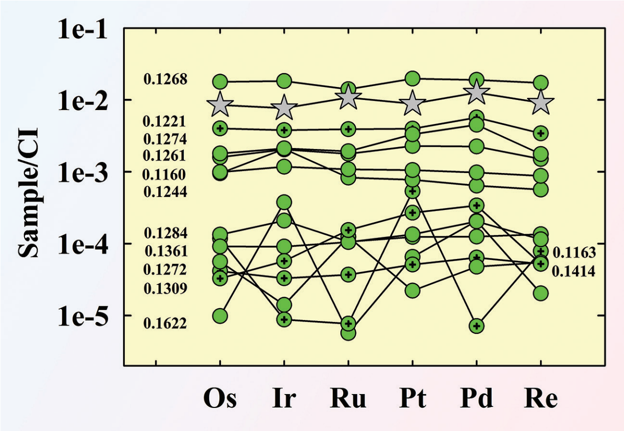


Figure 4.11 CI chondrite normalised HSE abundances for diogenites. The measured $^{187}Os/^{188}Os$ ratios of the meteorites are provided to the left or right of each pattern. Note that as abundances decrease, the pattern shapes become more fractionated and the Os isotopic ratios more suprachondritic. Data are from Day *et al.* (2012) (solid circles) and Dale *et al.* (2012) (circles with crosses). Data for BSE from Becker *et al.* (2006) are shown as grey stars for comparison.

Riches *et al*. (2012) and Dale *et al*. (2012) reported HSE data for angrite meteorites (Fig. 4.12). The results of both studies were broadly similar to the findings of Day *et al*. (2012) with regard to diogenite meteorites. The HSE absolute and relative abundances are highly variable, with chondrite-normalised HSE patterns flattening with increasing abundances. As with the diogenites, the meteorites with higher HSE abundances must result from either contamination of the parental melt passing through meteorite-contaminated crust of the parent body, or contaminated by late accretionary additions to the mantle of the parent body. As with the diogenites, the variability may reflect the unevenness of the late accretionary additions and the sluggishness of the parent body mantle to stir late accretionary additions efficiently into the major mantle domains that later melted to form these basaltic meteorites. As with two of the diogenites, four of the angrites evolved to sub-chondritic present day $^{187}Os/^{188}Os$, indicating that Re behaved less compatibly than Os as the rocks formed either as residues of partial melting or olivine-rich cumulates. This is unusual for achondrites, although some ureilites are also characterised by present day sub-chondritic $^{187}Os/^{188}Os$ (Rankenburg *et al*., 2007).

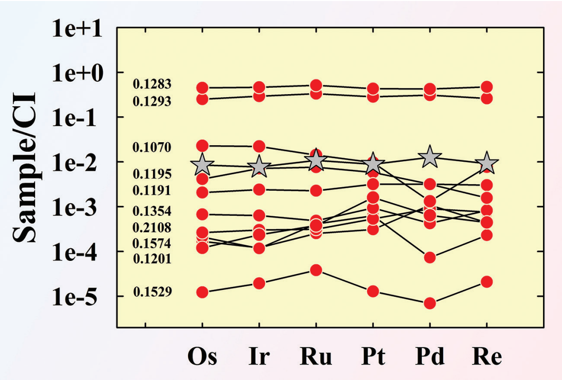


Figure 4.12 CI chondrite normalised HSE abundances for angrite meteorites. The measured $^{187}Os/^{188}Os$ ratios of the meteorites are provided to the left of each pattern. Note that as abundances decrease, the pattern shapes become more fractionated and the Os isotopic ratios become more supra- or sub-chondritic, possibly due to modifications to Re/Os resulting from crystal-liquid fractionation processes. Data are from Riches *et al*. (2012) and Dale *et al*. (2012). BSE pattern from Becker *et al*. (2006) (grey stars) is shown for comparison.

4.3 Putting the Planetary Data Together

When considering the broad spectrum of planetary igneous rocks for which we have HSE and Os isotopic data, it is clear that as concentrations decrease, the degree of fractionations among the HSE increases, especially for the slightly compatible to incompatible HSE, such as Pt, Pd and Re. This can be easily seen when examining a plot of Os *versus* Pt, or Os *versus* $^{187}Os/^{188}Os$ for terrestrial, lunar, SNC, diogenite/eucrites and angrites (Fig. 4.13a,b). The fact that the HSE abundances estimated for the lunar mantle are considerably lower than the terrestrial mantle is an observation that requires explanation. If the HSE in the mantles of both the Earth and Moon are to be attributed to late accretion, why did the Moon accrete proportionally much less stuff? There has always been the recognition that the Moon will accrete proportionally less material, by surface area, through any late accretionary processes, due to gravitational focusing by Earth, and diminished retention of late accreted materials on the Moon resulting from its weaker gravitational field. Even when this is taken into account, the Moon might be expected to have similar or higher abundances of HSE in its mantle, compared to the terrestrial mantle (see discussion in Walker *et al.*, 2004), yet the lunar mantle appears to be strongly depleted. Typical predictions for Earth/Moon influx ratios, when considering gravitational focusing and differential retention, range from about 20 to 50. The estimates presented above instead suggest a ratio of 1200 or greater.

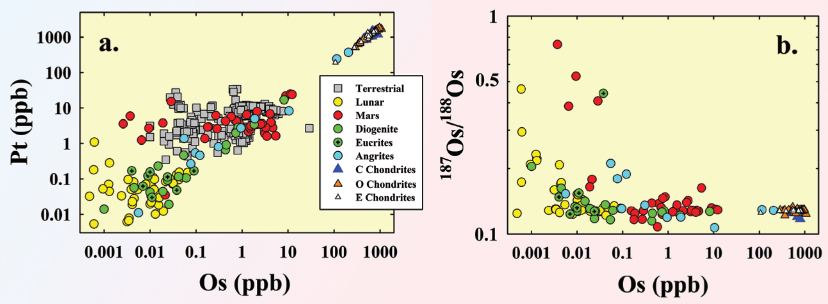


Figure 4.13 **(a)** Plot of Os *versus* Pt (in ppb) of planetary silicates and bulk chondrites. Note that both axes are logarithmic. **(b)** Plot of Os (in ppb) *versus* present day $^{187}Os/^{188}Os$ for planetary silicates and bulk chondrites. Note that terrestrial rocks have been removed to reduce the range in $^{187}Os/^{188}Os$. Note that both axes are logarithmic. Achondrite and lunar data are from Day *et al.* (2007, 2012), Riches *et al.* (2011), Brandon *et al.* (2012) and Dale *et al.* (2012). Bulk chondrite data are from Horan *et al.* (2003) and Fischer-Gödde *et al.* (2010).

There are several possible reasons for the large mismatch between late accretion to Earth and the Moon. One is that it reflects the timing of late accretion. If Earth's mantle began to accumulate HSE long before the Moon formed, then it could have accumulated a disproportionate share of late accreted materials. However, late accretion to the Earth and Moon must be placed within the context of lunar formation models. The current paradigm for Moon formation is that of a giant impact (*e.g.*, Hartmann and Davis, 1975). A giant impact likely resulted in the melting of a large proportion of the Earth's mantle. Further, at this time, most of the core of the giant impactor must have transited the Earth's mantle to merge with its core. It is plausible, maybe even likely, that this event stripped the Earth's mantle of any HSE that had been added to the mantle by prior late accretion. Thus, the accumulation clocks for the Earth and nascent Moon could have been started at essentially the same time. Later in this section, I'll present some ^{182}W isotopic data that appear to confirm this assumption. So we are back to square one. Why did the Moon experience proportionally less late accretion compared to the Earth?

When presenting this issue at a Lunar and Planetary Science Conference, I was approached by *Bill Bottke* of the Southwest Research Institute. He suggested that the late accretion process might best be modelled as a stochastic process, and proceeded to do this. In Bottke *et al.* (2010) his Monte Carlo simulations of late stages of planetary accretion suggested that the substantial mismatch in late accreted mass to Earth and Moon can be explained if it is assumed that late accretion was dominated by the addition of a few large bodies bodies to Earth, and that the Moon was simply not struck by any bodies of this size. This solution works if the remaining mass available for late accretion, following a giant impact, was mainly in the form of sizable (1500 to 2500 km diameter) bodies, rather than a large number of low mass bodies. The impact of a few large bodies may have created HSE rich and poor domains deep in the mantle, rather than a thin HSE-rich veneer resting at or near the surface. This is why I don't favour the term late veneer. As will be discussed below, there is some evidence in the variability of W isotopic compositions in early Earth rocks that are consistent with a grainy initial distribution of HSE and MSE in the mantle. This observation is more consistent with the stochastic bombardment interpretation.

An alternate possibility to explain the different HSE abundances in the terrestrial and lunar mantles is the recent recognition that metallic iron of impactor cores (bearing most of the impactor's budget of HSE) would partially or wholly vaporise upon impact onto larger bodies, such as the Earth (Kraus *et al.*, 2015). In this case, there would have been a much higher probability of the Earth retaining the vaporised Fe than the Moon. Hence the difference in HSE abundances in the silicate portions of the bodies could reflect the abilities of the two bodies to retain vaporised iron.

Regardless of the mechanism for the disproportional late accretion, two recent ^{182}W isotopic studies of lunar rocks may have firmed up some of the loose ends of this story (Kruijer *et al.*, 2015; Touboul *et al.*, 2015). Disproportional additions of broadly chondritic materials to the mantles of both the Earth and Moon, consistent with the late accretionary estimates above, should lead to modest isotopic heterogeneity between the two bodies, assuming that, as with other elements, the ^{182}W isotopic compositions of both bodies were identical after Moon formation. This is because W is in comparatively high abundance in materials with chondritic bulk compositions, relative to post-core-segregation mantle, and because the chondritic ^{182}W/^{184}W is about 200 ppm lower than the BSE today. This provides sufficient isotopic/elemental leverage so that addition of ~0.5 wt. % of Earth's mass by late accretion would lower the W isotopic composition of the mantle by ~20-30 ppm (Halliday, 2008; Willbold *et al.*, 2011; Walker, 2014). By contrast, the much smaller proportion of mass evidently added to the mantle of the Moon by late accretion would result in a smaller change in W isotopic composition. For this scenario, the lunar isotopic composition might have been lowered by only 1-4 ppm. Thus, a difference of approximately 20-25 ppm is expected if disproportional late accretion really did happen.

Prior studies did not detect a difference in the ^{182}W isotopic compositions of the Earth and Moon (*e.g.*, Touboul *et al.*, 2007), but also did not have the resolution to detect differences at the level predicted. Recent developments in W isotopic measurement capabilities provide the necessary level of resolution and reveal that the silicate Moon has a ^{182}W/^{184}W that is ~25 ppm higher than the present BSE (Kruijer *et al.*, 2015; Touboul *et al.*, 2015; Fig. 4.14), consistent with the predictions. These data strongly support the concept of disproportional late accretion to the Earth and Moon, and therefore, the assumption that the Earth's mantle and the nascent Moon had identical μ^{182}W values (~+27) immediately following the impact. If correct, this is important because the metallic core of the Moon-forming impactor would have to have stripped any HSE from the terrestrial mantle that had accreted late, prior to the giant impact. Thus, the giant impact event must have been a clearinghouse event for HSE from the proto-Earth's mantle. This is necessary so that the late accretionary accumulation clocks could be simultaneously started for both bodies immediately following the giant impact. So, allowing that our estimates of the HSE abundances in the lunar mantle are reasonably accurate, we have a strong explanation to account for the W isotope observation.

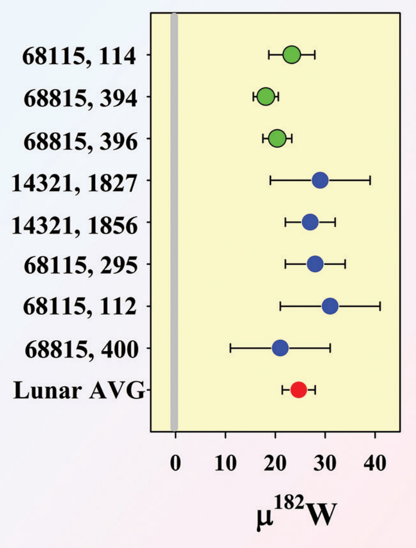


Figure 4.14 μ^{182}W values (parts per million deviation in the ^{182}W/^{184}W ratio of a sample relative to the average for terrestrial standards) from eight pieces of KREEP-rich, lunar impact melt rocks (sample numbers are given on the y-axis). By combining data from Kruijer *et al.* (2015) (blue circles) and Touboul *et al.* (2015) (green circles) an offset of the lunar samples of +24.7 ± 3.3 (2 SE) ppm (red circle) is obtained, relative to the silicate Earth (grey vertical bar).

Some potential problems still remain. For HSE to become emplaced and mixed within the lunar mantle requires late accretion to occur before formation of a permanent crust, presumably while lunar magma ocean crystallisation, and overturn could have led to mixing of HSE within the mantle. It has also been proposed that a major proportion of the Moon's late accretionary inventory of HSE may reside in metal at the base of the lunar crust (Schlichting *et al.*, 2012). This is an idea that merits further consideration, but appears to be an untestable model for the foreseeable future.

What about Mars? Bottke *et al.* (2010) concluded that stochastic late accretion could also account for the HSE abundances estimated for the silicate portion of Mars. However, for this aspect of the model to work, probabilities go down. Thus, it is rather unlikely that the mantles of Earth and Mars should end up with such similar HSE abundances. Using results from a new experimental partitioning study, Righter *et al.* (2014) concluded that the abundances of HSE observed in SNC meteorites could be accounted for by relatively high pressure-temperature metal-silicate partitioning at pressures of ~14 GPa in the early martian mantle. This would be a handy way to solve the martian conundrum. To achieve sufficiently high HSE in the martian mantle following core segregation, it must be assumed that the martian core is S-rich. Given the density of Mars, this is a reasonable assumption. However, under these conditions, the experiments show that Re would be more strongly partitioned into the martian core than Os. Using the projected martian mantle abundances cited by that study, a $^{187}Re/^{188}Os$ of 0.131 results. In 4.5 Ga of isotopic evolution, the $^{187}Os/^{188}Os$ of the mantle today would be only 0.1055 (γ_{Os} = -17; Fig. 4.10), well below the range of chondritic meteorites, yet virtually all martian meteorites for which there are Os isotopic data have calculated initial ratios that are chondritic or suprachondritic (Fig. 4.8c). This illustrates just how difficult it may be to achieve a precisely chondritic Re/Os in mantle by high pressure-temperature partitioning. Additional experiments may eventually find conditions under which core formation could leave a martian mantle with chondritic Re/Os, but this requires appealing to a special set of circumstances that could lead the BSE and shergottite source to evolve to essentially the same Os isotopic composition after 4.5 Ga of growth. How do these two planets know to segregate cores at unique sets of pressures and temperatures (different conditions for each planet) where the D values for Os and Re converge, such that more than 4 Ga later the dominant $^{187}Os/^{188}Os$ of their mantles are both within the range of chondrites? This strikes me as a very unlikely scenario.

4.4 Genetics of Late Stages of Earth's Accretion

The earlier mentioned Ru-Mo isotopic correlation provides some remarkable insights to planetary accretion. Most notably, Dauphas *et al.* (2004) recognised that most of the Mo present in the mantle today was added during the last 10-20 wt. % of Earth's accretion. As discussed above, the Mo present in the BSE is mainly the result of multiple stages of metal-silicate segregation at elevated temperatures and pressures, where D values for most MSE are substantially reduced. By contrast, the Ru present in the mantle was mainly added by late accretion of ~0.5 wt. % meteoritic matter, most likely soon after the Moon forming event. If the sources of the last 10-20 wt. % of material accreted differently from those of the final 0.5 wt. % (*i.e.* if their genetic origins differed), the Earth would not plot on the Ru-Mo correlation trend. The fact that it plots on or very near the trend suggests that the genetic makeup of at least the final 10-20 wt. % of Earth accretion did not vary greatly (Dauphas *et al.*, 2014). This means that even the putative Moon-forming giant impactor had very similar Mo and Ru to that of the proto-Earth.

As noted by Dauphas *et al*. (2014) the isotopic similarities between the Earth and Moon may simply mean the genetic properties of the building blocks (*e.g.*, O, Ti, Cr) of the proto-Earth and giant impactor were essentially the same. The conclusion that the silicate portions of the Earth and Moon had identical, pre-late accretionary ^{182}W isotopic compositions, however, remains problematic for this interpretation. This is because the radiogenic ^{182}W isotopic compositions of the proto-Earth and giant impactor, compared to bulk chondrites, did not reflect genetics, but rather the timing of the formation of their respective cores and Hf/W ratios of their mantles. It seems unlikely that two such bodies would have evolved to essentially identical W isotopic compositions by the time of the impact.

There remain many unanswered questions relating to the origins of siderophile elements in the terrestrial planets. For example, is the genetic similarity for Ru and Mo between Earth and enstatite chondrites a reflection of genetic homogeneity throughout the innermost solar system? If so, we would expect similar Ru and Mo isotopic compositions for Venus and Mercury. Did the much smaller proportion of materials that fell to the Earth and Moon during a putative late heavy bombardment, that some put at 3.9 Ga, consist of genetically similar or different materials? For the Mo-Ru isotopic correlation, why does the Earth appear to pin one end of the correlation? Answers to these questions will have to await future study.

5. SIDEROPHILE ELEMENTS IN THE DEPLETED MORB MANTLE

From here on I'll focus exclusively on siderophile elements in the silicate Earth, and try to ignore elusive, imaginary friends, such as the BSE, that represent model compositions. The largest mantle domain that we have more or less direct access to is the DMM, so it is a good place to begin. The DMM comprises most of the upper mantle, and chemically may extend well into the lower mantle (*e.g.*, Workman and Hart, 2005; Arevalo *et al.*, 2013). We have indirect access to it in the form of MORB, and may have direct access to it in the form of abyssal peridotites, and in limited instances, oceanic mantle xenoliths (*e.g.*, Bizimis *et al.*, 2007). We can also access the DMM in the mantle sections of some ophiolites, although the effects of supra-subduction zone and obduction processes must be filtered from any such data, if we wish to gain insight to the DMM.

In this section I discuss Os isotopic data referring to both $^{187}Os/^{188}Os$ ratios and the γ_{Os} notation (percent deviation of $^{187}Os/^{188}Os$ from a reference to chondritic evolution, for a specified time; Table 2.3). I know some people think in terms of ratios and some think in terms of normalised ratios (especially those of us who work with non-zero age rocks), so I try to provide Os isotopic compositions in both formats where possible. The γ_{Os} notation is most useful when comparing isotopic data of mantle and mantle-derived materials of different ages, and so it is used in most of the figures to follow.

5.1 Overview of the DMM

An important concept to recognise regarding the DMM is that it is chemically and isotopically heterogeneous. In addition to fertile and refractory peridotite, the DMM also includes recycled crust. So, even with this living, breathing, non-sedentary portion of the mantle that we can touch on occasion, it is not so easy to arrive at complete characterisation of its siderophile element budget. The heterogeneity is most amply evidenced by the diverse lithophile element compositions (chemical and isotopic) of derivative melts, such as those sampled by MORB (*e.g.*, Langmuir and Hanson, 1980; Cohen and O'Nions, 1982; Dupré and Allègre, 1983; Shirey *et al.*, 1987; Salters *et al.*, 2011), as well as by data generated through the direct analysis of mantle rocks accessible in the form of abyssal (oceanic) peridotites (Snow *et al.*, 1994; Warren *et al.*, 2009a; Stracke *et al.*, 2011), and the mantle sections of ophiolites (Sharma *et al.*, 1995; Büchl *et al.*, 2002; Dilek and Furnes, 2011). The processes that resulted in the creation of heterogeneities in the oceanic mantle most likely were dominated by multiple stages of partial melting and metasomatism, as well as lithospheric recycling, yet the relative impact of each of these processes, the timing of the processes, and the length scales and longevity of the resulting heterogeneities remain topics of considerable debate. Clarifying the causes, timing and spatial extent of chemical and isotopic heterogeneities in the DMM is, therefore, critical for refining our knowledge of the present bulk composition of this major terrestrial reservoir, for achieving a more complete understanding of how the chemical and isotopic composition of the DMM evolved through time, and for assessing the efficiency by which the DMM is convectively mixed today.

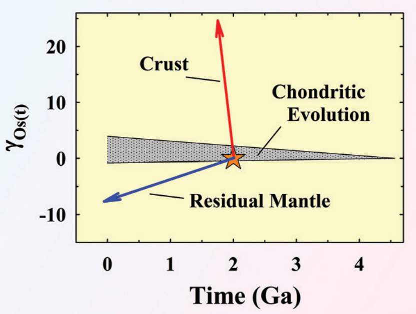
Much of the geochemical research directed at examining chemical and isotopic heterogeneities in the oceanic mantle has been understandably focused on lithophile elements in essentially modern MORB. Such research has been fruitful because of the extent to which MORBs have been sampled throughout all of the ocean basins (*e.g.*, Klein and Langmuir, 1987; Workman and Hart, 2005; Salters *et al.*, 2011). Thus, MORB research has elucidated global variations in the chemical and isotopic nature of the DMM. The study of MORB, however, is not sufficient for fully characterising the oceanic mantle (*e.g.*, Dick, 1989; Rampone and Hofmann, 2012), and given the youth of most MORB, it is not suitable for exploring the chemical evolution of the mantle. Numerous studies have shown that, because of the tendency of melting and melt transport at mid-ocean ridges to blend diverse melts and attenuate compositional extremes, basaltic melt products do not always reveal the complete extent of heterogeneities within their DMM sources. Further, some refractory portions of the DMM may not be accessed at all in the production of MORB. Evidence for considerable heterogeneity in the DMM, beyond the range sampled by MORB, includes the fact that some peridotites that directly sample the DMM have much more radiogenic ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf than any known MORB (*e.g.*, Sharma *et al.*, 1995; Warren *et al.*, 2009a; Salters *et al.*, 2011; Stracke *et al.*, 2011). Thus, the nature and scale of chemical heterogeneity in the modern DMM may be utilised to reveal important secrets of the mantle. In addition to limitations in our knowledge regarding the present chemical and isotopic structure of the oceanic mantle, the secular evolution of the chemical and isotopic structure of the oceanic mantle remains only partially revealed (*e.g.*, Bennett, 2003).

So, how can siderophile elements help us to understand better the present chemical structure, and long-term chemical evolution of the DMM? Following the large-scale primordial events that established the initial abundances of HSE and MSE in the mantle discussed in preceding sections, subsequent processes have acted to change the absolute and relative abundances of these elements (as well as lithophile elements) over Earth history. Such processes include mantle melting, coupled with melt extraction to form crust, mantle metasomatism/refertilisation, as well as crustal recycling via the plate tectonic cycle (*e.g.*, Martin, 1991; Rehkämper *et al.*, 1999a; Becker *et al.*, 2001b; Walker *et al.*, 2002b; Luguet *et al.*, 2007; Le Roux *et al.*, 2007; Lorand *et al.*, 2009). In the DMM, convective mixing has presumably acted in the opposing direction to these processes to reduce the range of some of the resulting chemical heterogeneities (*e.g.*, Allègre and Turcotte, 1986). The value of the HSE and MSE in the study of processes in the DMM, as well as other mantle domains, stems from the fact that the abundances of the HSE, and some of the MSE (*e.g.*, W, Mo), in the mantle are primarily controlled by diverse, trace sulphides and alloys whose stabilities can be strongly affected by melting and metasomatic processes in different ways from the hosts of lithophile elements. Thus, siderophile elements provide important complementary information about processes that occur in the DMM. For example, relatively large extents of partial mantle melting, coupled with melt removal, typically leads to the creation of residual mantle that is moderately to strongly depleted in incompatible HSE and MSE, including Pt, Pd, Re, Mo and W. Conversely, melt removal can lead to minor enrichment of the compatible HSE, Os, Ir and Ru, relative to fertile mantle. This results in the generation of characteristic siderophile element signatures, and can provide a robust means to constrain the extent and timing of the processes involved.

The resulting divergence in the evolution of isotopic composition of Os away from that of the ambient mantle is the basis of T_{MA} and T_{RD} Os model ages, which in some peridotites permits the placement of age constraints on the timing of primary melt extraction (Shirey and Walker, 1998; Rudnick and Walker, 2009) (Table 2.3). The two types of model ages reflect the observation that Re can be easily mobilised by metasomatic processes. T_{MA} ages are based on the assumption the measured Re/Os ratio of a rock reflects the ratio it held in the mantle, and that the Os isotopic composition of a peridotite can be projected backward in time from that measured to a mantle evolution trajectory to obtain a model age. If some Re was added prior to or during removal of the peridotite from the mantle, the model age will be older than the true age of melt depletion. A T_{RD} age, by contrast, is calculated based on the (probably incorrect) assumption that all Re present in a peridotite was introduced just prior to or during its removal from the mantle. As such, it is normally expected to provide a minimum age of melt depletion. The effects of melt depletion have been amply demonstrated for mantle domains that have become isolated from the DMM, such as SCLM and orogenic peridotite massifs, through correlations between $^{187}Os/^{188}Os$ and HSE ratios, such as Pd/Ir, *versus* elemental indicators of melt depletion, such as abundances of Al_2O_3 and Yb (*e.g.*, Pearson *et al.*, 1995a; Reisberg and Lorand, 1995; Luguet *et al.*, 2004), as also discussed in the preceding section. These effects have been less well documented for the DMM, but nevertheless appear to be broadly similar (*e.g.*, Liu *et al.*, 2009; Schulte *et al.*, 2009).

One important application of contrasting geochemical behaviours of siderophile elements stems from the incompatibility of Re and compatibility of Os during most types of mantle melting (Morgan, 1986). The loss of Re and retention of Os in mantle residues resulting from partial melting leads to a decrease in the Re/Os of the residual mantle, and consequent retardation in the growth of the $^{187}Os/^{188}Os$ ratio (decrease in γ_{Os} value) within the residue, compared to mantle that has not experienced prior melt removal (Fig. 5.1; *e.g.*, Walker *et al.*, 1989; Rudnick and Walker, 2009). Conversely, the somewhat higher concentrations of Re in crust, compared with the mantle, coupled with the much lower concentrations of Os in the crust, resulting from its mantle compatibility, leads to typically very high Re/Os in the crust, and increase in $^{187}Os/^{188}Os$ (and γ_{Os}).

Figure 5.1 Time *versus* γ_{Os} plot showing range of Os isotopic evolution of 95 % of bulk chondrites (grey field), as well as the schematic, long-term isotopic evolution effects of melt extraction from a chondritic mantle at 2.0 Ga (orange star) on both the residual mantle, and the melt which goes on to form crust. Note the rapid growth in γ_{Os} in the resulting crustal rock, due to high Re/Os.



Crustal recycling can also lead to the creation of domains within the DMM that are characterised by relatively high Re, Pt, Pd, Mo and W concentrations, and correspondingly lower Os, Ir and Ru concentrations. For example, W behaves as a highly incompatible trace element in the silicate Earth, showing greatest enrichments in continental crust, similar to Th and U (Newsom and Palme, 1984; Newsom *et al.*, 1996; Arevalo and McDonough, 2008). The recycling of crust, particularly continental crust, into the mantle can lead to the creation of W-enriched domains, relative to the ambient mantle (Ireland *et al.*, 2009a). Similarly, mantle lithologies such as pyroxenites, which may represent recycled oceanic crust (*e.g.*, Pearson *et al.*, 1991), can be characterised by relatively high Re/Os and Pt/Os ratios (Reisberg *et al.*, 1991; Smith, 2003; Pearson and Nowell, 2004; Luguet *et al.*, 2008a). Preferential melting of, or assimilation of such materials that have resided in the mantle for long periods of time can potentially lead to the generation of magmas with enrichments in ^{187}Os/^{188}Os and ^{186}Os/^{188}Os, relative to the ambient, depleted mantle. This process has been invoked in the generation of at least some OIB (*e.g.*, Hauri and Hart, 1993; Reisberg *et al.*, 1993; Lassiter *et al.*, 2000; Sobolev *et al.*, 2008), as will be discussed in Section 7, and has been suggested for the origins of some pyroxenitic materials present in the DMM (*e.g.*, Smith, 2003; Luguet *et al.*, 2008a).

Other processes, such as mantle metasomatism may also cause localised diversification of HSE and MSE ratios, as well as Os isotopic compositions within the mantle (*e.g.*, Büchl *et al.*, 2002; Luguet *et al.*, 2007; Lorand *et al.*, 2008, 2009). The effects of metasomatism, however, can vary, and there are no universal characteristics of metasomatised mantle with respect to HSE (*e.g.*, Rudnick and Walker, 2009). Some studies have also directly or indirectly attempted to assess the effects of metasomatism on MSE, such as Mo and W (Newsom and Palme, 1984; König *et al.*, 2011). As incompatible trace elements, they tend to be strongly affected by melt migration. On a global scale, the effects of the extraction of mafic oceanic lithosphere from the DMM over the course of Earth history has almost certainly led to changes in the average absolute and relative abundances of the HSE and MSE in the DMM, including the depletion of Re and consequent retardation in the growth of $^{187}Os/^{188}Os$. Yet our knowledge of secular changes to HSE and MSE in the oceanic mantle remains quite limited. Thus, improving our understanding of siderophile elements in the DMM through time is a critical complement to the major advances in mantle research that have already been made based on lithophile elements.

The siderophile elements may be particularly useful in extracting important information about the DMM from the mantle sections of ophiolites. As noted above, siderophile elements can be useful for monitoring some mantle processes to which lithophile elements are insensitive. This stems from the fact that some siderophile elements, especially the HSE, are relatively insensitive to metasomatic additions. They are also in much higher abundance in mantle peridotites than in crustal rocks and are comparatively insensitive to crustal recycling. Further, most siderophile elements are significantly less fluid mobile compared to some of the most important lithophile elements used for tracing the chemical evolution of the mantle, such as the Nd and Sr isotope systems. Although fluid/melt transport of typically radiogenic Os into mantle wedge peridotites above subduction zones has been well documented (*e.g.*, Brandon *et al.*, 1996; Widom *et al.*, 2003), most affected peridotites are typically also characterised by low (<1 ppb) Os abundances and may be easily identified. In some fluid-rich settings, such as mélange zones, the HSE and Os isotopes appear to be little affected by processes that have strongly modified lithophile elemental abundances and isotopic compositions, such as for Li (Penniston-Dorland *et al.*, 2010, 2012, 2014).

5.2 Mid-Ocean Ridge Basalts

Despite the volumes written about MORB, siderophile element abundances in MORB remain rather poorly characterised. This is not a major disaster from the standpoint of characterising the DMM. It turns out that data for at least some of the siderophile elements in MORB are of limited value in that task. This is because some siderophile elements are strongly compatible during mantle melting that produces MORB. In particular, the abundances of Os, Ir and Ru are typically very low in bulk samples of MORB, and problematic materials from which to characterise their abundances in the DMM (Hertogen *et al.*, 1980; Rehkämper *et al.*, 1999b; BÉzos *et al.*, 2005; Dale *et al.*, 2008; Gannoun *et al.*, 2016). Other HSE, such as Pd and Re, range from slightly compatible to moderately incompatible, during the production of MORB. The highly disparate natures of partitioning of individual HSE is manifested in chondrite normalised patterns for MORB that are characterised by steeply upward sloping patterns, proceeding from Os to Re (Fig. 5.2). These characteristics result in Os and Ir abundances that are always more than 1 order of magnitude lower than BSE, Pt and Pd abundances that can approach BSE, and Re abundances that commonly exceed BSE.

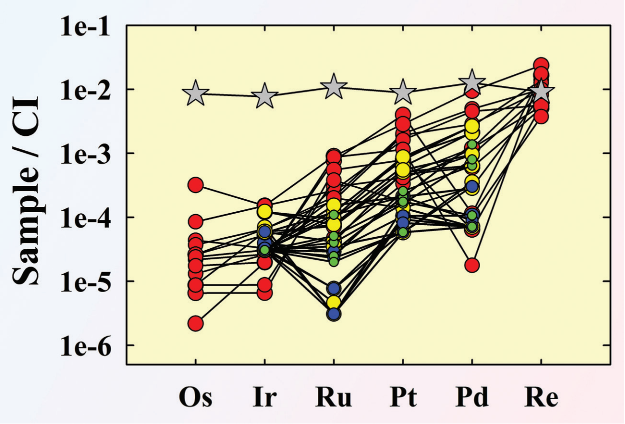


Figure 5.2 CI chondrite normalised HSE patterns for MORB and related mafic melts. Red symbols are for Philippine Sea Plate basalts from Dale *et al*. (2008). Blue, yellow and green symbols are for Pacific, Atlantic and Indian Ocean MORB basalts and glasses from Bézos *et al*. (2005). All patterns are broadly similar with positive slopes from Os to Re. The BSE composition of Becker *et al*. (2006) is shown in the grey stars for comparison.

The average $^{187}Os/^{188}Os$ ratio or γ_{Os} value of the DMM is an important geochemical parameter of the Earth to constrain, so if the production of MORB does a good job of averaging the Os isotopic composition of the DMM (as is commonly assumed for lithophile isotope systems, such as Sm-Nd, Lu-Hf and Rb-Sr) then MORB should be an important source of data regarding the Os isotopic composition of the modern DMM. Unfortunately, the very low Os concentrations in MORB weigh against it providing an unbiased view of the DMM source. This is because of the possibility/likelihood of contamination with more radiogenic materials.

There are at least two major possibilities for contamination. First, at least some MORB must transit highly radiogenic oceanic crust (*e.g.*, Blusztajn *et al.*, 2000). Contamination with crust would lead to a more radiogenic $^{187}Os/^{188}Os$ ratio in the MORB than is representative of the mantle source of the DMM. Second, seawater is highly radiogenic ($^{187}Os/^{188}Os \approx 1$; $\gamma_{Os} \approx +700$) (Sharma *et al.*, 1997) compared to the modern BSE ($^{187}Os/^{188}Os = 0.1296$; $\gamma_{Os} = +2$), so any hint of interaction between a MORB sample (basalt or glass) and seawater casts doubt on the primary Os isotopic characteristics of the MORB, and how it may relate to its mantle source. Seawater-deposited Mn crusts tend to have high Os concentrations and incorporate the isotopic composition of seawater, so even if there is no interaction between MORB and seawater, the presence of even small amounts of Mn crust can also bias MORB results. In addition, the typically high Re/Os of MORB means that any attempt to assess the isotopic compositions of the mantle sources of MORB may also require an age correction. Despite these problems, several studies have sought to determine the Os isotopic compositions of MORB, and through it, the isotopic composition of the DMM.

Initial attempts to determine the Os isotopic compositions of MORB were slowed by the very low abundances of Os in MORB, coupled with inefficient mass spectrometric techniques, such as SIMS and RIMS. Consequently, all meaningful measurements of bulk MORB followed the advent of NTIMS methods. The first successful study of Os isotopes in MORB was Roy-Barman and Allègre (1994). That study measured $^{187}Os/^{188}Os$ in 6 different samples of MORB, or phases separated from MORB, from the Atlantic, Pacific, and Indian Oceans. In an attempt to remove the possible effects of seawater alteration, they processed their samples through extensive leaching steps. They reported mean, age-corrected $^{187}Os/^{188}Os$ ratios of ~0.130 to 0.330 (γ_{Os} = +2 to +150) for North Atlantic MORB. Despite leaching, they measured $^{187}Os/^{188}Os$ ratios of 0.220 to 0.250 (γ_{Os} = +73 to +97) for Pacific MORB, and of 0.143 to 0.250 (γ_{Os} = +13 to +97) for basalts from the Central Indian Ridge. These authors cautiously concluded that most of the ratios they obtained were most likely not representative of their mantle sources, and may instead reflect varying degrees of contamination of lavas *en route* to the surface, or incomplete removal of seawater effects.

Soon thereafter, *Claude Allègre* and *Jean-Louis Birck* at Paris developed an effective, very low blank chemical separation method for Os that, when combined with NTIMS, allowed measurement of Os isotopic compositions of very small amounts of Os (<1 pg; Birck *et al.*, 1997). Schiano *et al.* (1997) quickly put the new methods to use and reported age-corrected $^{187}Os/^{188}Os$ ratios for a sizable, global suite of samples of MORB glass. The ratios they obtained ranged from 0.128 to 0.163 (γ_{Os} = +1 to +28). These authors noted correlations between Os isotopic compositions and Sr-Nd and Pb isotopic compositions. They argued that the correlations could not be attributed to lithospheric or seawater contamination, and concluded that Os is part of the global chemical heterogeneity that is present in the DMM. Subsequent advances in analytical methods, however, led Gannoun *et al.* (2007) to conclude that the correlations between Os isotopic composition and lithophile isotopes were largely analytical artefacts.

To further explore the effects of lithospheric or seawater contamination of MORB, Roy-Barman *et al.* (1998) examined Os present in sulphide globules extracted from MORB. The sulphide globules in MORB have the advantage of bearing comparatively high Os concentrations, making them resistant to the effects of contamination. They also tend to have low Re/Os, which makes them insensitive to age corrections. If they crystallise and become closed systems to Os exchange before crustal contamination, they should be ideal for defining the parental melt isotopic composition. For this study, the authors reported $^{187}Os/^{188}Os$ ratios ranging from 0.126 to 0.166 (γ_{Os} = -1 to +31).

Subsequent studies of Os in MORB (*e.g.*, Escrig *et al.*, 2005; Gannoun *et al.*, 2004, 2007; Dale *et al.*, 2008; Yang *et al.*, 2013) have reported generally similar results, with $^{187}Os/^{188}Os$ ratios ranging from chondritic to considerably suprachondritic. As will be discussed in the following section, there is only modest overlap between the Os isotopic compositions of MORB and the range of isotopic compositions of much more Os-rich abyssal peridotites, that presumably also sample the same DMM. The meaning of the apparent difference in isotopic compositions between MORB and abyssal peridotites has been vigorously debated.

The abundances of the MSE in MORB, as with HSE, are not well constrained at present. Tungsten is probably the best studied of the moderately siderophile trace elements in MORB. As noted above in Section 4.1, the W concentration in MORB has been compared with U, with a $W/U_{MORB} = 0.65 \pm 0.41$ ($n = 52$) (Arevalo and McDonough, 2008). From this ratio, Arevalo and McDonough (2008) estimated the W concentration of the DMM to be 3.0 ± 2.3 ppb. König *et al.* (2011) measured W in 40 MORB glasses and reported concentrations ranging from 0.005 to 0.70 ppm. They estimated the W concentration of the DMM to be 2.4 ppb.

5.3 Abyssal Peridotites

Abyssal (or oceanic) peridotites are tectonically exposed peridotites that are usually collected by dredging along, or near mid-ocean ridges. Although a few studies have concluded that some abyssal peridotites may represent SCLM that has gotten mixed into the DMM (*e.g.*, Parkinson *et al.*, 1998), most abyssal peridotites are indisputably samples of the DMM. Most abyssal peridotites have major element compositions that reflect one or more episodes of melt depletion at ridges (Dick *et al.*, 1984; Elthon, 1992; Snow *et al.*, 1994; Warren *et al.*, 2009a). Because they are peridotites, they have comparatively high concentrations of the HSE, and moderate to low concentrations of the MSE. As such, they would seem ideal rocks to study for siderophile element abundances and $^{187}Os/^{188}Os$ and $^{186}Os/^{188}Os$ ratios in the DMM. Indeed, data generated for abyssal peridotites have been critical to characterising siderophile elements abundances and isotopic compositions in the DMM. Abyssal peridotites, however, come with three major penalties. One penalty is that most abyssal peridotites are highly serpentinised, and often contain few primary mantle phases. A second problem is the lack of spatial control when sampling. Given that most abyssal peridotites are collected by shipboard dredging, the general location of collection is known, however there is rarely any spatial control over how different samples from a given dredging site may relate to one another. No outcrop-scale sampling is possible, except in very rare circumstances where the abyssal peridotites have been sampled by submersible, or are accessible at or near the surface, such as the Saint Peter and Saint Paul islets, Brazil (Sichel *et al.*, 2008). Finally, given that abyssal peridotites may owe their exposure on the seafloor to their buoyancy resulting from prior melt depletion, they may not be representative of the mean composition of the DMM. Thus, abyssal peridotites provide important, but fuzzy snapshots of the DMM.

Considerable high quality HSE data are now available for bulk samples of abyssal peridotites (*e.g.*, Rehkämper *et al.*, 1999a; Luguet *et al.*, 2001; Alard *et al.*, 2005; Becker *et al.*, 2006; Liu *et al.*, 2009). The BSE-normalised HSE patterns of abyssal peridotites are generally flat (Fig. 5.3). As might be expected, the greatest variations are in the incompatible HSE, Pd and Re, reflecting melt depletion events in some of the samples. It may not be so surprising that the HSE data for abyssal peridotites are broadly similar to estimates for the BSE discussed above. This, in part, is because data for three abyssal peridotites were included in projections of HSE data to BSE compositions by Becker *et al.* (2006). But it also signals that the average absolute and relative HSE abundances in abyssal peridotite are not very different from their concentrations in the BSE estimate. Note that there are no obvious negative Ru anomalies in the BSE normalised patterns, and only about half show evidence for negative Pd anomalies, as would be expected if suprachondritic Ru/Ir and Pd/Ir were characteristic of only the SCLM (Fig. 5.3). This is important because most of the rocks used for estimating the concentrations of HSE in the BSE are samples of SCLM. The usage of SCLM samples for defining the BSE compositions of HSE has been called into question because of possible secondary melting and metasomatic processes that commonly affect these types of rocks (*e.g.*, Lorand *et al.*, 2008).

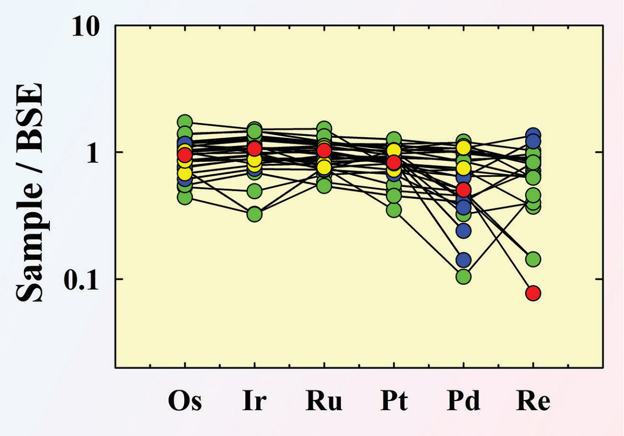


Figure 5.3 Bulk silicate Earth normalised abundances of HSE in abyssal peridotites from the Kane Fracture Zone, Atlantic Ocean (blue circles), the St. Paul Fracture Zone, Atlantic Ocean (red circle), the Southwest Indian Ridge, Indian Ocean (yellow circles) and the Gakkel Ridge, Arctic Ocean (green circles). Data are from Luguet *et al.* (2001), Alard *et al.* (2005), Becker *et al.* (2006) and Liu *et al.* (2009).

There are many more $^{187}Os/^{188}Os$ ratios reported for abyssal peridotites than complete HSE abundance data. Martin (1991) reported the first Re-Os isotopic data for abyssal peridotites from the Southwest Indian Ridge, Islas Orcadas Fracture Zone, and the Bouvet Fracture Zone. She found that Os isotopic compositions were variable, with ^{187}Os/^{188}Os ratios ranging from 0.120 to 0.132 (γ_{Os} = -9 to +4). This was followed by the study of Roy-Barman and Allègre (1994), which reported data for abyssal peridotites from the North Atlantic ridge, the East Pacific Rise and the Indian Ocean. They reported a somewhat diminished range in isotopic compositions, with ratios varying only from 0.122 to 0.128 (γ_{Os} = -7 to +1). Snow and Reisberg (1995) has been probably the most influential Os isotopic study of abyssal peridotites. In this paper the authors considered the effects of seawater alteration on abyssal peridotites and developed criteria, based on Sr and Nd isotopic data, as well as major element data, to filter out what they considered problematically altered rocks. They reported ^{187}Os/^{188}Os ratios for ten samples deemed free of alteration. The ratios ranged from 0.1221 to 0.1270 (γ_{Os} = -7 to 0), and averaged 0.1246 ± 0.0014 (2 S.E.) (γ_{Os} = -1.9 ± 1.1), which they promoted as the likely average composition of the DMM. There have been numerous ^{187}Os/^{188}Os ratio data published for abyssal peridotites since then (*e.g.*, Parkinson *et al*., 1998; Brandon *et al*., 2000b; Standish *et al*., 2002; Alard *et al*., 2005; Harvey *et al*., 2006; Liu *et al*., 2008; Lassiter *et al*., 2014). The Os isotopic data for 188 abyssal peridotites from these studies are shown in a histogram comparison with data for 81 bulk chondrites in Figure 5.4. The average ^{187}Os/^{188}Os for the abyssal peridotites is 0.1259 ± 0.0011 (2 S.E.) (γ_{Os} = -0.7 ± 0.9), with a median value of 0.1253 (γ_{Os} = -1.3). Remarkably, the mean ratio has not changed significantly since Snow and Reisberg (1995), and the range of isotopic compositions has only expanded modestly since Martin (1991). The database is unfiltered for alteration, so the true average of unaltered samples might be expected to be even closer to the average DMM composition proposed by Snow and Reisberg (1995). The most interesting observation resulting from this data comparison is that if the abyssal peridotite average is representative of the bulk DMM, and if the ^{187}Os/^{188}Os of the BSE is at the upper end of the chondritic range (0.1289; Meisel *et al*., 2001), then the isotopic composition of the DMM is ~3 % lower than the BSE. This means substantial Re has been removed from the DMM over Earth history, leading to retardation in the growth of ^{187}Os/^{188}Os relative to the BSE. Implications for this will be discussed below.

It is useful to briefly review the longstanding issue regarding the apparent offset between the average ^{187}Os/^{188}Os ratio of abyssal peridotites and MORB (Fig. 5.5). This offset was originally noted by Roy-Barman and Allègre (1994), and has been addressed by several papers since then (*e.g.*, Alard *et al*., 2005; Gannoun *et al*., 2007). There are at least three options to explain the offset. First, some portion, or all of the bulk MORB samples analysed have been contaminated while their parental melts transited the oceanic crust or the melts/rocks were directly contaminated with highly radiogenic seawater. Second, MORB may preferrentially sample a portion of DMM that is characterised by higher ^{187}Os/^{188}Os than that accessed by abyssal peridotites, *e.g.*, pyroxenitic veins. Third, melting of the upper mantle to produce MORB selectively involves some phases that are characterised by high ^{187}Os/^{188}Os, compared to average DMM, so the melt is not in isotopic equilibrium with the residue. These three options are not mutually exclusive, and all probably contribute to the differences to some extent. Let's consider these options in a little more detail.

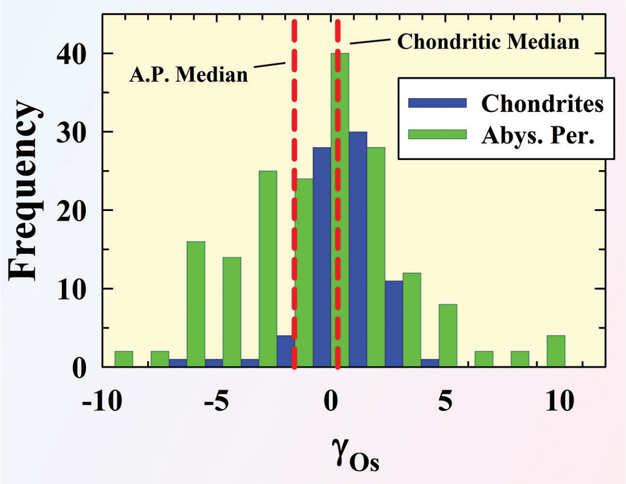


Figure 5.4 Histogram of γ_{Os} values for for 188 abyssal peridotites (see references in the text). Data for 81 bulk chondrites are from Walker *et al*. (2002a). Brandon *et al*. (2005) and Fischer Gödde *et al*. (2010) are shown for comparison. Median values for abyssal peridotites and chondrites are -1.3 and +0.3, respectively.

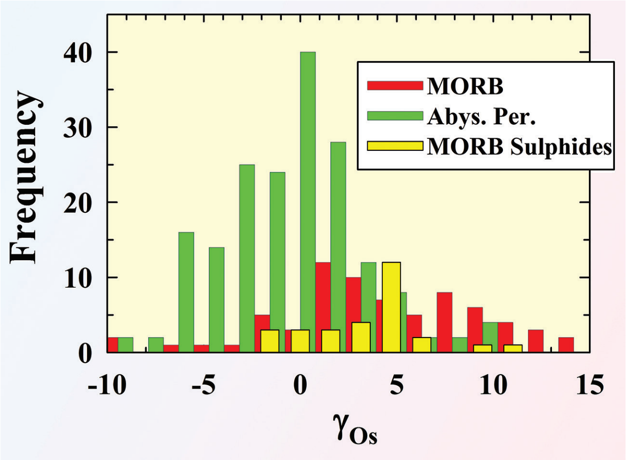


Figure 5.5 Histogram plot of γ_{Os} values for 188 abyssal peridotites (see references in the text) compared with data from 129 MORB glasses from Roy-Barman and Allègre (1994), Escrig *et al*. (2005), Gannoun *et al*. (2007) and Dale *et al.* (2008). Data for sulphides present in MORB are from Roy-Barman *et al*. (1998) and Gannoun *et al*. (2007).

Based on the Os isotopic and HSE elemental microanalysis of sulphides in abyssal peridotites, Alard *et al*. (2005) proposed that Os with relatively high ^{187}Os/^{188}Os is mobile in the upper mantle. Further, they argued that correlations between ^{187}Os/^{188}Os and Pd/Ir observed among some sulphides present in abyssal peridotites mean that the higher ^{187}Os/^{188}Os ratios present in some abyssal peridotites are the result of magmatic processes, rather than interactions with seawater. The study concluded that some abyssal peridotites commonly filtered from Os isotopic comparisons with MORB, because of high ^{187}Os/^{188}Os (*e.g.*, Snow and Reisberg, 1995), should not be filtered. If these samples are not filtered, there is more overlap between data for abyssal peridotites and MORB, and so Alard *et al*. (2005) concluded that there is no gap between the two types of rocks.

By contrast, Gannoun *et al*. (2007) concluded that there is a real difference between the average ^{187}Os/^{188}Os in abyssal peridotites and MORB, with a mean ratio of 0.133 (γ_{Os} = +4.7) for MORB, compared to ~0.125 (γ_{Os} = -1.3) for abyssal peridotites (Fig. 5.5). It was reported in the study that sulphides present in MORB are always less radiogenic than their glass hosts. From this they concluded that most MORB melts have been contaminated by older, more radiogenic oceanic crust. They also noted a correlation between ^{187}Os/^{188}Os and Os concentration in the sulphides. Those sulphides with the highest concentrations of Os have ^{187}Os/^{188}Os ratios similar to abyssal peridotites, yet most sulphides are more radiogenic than the abyssal peridotite mean (Fig. 5.5). This suggests that most sulphides present in MORB precipitated following some level of contamination. Gannoun *et al*. (2007) concluded that both abyssal peridotites and MORB sample the same DMM source, but that MORB glasses (and even sulphides) are not reliable recorders of their mantle sources. I have never worked with Os isotopes in MORB, but these studies lead me to the conclusion that it is really difficult to obtain reliable Os isotopic information about their mantle sources from them. I will continue to stay away from MORB!

Before leaving the topic of abyssal peridotites, it should be noted that, although we had previously analysed ^{186}Os/^{188}Os ratios in Os-Ir-Ru alloys (Walker *et al*., 1997; Brandon *et al*., 1999), the measurement of a suite of abyssal peridotites from the Kane Fracture Zone in the Atlantic Ocean by Brandon *et al*. (2000b) were the first *bona fide* rocks from the DMM to be analysed for ^{186}Os/^{188}Os. The 6 samples analysed gave uniform ^{186}Os/^{188}Os ratios within analytical uncertainties, averaging 0.1198353 ± 7 (2 S.E.). This is important because the chondritic ratio indicates that the Pt/Os ratio of the DMM, and presumably the BSE, did not deviate from the chondritic ratio by more than ±30 %. This provides a strong constraint on the long-term adherence of Pt/Os to chondritic ratios in the mantle. Changes in the Pt/Os ratio of the DMM, as a consequence of crustal extraction, is likely very limited, so the ^{186}Os/^{188}Os ratio of the DMM is indistinguishable from BSE at the current levels of isotopic resolution.

5.4 Ophiolites

Most ophiolites are believed to be tectonically obducted slivers of, broadly defined, oceanic lithosphere (*e.g.*, Miyashiro, 1975; Dilek and Furnes, 2011). Consequently, with some caveats, they can provide important information about the compositions of both the recent and ancient DMM, in some instances with excellent field control (Fig. 5.6a). Ophiolites are lots of fun if you are interested in the mantle because they allow you to walk around the upper mantle and see what is to be seen. The Leka ophiolite in Norway even provides a picnic table with seating right on the petrologic Moho, should your legs get wobbly from the exciting view (Fig. 5.6b). The primary mantle lithologies present in the upper mantle sections of ophiolites include harzburgites, lherzolites, dunites, pyroxenites and chromitites. The presence of these lithologies, in the context of their spatial associations allows detailed assessment of the distribution of siderophile elements within the DMM, the bulk composition of siderophile elements in the DMM, and in some instances permits determination of the timing of events acting upon this portion of the mantle (*e.g.*, Sharma *et al.*, 1995). Thus, ophiolites can provide an important, if imperfect, field-based means to examine the chemical/isotopic structure and evolution of the DMM, given the temporal extent of well-preserved ophiolites.

Figure 5.6 **(a)** Photo of the *ca*. 497 Ma Leka, Norway ophiolite. The Leka ophiolite is characterised by excellent exposure of upper mantle rocks. Subtle variations in the colours of the rocks reflect different lithologies present in this portion of the ophiolite, several hundred metres below the petrologic Moho. **(b)** The petrological Moho at Leka is well marked, and a picnic table is provided on which to sit and enjoy the scenery.

Although ophiolites offer an excellent opportunity for direct "hands on" study of the mantle, most ophiolites are structurally complex, and petrologically record multiple stages of melting, refertilisation and subsequent alteration (*e.g.*, Kelemen *et al.*, 1992). Further, ophiolites are formed in diverse tectonic settings. Based on structure, petrology and geochemistry, ophiolites are commonly divided into types that include those formed at mid-ocean ridges (MOR) and those formed in supra-subduction zone (SSZ) settings (Dilek and Furnes, 2011). Many ophiolites have, therefore, also been affected by SSZ processes, especially fluid transport of materials from slabs to mantle wedges. In particular, fluid mobilised lithophile elements, such as Ba, Sr and Li can be enriched in lithologies associated with SSZ settings, particularly gabbros and basaltic rocks associated with sheeted dikes and extrusive rocks. The general insensitivity of most siderophile elements to fluid transport is presumably advantageous when studying primary mantle features captured in ophiolites, although the effects of SSZ fluid transport on siderophile elements in ophiolites are still not yet well documented. Some prior studies have highlighted the variable effects SSZ processes may have on HSE (O'Driscoll *et al.*, 2012) and Os isotopes (*e.g.*, Brandon *et al.*, 1996). As an additional complexity, almost all upper mantle assemblages in ophiolites have been affected by serpentinisation, most likely through interactions with seawater. Fortunately, serpentinisation appears to have little impact on the HSE and Os isotopes in these rocks. This is likely a reflection of the highly reducing conditions that occur during serpentinisation, leading to the stabilisation of host sulphides (*e.g.*, Snow and Reisberg, 1995; Foustoukos *et al.*, 2015).

Considerable HSE and Os isotopic data have been published for mantle rocks present in ophiolites (*e.g.*, Luck and Allègre, 1991; Walker *et al.*, 1996; Snow *et al.*, 2000; Tsuru *et al.*, 2000; Büchl *et al.*, 2002, 2004; Meibom *et al.*, 2002; Walker *et al.*, 2002a; Frei *et al.*, 2006; Pearson *et al.*, 2007; Batanova *et al.*, 2008; Schulte *et al.*, 2009; Hanghøj *et al.*, 2010; O'Driscoll *et al.*, 2012; González-Jiménez *et al.*, 2014a). Some important observations can be made. For example, the HSE abundances in peridotitic rocks don't appear to have changed significantly over at least the past 2 Ga. The HSE patterns for relatively fertile peridotites sampled from the ~6 Ma Taitao ophiolite, Chile, the 497 Ma Leka ophiolite, Norway, and the 1.96 Ga Jormua ophiolite, Finland are all characterised by generally similar, flat, BSE-normalised patterns with respect to Os, Ir, Ru and Pt (Fig. 5.7a,b,c). Further, most peridotite samples from these ophiolites plot within the range of compositions reported for modern abyssal peridotites. These and comparable data for other ophiolites provide strong evidence that, with respect to HSE, at least some abyssal peridotites and some ophiolite peridotites sample the same mantle, and have been little modified by extra-mantle processes, such as seafloor alteration, in the case of abyssal peridotites, and SSZ processing and surface weathering, in the case of some ophiolite peridotites.

The mantle sections of ophiolites also allow us to target diverse mantle rocks for analysis. In particular, dunites are commonly interpreted to represent former melt channels within which basaltic melts reacted with peridotites to produce these olivine rich rocks (*e.g.*, Kelemen, 1990). This process can lead to considerable modification of original HSE and Os isotopic compositions (Büchl *et al.*, 2004). Bulk silicate Earth normalised HSE patterns for dunites from the Leka ophilite are shown in Figure 5.8. Although some of the dunites have patterns that are similar to spatially associated harzburgites and lherzolites, other dunites are characterised by much higher variations in absolute and relative abundances of HSE, compared to the Leka harzburgites and lherzolites (Fig. 5.8). Of note, Pt and Pd were strongly mobilised in some of the Leka dunites, with some rocks characterised by very high and low abundances of these elements. Dunites with similarly fractionated patterns have been reported for other ophiolites, such as Troodos and Unst (Büchl *et al.*, 2002; O'Driscoll *et al.*, 2012).

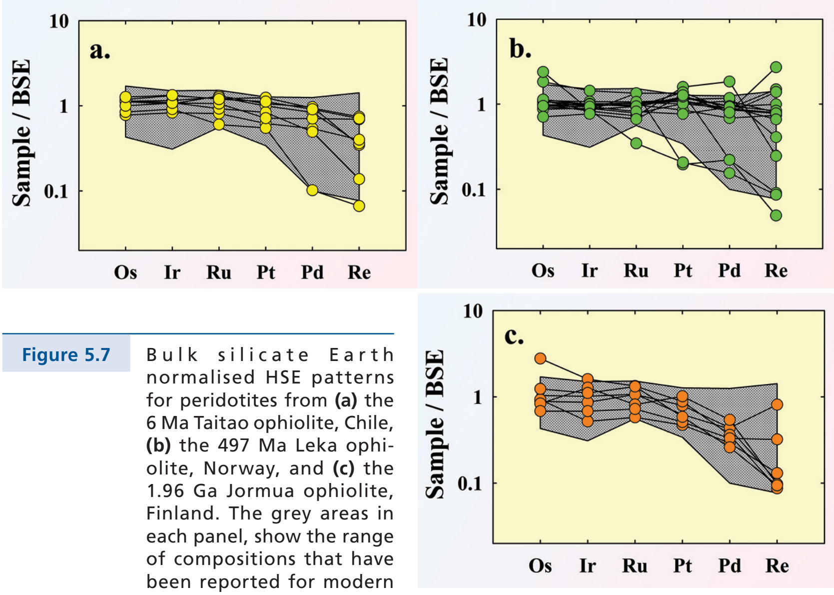


Figure 5.7 Bulk silicate Earth normalised HSE patterns for peridotites from **(a)** the 6 Ma Taitao ophiolite, Chile, **(b)** the 497 Ma Leka ophiolite, Norway, and **(c)** the 1.96 Ga Jormua ophiolite, Finland. The grey areas in each panel, show the range of compositions that have been reported for modern abyssal peridotites from Figure 5.3. Most of these ophiolite peridotites have HSE patterns that are indistinguishable from patterns for abyssal peridotites, regardless of their age. Data are from Schulte *et al.* (2009), O'Driscoll *et al.* (2015) and Ginley, unpublished.

Other types of upper mantle rocks are also worthy of note from the standpoint of HSE. Ophiolite chromitites in the form of pods and seams are known to incorporate high concentrations of HSE. In the case of the 492 Ma Unst (Shetland) ophiolite, very high concentrations of HSE (>1 ppm) are present in some chromitite seams, such as the Harold's Grave locale (Fig. 5.9). The origins of the Unst chromitites, and chromitites present in other ophiolites are much debated (*e.g.*, Prichard and Neary, 1982; O'Driscoll *et al.*, 2012; González-Jiménez *et al.*, 2014a,b). Despite questions regarding their mechanisms of formation, there is little doubt that they concentrate and fractionate the HSE. This may stem from the tendency of crystallising chromite to collect diverse platinum-group minerals, which are the actual hosts of the HSE in the chromitites (*e.g.*, Walker *et al.*, 1996; Prichard *et al.*, 2008). These minerals may partially or wholly precipitate from metasomatic fluids/melts that interacted with pre-existing chromitite (González-Jiménez *et al.*, 2014a). For the Unst chromitites, the seams with the highest concentrations are also characterised by highly fractionated HSE patterns, relative to BSE, as well as the DMM (Fig. 5.9).

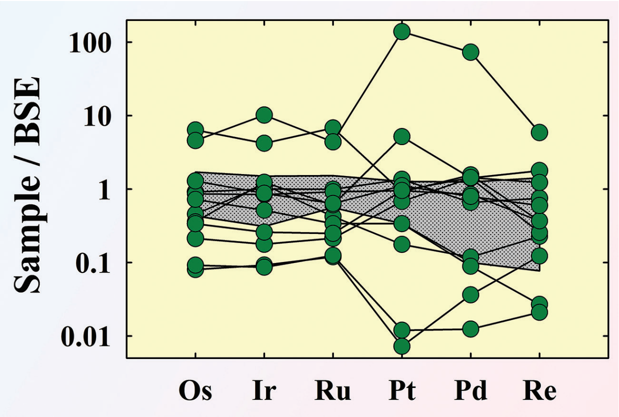


Figure 5.8 Bulk silicate Earth normalised HSE patterns for dunites from the Leka ophiolite, Norway. The grey area shows the range of compositions that have been reported for abyssal peridotites from Figure 5.3. Leka dunites are characterised by much greater variations in absolute and relative abundances of HSE compared to spatially associated harzburgites (Fig. 5.7b). Data are from O'Driscoll *et al.* (2015).

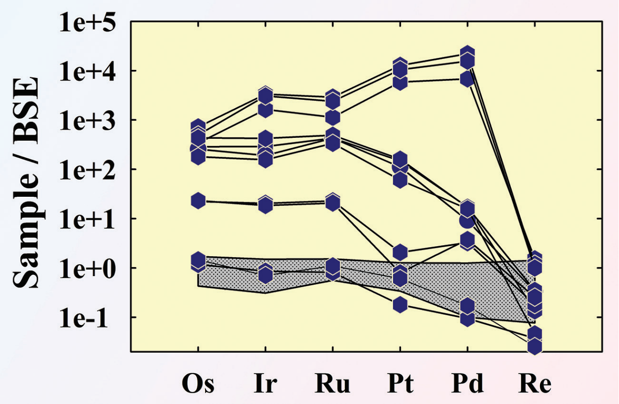


Figure 5.9 Bulk silicate Earth normalised HSE patterns for chromitites from the Unst (Shetland Islands) ophiolite, Scotland. The grey area shows the range of compositions that have been reported for abyssal peridotites from Figure 5.3. The chromitite data are from O'Driscoll *et al.* (2012).

Osmium isotopes provide complementary information to the absolute and relative HSE abundances in ophiolitic rocks. Because of the difficulties in measuring Os isotopic compositions in the 1960's, the pioneers of Os research, not surprisingly, focused attention on materials with very high concentrations of Os. These materials included iron meteorites (see above) and Os-Ir-Ru alloy grains (which include osmiridiums), some of which are weathered from the mantle sections of ophiolites, and collect as placers in streambeds. Hence, the ^{187}Os/^{188}Os ratios (initially reported as ^{187}Os/^{186}Os ratios) of certain components of the mantle sections of ophiolites have been studied for more than 50 years. I find the early studies to be very interesting because I well understand the analytical problems these authors faced. Further, we have periodically gone back to some of the same types of materials to study the evolution of ^{186}Os/^{188}Os in the mantle. Hirt *et al.* (1963b) reported the first Os isotopic data for what were likely ophiolite-derived alloys from Australia, Alaska, South Africa, South America and the Urals Mountains. These authors offered little interpretation of the variations observed in Os isotopic composition among the materials analysed. It was a major accomplishment just to get some reliable numbers. Riley and Delong (1970) eventually plotted the data from the Hirt *et al.* (1963b) study *versus* assumed ages for the alloy grains. From the observed linear trend, they concluded that the mantle evolved over Earth history with an approximately chondritic Re/Os ratio to the present time. This was an important bedrock observation that remains critical to our understanding of the origin of the HSE in the mantle.

As noted above, the next big advancement in our understanding of the Re-Os system in the DMM was the development of higher precision SIMS-based measurements, first published by Allègre and Luck (1980). In this study, the authors largely re-did the alloy study of Hirt *et al.* (1963b), examining alloy grains from mostly the same ophiolite locales. With more and higher precision data they came to the conclusion that the mantle evolved with an essentially constant Re/Os ratio through time. They recognised that this is a reasonable observation, given the fact that continental crust sequesters very little Re and Os from the mantle. They noted that this is in contrast to the major effects the growth of continental crust has had on the Rb-Sr, Sm-Nd and U-Pb isotopic systems in the mantle. They did not, however, note the peculiarity of a mantle that retained a chondritic Re/Os in a planet where the lion's share of the planet's Re and Os was sequestered into the core. It took until the study of Morgan (1985) to link the Os isotopic data for mantle-derived materials from Allègre and Luck (1980) to the concept of late accretion. There have been numerous subsequent studies of Os isotopic compositions (including ^{186}Os/^{188}Os) of ophiolite-derived Os-Ir-Ru alloys at increasingly higher levels of precision (Walker *et al.*, 1997; Brandon *et al.*, 1998; Meibom *et al.*, 2002; Malitch, 2004; Walker *et al.*, 2005; Brandon *et al.*, 2006; Pearson *et al.*, 2007). By and large, studies of alloy grains have provided results that continue to indicate that the DMM has evolved through time with "chondritic" long–term Re/Os and Pt/Os, and therefore, ^{187}Os/^{188}Os and ^{186}Os/^{188}Os ratios. For example, in Walker *et al.* (2005) we reported laser ablation ICP-MS data for 112 alloy grains from Port Orford, Oregon. These grains likely formed in the DMM as a result of S removal during partial melting (Fonseca *et al.*, 2012; Foustoukos *et al.*, 2015), and eventually weathered out of the 162 Ma Josephine ophiolite. Presumably these grains sample the Os present in random domains within the DMM, in some cases concentrating Os from as much as ~1 m^3 of peridotite. The median $\gamma_{Os(162\ Ma)}$ value for the Josephine grains from our study is -0.4. The median initial γ_{Os} value for the grains, as well as the modal distribution of compositions, is very similar to the median value of all published abyssal peridotite data of -1.3, and their modal distribution (Fig. 5.10).

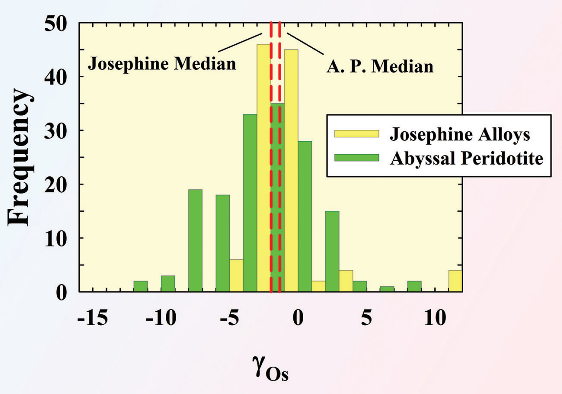


Figure 5.10 Histogram of data for Os isotopic data from abyssal peridotites (see references in text) compared with data for 110 Os-Ir-Ru alloy grains from the 162 Ma Josephine ophiolite (Walker *et al.*, 2005). Median values are within 1 % of each other, suggesting mantle Os recording similar average long-term Re/Os.

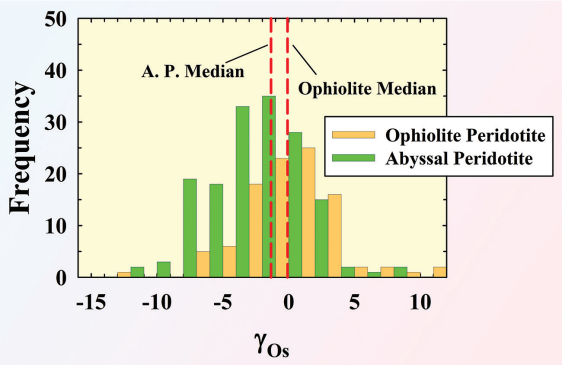


Figure 5.11 Histogram plot of bulk ophiolite (from Leka, Unst and Taitao ophiolites) *versus* data for modern abyssal peridotites. Median values for ophiolite and abyssal peridotites are shown for comparison. Abyssal peridotite data are from Snow

and Reisberg (1995), Luguet *et al*. (2001), Alard *et al*. (2005), Becker *et al*. (2006), Liu *et al*. (2009) and Lassiter *et al*. (2014). Ophiolite data are from Schulte *et al*. (2009) and O'Drisocoll *et al*. (2012, 2015).

Although fewer in number, the ^{187}Os/^{188}Os ratios of bulk peridotites from ophiolites provide results that are similar to those observed for alloy grains. For example, a comparison of combined ^{187}Os/^{188}Os isotopic data for bulk peridotites from our lab, produced using the same analytical methods for the Leka, Unst and Taitao ophiolites, with abyssal peridotites, also shows very similar median compositions and isotopic distributions (Fig. 5.11).

5.5 Summary Observations regarding Siderophile Elements in the DMM

In Walker *et al*. (2002b), we argued that the best way to characterise the evolution of ^{187}Os/^{188}Os in the DMM through time was to analyse chromitites from ophiolites of diverse age. If chromitites are major collectors of Os, then the Os contained within a chromitite seam or pod would provide an averaging of a large domain of the upper DMM. Further, chromitites are normally characterised by very low Re/Os ratios, so age corrections of ^{187}Os/^{188}Os in non-zero age ophiolites are typically minimal. Based on our projection of chromitite data to the present for a global suite of ophiolites, ranging in age from ~50 to 900 Ma, we concluded that the modern ^{187}Os/^{188}Os ratio of the DMM is 0.1281 ± 9 (γ_{Os} = +0.9 ± 0.7), placing the average only ~1 % lower than our estimate of 0.1296 ± 8 for the BSE (Meisel *et al*., 2001). As first noted by Allègre and Luck (1980), the formation of continental crust has had very little effect on the Re/Os of the DMM. By contrast, even relatively small changes in Re/Os in the DMM, compared to the BSE, must result from the production, recycling, and isolation of oceanic crust, with its comparatively high Re concentrations. The estimate for the DMM, based on chromitite data, requires ~1 to 3 wt. % of Re-bearing oceanic crust, relative to the BSE, to be removed and isolated from the DMM for periods of 2.5 to 1.0 Ga, respectively (Fig. 5.12).

With many more Os isotopic data in hand for chromitites and spatially associated bulk peridotites, however, it now seems apparent to me that the Os isotopic compositions of ophiolite chromitites are biased towards more radiogenic ratios than spatially associated peridoitites (*e.g.*, O'Driscoll *et al*., 2015). This may reflect preferential extraction of radiogenic Os from either mafic veins or sulphides, and the subsequent deposition of Os that is preferentially ^{187}Os-enriched into chromitites, forming as a result of metasomatic processes (*e.g.*, Alard *et al*., 2005; González-Jiménez *et al*., 2014a). Thus, the true HSE abundances and average ^{187}Os/^{188}Os ratio of the DMM are probably better determined through the averaging of data for ophiolite and abyssal periodites. If so, the data for ophiolite and abyssal peridotites support the contention, largely developed via the analysis of peridotite xenoliths from SCLM, that Ru/Ir ratios in the BSE really are higher than chondritic averages (*e.g.*, Becker *et al.*, 2006) (Fig. 5.13), and not the result of secondary processes (*e.g.*, Lorand *et al.*, 2008). By contrast, it is impossible to see a difference in Pd/Ir because partial melting has much more seriously compromised the Pd contents of these rocks than Ru. In my view, there are too many rocks from the DMM that show similar enrichments in Ru/Ir for the enrichment to result solely from secondary processes. In addition, the modern average $^{187}Os/^{188}Os$ ratio of the DMM appears to be very close to 0.125 (γ_{Os} = -1.6), which is in turn, quite similar to the original estimate by Snow and Reisberg (1995)! If this difference between the DMM and BSE is correct, the data require the removal and isolation of between ~3 and 9 wt. % of Re-bearing oceanic crust, relative to the BSE, for periods of 2.5 to 1.0 Ga, respectively (Fig. 5.12).

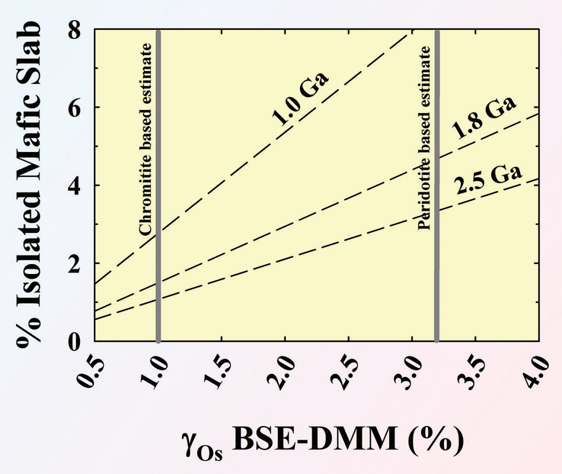


Figure 5.12 Plot showing the mass of recycled mafic slab (as percent of total mass of mantle) that must be isolated for periods of 1.0, 1.8 and 2.5 Ga to account for ^{187}Os depletion in the DMM as delineated by the difference between the γ_{Os} values of the BSE and the DMM (as %), based on estimates derived from chondritites and peridotites. Figure is modified from Walker *et al.* (2002b).

Osmium isotopes may even provide us with some important insights into the age structure of melting preserved in the DMM. Three of the Os isotope studies of alloy grains used *in situ* measurement methods to make $^{187}Os/^{188}Os$ ratio measurements of large numbers of grains from multiple sites (Meibom *et al.*, 2002; Walker *et al.*, 2005; Pearson *et al.*, 2007). Since these grains contain essentially no Re, they record the Os isotopic composition of their immediate surroundings in the DMM at the time they formed. The combined data for 1462 grains are interesting in that they show a generally normal distribution of initial γ_{Os} values (Fig. 5.14). The peak of 0.127 (γ_{Os} = 0), when normalised to the present time, is ~1 % higher than determined by averaging data from abyssal and ophiolite peridotites. It is clear from these data that, as with other radiogenic isotope

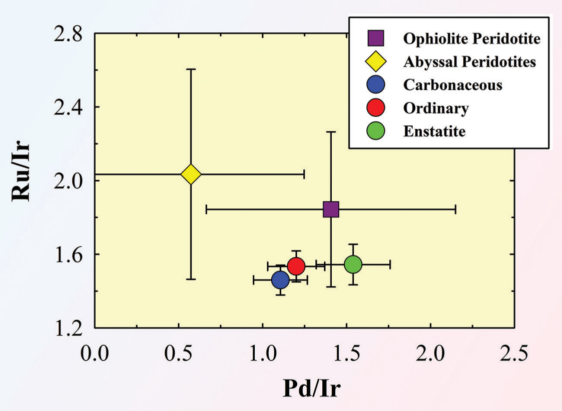
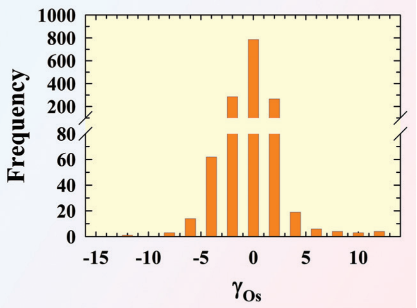


Figure 5.13 Average Pd/Ir *versus* Ru/Ir for bulk samples of ophiolite peridotites, abyssal peridotites, as well as ordinary, carbonaceous and enstatite chondrites. Ophiolite data are from Batanova *et al*. (2008), Schulte *et al*. (2009) and O'Driscoll *et al*. (2015). Abyssal peridotite data are from Luguet *et al*. (2001), Alard *et al*. (2005), Becker *et al*. (2006) and Liu *et al*. (2009). Chondrite data are from Horan *et al*. (2003), Brandon *et al*. (2005), Fischer-Gödde *et al*. (2010) and Van Acken *et al*. (2011). Error bars represent 1σ of data. On average ophiolite and abyssal peridoitites have higher Ru/Ir than chondrites. Pd/Ir is highly variable in ophiolite and abyssal peridotite data because of its incompatible nature during mantle melting.

systems, the ^{187}Os/^{188}Os of the DMM is variable. About 10 % of the alloy grains have Proterozoic model Os ages. One grain has an Archean model age. The isotopically depleted grains highlight the fact that the recent DMM harbours domains whose Os records ancient melting events, as previously shown for bulk rocks (*e.g.*, Snow and Reisberg, 1995; Standish *et al.*, 2002; Alard *et al.*, 2005; Warren, 2016). These types of Os isotopic heterogeneities are also manifested in bulk ophiolite and abyssal peridotites (*e.g.*, Standish *et al.*, 2002; Schulte *et al.*, 2009). For example, Schulte *et al.* (2009) reported a negative correlation between ^{187}Os/^{188}Os ratios of bulk peridotite samples and the Mg# of olivines for bulk peridotite samples from the Taitao, Chile ophiolite (Fig. 5.15a). This suggests that the whole rock samples of the DMM, in some cases, may retain major element evidence for the ancient events recorded by Os isotopes. There remain some observations relating to ophiolite peridotites that remain difficult to explain. One curious aspect of the Taitao dataset is the modest positive correlation between Al_2O_3 and ^{187}Os/^{188}Os for bulk peridotite samples (Fig. 5.15b). In Figure 4.1 it was shown, using a similar diagram, how a positive linear correlation might be present in modern mantle peridotites (either in DMM or SLM) as a result of variable extents of melting during a single, ancient melting event (grey to white symbol transition). In such a case, the trend might be expected to extend through the BSE composition, as is the case for trends for numerous SCLM peridotite suites (*e.g.*, Gao *et al.*, 2002). The Taitao trend (green symbols), however, does not pass through the BSE composition. These data are consistent with a second melting event that was superimposed on an earlier (Proterozoic) melting event if, for example, this portion of the mantle was reprocessed by additional melting under the nearby spreading centre (Chile Triple Junction). An additional stage of melting would drive the Al_2O_3 content down for individual samples. What is surprising is that a linear trend was maintained, suggesting that the less refractory peridotites melted more (and lost more Al_2O_3) compared to the more refractory rocks, in proportion to their prior proportions of melt removal.

Figure 5.14 Histogram of initial γ_{Os} values for 1462 Os-Ir-Ru alloy grains from the 162 Ma Josephine ophiolite, Oregon, the 119 Ma Lubuosa ophiolite, Tibet, the 387 Ma Urals ophiolite, and the 630 Ma Tasmanian ophiolite. Data are from Meibom *et al.* (2002), Walker *et al.* (2005) and Pearson *et al.* (2007). Seven of the grains measured have γ_{Os} ratios that are higher than shown here.



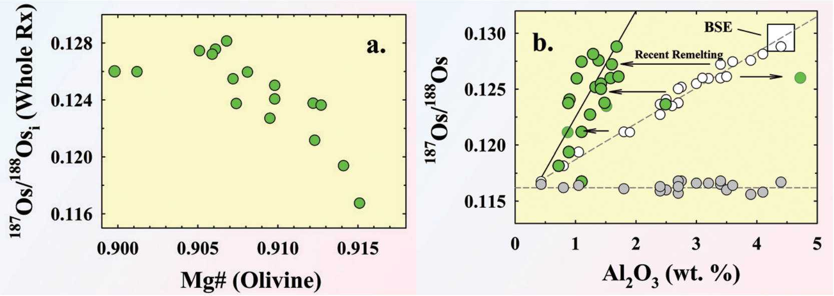


Figure 5.15 **(a)** Plot of Mg# in relict olivine *versus* initial $^{187}Os/^{188}Os$ in whole rock samples of peridotite from the 6 Ma Taitao ophiolite. For reference, the Mg# of primitive mantle peridotites has been estimated to be 0.88 (McDonough and Sun, 1995). **(b)** Al_2O_3 *versus* $^{187}Os/^{188}Os$ plot for the same peridotites shown in **(a)** (green circles). Grey and white symbols show hypothetical pathways the rocks may have taken to evolve to their present day compositions (see also Fig. 4.1). Figures are modified from Schulte *et al.* (2009).

One final issue regarding the DMM, for which siderophile elements may prove useful, is determining how the DMM chemically evolved through Earth history. As noted above, the Os isotopic composition of the DMM appears to have evolved with a lower Re/Os than the BSE. Most of the data upon which this observation is based, however, on rocks that are less than 1 Ga. Is there evidence for increasing removal and isolation of Re from the DMM as time progressed? If so, how did this change the evolutionary curve? There are only a few hints to the answer to this question at present, because very few initial Os isotopic data of sufficiently high precision are available for ancient DMM. Bennett *et al.* (2002) reported the first high precision Os isotopic data for early Earth rocks that may be representative of the DMM. They found chondritic initial $^{187}Os/^{188}Os$ for 3.8 Ga rocks from the Itsaq Gneiss Complex of southern West Greenland, and 3.46 Ga rocks from the Pilbara region of Western Australia. These results provide us with confidence in the assumption that the mantle became chondritic-like with regard to HSE within the first 1 Ga of Earth history.

In Tsuru *et al.* (2000) we reported initial Os isotopic data for peridotites from the 1.96 Ga Jormua ophiolite. Because of the Proterozoic age of the rocks, we considered only bulk peridotite samples with $^{187}Re/^{188}Os$ <0.5, in order to minimise inaccuracy in age correction. It can be seen in Figure 5.16 that initial γ_{Os} values for peridotitic samples from the Jormua ophiolite were offset downward by ~3 % compared to the average of the modern Gakkel Ridge abyssal peridotite suite from Liu *et al.* (2008), the best studied suite of modern abyssal peridotites for Os isotopes. This offset may indicate the Jormua peridotites do not sample the Proterozoic DMM, but instead sample SCLM that formed during the Archean, as suggested in Tsuru *et al.* (2000). Alternatively, it may mean that the Gakkel Ridge abyssal peridotite suite has Os isotopic compositions that are biased to higher, time normalised $^{187}Os/^{188}Os$ ratios than the true DMM. The range of isotopic compositions is similar for both Jormua and Gakkel Ridge, however, suggesting that the variable prior melt history observed in the modern DMM was equally well developed by 2 Ga.

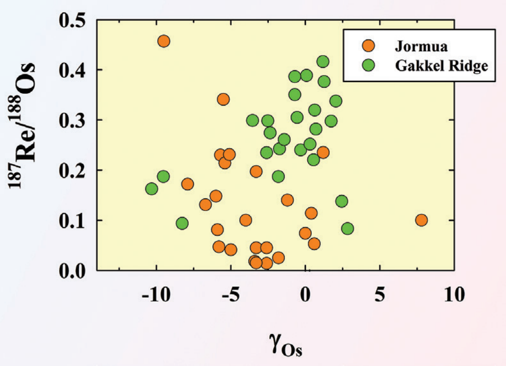


Figure 5.16 Plot of initial γ_{Os} values for bulk peridotites from the 6 Ma Taitao ophiolite and the 1.96 Ga Jormua ophiolite. Only samples with $^{187}Re/^{188}Os$ ratios <0.5 are included in order to minimise uncertainties resulting from age corrections for the Jormua data. Gakkel Ridge data are from Liu *et al.* (2008) and Jormua ophiolite data are from Tsuru *et al.* (2000) and Ginley (unpublished).

6. SIDEROPHILE ELEMENTS IN SUBCONTINENTAL LITHOSPHERIC MANTLE

Sub-continental lithospheric mantle (SCLM) is interpreted by many to be mantle that began life as DMM, then melted in a plume or subduction zone environment, and finally became emplaced under continental crust (Maaloe and Aoki, 1977; Boyd and Mertzman, 1987). This interpretation is based on both the spatial relations between crust and lithospheric mantle, and the observation that most lithospheric mantle is depleted in its basaltic component (Jordan, 1978). The formation of SCLM results in mantle that is chemically distinct, buoyant, and (at least for a time) physically isolated from the DMM. It is accessible to us in the form of peridotite xenoliths, which are small chunks of rock removed from the SCLM and brought to the surface in most cases by relatively young volcanic systems. Famous locations where such xenoliths can be collected include San Carlos, Arizona, Kilbourne Hole, New Mexico, Hannouba, China, and the Jagersfontein mine, South Africa. Sub-continental lithospheric mantle peridotite xenoliths can be very fresh, and easily accessible (Fig. 6.1). Subcontinental lithospheric mantle is also accessible to us in the form of orogenic peridotite complexes or massifs, which are tectonically emplaced slivers of SCLM into stable continental crust. Examples include the Ronda peridotite, Spain, and the Lherz massif in France.

In numerous instances it has been shown that the age of formation of SCLM is approximately the same as the age of formation of the overlying continental crust (Pearson *et al.*, 1995b; Carlson *et al.*, 2005), although there are also notable exceptions (Griffin *et al.*, 1998; Peslier *et al.*, 2000; McCoy-West *et al.*, 2013). The physical linkage of SCLM and overlying continental crust can last for billions of years. In some instances, however, the ancient SCLM is either delaminated from the overlying continental crust, or eroded by rising melts. In such instances, the age of the resulting SCLM may be indistinguishable from the modern DMM, despite the presence of overlying Archean crust (Gao *et al.*, 2002).

My first exposure to SCLM came in the form of little vials of peridotite powders provided to me by *Steve Shirey* and *Rick Carlson* during my postdoc at DTM (see Section 1). My group, especially postdocs *Thomas Meisel* and *Harry Becker*, periodically worked with samples of SCLM, again in the form of well-studied powders, within the context of our attempts to refine Os isotopic compositions and HSE abundances in the BSE (see Section 4 above). I didn't get to work with real rocks from the SCLM (not powders!) until I was contacted by *Professor Fu-yuan Wu*, then at Jilin University in China, to work on peridotites from the SCLM underlying the North China Craton. He came to the University of Maryland for a visit to analyse some xenoliths, and we were able to generate a paper showing that, for at least some portions of the craton, there was a strong mismatch between the age of overlying crust (older) and underlying SCLM (younger) (Wu *et al.*, 2003). This observation was consistent with some prior geophysical studies suggesting that the ancient SCLM had somehow been separated from the overlying Archean crust (*e.g.*, Menzies *et al.*, 1993; Griffin *et al.*, 1998). It turns out that several other groups were working with Os isotopes on the same general project, including a recent addition to our department, *Roberta Rudnick*, and her Chinese collaborator *Shan Gao* (Wuhan University) who had just published Gao *et al*. (2002). We soon agreed to collaborate on this very large project, and *Roberta* and I began to co-advise a new student to work on the project, *Jingao Liu*. *Jingao* proved to be a very talented and energetic student, and he ended up producing considerable data for xenoliths from various sites in the North China Craton, and ultimately generating a clearer picture of the highly variable age structure of this parcel of SCLM (*e.g.*, Liu *et al*., 2010, 2011).

Figure 6.1 **(top)** A large basaltic block hosting numerous peridotite xenoliths (green inclusions) at Yangyuan, China. In front row from left to right: Roberta Rudnick, Shan Gao, Jingao Liu, Yuan Yuan Xiao. In back row: myself, Fu-yuan Wu, Yong Xin Pan and Lei Wang. **(bottom)** The beautiful Xenolith Valley near Fansi, China, where numerous xenoliths were collected on a 2007 trip.

Most work on siderophile elements as related to SCLM has been directed at the HSE, and especially Os isotopes. Several reviews of this topic have been published within the past decade (*e.g.*, Rudnick and Walker, 2009; Lorand *et al.*, 2013; Aulbach *et al.*, 2016; Becker and Dale, 2016; Luguet and Reisberg, 2016), so there is no need to provide a detailed additional review of HSE in the SCLM here. Further, the basics of Re-Os dating melt depletion in mantle materials are discussed above in Section 4.1. Neverthless, some discussion of problems specific to the study of SCLM using siderophile elements is worthwhile.

One important lesson learned over the past two decades is that not all rocks from the SCLM were created equal for Os dating. Cratonic SCLM, sampled by kimberlite, is typically highly refractory and often provides robust Os model ages. By contrast, off cratonic SCLM, normally sampled by alkali basalts and massifs, is generally much less refractory. In off craton peridotites, the lack of high degrees of melt depletion, coupled with the corresponding lack of complete Re removal, usually means that Os T_{RD} ages do not reflect true melt depletion ages (*e.g.*, Luguet and Reisberg, 2016). Put another way, only the most refractory off craton peridotites are worth examining for Os T_{RD} ages. Such portions of the SCLM can potentially be dated using Os isotopes if you can find suitably refractory rocks, or where there are good correlations between ^{187}Os/^{188}Os and chemical indicators of melt depletion, such as Al_2O_3 or Lu (see Section 4.1 above).

There are a few additional observations that have gradually solidified into new ways of thinking about siderophile element data that need reiteration here. One observation is that the original assumption made in Walker *et al.* (1989) of closed-system behaviour of Re-Os systematics of SCLM peridotites, from the time of initial melt depletion to just prior eruption, must be critically assessed for all applications. As a result of numerous studies of large numbers of xenoliths from diverse areas (*e.g.*, Luguet *et al.*, 2007; Liu *et al.*, 2011; Lorand *et al.*, 2013) it has become increasingly obvious that the HSE, including Os isotopes, of SCLM underlying some portion of continental crust, can be modified by complex processes at disparate times. Early applications of Os isotopes to constrain the age of melting in the SCLM commonly made the assumption that the oldest model age of a given suite could be used to define the age of melting. In the past, if we found one out of ten rocks analysed from a given location to have a Proterozoic Os model age, we likely would have concluded that the SCLM formed during the Proterozoic. Although there are a few locales where SCLM evidently formed through variable extents of melting of DMM, with more or less uniform initial ^{187}Os/^{188}Os, resulting in surprisingly good isochron systematics (*e.g.*, Reisberg *et al.*, 1991; Gao *et al.*, 2002), we now know that the DMM is characterised by a broad range of Os isotopic compositions (see above), including a significant share of rocks and mineral or alloy grains with Proterozoic model ages (*e.g.*, Alard *et al.*, 2005). Thus, Os isotopic dating of melting for a given locale requires analysis of a substantial number of rocks, and the distribution of isotopic compositions must be compared with that observed in the modern DMM (Rudnick and Walker, 2009). In many cases the difference is very clear. For example, data reported by Gao *et al.* (2002) and Liu *et al.* (2011) indicate that the xenoliths from the

Trans-North China Orogen portion of the North China Craton (NCC) define a range in initial Os isotopic compositions of about 15 γ_{Os} units that is similar to modern abyssal peridotites, and the Josephine ophiolite alloy grains (Fig. 6.2). However, their mean isotopic composition is clearly offset nearly 5 % below the modern mantle. This provides robust evidence that the sampled SCLM underlying this portion of the NCC is of mid-Proterozoic age.

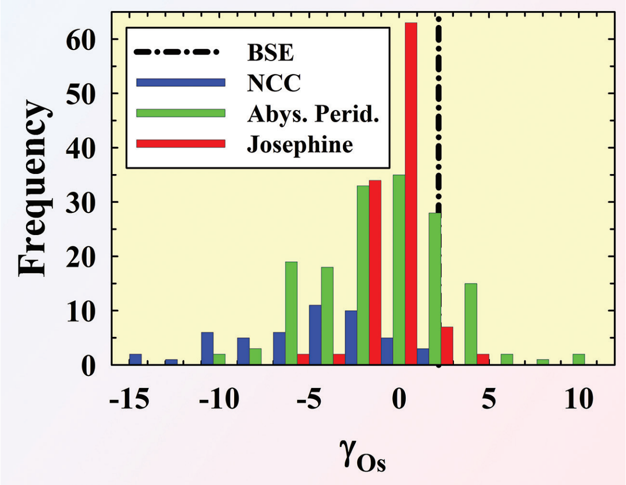


Figure 6.2 Histogram plot of Os isotopic data (in γ_{Os} notation) for peridotite xenoliths from the Trans-North China Orogen portion of the North China Craton (NCC) relative to Josephine ophiolite alloy data and data for modern abyssal peridotites. Data for the NCC are from Liu *et al.* (2010, 2011). Data for the alloy grains are from Walker *et al.* (2005). Data for abyssal peridotites are from Snow and Reisberg (1995), Parkinson *et al.* (1998), Brandon *et al.* (2000b), Standish *et al.* (2002), Alard *et al.* (2005), Harvey *et al.* (2006), Liu *et al.* (2008) and Lassiter *et al.* (2014).

As relates to the first observation, Os isotopic data are best interpreted within the context of the associated HSE concentration data. As noted above, the absolute and relative abundances of some of the HSE, most notably Pt, Pd and Re, record both melt removal events, and metasomatic additions of HSE to peridotitic rocks. Thus, the Os model age of a rock can only be considered potentially meaningful if the HSE pattern accompanying it appears to be consistent with a prior, single-stage melting event. Multiple stages of melting and/or metasomatic enrichments lead to complex HSE and Os isotopic compositions that may be impossible to deconvolute with respect to timing of melting (*e.g.*, Lorand *et al.*, 2013). Although this sounds really bad for Os dating, the reader is reminded that it is sometimes easy to lose sight of the forest for the trees. For regions that have been intensively studied, the application of Os isotopes to constraining the age structure of underlying SCLM has been quite successful! Perhaps the area that most exemplifies the power of Os isotopes to map the age of SCLM both laterally and with depth is the Kaapvaal craton, southern Africa. Work on xenoliths from this region by *Steve Shirey* and *Rick Carlson* and their colleagues at the Department of Terrestrial Magnetism continued for many years after the initial Walker *et al.* (1989) study. Their highly-focused work on xenoliths from across the craton ultimately filled in the melt depletion ages for mantle underlying both Archean and Proterozoic portions of the region. A nice summary of this work that describes the excellent symmetry found between Archean T_{RD} ages on craton and Proterozoic T_{RD} ages off craton can be found in Carlson *et al.* (2005).

7. SIDEROPHILE ELEMENTS IN THE MANTLE SOURCES OF OCEAN ISLAND BASALTS

7.1 Siderophile Element Abundances and ^{187}Os/^{188}Os

Ocean island basalts and related rocks are the surface manifestations of intraplate volcanism. Most OIB are chemically and isotopically distinct from MORB, and therefore, have been interpreted to sample mantle that is different from the DMM, although OIB can also include a DMM component (*e.g.*, Zindler and Hart, 1986; Hofmann, 2014). Ocean island basalts are also commonly associated with the concept of mantle plumes and hotspots, which are defined as the focused, upward flow of mantle materials that likely originate at different boundary layers within the Earth (Morgan, 1971; Campbell and Griffiths, 1990). The reasons for chemical and isotopic diversity in OIB sources, as well as their depth of origin remain controversial (Campbell and Griffiths, 1990; Hofmann, 1997; Anderson, 1998, 2010; Humayun *et al.*, 2004). Nevertheless, most will agree that there is strong evidence that at least some OIB systems incorporate recycled oceanic or continental crust, including sediments, as well as continental and oceanic lithospheric mantle (*e.g.*, White and Hofmann, 1982; Zindler and Hart, 1986; Workman *et al.*, 2004; Nielsen *et al.*, 2006; Hofmann, 2014). Abundances and isotopic compositions of siderophile elements can be used to provide new insights to the origin of OIB (see for example, reviews by Day, 2013 and Gannoun *et al.*, 2016).

Only a handful of prior studies have examined the absolute and relative abundances of HSE in OIB systems (Tatsumi *et al.*, 1999; Bennett *et al.*, 2000; Jamais *et al.*, 2008; Ireland *et al.*, 2009b; Day *et al.*, 2010b). Chondrite normalised patterns for rocks from Hawaii, the Azores and the Canary Islands are shown in Figure 7.1. As with MORB, concentration variations are large, and there is considerable overlap between OIB and MORB patterns. By and large, however, abundances of all HSE in these OIB, except Re, do not extend to the lowest concentrations observed for global MORB. Also, some of the OIB, most notably from Hawaii, are characterised by higher Os, Ir and Ru concentrations than are observed in MORB. This can be explained by the fact that these samples are picritic lavas with considerably higher MgO than MORB. This means higher extents of partial melting and greater removal of HSE-bearing mantle sulphides into the melt.

Most studies of HSE in OIB have focused on Hawaiian lavas. This is not surprising. The Hawaiian mantle plume is the largest, hottest, and longest-lived plume that is currently active (Sleep, 1990, 1992). It has been suggested by tomographic studies that the Hawaiian plume originates at the core-mantle boundary (CMB) (*e.g.*, Montelli *et al.*, 2004; French and Romanowicz, 2015). Thus, the Hawaiian plume has been the focus of numerous geochemical studies that have attempted to assess the chemical and isotopic characteristics of a purportedly deep mantle source (Norman and Garcia, 1999; Bennett *et al.*, 2000; Lassiter *et al.*, 2000; Humayun *et al.*, 2004; Bryce *et al.*, 2005; Nielsen *et al.*, 2006; Sobolev *et al.*, 2006; Bizimis *et al.*, 2007). Tatsumi *et al.* (1999) examined HSE abundances in tholeiites from Mauna Loa and Kilauea. They noted that the chondrite normalised HSE patterns of the different lavas examined differed only modestly. They hypothesised that the small observed fractionations of the HSE resulted from the crystallisation of phases such as chromite, olivine and clinopyroxene. However, they also suggested a role for the separation of sulphides from the parental magmas. Bennett *et al.* (2000) studied the concentrations of several HSE along with ^{187}Os/^{188}Os ratios in a suite of picritic rocks from six volcanic centres. They concluded that the variable HSE abundances in the picrites directly reflect plume source compositions, and suggested that residual sulphides in the plume source may be responsible for the absolute HSE abundance variations between the different Hawaiian volcanoes. They also noted that the effects of the residual sulphides may obscure the contributions of various HSE reservoirs present in the plume source.

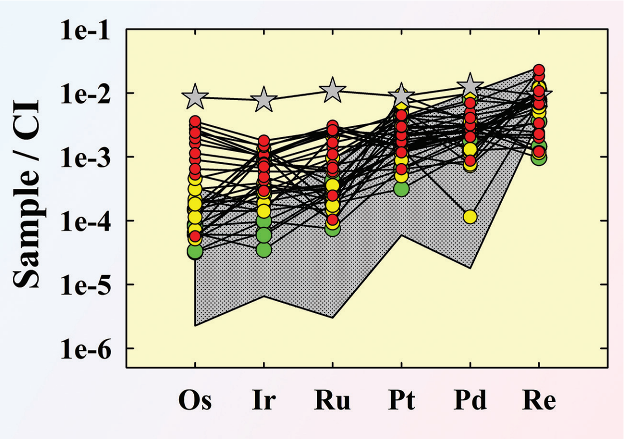


Figure 7.1 CI chondrite normalised HSE patterns for whole rock samples of ocean island basalts and picrites. Green symbols are from the Azores (Day *et al.*, 2016); yellow symbols are from the Canary Islands (Day *et al.*, 2010b), and red symbols are from Hawaii (Tatsumi *et al.*, 1999; Bennett *et al.*, 2000; Jamais *et al.*, 2008; Ireland *et al.*, 2009b). Note that the higher concentrations of Os, Ir and Ru in the Hawaiian samples, compared to Azores and Canary Island basalts reflects the picritic (high MgO) nature of most of the Hawaiian lavas analysed. The field for MORB from is from Figure 5.3; BSE concentrations are from Becker *et al.* (2006). Except for the Hawaiian picrites, there is considerable overlap between the data for OIB and MORB.

To further efforts to understand the HSE and ^{187}Os systematics of the mantle sources of Hawaiian lavas, in 2007, my Ph.D. student *Tom Ireland*, in collaboration with *Mike Garcia* (University of Hawaii at Manoa) began to examine a large suite of picrites (MgO >13 wt. %) collected from eight Hawaiian volcanic centres (Mauna Kea, Mauna Loa, Hualalai, Loihi, Kilauea, Kohala, Koolau and Lanai). The samples we studied represent some of the most primitive melts among the Hawaiian volcanic centres. Consequently, they are particularly useful in preserving information about the concentrations of trace elements, including HSE in the mantle sources of the Hawaiian plume (Norman and Garcia, 1999). Seven related tholeiitic basalts (MgO ~7 to 12 wt. %), which are more evolved than the associated picrites, were also included in the study as a means of considering the effects of crystal-liquid fractionation processes on HSE.

The data for the Hawaiian suite reported in Ireland *et al*. (2009b) are characterised by a moderate range of HSE concentrations (Fig. 7.1), comparable to the findings of prior studies by Bennett *et al*. (2000) and Jamais *et al*. (2008). We found that among the picrites, Os, Ir and Ru show good positive correlations with MgO. Platinum, Pd and Re showed much noisier negative correlations with MgO. Norman and Garcia (1999) had previously determined that the parental melts to the picrites averaged ~16 wt. % MgO. Consequently, *Tom* was able to define the HSE abundances of the parental melts to the picrites as the point of overlap between each trend and 16 wt. % MgO. Some of the variations in HSE abundances can be attributed to crystal-liquid fractionation effects, similar to the conclusion of Bennett *et al*. (2000). The variations are also consistent with the findings of our subsequent study of HSE fractionation in the Kilauea Iki lava lake, discussed next. Some of the variations, however, must ultimately be attributed to heterogeneities in parental liquids, and by inference, mantle source characteristics. For example, the concentration of Os in the parental liquid to the Hualalai picrites was estimated to be a factor of 2 higher than for the picrites from the other volcanic centres.

As part of the same project to understand HSE in Hawaiian picritic lavas, UMd undergraduate student *Lynnette Pitcher* analysed a suite of rocks from the Kilauea Iki lava lake for her senior thesis. We selected samples and interpreted the data in collaboration with *Roz Helz* of the U.S.G.S., an expert on the lava lake. Kilauea Iki provides a wonderful suite of samples for studying elemental and stable isotopic fractionation resulting from crystal-liquid fractionation of picritic lava. The lava lake eruption occurred in 1959, pooled in a prior depression, and quickly solidified a crust. At this point, the U.S.G.S. made the clever decision to periodically drill into the lake and collect samples as crystallisation proceeded. Full crystallisation required more than 30 years. We decided to measure HSE in rocks obtained from the drill cores, which had MgO ranging from as high as 26.9 wt. % to as low as 2.4 wt. %. Our results were published in Pitcher *et al*. (2009), which was not a bad outcome for *Lynnette*'s senior thesis project! Not surprisingly, chondrite normalised patterns were highly variable, ranging from relatively flat (high MgO), to strongly depleted in Os and Ir (low MgO; Fig. 7.2). Of note, Os and Ir concentrations were most highly variable, correlating positively with MgO. Platinum concentrations varied the least. The fractionations observed were broadly consistent with some of the major variations in pattern shape observed among the entire Hawaiian picrite suite examined by Ireland *et al*. (2009b).

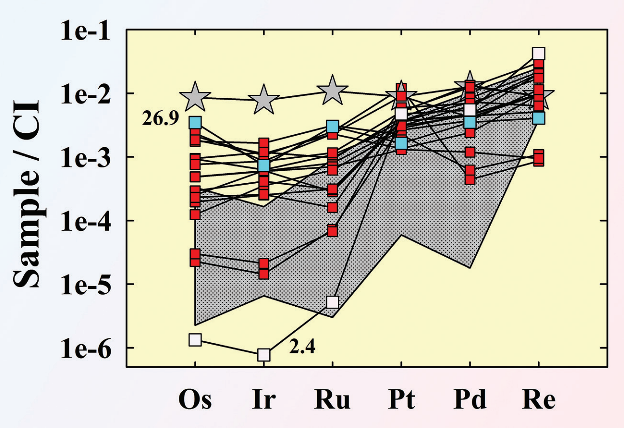


Figure 7.2 CI chondrite normalised HSE patterns for whole rock samples from different depths of the Kilauea Iki lava lake. Note the large range of concentrations present in different parts of the crystallisation sequence. The most evolved sample (KI-81-2-88.6), with 2.4 wt. % MgO, shown as white squares, has the lowest Os, Ir and Ru concentrations, and the highest Re concentration of the suite. The least evolved sample (KI-81-1-169) with 26.9 wt. % MgO), shown as cyan squares, has the highest Os and Ru concentrations of the suite. The field for MORB from Figure 5.2, as well as the BSE concentrations from Becker *et al.* (2006) are shown for comparison. Data for Kilauea Iki samples are from Pitcher *et al.* (2009).

Because of the difficulties in extrapolating from primitive melt compositions to precise mantle source compositions, it remains unclear whether the sources of the different Hawaiian volcanic centres have HSE abundances that are outside of the range estimated for the DMM, although as noted above, this seems likely for at least the Os in Hualalai lavas. The situation is a bit better for some MSE that are highly incompatible. Their mantle source abundances can be estimated much more accurately. For example, Ireland *et al.* (2009a) examined W concentrations in the sources of Hawaiian picrites. As with Arevalo and McDonough (2008), they also used the W/U of the rocks to project to mantle source W concentrations. There were no discernable differences in the W concentrations determined for the mantle sources of 7 volcanic centres. The average concentration of 10 ± 3 ppb they obtained is significantly higher than the 3.0 ± 2.3 ppb concentration for the DMM, so at least with regard to W, the picrites were derived from mantle that is less depleted in highly incompatible trace elements than the DMM.

Of course another way of characterising the long-term relative abundances of three siderophile elements (Re-Pt-Os) within the mantle sources of OIB is through the examination of Os isotopes. Here, I'll first discuss what I think we know about ^{187}Os/^{188}Os ratios in OIB. In the following section I'll discuss the puzzling issue of heterogeneity in ^{186}Os/^{188}Os ratios present in OIB, especially in the Hawaiian suite.

The first substantial, published Os isotopic data for an OIB was by *Candace Martin*, who as part of her Ph.D. dissertation at Yale University, reported Os isotopic compositions for basalts from Hawaii and Iceland (Martin, 1991). In this impressive seminal study, *Candace* recognised that, on average, OIB were more radiogenic than the DMM, and so require at least one additional mantle component to explain the offset. The samples she analysed all had $^{187}Os/^{188}Os > 0.13$ ($\gamma_{Os} > +3$). By plotting Os isotopic compositions *versus* $^3He/^4He$ and $^{87}Sr/^{86}Sr$, she demonstrated that there were likely more than two components involved in just the Hawaiian and Icelandic systems. Another important early study was Hauri and Hart (1993). This paper was a first attempt to place Os isotopes within the context of the mantle "zoo" of components defined by Zindler and Hart (1986). They reported Os isotopic compositions for EMII lavas to range from 0.123 to 0.136 (γ_{Os} = -3 to +7). They concluded that these ratios were within the range of the DMM and that these isotopic compositions offered no unique insights into the involvement of recycled continental crust. Recycled continental crust is presumed to be a major contributor to the enriched lithophile isotope characteristics of EMII lavas (*e.g.*, White and Hofmann, 1982; Zindler and Hart, 1986; Workman *et al.*, 2004). By contrast, they found HIMU lavas to have more radiogenic $^{187}Os/^{188}Os$ ratios, ranging from 0.134 to 0.150 (γ_{Os} = +6 to +18), which they attributed to the presence of appreciable recycled oceanic crust in the source. At about the same time, Reisberg *et al*. (1993) also reported a similar range of Os isotopic compositions for a variety of OIB sources, obtaining similar results to Hauri and Hart (1993). In addition, they reported a $^{187}Os/^{188}Os$ ratio of 0.163 (γ_{Os} = +28) for a basalt from Pitcairn Island, which they speculated may define the Os isotopic composition of the EMI component. That study also concluded, however, that samples with low Os concentrations were not necessarily reliable recorders of mantle source compositions, because of the possibility of contamination by incorporation of Mn-oxides or other seawater-derived phases. A subsequent study (Eisele *et al*., 2002) reported that Pitcairn lavas with ≥50 ppt Os have somewhat less radiogenic $^{187}Os/^{188}Os$ ratios, ranging from 0.131 to 0.148 (γ_{Os} = +3 to +17), and that the most radiogenic ratios of these are probably the most representative of the EMI component. They interpreted this to mean that SCLM, with low $^{187}Os/^{188}Os$, did not contribute Os to the EMI lavas (SCLM is commonly assumed to contribute to the EMI isotopic signature), and the radiogenic nature of the EMI instead reflects the involvement of Os from recycled oceanic crust.

There are now a substantial number of $^{187}Os/^{188}Os$ ratios published for OIB (*e.g.*, Pegram and Allègre, 1992; Marcantonio *et al*., 1995; Hauri *et al*., 1996; Widom and Shirey, 1996; Lassiter and Hauri, 1998; Brandon *et al*., 1999; Tatsumi *et al*., 1999; Widom *et al*., 1999; Bennett *et al*., 2000; Schiano *et al*., 2001; Workman *et al*., 2004; Bryce *et al*., 2005; Day *et al*., 2010b; Hanyu *et al*., 2011; Jackson and Shirey, 2011; Day, 2013). By and large the story has not changed greatly since the 1990's. In most cases, Os isotopic compositions of OIB lavas, with sufficiently high Os concentrations (≥50 ppt) generally range from the composition of the DMM, to 20-30 % higher (Fig. 7.3). In comparison to lithophile isotope systems, filtering the data for Os abundance is critical here because of the very low Os concentrations present in some lavas, coupled with the potentially very high $^{187}Os/^{188}Os$ present in possible crustal or seawater contaminants. Lavas with EMII affinities, as well as most Hawaiian lavas, are more radiogenic than DMM, but only by a few percent. There remain few data for EMI lavas with ≥50 ppt Os, yet the few that exist appear somewhat more radiogenic than EMII. Conversely, as originally noted by Hauri and Hart (1993), lavas with HIMU affinities have the highest average $^{187}Os/^{188}Os$ of all OIB.

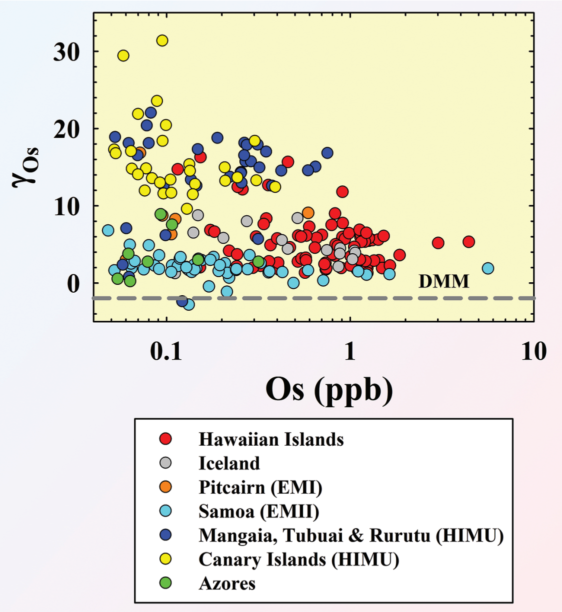


Figure 7.3 Plot of Os concentration in ppb *versus* initial γ_{Os} values for major ocean island basalts and related rocks. Data are filtered to exclude samples with <50 ppt Os. Note that for data from each of the island suites, there is no meaningful trend between Os concentration and isotopic composition. This suggests that direct crustal contamination played a minimal role in defining the isotopic compositions. The horizontal dashed line represents the best estimate for DMM by Snow and Reisberg (1995). OIB data are compiled from Pegram and Allègre (1992), Hauri and Hart (1993), Reisberg *et al*. (1993), Marcantonio *et al*. (1995), Hauri *et al*. (1996), Widom and Shirey (1996), Lassiter and Hauri (1998), Brandon *et al*. (1999), Widom *et al*. (1999), Bennett *et al*. (2000), Workman *et al*. (2004), Bryce *et al*. (2005), Brandon *et al*. (2007), Ireland *et al*. (2009b), Day *et al*. (2010b), Hanyu *et al*. (2011) and Jackson and Shirey (2011).

Osmium isotopic data provide supporting evidence for the prevailing models that have been proposed to generate the endmember mantle components delineated by OIB, but no unique insights. This should not be surprising. Remember that Os is a compatible trace element during mantle melting to form basaltic melts, so its abundance remains high in the mantle and is generally quite low in the melts and crust formed from those melts. It is often not realised that, although crustal rocks can evolve to very high $^{187}Os/^{188}Os$ ratios (see Fig. 5.1), they don't contain very many atoms of Os, compared to mantle peridotites. Thus, $^{187}Os/^{188}Os$ in peridotitic mantle is not very sensitive to crustal (continental or oceanic) recycling. This can be seen in a simple mixing model that considers the effect of recycling relatively young, 100 Ma oceanic crust into fertile peridotitic mantle (Fig. 7.4). Assuming simple mass transfer, the addition of 40 % of this basalt component, with a γ_{Os} value of +119, raises the value of the mixture only 1.2 γ units (%). The recycling of basaltic crust has a greater long-term effect resulting from the addition of Re to the mixture. This raises the Re/Os ratio of the mixture such that over time, the $^{187}Os/^{188}Os$ of the mixture will increase substantially. For peridotite-basalt mixing scenarios, Figure 7.4 highlights the fact that a typical OIB with a γ_{Os} value of +12 requires either a large proportion of the recycled basalt in the source, a long period of time, or both. For example,

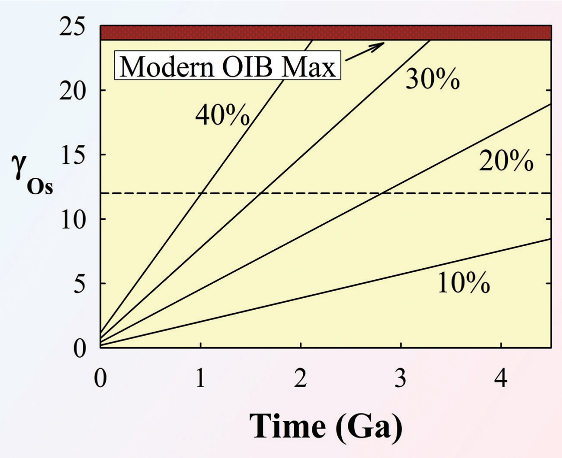


Figure 7.4 γ_{Os} *versus* Time (in Ga) for hybrid mantle reservoirs generated by mixing modern fertile peridotite with 100 Ma basaltic crust. Model mixing parameters are: fertile mantle: $^{187}Os/^{188}Os = 0.127$ ($\gamma_{Os} = 0$), Os = 3.3 ppb, Re = 0.27 ppb. Basalt component: $^{187}Os/^{188}Os = 0.278$ ($\gamma_{Os} = +120$), Os = 0.050 ppb, Re = 0.93 ppb. Mixing results show the insensitivity of the Os isotopic composition of the hybrid mix to the recycling of comparatively old basaltic crust into mantle peridotites. For example, addition of 40 % of the recycled crust raises the γ_{Os} value of the mix only 1.2 units. Diagonal lines indicate growth trajectories for different mantle/basalt mixtures with the percentage of basaltic crust additions labeled. Addition of basaltic crust to fertile mantle significantly changes the $^{187}Re/^{188}Os$ ratio of the hybrid mixture, as a result of the relatively high Re content of basalt. This figure shows that a considerable length of time and considerable contamination is necessary to generate a γ_{Os} of +12 via mixing oceanic basalt with fertile mantle.

a γ_{Os} value of +12 requires 1 Ga in a source with 40 % of the recycled basaltic component (or the recent involvement of recycled crust that is 1 Ga). The sensitivity of the Re-Os isotope system to recycled components may be increased for mantle domains in which peridotite has been infiltrated by pyronenite-derived melts (Yaxley and Green, 1998; Marchesi *et al.*, 2014), or converted to pyroxenite via interactions with melts derived from recycled crust, or metasomatised peridotites that have been modified by the addition of base metal sulphides (*e.g.*, Lassiter *et al.*, 2000; Sobolev *et al.*, 2006; Luguet *et al.*, 2008a). I'll return to this topic in the next section.

Returning briefly to Os in the Hawaiian suite, $^{187}Os/^{188}Os$ ratios for most Hawaiian volcanic centres vary only from ~0.129 to ~0.137 (γ_{Os} = +2 to +8) (*e.g.*, Martin, 1991; Lassiter and Hauri, 1998, Bryce *et al.*, 2005; Ireland *et al.*, 2009b). Lassiter and Hauri (1998) attributed these Os isotopic compositions to the incorporation of recycled oceanic lithosphere. They also reported that Koolau lavas are considerably more radiogenic, ranging from ~0.140 to 0.148 (γ_{Os} = +10 to +17). They attributed the more radiogenic compositions to the additional presence of pelagic sediments in their mantle source. Ireland *et al.* (2009b) noted that the Os isotopic variations don't correlate with projected absolute or relative abundances of the HSE in the parental liquids to the picrites. That study concluded that Os isotopic heterogeneities reflect heterogeneities in the sources of these rocks. By contrast, the HSE abundances were dominated by the effects of partial melting and crystal-liquid fractionation processes, which masked the source characteristics.

7.2 The Story of ^{186}Os

In Section 5.4 I mentioned that Riley and Delong (1970) took the first stab at defining the long-term Re/Os ratio of the mantle, using $^{187}Os/^{188}Os$ data they obtained from Hirt *et al.* (1963b). In addition to this advance, the authors were also prescient by stating: *"The intriguing possibility remains that, with a very major improvement in instrumentation, measurements of the coupled Re-Pt-Os isotopic systems in ultramafic rocks could yield information on the long-term chemical interaction of the earth's mantle and core"*.

My involvement with the ^{190}Pt-^{186}Os system came about initially because of work *Erik Krogstad* and I were conducting with a U.S. Geological Survey group consisting of *John Morgan*, *Gerry Czamanske*, *Mary Horan* and *Joe Wooden*, and Russian colleague *Victor Fedorenko*, on magmatic Cu-Ni sulphide ores, and spatially associated ultramafic and mafic rocks from Noril'sk, Russia. These rocks and ores were produced as part of the generation of the massive, *ca.* 251 Ma Siberian Flood Basalt Province, presumed by many to be associated with a particularly large mantle plume. A peculiar aspect of some samples was that they had excess ^{186}Os. The excess ^{186}Os was present only in ores with high Pt/Os ratios. *John* quickly put two and two together and concluded that the excesses were the result of the radioactive decay of ^{190}Pt to ^{186}Os, until then (the Riley and Delong proclamation notwithstanding) an obscure isotope system. This is what forced us to abandon using ^{186}Os in the denominator when reporting Os isotopic compositions (see Section 2). This also got us thinking about the ^{190}Pt-^{186}Os isotopic system and the challenge of Riley and Delong (1970).

As discussed in the previous section, considerable recycled crustal component is necessary to substantially increase the ^{187}Os/^{188}Os ratio of hybridised mantle sources. This is not a problem for generating most OIB. However, for some of the high MgO picritic rocks at Noril'sk, we found it problematic to envision a petrologically feasible mechanism to generate the parental melts from a mantle domain characterised by such a large proportion of recycled crust (*e.g.*, Walker *et al.*, 1994). At that time, we were also conducting a study of Re/Os fractionation in iron meteorites, and knew that solid metal-liquid metal partitioning in asteroidal cores initially leads to increasingly higher Re/Os in the evolving melt (see Section 3.2 above). As a consequence of this work, *John* proposed to me that maybe some of the high ^{187}Os/^{188}Os ratios observed in certain plumes (*e.g.*, the Siberian plume) obtained some or all of their Os isotopic compositions from the outer core, rather than the mantle. If Re and Os were partitioned between the inner and outer cores in a manner similar to what is observed in some iron meteorite systems, the 5.5 wt. % crystallisation of the Earth's core could have led to as much as an ~8 % increase in ^{187}Os/^{188}Os over the bulk core, assuming sufficient inner core crystallisation occurred in early Earth history. I thought this was a good idea. We did some modelling and published the idea in *Science* (Walker *et al.*, 1995). This idea is not so farfetched as it may sound. The outer core is likely enriched in HSE by a factor of ~300 compared to the ambient mantle. The isotopic signature of the core could be imprinted on a plume rising from the CMB, either through the direct incorporation of 1-3 wt. % metal in the rising plume, or as a result of isotopic exchange between the core and mantle. The idea was strengthened by the modelling of Os and Pb isotopes for lavas from the Azores by Widom and Shirey (1996), who argued that the relatively uniform, suprachondritic ^{187}Os/^{188}Os in these rocks, coupled with the more variable Pb isotopic compositions observed, could not be explained solely by appealing to the presence of recycled crust in the mantle source of the lavas.

In Walker *et al.* (1995) we proposed an alternative to recycled crust for generating enriched ^{187}Os/^{188}Os in the mantle sources of at least some plumes, but needed a way to test the hypothesis. Again, based on the iron meteorite analogue (*e.g.*, Pernicka and Wasson, 1987), *John Morgan* suggested that ^{186}Os might serve as a potential arbiter of Os derived from the outer core as compared with recycled crust. The idea was that, in addition to increasing the Re/Os ratio, crystallisation of liquid metal greatly increases the Pt/Os ratio. Thus, although the Pt-Os system is incredibly sluggish, because of the very small decay constant for ^{190}Pt, and the very low proportion of ^{190}Pt in Pt (Table 2.2), we nevertheless might expect to see unique, coupled enrichments in ^{187}Os and ^{186}Os in materials that sample outer core Os. Our simple fractional crystallisation models for the inner core suggested that 8 % enrichments in ^{187}Os/^{188}Os in the outer core would be accompanied by ^{186}Os/^{188}Os enrichments, relative to the chondritic mantle, by as much as 100 ppm. Equally important to the idea is the fact that the Re/Pt/Os ratios of known recycled materials were not appropriate to generate the isotopic offsets that we predicted for the outer core. Thus, we believed that if a plume source had coupled ^{187}Os-^{186}Os enrichments of the magnitude predicted, it was solid evidence for the involvement of Os derived from the outer core. We had no way to measure Os isotopes to the level of precision required to assess the hypothesis at that time, so it was safe to propose this test in our *Science* paper.

By and large, the mantle isotope community was not impressed with this idea. To advance it further, and to prove the critics wrong, we spent considerable effort developing a multi-dynamic Os method for our *Sector 54* mass spectrometer to measure ^{186}Os/^{188}Os to a sufficient level of precision to test the coupled isotope system idea. Of course we also had to obtain enough Os from a sample to run with sufficient signal to obtain useful data. We eventually succeeded with the mass spectrometry and were able to analyse some enstatite chondrites, group IIAB iron meteorites, Os-Ir-Ru alloy grains, and a variety of ores from Noril'sk (Walker *et al.*, 1997). The idea with the iron meteorites and Noril'sk samples was to generate isochrons by examining samples with highly variable Pt/Os ratios. This would allow us to better constrain the decay constant for ^{190}Pt. We also repeatedly analysed an ore from Noril'sk with high Os and relatively low Pt. We obtained pretty nice isochrons for the ores and iron meteorites, and also were able to define both chondritic and mantle ^{186}Os/^{188}Os to a never before obtained level of precision. Most exciting of all, we determined that the low Pt/Os Noril'sk ore was characterised by an ~120 ppm enrichment in ^{186}Os, compared to the alloy grains (mantle), which was coupled with an ~8 % enrichment in initial ^{187}Os/^{188}Os. This was very close to what we had projected for the outer core (Walker *et al.*, 1995). We proposed that the Noril'sk sample provided evidence for either the ancient formation of a Pt-rich domain in the mantle, or an outer core signature. Because it met our modelling predictions, we favoured the outer core explanation. Noril'sk, however, was not an ideal system for demonstrating core-mantle interaction because the igneous system also bears some geochemical evidence of continental crustal contributions. Following this study, we decided to set my recently-hired postdoc, *Alan Brandon*, onto this problem by working on *bona fide* OIB.

We decided to analyse ^{186}Os in Hawaiian picrites as our primary push to examine an OIB system. To harvest enough Os from the picrites, *Al* had to apply the exciting Ni-sulphide fire assay technique of Hoffman *et al.* (1978). This method requires mixing 100-200 g of sample powder with huge amounts of NiS and sodium tetraborate, then fusing the mix in a large ceramic crucible at 1100 °C. The sample Os is concentrated from the silicate-flux mixture into a NiS bead that forms and sinks to the bottom of the crucible. Once concentrated, the Os can then be separated from the NiS bead by filtration and further processing using standard techniques. In two studies (Brandon *et al.*, 1998, 1999) we reported coupled enrichments in ^{187}Os/^{188}Os and ^{186}Os/^{188}Os ratios that extended to about the same composition as observed for the Noril'sk sample. The only exceptions to the trend were lavas from Koolau. In addition to the Hawaiian samples, *Al* also analysed additional alloy grains, as well as a suite of 89 Ma komatiites from Gorgona Island, Colombia (Brandon *et al.*, 2003). Like the Hawaiian suite, the komatiites also showed a linear correlation between ^{187}Os and ^{186}Os, albeit with a different slope on a plot of ^{187}Os/^{188}Os *versus* ^{186}Os/^{188}Os (Fig. 7.5).

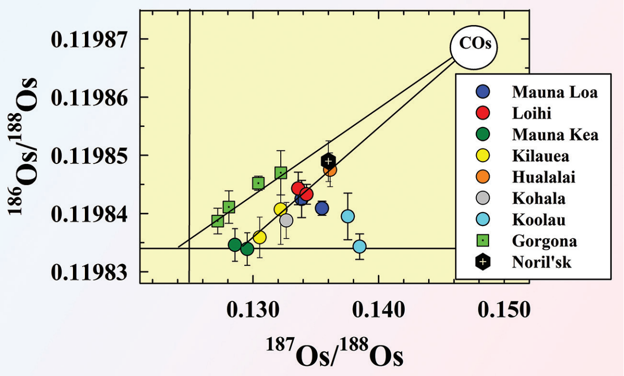


Figure 7.5 ^{187}Os/^{188}Os *versus* ^{186}Os/^{188}Os for a Noril'sk ore, picrite samples from Hawaii (Brandon *et al.*, 1999) and komatiites from Gorgona Island (Brandon *et al.*, 2003). The datum for the Noril'sk ore is from Walker *et al.* (1997). The COs is the point of Os isotopic convergence for the Hawaiian and Gorgona trends.

Although the error bars allowed for considerable uncertainty, the slopes of the different trends on this plot seemed to converge on a point, which *Al* defined as a common ^{187}Os- and ^{186}Os-enriched reservoir, or COs. We proposed that this point was the composition of the outer core (*e.g.*, Brandon *et al.*, 2003). It should be noted that not all putative plume derived systems show evidence for coupled Os isotopic enrichments. *Al* subsequently showed that despite variable ^{187}Os/^{188}Os, the Iceland plume is characterised by chondritic ^{186}Os/^{188}Os (Brandon *et al.*, 2007).

At the time, we thought the apparent COs made a pretty strong case for core-mantle interaction of some sort. For it to be true, however, requires some pretty special things to occur. First, both Os isotopic systems require considerable time for the isotopic heterogeneities to develop between the inner and outer cores. Conservative models, using solid metal-liquid metal D values for Re-Pt-Os appropriate for iron meteorite systems, require substantial growth of the inner core within the first 500 Ma of Earth history in order to generate ^{186}Os and ^{187}Os enrichments of the magnitude envisioned for the COs. However, subsequent thermal models suggested that the inner core started crystallisation relatively late (*e.g.*, Labrosse *et al.*, 2001; Labrosse, 2003; Lassiter, 2006). Second, conditions of inner core growth are very different from the low pressure and temperature asteroidal systems that were the basis for our modelling, and the claim of core-mantle interaction spurred some experimentalists to examine solid metal-liquid metal partitioning at more core-relevant conditions (*e.g.*, Chabot *et al.*, 2008; Van

Orman *et al.*, 2008). Although there is considerable composition parameter space for core crystallisation yet to be explored, these studies suggest that high pressure-temperature partitioning leads to less fractionation of Re-Pt-Os than occurs in much lower pressure-temperature asteroidal systems. This makes the generation of an outer core composition matching the COs even more problematic. Third, the concentrations of HSE in the isotopically enriched endmembers of the trends do not appear to be enriched. Thus, there is no accompanying evidence for the introduction of HSE to the plumes from the HSE-rich outer core. This means that isotopic exchange between the core and mantle would have to be more rapid than elemental exchange. Subsequent work we conducted with *Dave Walker* at Lamont, however, suggests that the opposite is true (Yokoyama *et al.*, 2009).

Although some potentially viable mechanisms to circumvent the problems related to the timing of inner core growth, and the limited fractionations of Re-Pt-Os at high pressures, have been proposed (*e.g.,* Humayun, 2011), most people I talk with consider the search for coupled Os isotopic enrichments as evidence for core-mantle interaction to be a provocative idea that came and went. This topic will return below when the application of tungsten isotopes, as relates to the detection of core-mantle interaction, is discussed.

Measurement capabilities have advanced and we are now able to measure ^{186}Os/^{188}Os better than in the studies noted above (*e.g.,* Brandon *et al.*, 2007; Luguet *et al.*, 2008b; Walker, 2012; Chatterjee and Lassiter, 2015). Thus, as part of his Ph.D. dissertation project, *Tom Ireland* analysed a sizable suite of Hawaiian picrites for ^{187}Os-^{187}Os (Ireland *et al.,* 2011). Although his results for samples that overlap with the suite from Brandon *et al*. (1999) were in good agreement, the greater numbers of data make the Hawaiian trend look a bit less impressive (Fig. 7.6a). *Tom*'s study revealed that some individual volcanic centres, most notably Kilauea, show as much variation in ^{186}Os/^{188}Os as the entire Hawaiian suite, yet there is still a general positive trend between ^{187}Os/^{188}Os and ^{186}Os/^{188}Os, when data for all volcanic centres (except Koolau), are combined. This is consistent with mixing between an ambient plume source that has normal chondritic mantle ^{186}Os/^{188}Os, but somewhat radiogenic ^{187}Os/^{188}Os, and a component that is characterised by suprachondritic ^{186}Os/^{188}Os, and ^{187}Os/^{188}Os that is enriched relative to the ambient plume source. The data also show a negative correlation between Os concentration and ^{186}Os/^{188}Os (Fig. 7.6b). This is the opposite of what might be expected from core-mantle interaction, and suggests that the isotopically enriched component in some Hawaiian lavas might be somewhat depleted in Os (and possibly other HSE), compared to the ambient plume source.

If the ^{186}Os-^{187}Os-enriched component is not the outer core, what can it be? Several studies have tendered alternate possibilities to account for coupled enrichments in ^{186}Os and ^{187}Os. Baker and Jensen (2004) suggested the enrichments may reflect the incorporation of Fe-Mn crusts in the mantle sources of isotopically enriched lavas. Iron-Mn crusts are commonly characterised by having high Pt/Os ratios, which over time, could evolve to the high ^{186}Os observed. The ability of a process to concentrate these types of materials sufficient to modify a plume source, however, seems unlikely. Smith (2003) and Luguet *et al.* (2008a) noted that some pyroxenites found in mantle assemblages have Re-Pt-Os relative abundances, as well as sufficiently high Os concentrations, that they could contribute the necessary Os to the enriched Hawaiian lavas. These high Pt/Os ratio pyroxenites may be explained as a result of peridotite-silicate melt interactions. Bockrath *et al.* (2004) noted that the fractionation of Os, Ir and Ru from Pt and Pd is a natural outcome of mantle melting and the removal of Pt and Pd in a sulphide melt, while Os, Ir and Ru are retained in monosulphide solid solutions. Thus, as proposed by Luguet *et al.* (2008a), and shown in detail by Marchesi *et al.* (2014), base metal sulphide-bearing melt may react with peridotites to produce rocks with high Pt/Os. Over time, these rocks could evolve to appropriately ^{186}Os- and ^{187}Os-enriched compositions to qualify as the enriched component necessary to explain the Hawaiian data.

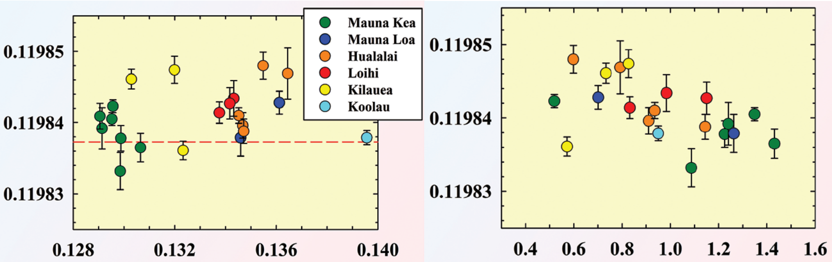


Figure 7.6 **(a)** ^{187}Os/^{188}Os *versus* ^{186}Os/^{188}Os for picritic lavas from Hawaii. The upper mantle average was obtained from the analysis of abyssal peridotites and Os-Ir-Ru alloy grains. **(b)** Osmium concentration (in ppb) *versus* ^{186}Os/^{188}Os for the same samples. Note the negative trend. Data are from Ireland *et al.* (2011).

Although initially a sceptic that such Pt-rich rocks really exist in sufficient quantities in the mantle, I have now seen them with my own eyes and believe. In the Leka ophiolite such rocks comprise roughly 2 % of the upper mantle section. We have sampled several pyroxenitic pods that are characterised by comparatively high Os and Pt/Os, but also moderate Re/Os. These rocks could evolve to Os isotopic compositions appropriate for mixing with ambient plume mantle to generate Hawaiian-like compositions. For example, Leka sample LK18 is characterised by concentrations of 2.05 ppb Re, 17.8 ppb Os, and 1060 ppb Pt (O'Driscoll *et al.*, 2015; Fig. 7.7). This suggests that the sulphide transport mechanism proposed by Bockrath *et al.* (2004) may be involved in the generation of rocks like this. As discussed in O'Driscoll *et al.* (2015), applying these Pt-Re-Os concentrations, assuming average chondritic ^{186}Os/^{188}Os and ^{187}Os/^{188}Os ratios at the time of formation, and allowing 1.5 Ga of radiogenic growth, would result in a rock with ^{186}Os/^{188}Os and ^{187}Os/^{188}Os ratios enriched by ~0.10 % (0.11997) and ~3.0 % (0.131), respectively, compared to mantle evolving along an average chondritic trajectory. Because of the high Os concentration in LK18, modal melting of a hybrid source consisting of only 2 % LK18, aged for 1.5 Ga, and fertile peridotite with the HSE characteristics of the bulk silicate Earth (Becker *et al.*, 2006), would result in a melt with $^{186}Os/^{188}Os = 0.119848$ and $^{187}Os/^{188}Os = 0.129$. These isotopic compositions are similar to Hawaiian sample Kil 2-4, from the Kilauea volcano, which has $^{186}Os/^{188}Os = 0.119847$ and $^{187}Os/^{188}Os = 0.1320$ (Ireland *et al.*, 2011).

Figure 7.7 Photo of an orthopyoxenite pod in the upper mantle section of the Leka ophiolite. It is characterised by high Pt/Os and moderate Re/Os, and if sufficiently aged, could potentially be an appropriate source of radiogenic ^{186}Os and ^{187}Os to generate compositions comparable to what is observed in some Hawaiian lavas.

Although pyroxenitic contributions to high $^{186}Os/^{188}Os$ lavas seem promising, I'm still not totally convinced the issue of ^{186}Os enrichment in Hawaii is resolved. The Leka orthopyroxenites are mainly associated with (or included within) dunitic channels. This suggests the pyroxenite and the dunites are manifestations of the same melt infiltration process (*e.g.*, Kelemen *et al.*, 1992). Consistent with this, the enrichment of Pt in the pyroxenite is matched by a strong depletion in Pt in the surrounding dunite (O'Driscoll *et al.*, 2015). Thus, on the scale of metres, the enrichments are a zero sum game, requiring a highly selective plumbing system to extract radiogenic ^{186}Os from the small proportion of rocks with the correct abundances of HSE. Wholesale melting of a comparatively large volume of this mantle would result in the production of melt with no distinguishing Os isotopic characteristics. On the other hand, if the same sulphide transport mechanism can work on a much grander scale, such as envisioned by Sobolev *et al.* (2008), Luguet *et al.* (2008a) or Marchesi *et al.* (2014) to generate a hybridised source for Hawaiian lavas, the generation of ^{186}Os-enriched lavas may not be so difficult. It will be critical to see whether other OIB sources that may consist largely of pyroxenites are also characterised by ^{186}Os enrichments. Alas, because of the difficulty of conducting ^{186}Os measurements on rocks with basaltic Os concentrations, measurements of ^{186}Os in other OIB systems are being produced very slowly.

Before leaving the topic of ^{186}Os it is worth mentioning that the ^{190}Pt-^{186}Os isotopic system is useful for chronologic purposes, in addition to mantle tracer studies. Perhaps the most interesting recent work has been the application of this system to model age dating single, Pt-rich minerals (Nowell *et al.*, 2008; Coggon *et al.*, 2011), as well as isochron dating of platinum group minerals (Coggon *et al.*, 2012). Although not for the faint hearted, this system seems poised to provide important new insights to the workings of the Earth.

8. TUNGSTEN ISOTOPES IN THE MANTLE

Some of the most important discoveries pertaining to the formation and early evolution of the Earth have come about through the measurement of short-lived radiogenic isotope systems. For example, the discovery of isotopic variations in ^{142}Nd ($^{146}Sm \rightarrow {}^{142}Nd$; $t_{½} = 103$ Ma) among early-Earth samples may reflect major silicate fractionation events, such as magma ocean crystallisation and turnover, during the first several hundred million years of terrestrial evolution (*e.g.*, Caro *et al.*, 2003; Bennett *et al.*, 2007; O'Neil *et al.*, 2008). Further, the surprising difference in the ^{142}Nd isotopic composition of the bulk silicate Earth, compared with the chondritic average, has been interpreted by various authors to suggest: 1) the existence of an early-formed, incompatible trace element enriched reservoir that was removed to the deep mantle and permanently isolated (Boyet and Carlson, 2005), 2) the possibility that bulk Earth has a fractionated Sm/Nd, relative to the chondritic average, because an early, incompatible trace element enriched component was removed via via collisional erosion (*e.g.*, O'Neill and Palme, 2008), or 3) construction of the Earth from materials that were originally enriched in ^{142}Nd, as are some enstatite chondrites, potentially a consequence of large-scale nucleosynthetic heterogeneities surviving mixing in the protosolar nebula (Gannoun *et al.*, 2011). Complementary to studies of the short-lived system, studies of the long-lived ^{147}Sm-^{143}Nd ($t_{½} = 106$ Ga) and ^{176}Lu-^{176}Hf ($t_{½} = 37.1$ Ga) isotopic systems in a wide variety of mantle and crustal rocks indicate their derivation from reservoirs strongly depleted in incompatible trace elements very early in Earth history (*e.g.*, Smith and Ludden, 1989; Vervoort *et al.*, 1994; Vervoort and Patchett, 1996; Blichert-Toft and Puchtel, 2010).

The Sm-Nd isotopic systems, as well as complementary Lu-Hf and Rb-Sr systems, are based upon lithophile elements whose elemental fractionations within planets are controlled by processes solely involving silicates. Siderophile element isotopic tracers provide additional leverage for geochemically tracking global geodynamic processes through time. The most promising of these tracers currently appears to be the ^{182}Hf-^{182}W isotope system, introduced in Section 3.2. This short-lived system ($t_{½}$ for $^{182}Hf = 8.9$ Ma; Vockenhuber *et al.*, 2004) can be used to trace the early fractionation of an incompatible lithophile trace element (Hf) from a highly incompatible MSE (W), as a result of processes that occurred within the first ~60 Ma of solar system history. For example, the observation that the $^{182}W/^{184}W$ of terrestrial rocks are ~200 ppm more radiogenic than chondrites (Kleine *et al.*, 2002; Schoenberg *et al.*, 2002; Yin *et al.*, 2002b; Burkhardt *et al.*, 2008) has led to the interpretation that the majority of terrestrial core formation occurred within the first 30 Ma of solar system history (Kleine *et al.*, 2002; Yin *et al.*, 2002b; Halliday, 2004; Kleine *et al.*, 2009). The isotopic difference between mantle and chondrites, together with mass balance constraints, also implies that the Earth's core is a W-rich reservoir with a $^{182}W/^{184}W$ ratio that is ~220 ppm lower than the BSE. Tungsten isotopic compositions are usually reported in ε or μ units, which are defined as the deviation in $^{182}W/^{184}W$ ratio of a sample in parts per 10,000 or parts per 1,000,000, respectively, relative to a standard (assumed to be representative of the BSE; Table 2.3). Hence, in $\mu^{182}W$ units, the core and BSE are defined as -220 and 0, respectively.

From the standpoint of studying the long-term workings of the terrestrial mantle, the fact that the core has a very different isotopic composition from the BSE is potentially very useful. As we have seen in the previous section, siderophile elements are the only hope we have for geochemical detection of core-mantle interactions of any type, should they occur. As noted, although coupled ^{187}Os-^{186}Os isotopic systematics originally seemed promising for examining this process, the apparent youth of the inner core means that the coupled ^{187}Os-^{186}Os variations observed in some OIB sources more likely reflect processes other than core-mantle interaction. By contrast, the ~220 ppm W isotopic contrast inferred between the core and the BSE makes ^{182}W a potentially powerful tracer to search for core-mantle interactions (*e.g.*, Walker and Walker, 2005). Unlike for Os, the isotopic offset of W of the core from the BSE is not a reflection of inner core growth, but of the timing of core-mantle segregation. The only downside to the application of W for this purpose is that the W concentration contrast between the core and mantle is much less than for Os. The W concentration in the core is ~470 ppb, compared with ~15 ppb in the BSE. By contrast, the Os concentration in the outer core is ~1100 ppb *versus* only ~3 ppb in the BSE.

Due to the promise of W isotopes for identifying core-mantle interactions, several studies have sought to measure W isotopes in OIB systems (Schersten *et al.*, 2004; Takamasa *et al.*, 2009; Iizuka *et al.*, 2010; Moynier *et al.*, 2010). Ocean island basalts were targeted because it has been argued by numerous studies that at least some such systems originate at the core-mantle boundary, where chemical exchange between metal and silicate could occur (*e.g.*, Montelli *et al.*, 2004). The studies reported uniform "normal" W isotopic compositions in all of the rocks analysed. Consequently, each of the studies concluded there was no core-mantle interaction evident in the rocks examined. At the precision of these studies (±25-30 ppm precision on the $^{182}W/^{184}W$ ratio) only massive exchange of W between the core and mantle could have been resolved. In the cases examined, massive exchange of core material into a mantle source could be ruled out because the rocks were not correspondingly highly enriched in HSE, as would be required by mass balance constraints. So these studies were brave initial attempts, but not definitive tests. My group at the UMd did not attempt to play in this game during the first decade of the 2000's because our aging *VG Sector 54* multi-collector TIMS was incapable of making better than ±20 ppm measurements on any isotope system, *let alone* W. Fortunately, in the early 2000's, a new generation of TIMS came on the market, the *Thermo-Finnigan Triton*. This instrument can make higher precision measurements than the prior generation of TIMS, which included the *Sector 54* and *Finnigan-MAT 261* and *262* instruments, and quickly proved its mettle by measuring $^{142}Nd/^{144}Nd$ ratios with <4 ppm external precision and definitively revealing terrestrial heterogeneities in ^{142}Nd (*e.g.*, Caro *et al.*, 2003).

While still working with me at UMd, *Harry Becker* traveled to Johnson Space Center to analyse W using *Al Brandon*'s new *Triton*. Results were mixed. He found that he could measure $^{182}W/^{184}W$ ratios for standards to better than ±10 ppm 2σ external precision for short periods of time, but these periods were always followed by jumps in the isotopic ratio before leading into another period of stability. Clearly appreciable time would have to be invested in refining the method. In 2007 we convinced NSF, NASA and UMd to jointly fund the purchase of a *Thermo-Fisher Triton* (the company had by now changed its name) for UMd. In 2009 I hired *Mathieu Touboul*, a leading expert in W chemical separation and analysis by multi-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS), to tackle the W isotope systematics for terrestrial samples using the new TIMS. This high risk effort was courageously supported by the NSF's Cooperative Studies of Earth's Deep Interior (CSEDI) program. *Mathieu* began analysis of W on the *Triton* in February of 2010 using mass spectrometric techniques that *Mary Horan* had developed previously for use on the UMd *Sector 54* (Horan *et al*., 1998). We run W as a negatively charged trioxide species, using La and Gd as electron emitters. Although the initial results were better than we obtained on the *Sector 54*, external precision remained at about the ±15-20 ppm level for the first year of development. This was a disappointment, as it did not provide the level of precision we assumed we would need in order to resolve a core component. *Mathieu* and I finally figured out that the oxygen that was combining with the W to form the trioxide was fractionating independently from W in the mass spectrometer, both from run to run, and even during the course of a run. We eventually learned we could correct for the oxygen fractionation by using the $^{183}W/^{186}W$ ratio for a second level of normalisation, after using $^{184}W/^{186}W$ to normalise for W fractionation (Touboul and Walker, 2012). Direct measurement of oxygen isotopic compositions associated with the Os trioxides formed by NTIMS have been previously measured and used in corrections for isobaric species (Luguet *et al*., 2008b; Chatterjee and Lassiter *et al*., 2015), but our high mass beams were rarely large enough to make sufficiently precise measurements of the ^{18}O species, *let alone* the ^{17}O species. Amazingly, using the two stage data reduction, our external precision dropped to <5 ppm, and we were ready to go with real samples. This was already nearly 2 years into *Mathieu*'s postdoc, and is a good example of why 2 years is sometimes inadequate for a difficult postdoc project. It was propitious that I could continue to fund him beyond the 2 year limit many institutions seem to establish as maximum terms for postdocs.

After the mass spectrometric measurement method achieved acceptable precision, we next had to decide which rocks to analyse first. We thought we had the perfect rocks to demonstrate what we believed would be the first W isotopic evidence for core-mantle exchange, so the choice was relatively easy. These rocks were the 2.8 Ga Kostomuksha komatiites from western Russia which my UMd colleague *Igor Puchtel* had collected, and for which he had already generated considerable data. Although as komatiites go, they are pretty pedestrian, Al-undepleted komatiites, they were noteworthy in having both enriched initial $^{187}Os/^{188}Os$ and $^{186}Os/^{188}Os$ ratios. The enrichments were about what we expected from modelling early inner core crystallisation (see prior section), so we were convinced that the mantle source of these komatiites had incorporated an outer core component (Puchtel *et al.*, 2005). *Mathieu* immediately started analytical work on these komatiites, and we collectively assumed he would find negative ^{182}W anomalies, confirming our core-mantle interaction story. At this point, I think *Mathieu*, *Igor* and I were already thinking about what we would wear for the ticker tape parades and celebrity balls that would soon follow publication of the expected, exciting findings! It didn't quite work out that way.

Mathieu spent several months conducting the analyses, all the while remaining very quiet about progress. He finally came to me, and with an exasperated tone told me that the komatiites do not have negative anomalies. Instead they have a positive 15 ppm anomaly! This was not what we expected, but we could learn to live with it. As part of the same analytical campaign, *Mathieu* also analysed the 3.5 Ga Komati komatiites, and a modern OIB from the Canary Islands, and found no anomalies in these rocks. We concluded that the key to understanding the W anomaly was the fact that the rocks were also characterised by coupled enrichments in ^{187}Os-^{186}Os. This meant that we needed a way to geochemically induce increases in Re/Os, Pt/Os, as well as Hf/W. The short half-life of ^{182}Hf appeared to place the fractionation event well within the first 60 Ma of solar system history. While we were writing this up, a paper by *Tim Elliott*'s Bristol group (Willbold *et al.*, 2011) was published in *Nature*, reporting ^{182}W enrichments of approximately the same magnitude as ours for early Archean rocks from Isua, Greenland. This made them the first to report a W anomaly in terrestrial rocks, which was a bit disappointing for us, but we were able to get our paper published in *Science* a few months later. Tungsten could now be added to the inventory of short-lived radiogenic isotope systems that showed variations among terrestrial rocks. Joint University of Maryland-Department of Terrestrial Magnetism postdoc *Hanika Rizo* subsequently analysed a larger suite of samples from Isua and obtained very similar results to those of the earlier study (Rizo *et al.*, 2016a). The anomalies are not analytical artefacts, as the two studies used completely different chemical separation methods and mass spectrometric techniques (multi-collector inductively-coupled plasma mass spectrometry *versus* thermal ionisation mass spectrometry).

In addition to the positive anomalies noted for the Kostomuksha and Isua rocks, there are also positive anomalies present in Eoarchean rocks from the Nuvvuagittuq, Quebec supracrustal rocks (Touboul *et al.*, 2014), the Acasta gneisses, Northwest Territories, Canada (Willbold *et al.*, 2015), and the Saglek Block, northern Labrador, Canada (Liu *et al.*, 2016; Fig. 8.1). There are also positive anomalies in komatiitic basalts from the 2.4 Ga Vetreny Belt, Fennoscandian Shield, although in this case we concluded the komatiitic basalts obtained the anomaly through contamination with spatially associated tonalites (Puchtel *et al.*, 2016a). We also found small negative anomalies in both ^{182}W and ^{142}Nd in 3.55 Ga komatiites from Schapenburg, South Africa, consistent with a contribution from an early magma ocean fractionation process (Puchtel *et al.*, 2016b). Perhaps most remarkable of all is the discovery that ^{182}W anomalies are present in the Phanerozoic rock record, with the discovery of positive anomalies in basalts from the 0.12 Ga Ontong Java plateau, and in 0.06 Ga picrites from Baffin Bay, Canada (Rizo *et al*., 2016b). It seems that however the anomalous W has been created and stored in the mantle, it is still down there somewhere.

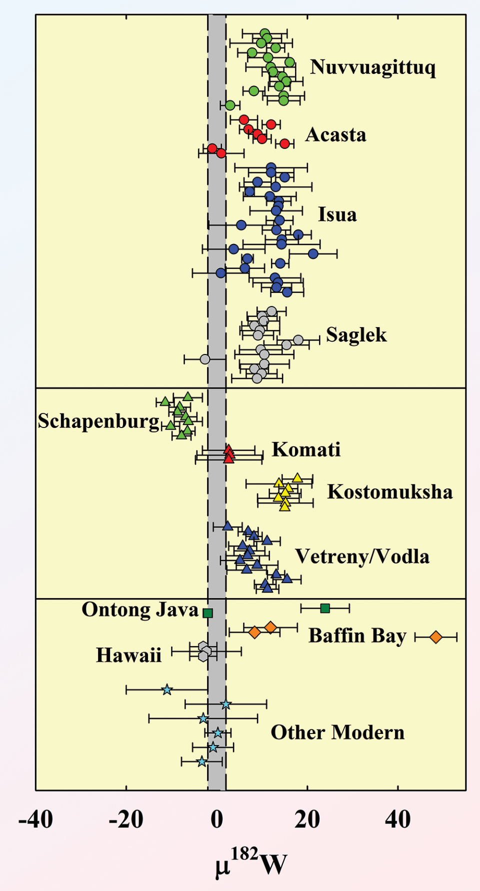


Figure 8.1 μ^{182}W values for various ancient and modern terrestrial rocks. The upper box includes mainly supracrustal rocks ≥3.4 Ga. The middle box includes mainly komatiites ranging in age from 3.55 Ga (Schapenburg) to 2.4 Ga (Vetreny). The lower box are data for Phanerozoic rocks including from Ontong Java (0.12 Ga), Baffin Bay (0.06 Ga) and modern oceanic and ocean island basalts. Note that in most instances, variability in isotopic composition relates to different rock types for a given location. Data are from Willbold *et al*. (2011, 2015), Touboul *et al*. (2012, 2014), Liu *et al*. (2016), Puchtel *et al*. (2016a,b) and Rizo *et al*. (2016a,b).

At the time of this writing, I admit that I am not very confident we understand the causes of the ^{182}W anomalies that have been found. Willbold *et al*. (2011) concluded that the positive anomalies for the Isua rocks reflect derivation from a mantle source that, at the time of melting to produce the rocks, had not yet acquired very much of its complement of late accreted siderophile elements. As noted above in Section 4.3, late accretion of materials with broadly chondritic compositions to the mantle leads to a lowering of the μ^{182}W value of the mantle, while increasing the HSE content. This is because the μ^{182}W value of chondrites is strongly negative (~-200). Based on mass balance arguments, Willbold *et al*. (2011) proposed that, prior to late accretion, the mantle had a μ^{182}W value 15-30 ppm higher than the modern mantle value, consistent with the enrichment observed in the rocks. Of course rocks generated from mantle without a late accretionary component should also have low HSE abundances. This study, however, did not measure HSE in the rocks analysed for W isotopes. If their interpretation is correct, and if it is assumed that late accreted materials to Earth were added soon after the Moon-forming event (see above), then the late accreted materials remained poorly mixed within the mantle for what was probably 100's of Ma. This paints a picture of a mantle that was convectively mixing much less efficiently than is typically suggested for the Hadean Earth.

Most Nuvvuagittuq rocks are enriched in ^{182}W by 10-15 ppm (Fig. 8.1), and are, therefore, similar to the results obtained by Willbold *et al*. (2011) and Rizo *et al*. (2016a) for Isua rocks. The highest MgO rocks from the Nuvvuagittuq suite appear to have been derived from mantle sources with "normal" mantle abundances of HSE (~80 % of BSE). This is also true for at least some of the rocks from Isua (Rizo *et al*., 2016a). Thus, despite their ^{182}W anomalies, some or all of these rocks were derived from mantle with more or less normal abundances of HSE. A major caveat with the results for rocks from both Isua and Nuvvuagittuq is that many of the rocks have much higher abundances of W than is possible by direct melting of an initially primitive mantle source. In the case of the Nuvvuagittuq suites, we concluded that the rocks were ultimately derived from mantle with "normal" abundances of HSE, but also that ^{182}W-enriched fluids, possibly derived from recycled earlier crust, transferred radiogenic W to the mantle sources, or parental melts, thus, accounting for the enriched ^{182}W but normal HSE abundances. This, admittedly, is an *ad hoc* model, and, of course, doesn't explain how the putative early crust attained its high ^{182}W/^{184}W ratio. Unfortunately, we don't have a better explanation at this time.

The positive ^{182}W anomaly in the mantle source of the Kostomuksha komatiites cannot be explained as the result of derivation from a mantle domain that had not yet received its full late accretionary complement of siderophile elements. The abundances of HSE in the komatiites had been previously measured, and the abundances of HSE in the Kostomuksha mantle source had been estimated (Puchtel and Humayun, 2005). Source abundances are essentially normal compared to estimates for the BSE. If the ^{182}W enrichment truly reflects the composition of its mantle source, then the short half-life of ^{182}Hf requires that the source included materials from a mantle reservoir created within the first 60 Ma of solar system history. This component, thus, survived convective mixing of the mantle in some form for >1.7 Gyr (Touboul *et al*., 2012). It even survived the putative giant impact that created the Moon! This event likely occurred more than 60 Ma after formation of the Solar System at 4.567 Ga, but before 4.374 Ga (Touboul *et al*., 2007; Borg *et al*., 2015).

Due to the isotopic requirements of suprachondritic Pt/Os, Re/Os and Hf/W in the mantle source, in Touboul *et al*. (2012) we proposed that this reservoir represents a by-product either of metal-silicate partitioning in a basal magma ocean (*e.g.*, Labrosse *et al*., 2007), or of silicate fractionation in an upper or whole mantle magma ocean. The first option is appealing in several ways. First, periodic equilibration of a lower basal magma with metal passing through it would likely produce a reservoir with very high Hf/W. Second, using what we know about Re-Pt-Os partitioning in high temperature and pressure metal silicate systems (*e.g.*, Van Orman *et al*., 2008), we might also expect that this reservoir would develop suprachondritic Re/Os and Pt/Os, albeit at the expense of low Os and fractionated HSE. Finally, if this reservoir is in the lowermost mantle, we can envision it surviving "big events", like the Moon-forming giant impact, while the overlying mantle developed "normal" HSE and W isotopic characteristics as a result of subsequent late accretion. Such an isotopically distinct lower mantle reservoir can then be tapped at any time in Earth history, potentially by incorporation of this material in a plume rising from the lower mantle. The contribution from this reservoir to upper mantle would have to be small, however, so that the abundances of the HSE of the resulting mixture would remain similar to BSE.

Other processes are also possible. For example, Willbold *et al*. (2015) modified their earlier model by appealing to retention of a small portion of metal from the Moon-forming giant impactor (high HSE) in the Earth's mantle as it cooled, then following this with a minor amount of additional late accretion. This model can potentially circumvent the problem of the apparently normal HSE abundances in the mantle sources of these rocks, but still requires some special things to happen (*e.g.*, metal retention in the mantle at the point in time when it likely reached its highest temperatures). Crystallisation and overturn in a large-scale, early-formed magma ocean also has some advantages, if you want to generate ^{182}W anomalies in the mantle. Most importantly, distribution coefficients for upper and lower mantle minerals suggest that Hf/W ratios would fractionate as a magma ocean evolved (*e.g.*, Brown *et al*., 2014). The fractionation processes would also likely lead to accompanying variations in Sm/Nd, so for this model one might expect a correlation between ^{182}W and ^{142}Nd. In the case of the Kostomuksha komatiites, no well-resolved correlation is noted. In the case of the 3.55 Ga komatiites from Schapenburg, South Africa, the coupled negative ^{182}W and ^{142}Nd anomalies are consistent with an early silicate fractionation process (Puchtel *et al*., 2016b).

Regardless of the true processes involved in generating the W and Os isotopic systematics of the Kostomuksha komatiites, the observed anomalies require the long-term survival of some mantle domain whose HSE and MSE were set by high temperature/pressure metal-silicate partitioning, as well as a major portion of the mantle that was stripped of HSE and (to a lesser extent) MSE, then re-enriched by late accretion. It remains unknown whether the W anomalies are related to the Os isotopic enrichments via the same process. Needless to say, there is much exciting work yet to be done with W isotopes in terrestrial rocks.

9. CONCLUDING REMARKS

The geochemical community has come a long way with respect to the measurement and interpretation of siderophile elements in cosmo- and geo-chemical materials. In my 30 years of working with the Re-Os isotope system, I have seen the precision in the measurement of ^{187}Os/^{188}Os and ^{186}Os/^{188}Os ratios decrease from about 1 % to about 10 parts per million. The improvements have paved the way for high precision geochronology, as well as the use of ^{187}Os and ^{186}Os as sensitive tracers of mantle processes. Similarly, during the past 20 years the Hf-W isotope system has been refined to such an extent that differences in the core segregation ages of asteroids of less than 1 Ma can now be resolved. These are truly exciting times to be working with siderophile elements!

My perspective of what is exciting and important will no doubt differ from those of most other proponents of these elements. I have not been able to cover many prominent topics that involve siderophile elements. For example, until now, I have not mentioned that one of the most famous applications of siderophile elements was the discovery of the Ir anomaly (actually an HSE anomaly) present in deposts resulting from a sizeable impact at the Cretaceous-Tertiary boundary. This discovery led to the conclusion that the major extinction event at this time was caused by an impact, most likely the Chixulub impactor. Nor have I discussed the exciting application of Re-Os dating of inclusions contained within diamonds. I have also only briefly mentioned siderophile elements in komatiites, although at UMd, we devote considerable attention to these rocks, and provide very little overview to applications of siderophile elements to the study of magmatic ores, an area of intense research. To fans of these topics, I apologise.

Here, I have also virtually ignored the application of siderophile elements to low temperature systems due to space and a lack of expertise, not because I believe these applications are unimportant or uninteresting. For example, in the last 15 years we have seen a huge increase in the number of applications of the Re-Os system for dating organic-rich sediments, and even the timing of oil formation. This is an exciting and very practical application of the system. Stable isotopes of Mo are now commonly used to study the redox conditions of aqueous systems at the surface of the Earth. The absolute and relative abundances of siderophile elements in loess and glacial diamictites are valuable tools for studying the chemical evolution and weathering history of the continental crust. However, these and other topics will have to wait for another author to address in a future *Geochemical Perspectives* article.

There is much left to do. Here are five examples of "important topics" that I believe bear significant further study:

1. The application of siderophile nucleosynthetic tracers, such as Mo and Ru, to study the genetics of late stages of planetary accretion has only begun. It is logical that these tracers should be applied to terrestrial

and lunar impact sites, to fingerprint the impactors, particularly those impactors involved in what some believe to be a late heavy bombardment stage of the Earth and Moon. Further, the Mo and Ru isotopic compositions of Mars, Vesta and the angrite parent body, among other inner solar system bodies, are either unknown or insufficiently well constrained. Hence, it remains important to determine how well these siderophile elements were mixed in the inner solar system by the time of large body formation.

2. The variability in the ^{182}W isotopic composition of terrestrial mantle-derived samples is an exciting discovery, yet the causes for the heterogeneities remain poorly constrained. Very few post-Archean rocks have been analysed to-date, so it remains unknown how long ^{182}W-enriched domains within the mantle remained isolated from the ambient mantle. High-precision re-measurement of the W isotopic compositions of potential plume-derived materials that may arise from the core-mantle boundary is also warranted. However, identifying the most appropriate materials for this type of study remains a challenge.
3. Estimates for the abundances of siderophile elements in the BSE will require constant updating and re-assessment as the database for these elements continues to grow.
4. Determination of how siderophile elements are distributed in the mantle. Are they homogeneously distributed on a global scale at present, and were they homogeneously distributed in the mantle as far back in time as we can look?
5. Although we know that siderophile elements prefer metal to silicate, we don't well know the rates of exchange of these elements between metal and silicate that can occur during core formation episodes. Thus, it remains problematic to model the passage of metal through silicate, as must occur during the giant impact stage of planetary growth. Perhaps even more important, we don't know how rapid isotopic exchange may be relative to elemental exchange. This needs to be much better constrained.

REFERENCES

Alard, O., Griffen, W.L., Lorrand, J.P., Jackson, S.E., O'Reilly, S.Y. (2000) Non-chondritic distribution of the highly siderophile elements in mantle sulfides. *Nature* 407, 891-894.

Alard, O., Luguet, A., Pearson, N.J., Griffen, W.L., Lorand, J.-P., Gannoun, A., Burton, K.W., O'Reilly, S.Y. (2005) *In situ* Os isotopes in abyssal peridotites bridge the isotopic gap between MORBs and their source mantle. *Nature* 436, 1005-1008.

Allègre, C.J., Luck, J.-M. (1980) Osmium isotopes as petrogenetic and geological tracers. *Earth and Planetary Science Letters* 48, 148-154.

Allègre, C.J., Turcotte, D.L. (1986) Implications of a two-component marble-cake mantle. *Nature* 323, 123-127.

Amelin, Y., Krot, A.N., Hutcheon, I.D., Ulyanov, A.A. (2002) Lead isotopic ages of chondrules and calcium-aluminum-rich inclusions. *Science* 297, 1678-1683.

Amelin, Y., Ghosh, A., Rotenberg, E. (2005) Unravelling the evolution of chondrite parent asteroids by precise U-Pb dating and thermal modelling. *Geochimica et Cosmochimica Acta* 69, 505-518.

Anders, E., Grevesse, N. (1989) Abundances of the elements: Meteoritic and solar. *Geochimica et Cosmochimica Acta* 53, 197-214.

Anders, E., Ganapathy, R., Keays, R.R., Laul, J.C., Morgan, J.W. (1971) Volatile and siderophile elements in lunar rocks: comparison with terrestrial and meteoritic basalts. *Proceedings of the Second Lunar Science Conference*, V. 2, 1021-1036.

Anderson, D.L. (1998) A model to explain the various paradoxes associated with mantle noble gas geochemistry. *Proceedings of the National Academy of Sciences* 95, 9087–9092.

Anderson, D.L. (2010) Top down tectonics. *Science* 293, 2016-2018.

Andreasen, R., Sharma, M. (2007) Mixing and homogenization in the early Solar System: clues from Sr, Ba, Nd, and Sm isotopes in meteorites. *Astrophysical Journal* 665, 874-883.

Archer, G.J., Bullock, E.S., Ash, R.D., Walker, R.J. (2014) ^{187}Re-^{187}Os isotopic and highly siderophile element systematics of the Allende meteorite: evidence for primary nebular processes and late-stage alteration. *Geochimica et Cosmochimica Acta* 131, 402-414.

Arevalo Jr., R., McDonough, W.F. (2008) Tungsten geochemistry and implications for understanding the Earth's interior. *Earth and Planetary Science Letters* 272, 656–665.

Arevalo Jr., R., McDonough, W.F., Stracke, A., Willbold, M., Ireland, T.J., Walker, R.J. (2013) Simplified mantle architecture and distribution of radiogenic power. *Geochemistry Geophysics Geosystems* 14, 2265-2285.

Arndt, N.T., Lesher, C.M., Barnes, S.J. (2008) Komatiite. Cambridge University Press, Cambridge, UK, 488pp.

Asphaug, E., Agnor, C.B., Williams, Q. (2006) Hit and run planetary collisions. *Nature* 439, 155-160.

Aulbach, S., Mungall, J.E., Pearson, D.G. (2016) Distribution and processing of highly siderophile elements in cratonic mantle lithosphere. *Reviews in Mineralogy & Geochemistry* V. 81, 239-304.

Baker, J.A., Jensen, K.K. (2004) Coupled ^{186}Os-^{187}Os enrichments in the Earth's mantle – core-mantle interaction or recycling of ferromanganese crusts and nodules? *Earth and Planetary Science Letters* 220, 277-286.

Baker, J.A., Schiller, M., Bizzarro, M. (2012) ^{26}Al-^{26}Mg deficit dating ultramafic meteorites and silicate planetesimal differentiation in the early Solar System? *Geochimica et Cosmochimica Acta* 77, 415-431.

Barnes, S.-J., Naldrett, A.J., Gorton, M.P. (1985) The origin of the fractionation of platinum-group elements in terrestrial magmas. *Chemical Geology* 53, 303-323.

Bate, G.L., Huizenga, J.R. (1963) Abundances of ruthenium, osmium and uranium in some cosmic and terrestrial sources. *Geochimica et Cosmochimica Acta* 27, 345-360.

Barrat, J.A., Yamaguchi, A., Zanda, B., Bollinger, C., Bohn, M. (2010) Relative chronology of crust formation on asteroid Vesta: Insights from the geochemistry of diogenites. *Geochimica et Cosmochimica Acta* 74, 6218-6231.

Batanova, V.G., Brügmann, G.E., Bazylev, B.A., Sobolev, A.V., Kamenestsky, V.S., Hofmann, A.W. (2008) Platinum-group element abundances and Os isotope composition of mantle peridotites from the Mamonia complex, Cyprus. *Chemical Geology* 248, 195-212.

Becker, H., Walker, R.J. (2003) The ^{98}Tc-^{98}Ru and ^{99}Tc-^{99}Ru chronometers: new results on iron meteorites and chondrites. *Chemical Geology* 196, 43-56.

Becker, H., Dale, C.W. (2016) Re-Pt-Os isotopic and highly siderophile element behavior in oceanic and continental mantle tectonites. *Reviews in Mineralogy & Geochemistry* V. 81, 369-440.

Becker, H., Walker, R.J., MacPherson, G.J., Morgan, J.W., Grossman, J.N. (2001a) Rhenium-osmium systematics of calcium-aluminum-rich inclusions in carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 65, 3379-3390.

Becker, H., Shirey, S.B., Carlson, R.W. (2001b) Effects of melt percolation on the Re-Os systematics of peridotites from a Paleozoic convergent plate margin. *Earth and Planetary Science Letters* 188, 107-121.

Becker, H., Horan, M.F., Walker, R.J., Gao, S., Lorand, J.-P., Rudnick, R.L. (2006) Highly siderophile element composition of the Earth's primitive upper mantle: Constraints from new data on peridotite massifs and xenoliths. *Geochimica et Cosmochimica Acta* 70, 4528-4550.

Bennett, N., Brenan, J.M. (2013) Controls on the solubility of rhenium in silicate melt: implications for the osmium isotopic composition of Earth's mantle. *Earth and Planetary Science Letters* 361, 320-332.

Bennett, N., Brenan, J.M., Koga, K.T. (2014) The solubility of platinum in silicate melt under reducing conditions: results from experiments without metal inclusions. *Geochimica et Cosmochimica Acta* 133, 422-442.

Bennett, V.C. (2003) Compositional evolution of the mantle. In: Holland, H.D., Turekian, K.K. (Eds.) *Treatise on Geochemistry* 2, *The Mantle and the Core*, 493-519.

Bennett, V.C., Norman M.D., Garcia, M.O. (2000) Rhenium and platinum group element abundances correlated with mantle source components in Hawaiian picrites: sulphides in the plume. *Earth and Planetary Science Letters* 183, 513-526.

Bennett, V.C., Nutman, A.P., Esat, T. (2002) Constraints on mantle evolution from ^{187}Os/^{188}Os isotopic compositions of Archean ultramafic rocks from southern West Greenland (3.8 Ga) and Western Australia (3.46 Ga). *Geochimica et Cosmochimica Acta* 66, 2615–2630.

Bennett, V.C., Brandon, A.D., Nutman, A.P. (2007) Coupled ^{142}Nd-^{143}Nd isotopic evidence for Hadean mantle dynamics. *Science* 318, 1907-1910.

Bézos, A., Lorand, J.-P., Humler, E., Gros, M. (2005) Platinum-group element systematics in Mid-Oceanic Ridge basaltic glasses from the Pacific, Atlantic, and Indian Oceans. *Geochimica et Cosmochimica Acta* 69, 2613–2627.

Birck, J.L., Allègre, C.J. (1994) Contrasting Re/Os magmatic fractionation in planetary basalts. *Earth and Planetary Science Letters* 124, 139–148.

Birck, J.L., Roy-Barman, M., Capmas, F. (1997) Re-Os isotopic measurements at the femtomole level in natural samples. *Geostandards Newsletter* 20, 19-27.

Bizimis, M., Griselin, M., Lassiter, J.C., Salkters, V.J.M., Sen, G. (2007) Ancient recycled mantle lithosphere in the Hawaiian plume: Osmium–Hafnium isotopic evidence from peridotite mantle xenoliths. *Earth and Planetary Science Letters* 257, 259–273.

Blichert-Toft, J., Puchtel, I.S. (2010) Depleted mantle sources through time: evidence from Lu-Hf and Sm-Nd isotope systematics of Archean komatiites. *Earth and Planetary Science Letters* 297, 598-606.

Blusztajn, J., Hart, S.R., Ravizza, G., Dick, H.J.B. (2000) Platinum-group elements and Os isotopic characteristics of the lower oceanic crust. *Chemical Geology* 168, 113–122.

Bockrath, C., Ballhaus, C., Holzheid, A. (2004) Fractionation of the platinum-group elements during mantle melting. *Science* 305, 1951–1953.

Borg, L.E., Nyquist, L., Taylor, L., Wiesmann, H., Shih, C.-Y. (1997) Constraints on Martian differentiation processes from Rb–Sr and Sm–Nd isotopic analyses of the basaltic shergottite QUE 94201. *Geochimica et Cosmochimica Acta* 61, 4915–4931.

Borg, L.E., Nyquist, L.E., Wiesmann, H., Reese, Y. (2002) Constraints on the petrogenesis of Martian meteorites from the Rb–Sr and Sm–Nd isotopic systematics of the ultramafic shergottites ALH77005 and LEW88516. *Geochimica et Cosmochimica Acta* 66, 2037–2053.

Borg, L.E., Nyquist, L.E., Wiesmann, H., Shih, C.-Y., Reese, Y. (2003) The age of Dar al Gani 476 and the differentiation history of the martian meteorites inferred from their radiogenic isotopic systematics. *Geochimica et Cosmochimica Acta* 67, 3519–3536.

Borg, L.E., Gaffney, A.M., Shearer, C.K. (2015) A review of lunar chronology revealing a preponderance of 4.34-4.37 Ga ages. *Meteoritics and Planetary Science* 50, 715-732.

Boyd, F.R., Mertzman, S.A. (1987) Composition and structure of the Kaapvaal lithosphere, Southern Africa. In: Mysen, B.O. (Ed.) *Magmatic Processes: Physicochemical Principles*. Geochemical Society Special Publication 1, 3-12.

Bottke, W.F., Walker, R.J., Day, J.M.D., Nesvorny, D., Elkins-Tanton, L. (2010) Stochastic late accretion to Earth, the Moon and Mars. *Science* 330, 1527-1530.

Bouvier, A., Blichert-Toft, J., Moynier, F., Vervoort, J.D., Albarède, F. (2007) Pb-Pb dating constriants on the accretion and cooling history of chondrites. *Geochimica et Cosmochimica Acta* 71, 1583-1604.

Bouvier, A., Blichert-Toft, J., Albarède, F. (2009) Martian meteorite chronology and the evolution of the interior of Mars. *Earth and Planetary Science Letters* 280, 285-295.

Boyet, M., Carlson, R.W. (2005) ^{142}Nd evidence for early (>4.53 Ga) global differentiation of the silicate Earth. *Science* 309, 576-581.

Brandon, A.D., Creaser, R.A., Shirey, S.B., Carlson, R.W. (1996) Osmium recycling in subduction zones. *Science* 272, 861-864.

Brandon, A.D., Walker, R.J., Morgan, J.W., Norman, M.D., Prichard, H.M. (1998) Coupled ^{186}Os and ^{187}Os evidence for core-mantle interaction. *Science* 280, 1570-1573.

Brandon, A.D., Norman, M.D., Walker, R.J., Morgan, J.W. (1999) ^{186}Os-^{187}Os systematics of Hawaiian picrites. *Earth and Planetary Science Letters* 172, 25-42.

Brandon, A.D., Walker, R.J., Morgan, J., Goles, G.G. (2000a) Re–Os isotopic evidence for early differentiation of the Martian mantle. *Geochimica et Cosmochimica Acta* 64, 4083–4095.

Brandon, A.D., Snow, J.E., Walker, R.J., Morgan, J.W., Mock, T.D. (2000b) ^{190}Pt-^{186}Os and ^{187}Re-^{187}Os systematics of abyssal peridotites. *Earth and Planetary Science Letters* 177, 319-335.

Brandon, A.D., Walker, R.J., Puchtel, I.S., Becker, H, Humayun, M., Revillon, S. (2003) ^{186}Os-^{187}Os systematics of Gorgona Island komatiites: implications for early growth of the inner core. *Earth and Planetary Science Letters* 206, 411-426.

Brandon, A.D., Humayun, M., Puchtel, I.S., Leya, I., Zolensky, M. (2005) Osmium isotope evidence for an *s*-process carrier in primitive chondrites. *Science* 309, 1233-1236.

Brandon, A.D., Walker, R.J., Puchtel, I.S. (2006) Platinum-Os isotope evolution of the Earth's mantle: constraints from chondrites and Os-rich alloys. *Geochimica et Cosmochimica Acta* 70, 2093-2103.

Brandon, A.D., Graham, D.W., Waight, T., Gautason, B. (2007) ^{186}Os and ^{187}Os enrichments and high-^{3}He/^{4}He sources in the Earth's mantle: evidence from Icelandic picrites. *Geochimica et Cosmochimica Acta* 71, 4570–4591.

Brandon, A.D., Puchtel, I.S., Walker, R.J., Day, J.M.D., Irving, A.J., Taylor, L.A. (2012) Evolution of the martian mantle inferred from the ^{187}Re-^{187}Os isotope and highly siderophile element systematics of shergottites meteorites. *Geochimica et Cosmochimica Acta* 76, 206-235.

Brearley, A.J. (2003) Classification of meteorites. In: Holland, H.D., Turekian, K.K. (Eds.) *Treatise on Geochemistry*. Elsevier B.V., Amsterdam, 247-268.

Brenan, J.M., McDonough, W.F. (2009) Core formation and metal–silicate fractionation of osmium and iridium from gold. *Nature Geoscience* 2, 798-801.

Brenan, J.M., Bennett, N.R., Zajacz, Z. (2016) Experimental results on fractionation of the highly siderophile elements (HSE) at variable pressures and temperatures during planetary and magmatic differentiation. *Reviews in Mineralogy & Geochemistry* V. 81, 1-87.

Brown, S., Elkins-Tanton, L., Walker, R.J. (2014) Effects of magma ocean crystallization and overturn on the development of ^{142}Nd and ^{182}W isotopic heterogeneities in the primordial mantle. *Earth and Planetary Science Letters* 408, 319-330.

Bryce, J.G., DePaolo, D.J., Lassiter, J.C. (2005) Geochemical structure of the Hawaiian plume: Sr, Nd, and Os isotopes in the 2.8 km HSDP-2 section of Mauna Kea volcano. *Geochemistry Geophysics Geosystems* 6, 1–36.

Büchl, A., Brügmann, G., Batanova, V.G., Münker, C., Hofmann, A.W. (2002) Melt percolation monitored by Os isotopes and HSE abundances: a case study from the mantle section of the Troodos Ophiolite. *Earth and Planetary Science Letters* 204, 385-402.

Büchl, A., Brügmann, G.E., Batanova, V.G., Hofmann, A.W. (2004) Os mobilization during melt percolation: The evolution of Os isotope heterogeneities in the mantle sequence of the Troodos ophiolite, Cyprus. *Geochimica et Cosmochimica Acta* 68, 3397-3408.

Burbidge, E.M., Burbidge, G.R., Fowler, W.A., Hoyle, F. (1957) Synthesis of the elements in stars. *Reviews of Modern Physics* 29, 547-650.

Burkhardt, C., Kleine, T., Palme, H., Bourdon, B., Zipfel, J., Friedrich, J., Ebel, D. (2008) Hf–W mineral isochron for Ca, Al-rich inclusions: Age of the solar system and the timing of core formation in planetesimals. *Geochimica et Cosmochimica Acta* 72, 6177-6197.

Burkhardt, C., Kleine, T., Oberli, F., Pack, A., Bourdon, B., Wieler, R. (2011) Molybdenum isotope anomalies in meteorites: constraints on solar nebula evolution and origin of the Earth. *Earth and Planetary Science Letters* 312, 390-400.

Campbell, A.J., Humayun, M. (1999) Trace element microanalysis in iron meteorites by laser ablation ICPMS. *Analytical Chemistry* 71, 939-946.

Campbell, I.H., Griffiths, R.W. (1990) Implications of mantle plume structure for the evolution of flood basalts. *Earth and Planetary Science Letters* 99, 79–93.

Capobianco, C.J., Dranke, M.J., De'Aro, J. (1999) Siderophile geochemistry of Ga, Ge, and Sn: cationic oxidation states in silicate melts and the effect of composition in iron-nickel alloys. *Geochimica et Cosmochimica Acta* 63, 2667-2677.

Carlson, R.W., Pearson, D.G., James, D.E. (2005) Physical, chemical, and chronological characteristics of continental mantle. *Reviews of Geophysics* 43, doi: 10.1029/2004RG000156.

Carlson, R.W., Boyet, M., Horan, M.F. (2007) Chondrite barium, neodymium, and samarium isotopic heterogeneity and early earth differentiation. *Science* 316, 1175–1178.

Caro, G., Bourdon, B., Birck, J.-L., Moorbath, S. (2003) ^{146}Sm–^{142}Nd evidence from Isua metamorphosed sediments for early differentiation of the Earth's mantle. *Nature* 423, 428-432.

Chabot, N.L. (2004) Sulfur contents of the parental metallic cores of magmatic iron meteorites. *Geochimica et Cosmochimica Acta* 68, 3607–3618.

Chabot, N.L., Jones, J.H. (2003) The parameterization of solid metal-liquid metal partitioning of siderophile elements. *Meteoritics and Planetary Science* 38, 1425-1436.

Chabot, N.L., Campbell, A.J., McDonough, W.F., Draper, D.S., Agee, C.B., Humayun, M., Watson, H.C., Cottrell, E., Saslow, S.A. (2008) The Fe–C system at 5 GPa and implications for Earth's core. *Geochimica et Cosmochimica Acta* 72, 4146–4158.

Chatterjee, R., Lassiter, J.C. (2015) High precision Os isotopicmeasurement using N-TIMS: Quantification of various sources of error in ^{186}Os/^{188}Os measurements. *Chemical Geology* 396, 112–123.

Chen, J.H., Papanastassiou, D.A., Wasserburg, G.J. (2010) Ruthenium endemic isotope effects in chondrites and differentiated meteorites. *Geochimica et Cosmochimica Acta* 74, 3852-3862.

Chou, C.-L. (1978) Fractionation of siderophile elements in the earth's upper mantle. *Proceeding of the Lunar and Planetary Science Conference* 9th, 219-230.

Chou, C.-L., Boynton, W.V., Sundberg, L.L., Wasson, J.T. (1975) Volatiles on the surface of Apollo 15 green glass and trace-element distributions among Apollo 15 soils. *Proceedings of the Lunar Science Conference* 6th, 1701-1727.

Clayton, R.N. (2003) Oxygen isotopes in meteorites. In: Davis, A.M. (Ed.) *Treatise on Geochemistry, Volume 1, Meteorites, Comets, and Planets*. Elsevier B.V., Amsterdam, 129-142.

Coggon, J.A., Nowell, G.M., Pearson, D.G., Parman, S.W. (2011) Application of the ^{190}Pt–^{186}Os isotope system to dating platinum mineralization and ophiolite formation — an example from the Meratus Mountains, Borneo. *Economic Geology* 106, 93–117.

Coggon, J.A., Nowell, G.M., Pearson, D.G., Oberthür, T., Lorand, J.-P., Melcher, F., Parman, S.W. (2012) The ^{190}Pt-^{186}Os decay system applied to dating platinum-group element mineralization of the Bushveld Complex, South Africa. *Chemical Geology* 302-303, 48-60.

Coggon, J.A., Luguet, A., Nowell, G.M., Appel, P.U. (2013) Hadean mantle melting recorded by southwest Greenland chromitite ^{186}Os signatures. *Nature Geoscience* 6, 871-874.

Cohen, A.S., Waters, F.G. (1996) Separation of osmium from geological materials by solvent extraction for analysis by thermal ionization mass spectrometry. *Analytica Chimica Acta* 332, 269-275.

Cohen, R.S., O'Nions, R.K. (1982) Identification of recycled continental material in the mantle from Sr, Nd and Pb isotope investigations. *Earth and Planetary Science Letters* 61, 73-84.

Cook, D.L., Walker, R.J., Horan, M.F., Wasson, J.T., Morgan, J.W. (2004) Pt-Re-Os systematics of group IIAB and IIIAB iron meteorites. *Geochimica et Cosmochimica Acta* 68, 1413-1431.

Cottrell, E., Walker, D. (2006) Constraints on core formation from Pt partitioning in mafic silicate liquids at high temperatures. *Geochimica et Cosmochimical Acta* 70, 1565-1580.

Creaser, R.A., Papanastassiou, D.A., Wasserburg, G.J. (1991) Negative thermal ion mass spectrometry of osmium, rhenium, and iridium. *Geochimica et Cosmochimica Acta* 55, 397-401.

Dale, C.W., Luguet, A., Macpherson, C.G., Pearson, D.G., Hickey-Vargas, R. (2008) Extreme platinum-group element fractionation and variable Os isotope compositions in Philippine Sea Plate basalts: tracing mantle source heterogeneity. *Chemical Geology* 248, 213–238.

Dale, C.W., Burton, K.W., Greenwood, R.C., Gannoun, A., Wade, J., Wood, B.J., Pearson, D.G. (2012) Late accretion on the earliest planetesimals revealed by the highly siderophile elements. *Science* 336, 72-75.

Dauphas, N., Marty, B., Reisberg, L. (2002) Molybdenum evidence for inherited planetary scale isotope heterogeneity of the protosolar nebula, *Astrophysical Journal* 565, 640–644.

Dauphas, N., Davis, A.M., Marty, B., Reisberg, L. (2004) The cosmic molybdenum-ruthenium isotope correlation. *Earth and Planetary Science Letters* 226, 465-476.

Dauphas, N., Burkhardt, C., Warren, P.H., Teng, F.-Z. (2014) Geochemical arguments for an Earth-like Moon-forming impactor. *Philosophical Transactions of the Royal Society of London* A 372, 20130244.

Davison, T.M., Ciesla, F.J., Collins, G.S. (2012). Post impact thermal evolution of porous planetesimals. *Geochimica et Cosmochimica Acta* 95, 252–269.

Day, J.M.D. (2013) Hotspot volcanism and highly siderophile elements. *Chemical Geology* 341, 50-74.

Day, J.M.D., Walker, R.J. (2015) Highly siderophile element depletion in the Moon. *Earth and Planetary Science Letters* 423, 114-124.

Day, J.M.D., Pearson, D.G., Taylor, L.A. (2007) Highly siderophile element constraints on accretion and differentiation of the Earth-Moon system. *Science* 315, 217-219.

Day, J.M.D., Walker, R.J., James, O.B., Puchtel, I.S. (2010a) Osmium isotope and highly siderophile element systematics of the lunar crust. *Earth and Planetary Science Letters* 289, 595-605.

Day, J.M.D., Pearson, D.G., Macpherson, C.G., Lowry, D., Carracedo, J.C. (2010b) Evidence for distinct proportions of subducted oceanic crust and lithosphere in HIMU-type mantle beneath El Hierro and La Palma, Canary Islands. *Geochimica et Cosmochimica Acta* 74, 6565–6589.

Day, J.M.D., Walker, R.J., Qin, L., Rumble, D. (2012) Early timing of late accretion in the solar system. *Nature Geoscience* 5, 614-617.

Day, J.M.D., Waters, C.L., Schaefer, B.F., Walker, R.J., Turner, S. (2016) Use of hydrofluoric acid desilicification in the determination of highly siderophile element abundances and Re-Pt-Os isotope systematics in mafic-ultramafic rocks. *Geostandards and Geoanalytical Research* 40, 49-65.

Debaille, V., Yin, Q.-Z., Brandon, A., Jacobsen, B. (2008) Martian mantle mineralogy investigated by the ^{176}Lu–^{176}Hf and ^{147}Sm–^{143}Nd systematics of shergottites. *Earth and Planetary Science Letters* 269, 186–199.

DeGrazia, A.R., Haskins, L. (1964) On the gold contents of rocks. *Geochimica et Cosmochimica Acta* 28, 559-564.

Dick, H.J.B. (1989) Abyssal peridotites, very slow spreading ridges and ocean ridge magmatism. In: Saunders, A.D., Norry, M.J. (Eds.) *Magmatism in the Ocean Basins*. Geological Society of London, Special Publication 42, 71–105.

Dick, H.J.B., Fisher, R.L., Bryan, W.B. (1984) Mineralogic variability of the uppermost mantle along mid-ocean ridges. *Earth and Planetary Science Letters* 69, 88-106.

Dilek, Y., Furnes, H. (2011) Ophiollite genesis and global tectonics: geochemical and tecton fingerprinting of anciet oceanic lithosphere. *Geological Society of America Bulletin* 123, 387-411.

Dupré, B., Allègre, C.J. (1983) Pb-Sr isotope variation in Indian Ocean basalts and mixing phenomena. *Nature* 303, 142-146.

Eisele, J., Sharma, M., Galer, S.J.G., Blichert-Toft, J., Devey, C.W., Hofmann, A.W. (2002) The role of sediment recycling in EM-1 inferred from Os, Pb, Hf, Nd, Sr isotope and trace element systematics of the Pitcairn hotspot. *Earth and Planetary Science Letters* 196, 197-212.

Elkins-Tanton, L.T. (2012) Magma oceans in the inner solar system. *Annual Reviews of the Earth and Planetary Sciences* 40, 113-139.

Elthon, D. (1992) Chemical trend in abyssal peridotites: refertilization of depleted suboceanic mantle. *Journal of Geophysical Research* 97, 9015-9025.

Escrig, S., Schiano, P., Schilling, J.-G., Allègre, C.J. (2005) Rhenium–osmium isotope systematics in MORB from the Southern Mid-Atlantic Ridge (40°–50° S). *Earth and Planetary Science Letters* 235, 528– 548.

Fischer-Gödde, M., Becker, H. (2012) Osmium isotope and highly siderophile element constraints on ages and nature of meteoritic components in ancient lunar impact melt rocks. *Geochimica et Cosmochimica Acta* 77, 135-156.

Fischer-Gödde, M., Becker, H., Wombacher, F. (2010) Rhodium, gold and other highly siderophile element abundances in chondritic meteorites. *Geochimica et Cosmochimica Acta* 74, 356-379.

Fischer-Gödde, M., Becker, H., Wombacher, F. (2011) Rhodium, gold and other highly siderophile element abundances in orogenic peridotites and peridotite xenoliths. *Chemical Geology* 280, 365-383.

Fischer-Gödde, M., Burkhardt, C., Kruijer, T.S., Kleine, T. (2015) Ru isotope heterogeneity in the solar protoplanetary disk. *Geochimica et Cosmochimica Acta* 168, 151-171.

Foley, N.C., Wadhwa, M., Borg, L.E., Janney, P.E., Hines, R., Grove, T.L. (2005) The early differentiation history of Mars from ^{182}W–^{142}Nd isotope systematics in the SNC meteorites. *Geochimica et Cosmochimica Acta* 69, 4557–4571.

Fonseca, R.O.C., Laurenz, V., Mallmann, G., Luguet, A., Hoehne, N., Jochum, K.P. (2012) New constraints on the genesis and long-term stability of Os-rich alloys in the Earth's mantle. *Geochimica et Cosmochimica Acta* 87, 227-242.

Fouché, K.F., Smales, A.A. (1967a) The distribution of trace elements in chondritic meteorites. 1. Antimony, arsenic, gold, palladium and rhenium. *Chemical Geology* 2, 5-33.

Fouché, K.F., Smales, A.A. (1967b) The distribution of trace elements in chondritic meteorites. 2. gallium, germanium and indium. *Chemical Geology* 2, 105-134.

Foustoukos, D.I., Bizimis, M., Frisby, C., Shirey, S.B. (2015) Redox controls on Ni–Fe–PGE mineralization and Re/Os fractionation during serpentinization of abyssal peridotite. *Geochimica et Cosmochimica Acta* 150, 11-25.

Frei, R., Gervilla, F., Meibom, A., Proenza, J.A., Garrido, C.J. (2006) Os isotope heterogeneity of the upper mantle: evidence from the Mayarí–Baracoa ophiolite belt in eastern Cuba. *Earth and Planetary Science Letters* 241, 466–476.

French, S.W., Romanowicz, B. (2015) Broad plumes rooted at the base of the Earth's mantle beneath major hotspots. *Nature* 525, 95-99.

Ganapathy, R., Morgan, J.W., Krähenbühl, U., Anders, E. (1973) Ancient meteoritic components in lunar highland rocks: clues from trace elements in Apollo 15 and 16 samples. *Proceedings of the Lunar Science Conference* 4th, 1239–1261.

Ganapathy, R., Morgan, J.W., Higuchi, H., Anders, E. (1974) Meteoritic and volatile elements in Apollo 16 rocks and in separated phases from 14306. *Proceedings of the Fifth Lunar Conference* V. 2, 1659-1683.

Ganguly, J., Tirone, M., Chakraborty, S., Domanik, K. (2013) H-chondrite parent asteroid: a multistage cooling, fragmentation and re-accretion history constrained by thermometric studies, diffusion kinetic modeling and geochronological data. *Geochimica et Cosmochimica Acta* 105, 206-220.

Gannoun, A., Burton, K.W., Thomas, L.E., Parkinson, I.J., Van Calsteren, P., Schiano, P. (2004) Osmium isotope heterogeneity in the constituent phases of mid-ocean ridge basalts. *Science* 303, 70-72.

Gannoun, A., Burton, K.W., Parkinson, I.J., Alard, O., Schiano, P., Thomas, L.E. (2007) The scale and origin of the osmium isotope variations in mid-ocean ridge basalts. *Earth and Planetary Science Letters* 259, 541–556.

Gannoun, A., Boyet, M., Rizo, H., Goresy, A.E. (2011) ^{146}Sm–^{142}Nd systematics measured in enstatite chondrites reveals a heterogeneous distribution of ^{142}Nd in the solar nebula. *Proceedings of the National Academy of Sciences* 108, 7693-7697.

Gannoun, A., Burton, Day, J.M.D., Harvey, J., Schiano, P., Parkinson, I. (2016) Highly siderophile element and Os isotopic systematics of volcanic rocks at divergent and convergent plate boundaries and in intraplate settings. *Reviews in Mineralogy & Geochemistry* V. 81, 651-724.

Gao, S., Rudnick, R.L, Carlson, R.W., McDonough, W.F., Liu, Y.-S. (2002) Re-Os evidence for replacement of ancient mantle lithosphere beneath the North China craton. *Earth and Planetary Science Letters* 198, 307-322.

Goldschmidt, V.M. (1937) The principles of distribution of chemical elements in minerals and rocks. *Journal of the Chemical Society,* 655-673.

González-Jiménez, J.M., Griffin, W.L., Gervilla, F., Proenza, J.A., O'Reilly, S.Y., Pearson, N.J. (2014a) Chromitites in ophiolites: How, where, when, why? Part I. A review and new ideas on the origin and significance of platinum-group minerals. *Lithos* 189, 127-139.

González-Jiménez, J.M., Griffin, W.L., Proenza, J.A., Gervilla, F., O'Reilly, S.Y., Akbulut, M., Pearson, N.J., Arai, S. (2014b) Chromitites in ophiolites: How, where, when, why? Part II. The crystallization of chromitites. *Lithos* 189, 140-158.

Göpel, C., Manhès, G., Allègre, C.J. (1994) U-Pb systematics of phosphates from equilibrated ordinary chondrites. *Earth and Planetary Science Letters* 121, 153-171.

Gordon, C.L., Schlecht, W.G., Wichers, E. (1944) Use of sealed tubes for the preparation of acid solutions of samples for analysis, or for small-scale refining: pressures of acids heated above 100°C. *Journal of Research of the National Bureau of Standards* 33, 457-470.

Gramlich, J.W., Murphy, T.J., Garner, E.L., Shields, W.R. (1973) The atomic weight of rhenium. *Journal of Research of the National Bureau of Standards*, Section A 77, 691-698.

Griffin, W.L., Zhang, A.D., O'Reilly, S.Y., Ryan, C.G. (1998) Phanerozoic evolution of the lithosphere beneath the Sino-Korean Craton. In: Flower, M., Chung, S.-L., Lo, C.-H., Lee, T.-Y. (Eds.) *Mantle Dynamics and Plate Interactions in East Asia.* American Geophysical Union, Washington, DC, 107-126.

Griffin, W.L., Graham, S., O'Reilly, S.Y., Pearson, N.J. (2004) Lithosphere evolution beneath the Kaapvaal craton. Re–Os systematics of sulfides in mantle-derived peridotites. *Chemical Geology* 208, 89–118.

Grossman, J.N., Wasson, J.T. (1985) The origin and history of the metal and sulfide components of chondrules. *Geochimica et Cosmochimica Acta* 49, 925-939.

Grossman, L. (1972) Condensation in the primitive solar nebula. *Geochimica et Cosmochimica Acta* 36, 597-619.

Halliday, A.N. (2004) Mixing, volatile loss and compositional change during impact-driven accretion of the Earth. *Nature* 427, 505–509.

Halliday, A.N. (2008) A young Moon-forming giant impact at 70-110 million years accompanied by late-stage mixing, core formation and degassing of the Earth. *Philosophical Transactions of the Royal Society* A 366, 4163-4181.

Handler, M.R., Bennett, V.C., Esat, T.M. (1997) The persistence of off-cratonic lithospheric mantle: Os isotopic systematics of variably metasomatised southeast Australian xenoliths. *Earth and Planetary Science Letters* 151, 61–75.

Hanghøj, K., Keleman, P.B., Hassler, D., Godard, M. (2010) Composition and genesis of depleted mantle peridotites from the Wadi Tayin Massif, Oman Ophiolite; major and trace element geochemistry, and Os isotope and PGE systematics. *Journal of Petrology* 51, 201-227.

Hanyu, T., Tatsumi, Y., Senda, R., Miyazaki, T., Chang, Q., Hirahara, Y., Takahashi, T., Kawabata, H., Suzuki, K., Kimura, J.-I., Nakai, S. (2011) Geochemical characteristics and origin of the HIMU reservoir: A possible mantle plume source in the lower mantle. *Geochemistry Geophysics Geosystems* 12.

Harper, Jr., C.L., Jacobsen, S.B. (1996) Evidence for ^{182}Hf in the early Solar System and constraints on the timescale of terrestrial accretion and core formation. *Geochimica et Cosmochimica Acta* 60, 1131-1153.

Harrison, K.P., Grimm, R.E. (2010) Thermal constraints on the early history of the H-chondrite parent body reconsidered. *Geochimica et Cosmochimica Acta* 74, 5410-5423.

Hartmann, W.K., Davis, D.R. (1975) Satellite-sized planetesimals and lunar origin. *Icarus* 24, 504-515.

Harvey, J., Gannoun, A., Burton, K.W., Rogers, N.W., Alard, O., Parkinson, I.J. (2006) Ancient melt extraction from the oceanic upper mantle revealed by Re–Os isotopes in abyssal peridotites from the Mid-Atlantic ridge. *Earth and Planetary Science Letters* 244, 606-621.

Hauri, E.H., Hart, S.R. (1993) Re-Os isotope systematics of HIMU and EMII oceanic island basalts from the south Pacific Ocean. *Earth and Planetary Science Letters* 114, 353-371.

Hauri, E.H., Lassiter, J.C., DePaolo, D.J. (1996) Osmium isotope systematics of drilled lavas from Mauna Loa, Hawaii. *Journal of Geophysical Research* B101, 11793-11806.

Henke, S., Gail, H.-P., Trieloff, M., Schwarz, W.H., Kleine, T. (2012) Thermal history modelling of the H chondrite parent body. *Astronomy and Astrophysic* 545, A135.

Herr, W., Wölfe, R., Eberhardt, P., Kopp, E. (1967) Development and recent applications of the Re/Os dating method. In: *Radioactive Dating and Methods of Low-Level Counting*. International Atomic Energy Agency, Vienna.

Hertogen, J., Janssens, M.J., Palme, H. (1980) Trace-elements in ocean ridge basalt glasses - implications for fractionations during mantle evolution and petrogenesis. *Geochimica et Cosmochimica Acta* 44, 2,125-2,143.

Hertogen, J., Janssens, M.-J., Takahashi, H., Morgan, J.W., Anders, E. (1983) Enstatite chondrites: trace element clues to their origins. *Geochimica et Cosmochimica Acta* 47, 2241-2255.

Hirt, B., Tilton, G.R., Herr, W., Hoffmeister, W. (1963a) The half-life of ^{187}Re. In: Geiss, J., Goldberg, E.D. (Eds.) *Earth Science and Meteoritics*. North-Holland Publishing Co., Amsterdam, 273-280.

Hirt, B., Herr, W., Hoffmeister, W. (1963b) Age determinations by the rhenium-osmium method. In: *Radioactive Dating*. International Atomic Energy Agency, Vienna.

Hoffman, E.L., Naldrett, A.J., Vanloon, J.C., Hancock, R.G.V., Manson, A. (1978) Determination of all platinum group elements and gold in rocks and ore by neutron-activation analysis after pre-concentration by a nickel sulfide fire-assay technique on large samples. *Analytica Chimica Acta* 102, 157–166.

Hofmann, A.W. (1997) Mantle geochemistry: the message from oceanic volcanism. *Nature* 385, 219-229.

Hofmann, A.W. (2014) Sampling mantle heterogeneity through ocenic basalts: isotopes and trace elements. In: Holland, H.D., Turekian, K.K. (Eds.) *Treatise on Geochemistry (second edition), The Mantle and the Core*. Elsevier B.V., Amsterdam, 67-101.

Holzheid, A., Sylvester, P., O'Neill, H.St.C. (2000) Evidence for a late chondritic veneer in the Earth's mantle from high-pressure partitioning of palladium and platinum. *Nature* 406, 396-399.

Horan, M.F., Morgan, J.W., Walker, R.J., Grossman, J.N. (1992) Re-Os isotope constraints on the age of iron meteorites. *Science* 255, 1118-1121.

Horan, M.F., Smoliar, M.I., Walker, R.J. (1998) ^{182}W and ^{187}Re-^{187}Os systematics of iron meteorites: chronology for melting, differentiation and crystallization in asteroids. *Geochimica et Cosmochimica Acta* 62, 545-554.

Horan, M.F., Walker, R.J., Morgan, J.W., Grossman, J.N., Rubin, A. (2003) Highly siderophile elements in chondrites. *Chemical Geology* 196**,** 5-20.

Horan, M.F., Alexander, C.M.O'D., Walker, R.J. (2009) Highly siderophile element evidence for early solar system processes in components from ordinary chondrites. *Geochimica et Cosmochimica Acta* 73, 6984-6997.

Humayun, M. (2011) A model for osmium isotopic evolution of metallic solids at the core-mantle boundary. *Geochemistry, Geophysics, Geosystems* 12, Q03007, doi: 10.1029/2010GC003281.

Humayun, M., Campbell, A.J. (2002) The duration of ordinary chondrite metamorphism inferred from tungsten microdistribution in metal. *Earth and Planetary Science Letter*s 198, 225-243.

Humayun, M., Qin, L., Norman, M.D. (2004) Geochemical evidence for excess iron in the mantle beneath Hawaii. *Science* 306, 91–94.

Hutcheon, I.D., Olsen, E., Zipfel, J., Wasserburg, G.J. (1992) Cr isotopes in differentiated meteorites: evidence for ^{53}Mn. *Lunar and Planetary Science Conference* (abstracts) 23, 569.

Hutson, M., Ruzicka, A., Pugh, R., Sloan, L., Thompson, E. (2007) Complex brecciation and shock effects in the Buck Mountain Wash (H3-5) chondrite. *Meteoritics and Planetary Science* 42, 963-978.

Iizuka, T., Nakai, S., Sahoo, Y.V., Takamasa, A., Hirata, T., Maruyama, S. (2010) The tungsten isotopic composition of Eoarchean rocks: implications for early silicate differentiation and core-mantle interaction, *Earth and Planetary Science Letters* 291, 189-200.

Ireland, T.J., Arevalo, R.D., Walker, R.J., McDonough, W.F. (2009a) Tungsten in Hawaiian picrites: a compositional model for the source of Hawaiian lavas. *Geochimica et Cosmochimica Acta* 73, 4517-4530.

Ireland, T.J., Walker, R.J., Garcia, M.O. (2009b) Highly siderophile element and ^{187}Os isotopes systematics of Hawaiian picrites: Implications for parental melt composition and source heterogeneity. *Chemical Geology* 260, 112-128.

Ireland, T.J., Walker, R.J., Brandon, A.D. (2011) ^{186}Os-^{187}Os systematics of Hawaiian picrites revisited: additional insights into the causes of Os isotopic variations in ocean island basalts. *Geochimica et Cosmochimica Acta* 75, 4456-4475.

Jackson, M.G., Shirey, S.B. (2011) Re–Os isotope systematics in Samoan shield lavas and the use of Os-isotopes in olivine phenocrysts to determine primary magmatic compositions. *Earth and Planetary Science Letters* 312, 91–101.

Jamais, M., Lassiter, J.C., Brügmann, G. (2008) PGE and Os-isotopic variations in lavas from Kohala Volcano, Hawaii: constraints on PGE behavior and melt/crust interaction. *Chemical Geology* 250, 16-28.

Jones, J.H. (1994) Fractional crystallization of iron meteorites – constant *versus* changing partition coefficients. *Meteoritics* 29, 423-426.

Jones, J.H., Drake, M.J. (1986) Geochemical constraints on core formation in the Earth. *Nature* 322, 221-228.

Jordan, T.H. (1978) Composition and development of the continental tectosphere. *Nature* 274, 544-548.

Kelemen, P.B. (1990) Reaction between ultramafic rock and fractionating basaltic magma I. Phase relations, the origin of calc-alkaline magma series, and the formation of discordant dunite. *Journal of Petrology* 31, 51-98.

Kelemen, P.B., Dick, H.J.B., Quick, J.E. (1992) Formation of harzburgite by pervasive melt/rock reaction in the upper mantle. *Nature* 358, 635-641.

Kimura, K., Lewis, R.S., Anders, E. (1974) Distribution of gold and rhenium between nickel-iron and silicate melts: implications for the abundance of siderophile elements on the Earth and Moon. *Geochimica et Cosmochimica Acta* 38, 683-701.

Klein, E., Langmuir, C.H. (1987) Global Correlations of Ocean ridge basalt chemistry, axial depth, crustal thickness. *Journal of Geophysical Research* 92, 8089-8115.

Kleine, T., Münker, C., Mezger, K., Palme, H. (2002) Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf-W chronometry. *Nature* 418, 952-955.

Kleine, T., Mezger, K., Palme, H., Scherer, E., Münker, C. (2005) Early core formation in asteroids and late accretion of chondrite parent bodies: evidence from ^{182}Hf–^{182}W in CAIs, metal-rich chondrites and iron meteorites. *Geochimica et Cosmochimica Acta* 69, 5805–5818.

Kleine, T., Touboul, M., van Orman, J.A., Bourdon, B., Maden, C., Mezger, K., Halliday, A.N. (2008) Hf-W thermochronometry: closure temperature and constraints on the accretion and cooling history of the H chondrite parent body. *Earth and Planetary Science Letters* 270, 106-118.

Kleine, T., Touboul, M., Bourdon, B., Nimmo, F., Mezger, K., Palme, H., Jacobsen, S.B., Yin, Q.-Z., Halliday, A.N. (2009) Hf-W chronology of the accretion and early evolution of asteroids and terrestrial planets. *Geochimica et Cosmochimica Acta* 73, 5150-5188.

Kong, P., Ebihara, M. (1996) Distribution of W and Mo in ordinary chondrites and implications for nebular and parent body thermal processes. *Earth and Planetary Science Letter*s 137, 83-93.

Kong, P., Ebihara, M., Palme, H. (l999) Siderophile elements in Martian meteorites and implications for core formation in Mars. *Geochimica et Cosmochimica Acta* 63, 1865–1875.

König, S., Münker, C., Hohl, S., Paulick, H., Barth, A.R., Lagos, M., Pfänder, J., Büchl, A. (2011) The Earth's tungsten budget during mantle melting and crust formation. *Geochimica et Cosmochimica Acta* 75, 2119-2136.

Korotev, R.L., Zeigler, R.A., Jolliff, B.L., Irving, A.J., Bunch, T.E. (2009) Compositional and lithological diversity among brecciated lunar meteorites of intermediate iron concentration. *Meteoritics and Planetary Science* 44, 1287-1322.

Krähenbühl, U. (1980) Distribution of volatile and non-volatile elements in grain-size fractions of Apollo 17 drive tube 74001/2. *Proceedings of the Lunar and Planetary Science Conference* 11th, 1551–1564.

Krähenbühl, U., Geissbühler, M., Bühler, F., Berhardt, P., Finnegan, D.L. (1992) Osmium isotopes in the aerosols of the mantle volcano Mauna Loa. *Earth and Planetary Science Letters* 110, 95-98.

Kraus, R.G., Root, S., Lemke, R.W., Stewart, S.T., Jacobsen, S.B., Mattsson, T.R. (2015) Impact vaporization of planetesimal cores in the late stages of planet formation. *Nature Geoscience* 8, 269-272.

Krot, A.N., Keil, K., Goodrich, C.A., Scott, E.R.D., Weisberg, M.K. (2003) Classification of meteorites. In: Davis, A.M. (Ed.) *Treatise on Geochemistry, Volume 1, Meteorites, Comets, and Planets*. Elsevier B.V., Amsterdam, 83-128.

Kruijer, T.S., Fischer-Gödde, M., Kleine, T., Sprung, P., Leya, I., Wieler, R. (2013) Neutron capture on Pt isotopes in iron meteorites and the Hf-W chronology of core formation in planetesimals. *Earth and Planetary Science Letters* 361, 162-172.

Kruijer, T.S., Touboul, M., Fischer-Gödde, M., Bermingham, K.R., Walker, R.J., Kleine, T. (2014a) Protracted core formation and rapid accretion of protoplanets. *Science* 344, 1150-1154.

Kruijer, T.S., Kleine, T., Fischer-Gödde, M., Burkhardt, C., Wieler, R. (2014b) Nucleosynthetic W isotope anomalies and the Hf-W chronometry of Ca-Al-rich inclusions. *Earth and Planetary Science Letters* 403, 317-327.

Kruijer, T.S., Kleine, T., Fischer-Gödde, M., Sprung, P. (2015) Lunar tungsten isotopic evidence for the late veneer. *Nature* 520, 534-537.

Labrosse, S. (2003) Thermal and magnetic evolution of the Earth's core. *Physics of Earth and Planetary Interiors* 140, 127–143.

Labrosse, S., Poirier, J.P., Le Mouel, J.L. (2001) The age of the inner core. *Earth and Planetary Science Letters* 190, 111–123.

Labrosse, S., Hernlund, J.W., Coltice, N. (2007) A crystallizing dense magma ocean at the base of the Earth's mantle. *Nature* 450, 866-869.

Lambert, D.D., Morgan, J.W., Walker, R.J., Shirey, S.B., Carlson, R.W., Zientek, M.L., Koski, M.S. (1989) Rhenium-osmium and samarium-neodymium isotopic systematics of the Stillwater Complex. *Science* 244, 1169-1174.

Langmuir, C.H., Hanson, G.N. (1980) An evaluation of major element heterogeneity in the mantle sources of basalts. *Philosophical Transactions of the Royal Society of London* A297, 383-407.

Lassiter, J.C. (2003) Rhenium volatility in subaerial lavas: constraints from subaerial and submarine portions of the HSDP-2 Mauna Kea drillcore. *Earth and Planetary Science Letters* 2014, 311-325.

Lassiter, J.C. (2006) Constraints on the coupled thermal evolution of the Earth's core and mantle, the age of the inner core, and the origin of the ^{186}Os/^{188}Os "core signal" in plume-derived lavas. *Earth and Planetary Science Letters* 250, 306–317.

Lassiter, J.C., Hauri, E.H. (1998) Osmium-isotope variations in Hawaiian lavas: evidence for recycled oceanic lithosphere in the Hawaiian plume. *Earth and Planetary Science Letters* 164, 483–496.

Lassiter, J.C., Hauri, E.H., Reiners, P.W., Garcia, M.O. (2000) Generation of Hawaiian post-erosional lavas by melting of a mixed lherzolite/pyroxenite source. *Earth and Planetary Science Letters* 178, 269-284.

Lassiter, J.C., Byerly, B.L., Snow, J.E., Hellebrand, E. (2014) Constraints from Os-isotope variations on the origin of Lena Trough abyssal peridotites and implications for the composition and evolution of the depleted upper mantle. *Earth and Planetary Science Letters* 403, 178-187.

Lazar, G.C., Walker, D., Walker, R.J. (2004) Experimental partitioning of Tc, Mo, Ru and Re between solid and liquid during crystallization in Fe-Ni-S. *Geochimica et Cosmochimica Acta* 68, 643-652.

Le Roux, V., Bodinier, J.-L., Tommasi, A., Alard, O., Dautria, J.-M., Vauchez, A., Riches, A.J.V. (2007) The Lherz spinel lherzolite: Refertilized rather than pristine mantle. *Earth and Planetary Science Letters* 259, 599–612.

Lee, D.-C., Halliday, A.N. (1995a) Precise determination of the isotopic compositions and atomic weights of molybdenum, tellurium, tin and tungsten using ICP-magnetic sector multiple collector mass spectrometry. *International Journal of Mass Spectrometry and Ion Processes* 146/147, 35-46.

Lee, D.-C., Halliday, A.N. (1995b) Hafnium-tungsten chronometry and the timing of terrestrial core formation. *Nature* 378, 771-774.

Lee, D-C., Halliday, A.N. (2000) Hf-W internal isochrons for ordinary chondrites and the initial ^{182}Hf-^{180}Hf of the solar system. *Chemical Geology* 169, 35-43.

Li, J., Agee, C.B. (1996) Geochemistry of mantle-core differentiation at high pressure. *Nature* 381, 686-689.

Liu, C.-Z., Snow, J.E., Hellebrand, E., Brügmann, G., von der Handt, A., Büchl, A., Hofmann, A.W. (2008) Ancient, highly heterogeneous mantle beneath Gakkel ridge, Arctic Ocean. *Nature* 452, 311-316.

Liu, C.-Z., Snow, J.E., Brügmann, G., Hellebrand, E., Hofmann, A.W. (2009) Non-chondritic HSE budget in Earth's upper mantle evidenced by abyssal peridotites from Gakkel ridge (Arctic Ocean). *Earth and Planetary Science Letters* 283, 122-132.

Liu, J., Rudnick, R.L., Walker, R.J., Gao, S., Wu, F., Piccoli, P. (2010) Processes controlling highly siderophile element fractionations in xenolithic peridotites and their influence on Os isotopes. *Earth and Planetary Science Letters* 297, 287-297.

Liu, J., Rudnick, R.L., Walker, R.J., Gao, S., Wu, F.-Y., Piccoli, P.M., Yuan, H., Xu, W.-L., Xu, Y.-G. (2011) Mapping lithospheric boundaries using Os isotopes of mantle xenoliths: an example from the North China Craton. *Geochimica et Cosmochimica Acta* 75, 3881-3902.

Liu, J., Sharp, M., Ash, R.D., Kring, D.A., Walker, R.J. (2015) Diverse impactors in Apollo 15 and 16 impact melt rocks: evidence from osmium isotopes and highly siderophile elements. *Geochimica et Cosmochimica Acta* 155, 122-153.

Liu, J., Touboul, M., Ishikawa, A., Walker, R.J., Pearson, D.G. (2016) Widespread tungsten isotope anomalies and W mobility in crustal and mantle rocks of the Eoarchean Saglek Block, northern Labrador, Canada: implicatinos for early Earth processes and W recycling. *Earth and Planetary Science Letters* 448, 13-23.

Lodders, K. (2003) Solar system abundances and condensation temperatures of the elements. *The Astrophysical Journal* 591, 1220-1247.

Lodders, K., Fegley, Jr., B. (1998) The Planetary Scientist's Companion. Oxford University Press, New York and Oxford, 371pp.

Lorand, J.-P., Luguet, A., Alard, O., Bezos, A., Meisel, T. (2008) Abundance and distribution of platinum-group elements in orogenic lherzolites; a case study in a Fontete Rouge lherzolite (French Pyrénées). *Chemical Geology* 248, 174-194.

Lorand, J.-P., Alard, O., Godard, M. (2009) Platinum-group element signature of the primitive mantle rejuvenated by melt-rock reactions: evidence from Sumail peridotites (Oman Ophiolite). *Terra Nova* 21, 35–40.

Lorand, J.-P., Luguet, A., Alard, O. (2013) Platinum-group element systematics and petrogenetic processing of the continental upper mantle: A review. *Lithos* 164-167, 2-21.

Luck, J.-M., Allègre, C.J. (1983) ^{187}Re-^{187}Os systematics in meteorites and cosmochemical consequences. *Nature* 302, 130-132.

Luck, J.-M., Allègre, C.J. (1991) Osmium isotopes in ophiolites. *Earth and Planetary Science Letters* 107, 406-415.

Luck, J.-M., Birck, J.-L., Allègre, C.J. (1980) ^{187}Re-^{187}Os systematics in meteorites: early chronology of the solar system and age of the galaxy. *Nature* 283, 256-259.

Lugmair, G.W., Galer, S.J. (1992) Age and isotopic relationships among the angrites Lewis Cliff 86010 and Anga dos Reis. *Geochimica et Cosmochimica Acta* 56, 1673-1694.

Lugmair, G.W., Shukolyukov, A. (1998) Early solar system timescales according to ^{53}Mn-^{53}Cr systematics. *Geochimica et Cosmochimica Acta* 62, 2863-2886.

Luguet, A., Reisberg, L. (2016) Highly siderophile element and ^{187}Os sigantures in non-cratonic basalt-hosted peridotite xenoliths: post-Archean lithospheric mantle. *Reviews in Mineralogy & Geochemistry* V. 81, 305-367.

Luguet, A., Alard, O., Lorand, J.P., Pearson, N.J., Ryan, C., O'Reilly, S.Y. (2001) Laser-ablation microprobe (LAM)-ICPMS unravels the highly siderophile element geochemistry of the oceanic mantle. *Earth and Planetary Science Letters* 189, 285-294.

Luguet, A., Lorand, J.P., Alard, O., Cottin, J.-Y. (2004) A multi-technique study of platinum group element systematic in some Ligurian ophiolitic peridotites, Italy. *Chemical Geology* 208, 175-194.

Luguet, A., Shirey, S.B., Lorand, J.P., Horan, M.F., Carlson, R.W. (2007) Resdiual platinum-group minerals from highly depleted harzburgites of the Lherz massif (France) and their role in HSE fractionation of the mantle. *Geochimica et Cosmochimica Acta* 71, 3082-3097.

Luguet, A., Pearson, D.G., Nowell, G.M., Dreher, S.T., Coggon, J.A., Spetsius, Z.V., Parman, S.W. (2008a) Enriched Pt-Re-Os isotope systematics in plume lavas explained by metasomatic sulfides. *Science* 319, 453-456.

Luguet, A., Nowell, G.M., Pearson, D.G. (2008b) ^{184}Os/^{188}Os and ^{186}Os/^{188}Os measurements by negative thermal ionisation mass spectrometry (N-TIMS): effects of interfering element and mass fractionation corrections on data accuracy and precision. *Chemical Geology* 248, 342–362.

Luguet, A., Behrens, M., Pearson, D.G., König, S., Herwartz, D. (2015) Significance of the whole rock Re–Os ages in cryptically and modally metasomatised cratonic peridotites: Constraints from HSE–Se–Te systematics. *Geochimica et Cosmochimica Acta* 164, 441-463.

Maaloe, S., Aoki, K. (1977) The major element composition of the upper mantle estimated from the composition of ilherzolites. *Contributions to Mineralogy and Petrology* 63, 161-173.

Malitch, K.N. (2004) Osmium isotope constraints on contrasting sources and prolonged melting in the Proterozoic upper mantle: evidence from ophiolitic Ru–Os sulfides and Ru–Os–Ir alloys. *Chemical Geology* 208, 157-173.

Malvin, D.J., Jones, J.H., Drake, M.J. (1986) Experimental investigations of trace element fractionation in iron meteorites. III: Elemental partitioning in the system Fe-Ni-S-P. *Geochimica et Cosmochimica Acta 50*, 1221–1231.

Mann, U., Frost, D.J., Rubie, D.C., Becker, H., Audétat, A. (2012) Partitioning of Ru, Rh, Pd, Re, Ir and Pt between liquid metal and silicate at high pressures and high temperatures - implications for the origin of highly siderophile element concentrations in the Earth's mantle. *Geochimica et Cosmochimica Acta* 84, 593-613.

Marcantonio, F., Zindler, A., Elliott, T.R., Staudigel, H. (1995) Os isotope systematics of La Palma, Canary Islands: Evidence for recycled crust in the mantle source of HIMU ocean island. *Earth and Planetary Science Letters* 133, 397-410.

Marchesi, C., Dale, C.W., Garrido, C.J., Pearson, D.G., Bosch, D., Bodinier, J.-L., Gervilla, F., Hida, K. (2014) Fractionation of highly siderophile elements in refertilized mantle: implications for the Os isotope composition of basalts. *Earth and Planetary Science Letters* 400, 33-44.

Marchi, S., Bottke, W.F., Elkins-Tanton, L.T., Bierhaus, M., Wuennermann, K., Morbidelli, A., Kring, D.A. (2014) Widespread mixing and burial of Earth's Hadean crust by asteroid impacts. *Nature* 511, 578-582.

Markowski, A., Leya, I., Quitté, G., Ammon, K., Halliday, A.N., Wieler, R. (2006) Correlated helium-3 and tungsten isotopes in iron meteorites: quantitative cosmogenic corrections and planetesimal formation times. *Earth and Planetary Science Letters* 250, 104-115.

Martin, C.E. (1991) Osmium isotopic characteristics of mantle-derived rocks. *Geochimica et Cosmochimica Acta* 55, 1421-1434.

Mason, B., Taylor, S.R. (1982) Inclusions in the Allende meteorite. *Smithsonian Contributions to Earth Science* 25, 1–30.

McCoy, T.J., Walker, R.J., Goldstein, J.I., Yang, J., McDonough, W.F., Rumble, D., Chabot, N.L., Ash, R.D., Corrigan, C.M., Michael, J.R., Kotula, P.G. (2011) Group IVA irons: new constraints on the crystallization and cooling history of an asteroidal core with a complex history. *Geochimica et Cosmochimica Acta* 75, 6821-6843.

McCoy-West, A.J., Bennett, V.C., Puchtel, I.S., Walker, R.J. (2013) Extreme persistence of cratonic lithosphere in the southwest Pacific: Paleoproterozoic Os isotopic signatures in Zealandia. *Geology* 41, 231-234.

McDonough, W.F., Sun, S.-S. (1995) The composition of the Earth. *Chemical Geology* 120, 223-253.

McSween, H.Y. (2003) Mars. In: Davis, A.M. (Ed.) *Treatise on Geochemistry, Volume 1, Meteorites, Comets, and Planets*. Elsevier B.V., Amsterdam, 601-621.

Médard, E., Schmidt, M.W., Wälle, M., Keller, N.S., Günther, D. (2015) Platinum partitioning between metal and silicate melts: core formation, late veneer and the nononuggets issue. *Geochimica et Cosmochimica Acta* 162, 183-201.

Meibom, A., Sleep, N.H., Chamberlain, C.P., Coleman, R.G., Frei, R., Hren, M.T., Wooden, J.T. (2002) Re-Os isotopic evidence for long-lived heterogeneity and equilibration processes in the Earth's upper mantle. *Nature* 419, 705-708.

Meisel, T., Walker, R.J., Morgan, J.W. (1996) The osmium isotopic composition of the Earth's primitive upper mantle. *Nature* 383, 517-520.

Meisel, T., Walker, R.J., Irving, A.J., Lorand, J.-P. (2001) Osmium isotopic compositions of mantle xenoliths: a global perspective. *Geochimica et Cosmochimica Acta* 65, 1311-1323.

Menzies, M.A., Fan, W.-M., Zhang, M. (1993) Palaeozoic and Cenozoic lithoprobe and the loss of >120 km of Archean lithosphere, Sino-Korean craton, China. In: Prichard, H.M., Alabaster, T., Harris, N.B.W., Neary, C.R. (Eds.) *Magmatic Processes and Plate Tectonics. Geological Society Special Publication* 76, 71– 81.

Misawa, K, Yamaguchi, A., Kaiden, H. (2005) U-Pb and ^{207}Pb-^{206}Pb ages of zircons from basaltic eucrites: Implications for early basaltic volcanism on the eucrite parent body. *Geochimica et Cosmochimica Acta* 69, 5847-5861.

Miyashiro, A. (1975) Classification, characteristics and origin of ophiolites. *Journal of Petrology* 83, 249-281.

Montelli, R., Nolet, G., Dahlen, F.A., Masters, G., Engdahl, E.R., Hung, S.-H. (2004) Finite-frequency tomography reveals a variety of plumes in the mantle. *Science* 303, 338-342.

Morbidelli, A., Lunine, J.I., O'Brien, D.P., Raymond, S.N., Walsh, K.J. (2012) Building terrestrial planets. *Annual Reviews of the Earth and Planetary Sciences* 40, 251–275.

Morgan, J.W. (1985) Osmium isotope constraints on Earth's late accretionary history. *Nature* 317, 703-705.

Morgan, J.W. (1986) Ultramafic xenoliths: clues to Earth's late accretionary history. *Journal of Geophysical Research* 91, 12375–12387.

Morgan, J.W., Lovering, F. (1967a) Rhenium and osmium abundances in some igneous and metamorphic rocks. *Earth and Planetary Science Letters* 3, 219-224.

Morgan, J.W., Lovering, F. (1967b) Rhenium and osmium abundances in chondritic meteorites. *Geochimica et Cosmochimica Acta* 31, 1893-1909.

Morgan, J.W., Wandless, G.A. (1979) 74001 drive tube: Siderophile elements match II B iron meteorite pattern. *Proceedings of the Lunar and Planetary Science Conference* 10th, 327-340.

Morgan, J.W., Wandless, G.A. (1984) Surface correlated trace elements in 15426 lunar glasses (abstract). *Lunar and Planetary Science* XV, 562– 563.

Morgan, J.W., Walker, R.J. (1989) Isotopic determinations of rhenium and osmium using fusion, distillation and ion exchange separations, as applied to meteorites. *Analytica Chimica Acta* 222, 291-300.

Morgan, J.W., Laul, J.C., Krähenbühl, U., Ganapathy, R., Anders, E. (1972) Major impacts on the moon: characterization from trace elements in Apollo 12 and 14 samples. *Proceedings of the Third Lunar Science Conference* (Supplement 3, *Geochimica et Cosmochimica Acta*) V. 2, 1377-1395.

Morgan, J.W., Ganapathy, R., Higuchi, H., Krähenbühl, U., Anders, E. (1974) Lunar basins: tentative characterization of projectiles, from meteoritic elements in Apollo 17 boulders. *Proceedings of the Fifth Lunar Science Conference* (Supplement 5, *Geochimica et Cosmochimica Acta*) V. 2, 1703-1736.

Morgan, J.W., Wandless, G.A., Petrie, R.K., Irving, A.J. (1981) Composition of the Earth's upper mantle – I. Siderophile trace elements in ultramafic nodules. *Tectonophysics* 75, 47-67.

Morgan, J.W., Walker, R.J., Grossman, J.N. (1992) Rhenium-osmium isotope systematics in meteorites I: Magmatic iron meteorite groups IIAB and IIIAB. *Earth and Planetary Science Letters* 108, 191-202.

Morgan, J.W., Walker, R.J., Brandon, A.D., Horan, M.F. (2001) Siderophile elements in Earth's upper mantle and lunar breccias: Data synthesis suggests manifestations of the same late influx. *Meteoritics and Planetary Science* 36, 1257-1275.

Morgan, J.W., Walker, R.J., Horan, M.F., Beary, E.S. (2002) ^{190}Pt-^{186}Os and ^{187}Re-^{187}Os systematics of the Sudbury Igneous Complex, Ontario. *Geochimica et Cosmochimica Acta* 66, 273-290.

Morgan, W.J. (1971) Convection plumes in the lower mantle. *Nature* 230, 42–43.

Moynier, F., Yin, Q.-Z., Irisawa, K., Boyet, M., Jacobsen, B., Rosing, M.T. (2010) Coupled ^{182}W-^{142}Nd constraint for early Earth differentiation. *Proceedings of the National Academy of Sciences* 107, 10810-10814.

Murthy, R. (1991) Early differentiation of the Earth and the problem o mantle siderophile elements: a new approach. *Science* 253, 303-306.

Newsom, H.E., Palme, H. (1984) The depletion of siderophile elements in the Earth's mantle - new evidence from molybdenum and tungsten. *Earth and Planetary Science Letters* 69, 354–364.

Newsom, H.E., White, W.M., Jochum, K.P., Hofmann, A.W. (1986) Siderophile and chalcophile element abundances in oceanic basalts, lead isotope evolution and growth of the Earth's core. *Earth and Planetary Science Letters* 80, 299-313.

Newsom, H.E., Sims, K.W., Noll Jr., P.D., Jaeger, W.L., Maehr, S.A., Beserra, T.B. (1996) The depletion of tungsten in the bulk silicate earth: Constraints on core formation. *Geochimica et Cosmochimica Acta* 60, 1155-1169.

Nielsen, S.G., Rehkämper, M., Norman, M.D., Halliday, A.N., Harrison, D. (2006) Thallium isotopic evidence for ferromanganese sediments in the mantle source of Hawaiian basalts. *Nature* 439, 314–317.

Nittler, L.R. (2003) Presolar stardust in meteorites: recent advances and scientific frontiers. *Earth and Planetary Science Letters* 209, 259–273.

Norman, M.D., Garcia, M.O. (1999) Primitive magmas and source characteristics of the Hawaiian plume petrology and geochemistry of shield picrites. *Earth and Planetary Science Letters* 168, 27–44.

Nowell, G.M., Pearson, D.G., Parman, S.W., Luguet, A., Hanski, E. (2008) Precise and accurate ^{186}Os/^{188}Os and ^{187}Os/^{188}Os measurements by Multi-collector Plasma Ionisation Mass Spectrometry, part II: laser ablation and its application to single-grain Pt–Os and Re–Os geochronology. *Chemical Geology* 248, 394–426.

Nyquist, L.E., Bansal, B., Wiesmann, H., Shih, C.-Y. (1994) Neodymium, strontium and chromium isotopic studies of the LEW86010 and Angr dos Reis meteorites and the chronology of the angrite parent body. *Meteoritics* 29, 872-885.

O'Driscoll, B., Day, J.M.D., Daly, J.S., Walker, R.J., McDonough, W.F. (2009) Rhenium-osmium isotopes and platinum-group elements in the Rum Layered Suite, Scotland: implications for Cr-spinel seam formation and the longevity of the Iceland mantle anomaly. *Earth and Planetary Science Letters* 286, 41-51.

O'Driscoll, B., Day, J.M.D., Walker, R.J., Daly, S., McDonough, W.F., Piccoli, P.M. (2012) Chemical heterogeneity in the upper mantle recorded by peridotites and chromitites from the Shetland Ophiolite Complex, Scotland. *Earth and Planetary Science Letters* 333-334, 226-237.

O'Driscoll, B., Walker, R.J., Day, J.M.D., Ash, R.D., Daly, S.J. (2015) Generations of melt extraction, melt-rock interaction and high-temperature metasomatism preserved in peridotites of the ~497 Ma Leka Ophiolite Complex, Norway. *Journal of Petrology* 56, 1797-1828.

O'Neill, H.St.C., Palme, H. (2008) Collisional erosion and the non-chondritic composition of the terrestrial planets. *Philosophical Transactions of the Royal Society* A, 4205-4238.

O'Neil, J., Carlson, R.W., Francis, D., Stevenson, R.K. (2008) Neodymium-142 evidence for Hadean mafic crust. *Science* 321, 1828-1831.

Orwell, G. (1954) Animal Farm. Harcourt, Brace and Jovanovich, New York.

Parkinson, I.J., Hawkesworth, C.J., Cohen, A.S. (1998) Ancient mantle in a modern arc: osmium isotopes in Izu-Bonin-Mariana forearc peridotites. *Science* 281, 2011-2013.

Pattou, L., Lorand, J.P., Gros, M. (1996) Non-chondritic platinum-group element ratios in the Earth's mantle. *Nature* 379, 712-715.

Pearson, D.G., Woodland, S.J. (2000) Solvent extraction/anion exchange separation and determination of PGEs (Os, Ir, Pt, Pd, Ru) and Re-Os isotopes in geological samples by isotope dilution ICP-MS. *Chemical Geology* 165, 87-107.

Pearson, D.G., Nowell, G.M. (2004) Re-Os and Lu-Hf isotope constraints on the origin and age of pyroxenites from the Beni Bousera peridotite massif: implications for mixed peridotite-pyroxenite mantle sources. *Journal of Petrology* 45, 439-455.

Pearson, D.G., Davies, G.R., Nixon, P.H., Greenwood, P.B., Mattey, D.P. (1991) Oxygen isotope evidence for the origin of pyroxenites in the Beni Bousera peridotite massif, North Morocco – derivation from subducted oceanic lithosphere. *Earth and Planetary Science Letters* 102, 289-301.

Pearson, D.G., Carlson, R.W., Shirey, S.B., Boyd, F.R., Nixon, P.H. (1995a) Stabilisation of Archean lithospheric mantle: a Re-Os isotope study of peridotite xenoliths from the Kaapvaal craton. *Earth and Planetary Science Letters* 134, 341-357.

Pearson, D.G., Shirey, S.B., Carlson, R.W., Boyd, F.R., Pokhilenko, N.P., Shimizu, N. (1995b) Re–Os, Sm–Nd and Rb–Sr isotope evidence for thick Archaean lithospheric mantle beneath the Siberian craton modified by multistage metasomatism. *Geochimica et Cosmochimica Acta* 59, 959– 977.

Pearson, D.G., Irvine, G.J., Ionov, D.A., Boyd, F.R., Dreibus, G.E. (2004) Re–Os isotope systematics and platinum group element fractionation during mantle melt extraction: a study of massif and xenolith peridotite suites. *Chemical Geology* 208, 29-59.

Pearson, D.G., Parman, S.W., Nowell, G.M. (2007) A link between large mantle melting events and continent growth seen in osmium isotopes. *Nature* 449, 202-205.

Pegram, W.J., Allègre, C.J. (1992) Osmium isotopic compositions from oceanic basalts. *Earth and Planetary Science Letters* 111, 59-68.

Pellas, R., Storzer, D. (1981) ^{244}Pu fission track thermometry and its application to stony meteorites. *Proceedings of the Royal Society of London Series* A 374, 253–270.

Penniston-Dorland, S.C., Sorensen, S.S., Ash, R.D., Khadke, S.V. (2010) Lithium isotopes as a tracer of fluids in a subduction zone mélange: Franciscan Complex, CA. *Earth and Planetary Science Letters* 292, 181–190.

Penniston-Dorland, S.C., Walker, R.J., Pitcher, L., Sorensen, S.S. (2012) Mantle-crust interactions in a paleosubduction zone: evidence from highly siderophile element systematics of eclogite and related rocks. *Earth and Planetary Science Letters* 319-320, 295-306.

Penniston-Dorland, S.C., Gorman, J.K., Bebout, G.E., Piccoli, P.M., Walker, R.J. (2014) Reaction rind formation in the Catalina Schist: deciphering a history of mechanical mixing and metasomatic alteration. *Chemical Geology* 384, 47-61.

Pernicka, E., Wasson, J.T. (1987) Ru, Re, Os, Pt and Au in iron meteorites. *Geochimica et Cosmochimica Acta* 51, 1717-1726.

Peslier, A.H., Reisberg, L., Ludden, J., Francis, D. (2000) Os isotopic systematics in mantle xenoliths; age constraints on the Canadian Cordillera lithosphere. *Chemical Geology* 166, 85–101.

Pitcher, L., Helz, R.T., Walker, R.J., Piccoli, P.M. (2009) Fractionation of the platinum-group elements and Re during crystallization of basalt in Kilauea Iki lava lake, Hawaii. *Chemical Geology* 260, 196-210.

Plessen, H.-G., Erzinger, J. (1998) Determination of the platinum-group elements and gold in twenty rock reference materials by inductively coupled plasma-mass spectrometry (ICP-MS) after pre-concentration by nickel sulfide fire assay. *Geostandards Newsletter* 22, 187-194.

Podosek, F.A., Huneke, J.C. (1973) Argon in Apollo 15 green glass spherules (15426): Ar-40 –Ar-39 age and trapped argon. *Earth and Planetary Science Letters* 19, 413–421.

Prichard, H.M., Neary, C.R. (1982) Some observations of chromite in the Shetland ophiolite complex. *Ofioliti* 2/3, 455–466.

Prichard, H.M., Neary, C.R., Fisher, F.C., O'Hara, M.J. (2008) PGE-rich Podiform chromitites in the Al'Ays ophiolite complex, Saudi Arabia: an example of critical mantle melting to extract and concentrate PGE. *Economic Geology* 103, 1507–1529.

Puchtel, I.S., Humayun, M. (2005) Highly siderophile element geochemistry of ^{187}Os-enriched 2.8 Ga Kostomuksha komatiites, Baltic Shield. *Geochimica et Cosmochimica Acta* 69, 1607-1618.

Puchtel, I.S., Brandon, A.D., Humayun, M., Walker, R.J. (2005) Evidence for the early differentiation of the core from Pt-Re-Os isotope systematics of 2.8-Ga komatiites. *Earth and Planetary Science Letters* 237, 118-134.

Puchtel, I.S., Humayun, M., Walker, R.J. (2007) Os-Pb-Nd isotope and highly siderophile and lithophile trace element systematics of komatiitic rocks from the Volotsk suite, SE Baltic Shield. *Precambrian Research* 158, 119-137.

Puchtel, I.S., Walker, R.J., Brandon, A.D., Nisbet, E.G. (2009) Pt-Re-Os and Sm-Nd isotope and HSE and REE systematics of the 2.7 Ga Belingwe and Abitibi komatiites. *Geochimica et Cosmochimica Acta* 73, 6367-6389.

Puchtel, I.S., Walker, R.J., Touboul, M., Nisbet, E.G., Byerly, G.R. (2014) Insights into early Earth from the Pt-Re-Os isotope and highly siderophile element abundance systematics of Barberton komatiites. *Geochimica et Cosmochimica Acta* 125, 394-413.

Puchtel, I.S., Touboul, M., Blichert-Toft, J., Walker, R.J., Brandon, A.D., Nicklas, R.W., Kulikov, V.S., Samsonov, A.V. (2016a) Lithophile and siderophile element systematics of Earth's mantle at the Archean-Proterozoic boundary: evidence from 2.4 Ga komatiites. *Geochimica et Cosmochimica Acta* 180, 227-255.

Puchtel, I.S., Blichert-Toft, J., Touboul, M., Horan, M.F., Walker, R.J. (2016b) The coupled ^{182}W-^{142}Nd record of early terrestrial mantle differentiation. *Geochemistry, Geophysics, Geosystems*, doi: 10.1002/2016GC006324.

Qin, L., Dauphas, N., Wadhwa, M., Masarik, J., Janney, P.E. (2008) Rapid accretion and differentiation of iron meteorite parent bodies inferred from ^{182}Hf–^{182}W chronometry and thermal modeling. *Earth and Planetary Science Letters* 273, 94-104.

Qin, L., Dauphas, N., Horan, M.F., Leya, I., Carlson, R.W. (2015) Correlated cosmogenic W and Os isotopic variations in Carbo and implications for Hf-W chronology. *Geochimica et Cosmochimica Acta* 153, 91-104.

Rampone, E., Hofmann, A.W. (2012) A global overview of isotopic heterogeneities in the oceanic mantle. *Lithos* 148, 247-261.

Rankenburg, K., Brandon, A.D., Humayun, M. (2007) Osmium isotope systematics of ureilites. *Geochimica et Cosmochimica Acta* 71, 2402-2413.

Raymond, S.N., Quinn, T., Lunine, J.I. (2006) High-resolution simulations of the final assembly of Earth-like planets I. terrestrial accretion and dynamics. *Icarus* 183, 265-282.

Regelous, M., Elliott, T., Coath, C.D. (2008) Nickel isotope heterogeneity in the early Solar System. *Earth and Planetary Science Letters* 272, 330–338.

Rehkämper, M., Halliday, A.N. (1997) Development and application of new ion-exchange techniques for the separation of the platinum group and other siderophile elements from geological samples. *Talanta* 44, 663-672.

Rehkämper, M., Halliday, A.N., Alt, J., Fitton, J.G., Zipfel, J., Takazawa, E. (1999a) Non-chondritic platinum-group element ratios in oceanic mantle lithosphere: petrogenetic signature of melt percolation? *Earth and Planetary Science Letters* 172, 65–81.

Rehkämper, M., Halliday, A.N., Fitton, J.G., Lee, D.C., Wieneke, M., Arndt, N.T. (1999b) Ir, Ru, Pt, and Pd in basalts and komatiites: New constraints for the geochemical behavior of the platinum-group elements in the mantle. *Geochimica et Cosmochimica Acta* 63, 3915–3934.

Reisberg, L., Lorand, J.P. (1995) Longevity of sub-continental mantle lithosphere form osmium isotope systematics in orogenic peridotite massifs. *Nature* 376, 159–162.

Reisberg, L.C., Allègre, C.J., Luck, J.-M. (1991) Re-Os systematics of the Ronda ultramafic complex of southern Spain. *Earth and Planetary Science Letters* 105, 196-213.

Reisberg, L., Zindler, A., Marcantonio, F., White, W., Wyman, D., Weaver, B. (1993) Os isotope systematics in ocean island basalts. *Earth and Planetary Science Letters* 120, 149-167.

Riches, A.J.V., Liu, Y., Day, J.M.D., Puchtel, I.S., Rumble, D., McSween, H.Y., Walker, R.J., Taylor, L.A. (2011) The petrology and geochemistry of Yamato 984028: a cumulate lherzolitic shergottites with affinities to Y 000027, Y 000047, and Y 000097. *Polar Science* 4, 497-514.

Riches, A.J.V., Day, J.M.D., Walker, R.J., Simonetti, A., Liu, Y., Neal, C.R., Taylor, L.A. (2012) Rhenium-osmium isotope and highly-siderophile element abundance systematics of angrite meteorites. *Earth and Planetary Science Letters* 353-354, 208-218.

Righter, K. (2011) Prediction of metal-silicate partition coefficients for siderophile elements: an update and assessment of PT conditions for metal-silicate equilibrium during accretion of the Earth. *Earth and Planetary Science Letters* 304, 158-167.

Righter, K., Drake, M.J. (1997) Metal-silicate equilibrium in a homogeneously accreting earth: new results for Re. *Earth and Planetary Science Letters* 146, 541-553.

Righter, K., Drake, M.J., Yaxley, G. (1997) Prediction of siderophile element metal-silicate partition coefficients to 20 GPa and 2800°C: the effects of pressure, temperature, oxygen fugacity, and silicate and metallic melt compositions. *Physics of the Earth and Planetary Interiors* 100, 115-134.

Righter, K., Danielson, L.R., Pando, K.M., Williams, J., Humayun, M., Hervig, R.L., Sharp, T.G. (2014) Highly siderophile element (HSE) abundances in the mantle of Mars are due to core formation at high pressure and temperature. *Meteoritics and Planetary Science* 50, 604-631.

Riley, G.H., Delong, S.E. (1970) Osmium isotopes in geology. *International Journal of Mass Spectrometry and Ion Physics* 4, 297-304.

Ringwood, A.E. (1966) Chemical evolution of the terrestrial planets. *Geochimica et Cosmochimica Acta* 30, 41-104.

Ringwood, A.E., Kesson, S.E. (1977) Basaltic magmatism and the bulk composition of the Moon; II, Siderophile and volatile elements in Moon, Earth and chondrites; implications for lunar origin. *The Moon* 16, 425-464.

Rizo, H., Walker, R.J., Carlson, R.W., Touboul, M., Horan, M.F., Puchtel, I.S., Boyet, M., Rosing, M.T. (2016a) Early Earth differentiation investigated through ^{142}Nd, 182W, and highly siderophile element abundances in samples from Isua, Greenland. *Geochimica et Cosmochimica Acta* 175, 319-336.

Rizo, H., Walker, R.J., Carlson, R.W., Horan, M.F., Mukhopadhyay, S., Manthos, V., Francis, D., Jackson, M.G. (2016b) Preservation of Earth-forming events in the tungsten isotopic composition of modern flood basalts. *Science* 352, 809-812.

Rocha-Júnior, E.R.V., Puchtel, I.S., Marques, L.S., Walker, R.J., Machado, F.B., Nardy, A.J.R., Babinski, M., Figueiredo, A.M.G. (2012) Re-Os isotope and highly siderophile element systematics of the Paraná continental flood basalts (Brazil). *Earth and Planetary Science Letters* 337-338, 164-173.

Roy-Barman, M., Allègre, C.J. (1994) ^{187}Os/^{186}Os ratios of mid-ocean ridge basalts and abyssal peridotites. *Geochimica et Cosmochimica Acta* 58, 5043-5054.

Roy-Barman, M., Wasserburg, G.J., Papanastassiou, D.A., Chaussidon, M. (1998) Osmium isotopic compositions and Re–Os concentrations in sulfide globules from basaltic glasses. *Earth and Planetary Science Letters* 154, 331–347.

Rubie, D.C., Jacobson, S.A., Morbidelli, A., O'Brien, D.P., Young, E.D., de Vries, J., Nimmo, F., Palme, H., Frost, D.J. (2015) Accretion and differentiation of the terrestrial planets with implications for the compositions of early-formed Solar System bodies and accretion of water. *Icarus* 248, 89-108.

Rubin, A.E. (2004) Post shock annealing and post annealing shock in equilibrated ordinary chondrites: implications for the thermal and shock histories of chondritic asteroids. *Geochimica et Cosmochimica Acta* 68, 673-689.

Rudnick, R.L., Walker, R.J. (2009) Ages from Re-Os isotopes in peridotites. Proceedings of the 9th Kimberlite Conference, *Lithos* 112S, 1083-1095.

Ryder, G., Norman, M.D., Taylor, J. (1997) The complex stratigraphy of the highland crust in the Serenitatis region of the Moon inferred from mineral fragment chemistry. *Geochimica et Cosmochimica Acta* 61, 1083-1105.

Salters, V.J.M., Mallick, S., Hart, S.R., Langmuir, C.E., Stracke, A. (2011) Domains of depletedmantle: new evidence from hafnium and neodymium isotopes. *Geochemistry, Geophysics, Geosystems*, doi: 10.1029/2011GC003617.

Schaudy, R., Wasson, J.T., Buchwald, V.F. (1972) The chemical classification of iron meteorites, VI. A reinvestigation of irons with Ge concentrations lower than 1 ppm. *Icarus* 17, 174-192.

Scherstén, A., Elliott, T., Hawkesworth, C., Norman, M. (2004) Tungsten isotope evidence that mantle plumes contain no contribution from the Earth's core. *Nature* 427, 234-237.

Scherstén, A., Elliott, T., Hawkesworth, C., Russell, S., Masarik, J. (2006) Hf-W evidence for rapid differentiation of iron meteorite parent bodies. *Earth and Planetary Science Letters* 241, 530-542.

Schiano, P., Birck, J.L., Allègre, C.J. (1997) Osmium-strontium-neodymium-lead isotopic covariations in mid-ocean ridge basalt glasses and the heterogeneity of the upper mantle. *Earth and Planetary Science Letters* 150, 363-379.

Schiano, P., Burton, K.W., Dupré, B., Birck, J.L., Guille, G., Allègre, C.J. (2001) Correlated Os-Pb-Nd-Sr isotopes in the Austral-Cook chain basalts: the nature of mantle components in plume sources. *Earth and Planetary Science Letters* 186, 527-537.

Schlichting, H.E., Warren, P.H., Yin, Q.-Z. (2012) The last stages of terrestrial planet formation: dynamical friction and the late veneer. *Astrophysical Journal* 752, 8.

Schmidt, G., Palme, H., Kratz, K.-L., Kurat, G. (2000) Are highly siderophile elements (PGE, Re and Au) fractionated in the upper mantle of the earth? New results on peridotites from Zabargad. *Chemical Geology* 163, 167-188.

Schmitt, W., Palme, H., Wänke, H. (1989) Experimental determination of metal/silicate partition coefficients for P, Co, Ni, Cu, Ga, Ge, Mo, and W and some implications for the early evolution of the Earth. *Geochimica et Cosmochimica Acta* 53, 173-185.

Schoenberg, R., Nägler, T.J., Kramers, J.D. (2000) Precise Os isotope ratio and Re-Os isotope dilution measurements down to the pictogram level using multicollector inductively coupled plasma mass spectrometry. *International Journal of Mass Spectrometry* 197, 85-94.

Schoenberg, R., Kamber, B.Z., Collerson, K.D., Eugster, O. (2002) New W-isotope evidence for rapid terrestrial accretion and very early core formation. *Geochimica et Cosmochimica Acta* 66, 3151-3159.

Schulte, R.F., Schilling, M., Horan, M.F., Anma, R., Komiya, T., Farquhar, J., Piccoli, P.M., Pitcher, L., Walker, R.J. (2009) Chemical and chronologic complexity in the convecting upper mantle: evidence from the Taitao Ophiolite, southern Chile. *Geochimica et Cosmochimica Acta* 73, 5793-5819.

Schulz, T., Upadhyay, D., Münker, C., Mezger, K. (2012) Formation and exposure history of non-magmatic iron meteorites and winonaites: clues from Sm and W isotopes. *Geochimica et Cosmochimica Acta* 86, 200-212.

Scott, E.R.D., Krot, T.V., Goldstein, J.I., Wakita, S. (2014) Thermal and impact history of the H chondrite parent asteroid during metamorphism: constraints from metallic Fe-Ni. *Geochimica et Cosmochimica Acta* 136, 13-37.

Seibert, J., Corgne, A., Ryerson, F.J. (2011) Systematics of metal–silicate partitioning for many siderophile elements applied to Earth's core formation. *Geochimica et Cosmochimica Acta* 75, 1451–1489.

Sharma, M., Wasserburg, G.J., Papanastassiou, D.A., Quick, J.E., Sharlov, E.V., Laz'ko, E.E. (1995) High ^{143}Nd/^{144}Nd in extremely depleted mantle rocks. *Earth and Planetary Science Letters* 135, 101-114.

Sharma, M., Papanastassiou, D.A., Wasserburg, G.J. (1997) The concentration and isotopic composition of osmium in the oceans. *Geochimica et Cosmochimica Acta* 61, 3287-3299.

Sharp, M., Righter, K., Walker, R.J. (2015) Estimation of trace element concentrations of the lunar magma ocean using mineral-melt and metal-silicate partition coefficients. *Meteoritics and Planetary Science* 50, 733-758.

Shearer, C.K., Papike, J.J. (1993) Basaltic magmatism on the Moon. A perspective from volcanic picritic glass beads. *Geochimica et Cosmochimica Acta* 57, 4785– 4812.

Shen, J.J., Papanastassiou, D.A., Wasserburg, G.J. (1996) Precise Re-Os determinations and systematics of iron meteorites. *Geochimica et Cosmochimica Acta* 60, 2887-2900.

Shirey, S.B., Walker, R.J. (1995) Carius tube digestion for low-blank rhenium-osmium analysis. *Analytical Chemistry* 34, 2136-2141.

Shirey, S.B., Walker, R.J. (1998) Re-Os isotopes in cosmochemistry and high-temperature geochemistry. *Annual Reviews of the Earth and Planetary Sciences* 26, 423-500.

Shirey, S.B., Bender, J.F., Langmuir, C.H. (1987) Three-component isotopic heterogeneity near the Oceanographer Transform, Mid-Atlantic Ridge. *Nature* 325, 217-223.

Shu, F., Shang, H., Glassgold, A.E., Lee, T. (1997) Towards an astrophysical theory of chondrites. *Science* 271, 1545-1552.

Sichel, S.E., Esperança, S., Motoki, A., Maia, M., Horan, M.F., Szatmari, P., da Costa Alves, E., Mello, S.L.M. (2008) Geophysical and geochemical evidence for cold upper mantle beneath the equatorial Atlantic Ocean. *Revista Brasileira de Geofisica* 26, 69-86.

Sims, K.W.W., Newsom, H.E., Gladney, E.S. (1990) Chemical fractionation during formation of the Earth's core and continental crust: clues from As, Sb, W, and Mo. In: Newsom, H.E., Jones, J.H. (Eds.) *Origin of the Earth*. Oxford University Press, New York, 29l-317.

Sleep, N.H. (1990) Hotspots and mantle plumes—some phenomenology. *Journal of Geophysical Research-Solid Earth Planets* 95, 6715–6736.

Sleep, N.H. (1992) Hotspot volcanism and mantle plumes. *Annual Reviews of the Earth and Planetary Sciences* 20, 19–43.

Smith, A.D. (2003) Critical evaluation of Re–Os and Pt–Os isotopic evidence on the origin of intraplate volcanism. *Journal of Geodynamics* 36**,** 469-484.

Smith, A.D., Ludden, J.N. (1989) Nd isotopic evolution of the precambrian mantle. *Earth and Planetary Science Letters* 93, 14-22.

Smoliar, M.I., Walker, R.J., Morgan, J.W. (1996) Re-Os ages of group IIA, IIIA, IVA and IVB iron meteorites. *Science* 271, 1099-1102.

Snow, J.E., Reisberg, L. (1995) Os isotopic systematics of the MORB mantle: results from altered abyssal peridotites. *Earth and Planetary Science Letters* 133**,** 411-421.

Snow, J.E., Hart, S.R., Dick, H.J.B. (1994) Nd and Sr isotopic evidence for a link between mid-ocean ridge basalts and abyssal peridotites. *Nature* 371**,** 57-60.

Snow, J.E., Schmidt, G., Rampone, E. (2000) Os isotopes and highly siderophile elements (HSE) in the Ligurian ophiolites, Italy. *Earth and Planetary Science Letters* 175, 119-132.

Sobolev, A.V., Hofmann, A.W., Kuzmin, D.V., Yaxley, G.M., Arndt, N.T., Chung, S.-L., Danyushevsky, L.V., Elliott, T., Frey, F.A., Garcia, M.O., Gurenko, A.A., Kamenetsky, V.S., Kerr, A.C., Krivolutskaya, N.A., Matvienkov, V.V., Nikogosian, I.K., Rocholl, A., Sigurdsson, I.A., Sushchevskaya, N.M., Teklay, M. (2006) The amount of recycled crust in sources of mantle-derived melts. *Science* 316, 412-417.

Sobolev, A.V., Hofmann, A.W., Brügmann, G., Batanova, V.G., Kuzmin, D.V. (2008) A quantitative link between recycling and osmium isotopes. *Science* 321, 536.

Srinivasan, G., Goswami, J. N., Bhandari N. (1999) Al-26 in eucrite Piplia Kalan: plausible heat source and formation chronology. *Science* 284, 1348–1350.

Standish, J.J., Hart, S.R., Blusztajn, J., Dick, H.J.B., Lee, K.L. (2002) Abyssal peridotite osmium isotopic compositions from Cr-spinel. *Geochemistry, Geophysics, Geosystems* 3, 1004.

Stracke, A., Snow, J.E., Hellebrand, E., von der Handt, A., Bourdon, B., Birbaum, K., Günther, D. (2011) Abyssal peridotite Hf isotopes identify extreme mantle depletion. *Earth and Planetary Science Letters* 308, 359-368.

Tagle, R., Berlin, J. (2008) A database of chondrite analysis including platinum group elements, Ni, Co, Au, and Cr: implications for the identification of chondritic projectiles. *Meteoritics and Planetary Science* 43, 541–559.

Takahashi, H., Janssens, M.-J., Morgan, J.W, Anders, E. (1978) Further studies of trace elements in C3 chondrites. *Geochimica et Cosmochimica Acta* 42, 97-106.

Takamasa, A., Nakai, S., Sahoo, Y., Hanyu, T., Tatsumi, Y. (2009) W isotope compositions of oceanic island basalts from French Polynesia and their meaning for core-mantle interaction. *Chemical Geology* 260, 37-46.

Tandon, S.N., Wasson, J.T. (1968) Gallium, germanium, indium and iridium variations in a suite of L-group chondrites. *Geochimica et Cosmochimica Acta* 32, 1087-1109.

Tatsumi, Y., Oguri, K., Shimoda, G. (1999) The behaviour of platinum-group elements during magmatic differentiation in Hawaiian tholeiites. *Geochemical Journal* 33, 237-247.

Touboul, M., Walker, R.J. (2012) High precision tungsten isotope measurement by thermal ionization mass spectrometry. *International Journal of Mass Spectrometry* 309, 109-117.

Touboul, M., Kleine, T., Bourdon, B., Palme, H., Wieler, R. (2007) Late formation and prolonged differentiation of the Moon inferred from W isotopes in lunar metals. *Nature* 450, 1206–1209.

Touboul, M., Puchtel, I.S., Walker, R.J. (2012) ^{182}W evidence for long-term preservation of early mantle differentiation products. *Science* 335, 1065-1069.

Touboul, M., Liu, J., O'Neil, J., Puchtel, I.S., Walker, R.J. (2014) New insights into the Hadean mantle revealed by ^{182}W and highly siderophile element abundances of supracrustal rocks from the Nuvvuagittuq Greenstone Belt, Quebec, Canada. *Chemical Geology* 383, 63-75.

Touboul, M., Puchtel, I.S., Walker, R.J. (2015) Tungsten isotopic evidence for disproportional late accretion to the Earth and Moon. *Nature* 520, 530-533.

Trieloff, M., Jessburger, E.K., Herrwerth, I., Hopp, J., Fieni, C., Ghelis, M., Bourot-Denise, M., Pellas, P. (2003) Structure and thermal history of the H-chondrite parent asteroid revealed by thermochronometry. *Nature* 422, 502-506.

Trinquier, A., Birck, J.-L., Allègre, C.J. (2007) Widespread ^{54}Cr heterogeneity in the inner solar system. *Astrophysical Journal* 655, 1179–1185.

Tsuru, A., Walker, R.J., Kontinen, A., Peltonen, P., Hanski, E. (2000) Re-Os isotopic systematics of the Jormua Ophiolite Complex, NW Finland. *Chemical Geology* 164, 123-141.

Van Acken, D., Brandon, A.D., Humayun, M. (2011) High-precision osmium isotopes in senstatite and Rumuruti chondrites. *Geochimica et Cosmochimica Acta* 75, 4020-4036.

Van Orman, J., Keshav, S., Fei, Y. (2008) High-pressure solid/liquid partitioning of Os, Re and Pt in the Fe–S system. *Earth and Planetary Science Letters* 274, 250–257.

Vervoort, J.D., Patchett, P.J. (1996) Behavior of hafnium and neodymium isotopes in the crust: Constraints from Precambrian crustally derived granites. *Geochimica et Cosmochimica Acta* 60, 3717-3733.

Vervoort, J.D., White, W.M., Thorpe, R.I. (1994) Nd and Pb isotope ratios of the Abitibi Greenstone Belt – New evidence for very early differentiation of the Earth. *Earth and Planetary Science Letters* 128, 215-229.

Vincent, E.A., Crocket, J.H. (1960) Studies in the geochemistry of gold – II the gold content of some basic and ultrabasic rocks and stone meteorites. *Geochimica et Cosmochimica Acta* 1, 143-148.

Vockenhuber, C., Oberli, F., Bichler, F., Ahmad, I., Quitté, G., Meier, M., Halliday, A.N., Lee, D.C., Kutschera, W., Steier, P., Gehrke, R.J., Helmer, R.G. (2004) New half-life measurement of ^{182}Hf: improved chronometer for the early solar system. *Physical Review Letters* 93, 172501.

Völkening, J., Walczyk, T., Heumann, K.G. (1991) Osmium isotope ratio determinations by negative thermal ionization mass spectrometry. *International Journal of Mass Spectrometry and Ion Processes* 105, 147-159.

Wade, J., Wood, B.J. (2005) Core formation and the oxidation state of the Earth. *Earth and Planetary Science Letters* 236, 78–95.

Wade, J., Wood, B.J., Tuff, J. (2012) Metal–silicate partitioning of Mo and W at high pressures and temperatures: Evidence for late accretion of sulphur to the Earth. *Geochimica et Cosmochimica Acta* 85, 58-74.

Walczyk, T., Hebeda, E.H., Heumann, K.G. (1991) Osmium isotope ratio measurements by negative thermal ionization mass spectrometry (NTI-MS). *Fresenius Journal of Analytical Chemistry* 341, 537-541.

Walker, R.J. (1988) Low-blank chemical separation of osmium and rhenium from gram quantities of silicate rock for measurement by resonance ionization mass spectrometry. *Analytical Chemistry* 60, 1231-1234.

Walker, R.J. (2012) Evidence for homogeneous distribution of osmium in the protosolar nebula. *Earth and Planetary Science Letters* 351-352, 36-44.

Walker, R.J. (2014) Siderophile element constraints on the origin of the Moon. *Philosophical Transactions of the Royal Society* A 372, 20130258.

Walker, R.J., Fassett, J.D. (1986) Isotopic measurement of subnanogram quantities of rhenium and osmium by resonance ionization mass spectrometry. *Analytical Chemistry* 58, 2923-2927.

Walker, R.J., Morgan, J.W. (1989) Rhenium-osmium isotope systematics of carbonaceous chondrites. *Science* 243, 519-522.

Walker, R.J., Walker, D. (2005) Does the core leak? *EOS* 86, 237-242.

Walker, R.J., Hanson, G.N, Papike, J.J., O'Neil, J.R. (1986) Nd, O and Sr isotopic constraints on the origin of Precambrian rocks, southern Black Hills, South Dakota. *Geochimica et Cosmochimica Acta* 50, 2833-2846.

Walker, R.J., Shirey, S.B., Stecher, O. (1988) Comparative Re-Os, Sm-Nd and Rb-Sr isotope and trace element systematics for Archean komatiite flows from Munro Township, Abitibi Belt, Ontario. *Earth and Planetary Science Letters* 87, 1-12.

Walker, R.J., Carlson, R.W., Shirey, S.B., Boyd, F.R. (1989) Os, Sr, Nd, and Pb isotope systematics of southern African peridotite xenoliths: Implications for the chemical evolution of subcontinental mantle. *Geochimica et Cosmochimica Acta* 53, 1583-1595.

Walker, R.J., Morgan, J.W., Naldrett, A.J., Li, C., Fassett, J.D. (1991) Re-Os isotope systematics of Ni-Cu Sulfide Ores, Sudbury Igneous Complex, Ontario: Evidence for a major crustal component. *Earth and Planetary Science Letters* 105, 416-429.

Walker, R.J., Morgan, J.W., Horan, M.F., Czamanske, G.F., Krogstad, E.J., Fedorenko, V., Kunilov, V.E. (1994) Re-Os isotopic evidence for an enriched-mantle source for the Noril'sk-type ore-bearing intrusions, Siberia. *Geochimica et Cosmochimica Acta* 58, 4179-4197.

Walker, R.J., Morgan, J.W., Horan, M.F. (1995) ^{187}Os enrichment in some mantle plume sources: evidence for core-mantle interaction? *Science* 269, 819-822.

Walker, R.J., Hanski, E.J., Vuollo, J., Liipo, J. (1996) The Os isotopic composition of Proterozoic upper mantle evidence for chondritic upper mantle from the Outokumpu ophiolite, Finland. *Earth and Planetary Science Letters* 141, 161-173.

Walker, R.J., Morgan, J.W., Beary, E., Smoliar, M.I., Czamanske, G.K., Horan, M.F. (1997) Applications of the ^{190}Pt-^{186}Os isotope system to geochemistry and cosmochemistry. *Geochimica et Cosmochimica Acta* 61, 4799-4808.

Walker, R.J., Horan, M.F., Morgan, J.W., Becker, H., Grossman, J.N., Rubin, A. (2002a) Comparative ^{187}Re-^{187}Os systematics of chondrites: Implications regarding early solar system processes. *Geochimica et Cosmochimica Acta* 66, 4187-4201.

Walker, R.J., Prichard, H.M., Ishiwatari, A., Pimentel, M. (2002b) The osmium isotopic composition of convecting upper mantle deduced from ophiolite chromitites. *Geochimica et Cosmochimica Acta* 66, 329-345.

Walker, R.J., Horan, M.F., Shearer, C.K., Papike, J.J. (2004) Depletion of highly siderophile elements in the lunar mantle: evidence for prolonged late accretion. *Earth and Planetary Science Letters* 224, 399-413.

Walker, R.J., Brandon, A.D., Bird, J.M., Piccoli, P.M., McDonough, W.F., Ash, R.D. (2005) ^{186}Os-^{187}Os systematics of Os-Ir-Ru alloy grains, southwestern Oregon. *Earth and Planetary Science Letters* 230, 211-226.

Walker, R.J., Böhlke, J.-K., McDonough, W.F., Li, J. (2007) Combined Re-Os isotope, gold and platinum-group element study of epigenetic gold ores, Alleghany District, California. *Economic Geology* 102, 1079-1089.

Walker, R.J., McDonough, W.F., Honesto, J., Chabot, N.L., McCoy, T.J., Ash, R.D., Bellucci, J.J. (2008) Origin and chemical evolution of group IVB iron meteorites. *Geochimica et Cosmochimica Acta* 72, 2198-2216.

Walter, M.J., Newsom, H.E., Ertel, W., Holzheid, A. (2000) Siderophile elements in the Earth and Moon: metal/silicate partitioning and implications for core formation. In: Canup, R.M., Righter, K. (Eds.) *Origin of the Earth and Moon*. University of Arizona Press, Tucson, 265-289

Warren, J.M. (2016) Global variations in abyssal peridotite compositions. *Lithos* 248-251, 193-219.

Warren, J.M., Shimizu, N., Sakaguchi, C., Dick, H.J.B., Nakamura, E. (2009a) An assessment of upper mantle heterogeneity based on abyssal peridotite compositions. *Journal of Geophysical Research* 114, B12203.

Warren, P.H. (2004) The Moon. In: Davis, A.M. (Ed.) *Treatise on Geochemistry, Volume 1, Meteorites, Comets, and Planets*. Elsevier B.V., Amsterdam, 559–599.

Warren, P.H., Kalleymeyn, G.W. (1996) Siderophile trace elements in ALH84001, other SNC meteorites and eucrites: evidence of heterogeneity, possibly time-linked, in the mantle of Mars. *Meteoritics and Planetary Science* 31, 97–105.

Warren, P.H., Kallemeyn, G.W., Huber, H., Ulff-Møller, F., Choe, W. (2009b) Siderophile and other geochemical constraints on mixing relationships among HED-meteoritic breccias. *Geochimica et Cosmochimica Acta* 73, 5918–5943.

Wasserburg, G.J., Papanastassiou, D.A., Sanz, H.G. (1969) Initial strontium for a chondrite and the determinations of a metamorphism or formation interval. *Earth and Planetary Science Letters* 7, 33-43.

Wasson, J.T., Richardson, J.W. (2001) Fractionation trends among IVA iron meteorites: contrasts with IIIAB trends. *Geochimica et Cosmochimica Acta* 65, 951-970.

Wasson, J.T., Kallemeyn, G.W. (2002) The IAB iron meteorite complex: A group, five subgroups, numerous grouplets, closely related, mainly formed by crystal segregation in rapidly cooling melts. *Geochimica et Cosmochimica Acta* 66, 2445–2473.

Wasson, J.T., Huber, H. (2006) Compositional trends among IID irons; their possible formation from the P-rich lower magma in a two-layer core. *Geochimica et Cosmochimica Acta* 70, 6153–6167.

Wasson, J.T., Isa, J., Rubin, A.E. (2013) Compositional and petrographic similarities of CV and CK chondrites: A single group with variations in textures and volatile concentrations attributable to impact heating, crushing and oxidation. *Geochimica et Cosmochimica Acta* 108, 45-62.

Wheeler, K.T., Walker, D., McDonough, W.F. (2011) Pd and Ag metal-silicate partitioning applied to Earth differentiation and core-mantle exchange. *Meteoritics and Planetary Science* 46, 199-217.

White, W.M., Hofmann, A.W. (1982) Sr and Nd isotope geochemistry of oceanic basalts and mantle evolution. *Nature* 296, 821–825.

Wichers, E., Schlecht, W.G., Gordon, C.L. (1944) Attack of refractory platiniferous materials by acid mixtures at elevated temperatures. *Journal of Research of the National Bureau of Standards* 33, 363-381.

Widom, E., Shirey, S.B. (1996) Os isotope systematics in the Azores: implications for mantle plume sources. *Earth Planetary Science Letters* 142, 451–465.

Widom, E., Hoernle, K.A., Shirey, S.B., Schmincke, H.-U. (1999) Os isotope systematics in the Canary Islands and Madeira: lithospheric contamination and mantle plume signatures. *Journal of Petrology* 40, 279– 296.

Widom, E., Kepezhinskas, P., Defant, M. (2003) The nature of metasomatism in the sub-arc mantle wedge: evidence from Re–Os isotopes in Kamchatka peridotite xenoliths. *Chemical Geology* 196, 283-306.

Willbold, M., Elliott, T., Moorbath, S. (2011) The tungsten isotopic composition of the Earth's mantle before the terminal bombardment. *Nature* 477, 195-198.

Willbold, M., Mojzsis, S.J., Chen, H.-W., Elliott, T. (2015) Tungsten isotope composition of the Acasta Gneiss Complex. *Earth and Planetary Science Letters* 419, 168–177.

Wittig, N., Humayun, M., Brandon, A.D., Huang, S., Leya, I. (2013) Coupled W-Os-Pt isotope systematics in IVB ironmeteorites: in situ neutron dosimetry for W isotope chronology. *Earth and Planetary Science Letters* 361, 152-161.

Wolf, R., Woodrow, A., Anders, E. (1979) Lunar basalts and pristine highland rocks: comparison of siderophile and volatile elements. *Proceedings of the Lunar and Planetary Science Conference* 10th, 2107– 2130.

Wolf, R., Richter, G.R., Woodrow, A.B., Anders, E. (1980) Chemical fractionations in meteorites – XI. C2 chondrites. *Geochimica et Cosmochimica Acta* 44, 711-717.

Woodland, S.J., Pearson, D.G., Thirlwall, M.F. (2002) A platinum group element and Re-O isotope investigation of siderophile element recycling in subduction zones: comparison of Grenada, Lesser Antilles arc, and the Izu-Bonin arc. *Journal of Petrology* 43, 171-198.

Workman, R.K., Hart, S.R. (2005) Major and trace element composition of the depleted MORB mantle (DMM). *Earth and Planetary Science Letters* 231, 53– 72.

Workman, R.K., Hart, S.R., Jackson, M., Regelous, M., Farley, K.A., Blusztajan, J., Kurz, M., Staudigel, H. (2004) Recycled metasomatized lithosphere as the origin of the Enriched Mantle II (EM2) end-member: evidence from the Samoan Volcanic Chain. *Geochemistry, Geophysics, Geosystems* 5, 4.

Wu, F.-Y., Walker, R.J., Ren, X.-W., Sun, D.-Y., Zhou, X.-H. (2003) Osmium isotopic constraints on the age of lithospheric mantle beneath northeastern China. *Chemical Geology* 196, 107-129.

Yamamoto, S., Nakamura, R., Matsunaga, T., Ogawa, Y., Ishihara, Y., Morota, T., Hirata, N., Ohtake, M., Hiroi, T., Yokota, Y., Haruyama, J. (2010) Possible mantle origin of olivine around lunar impact basins detected by SELENE. *Nature Geoscience* 3, 533-536.

Yang, J., Goldstein, J.I., Scott, E.R.D. (2007) Iron meteorite evidence for early catastrophic disruption of protoplanets. *Nature* 446, 888–891.

Yang, J., Goldstein, J.I., Scott, E.R.D. (2008) Metallographic cooling rates of the IVA iron meteorites. *Geochimica et Cosmochimica Acta* 72, 3043–3061.

Yang, J., Goldstein, J.I., Michael, J.R., Kotula, P.G., Scott, E.R.D. (2010) Thermal history and origin of the IVB iron meteorites and their parent body. *Geochimica et Cosmochimica Acta* 74, 4493–4506.

Yang, A.Y., Zhao, T.-P., Zhou, M.-F., Deng, X.-G., Wang, G.-Q., Li, J. (2013) Os isotopic compositions of MORBs from ultra-slow spreading Southwest Indian Ridge: constraints on the assimilation and fractional crystallization (AFC) processes. *Lithos* 179, 28-35.

Yang, S., Humayun, M., Righter, K., Jefferson, G., Fields, D., Irving, A.J. (2015) Siderophile and chalcophile element abudances in shergottites: implications for Martian core formation. *Meteoritics and Planetary Science* 50, 691-714.

Yaxley, G.M., Green, D.H. (1998) Reactions between eclogite and peridotite: mantle refertilisation by subduction of oceanic crust. *Schweizerische Mineralogische und Petrographische Mitteilungen* 78, 243-255.

Yin, Q.-Z., Jacobsen, S.B., Yamashita, K. (2002a) Diverse supernova sources of pre-solar material inferred from molybdenum isotopes in meteorites. *Nature* 415, 881-883.

Yin, Q.-Z., Jacobsen, S.B., Yamashita, K., Blichert-Toft, J., Telouk, P., Albarède, F. (2002b) A short timescale for terrestrial planet formation from Hf–W chronometry of meteorites. *Nature* 418, 949–952.

Yokoyama, T., Walker, R.J. (2016) Nucleosynthetic isotope variations of siderophile and chalcophile elements in the Solar System. *Reviews in Mineralogy & Geochemistry* V. 81, 107-160.

Yokoyama, T., Walker, D., Walker, R.J. (2009) Low osmium solubility in silicate at high pressures and temperatures. *Earth and Planetary Science Letters* 279, 165-173.

Zindler, A., Hart, S.R. (1986) Chemical geodynamics. *Annual Reviews of the Earth and Planetary Sciences* 14, 493–571.

Zinner, E. (1998) Stellar nucleosynthesis and the isotopic composition of presolar grains from primitive meteorites. *Annual Review of the Earth and Planetary Science* 26, 147–188.

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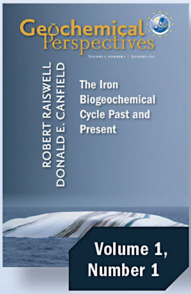
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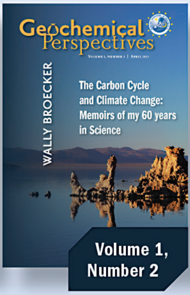
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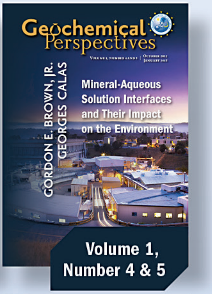
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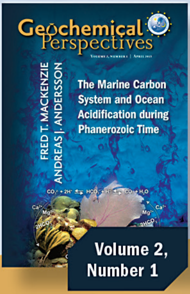
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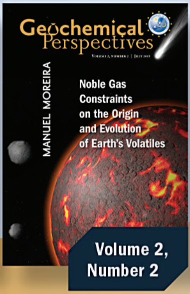
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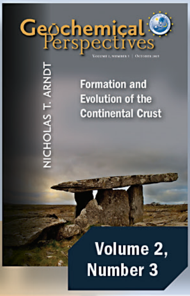
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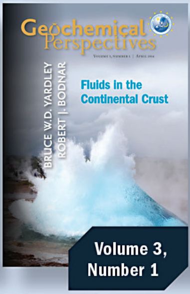
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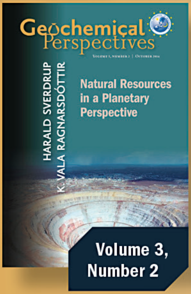
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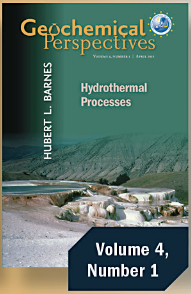
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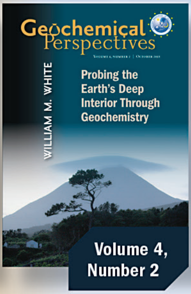
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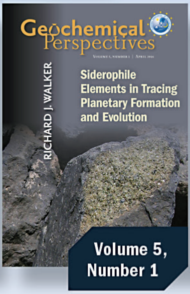
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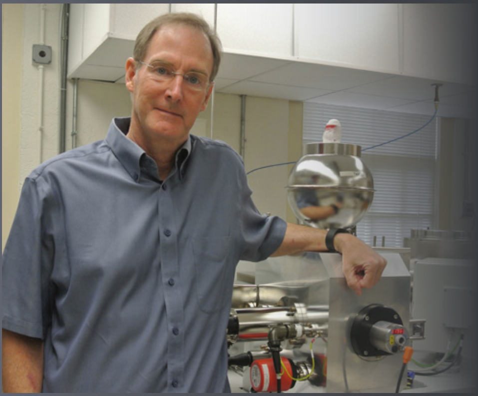

RICHARD J. WALKER is a Professor and currently the Chair in the Department of Geology, at the University of Maryland. He obtained a B.S. degree in Geology from the College of William and Mary in 1979. He completed both M.S. and Ph.D. degrees in geology from the State University of New York at Stony Brook in 1981 and 1984, respectively. After this, he did postdoctoral work at the U.S. National Bureau of Standards, the Carnegie Institution of Washington's Department of Terrestrial Magnetism, and the U.S. Geological Survey. He became a member of the faculty at the University of Maryland in 1990. He was the 1990 recipient of the Clarke Medal of the Geochemical Society. He is a fellow of the American Geophysical Union, the European Association of Geochemistry and the Geochemical Society.

Professor Walker utilises radiogenic isotopes and trace elements to conduct research in several areas of geo- and cosmo-chemistry including the chemical evolution of Earth's mantle, the formation and crystallisation histories of early solar system planetesimals, the origin of ore deposits and the accretional and differentiation histories of the Earth, Moon and Mars. He was a pioneer in the application of the Re-Os isotope system to high temperature geochemistry, and he and colleagues still specialise in the applications of siderophile elements to these topics.