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,

![Resonance ionisation 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.](https://pubs.geoscienceworld.org/perspectives/article-pdf/5/1/3/3716248/gsgp_5_1_section1_OA.pdf)
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).

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](https://pubs.geoscienceworld.org/perspectives/article-pdf/5/1/3/3716248/gsgp_5_1_section1_OA.pdf)

(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 \textit{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 \textit{aqua regia} would be just the thing.
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.


