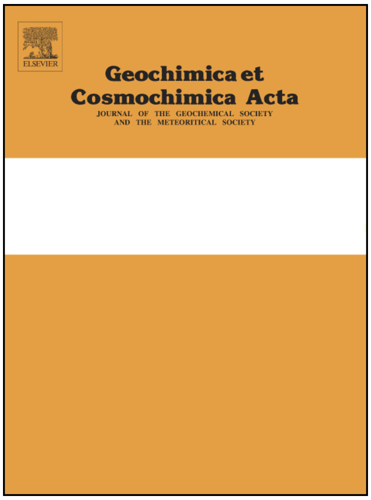

Preface to Highly Siderophile Element Constraints on Earth and Planetary Processes

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Figure 1: Delegates of the 4th International Workshop on Highly Siderophile Element Geochemistry

1.1 Overview

The geochemical properties of the highly siderophile elements (HSEs; Os, Ir, Ru, Rh, Pt, Pd, Re and Au) - being strongly iron-loving, but also chalcophile (i.e., having an affinity for sulphide), and generally occurring at ultra-trace levels in silicate rocks, their weathered products, and oceanic waters - mean that this suite of elements and their isotopic compositions are useful in tracing a wide variety of processes. Thus, the HSEs are useful tracers with which to tackle major research questions pertinent to past and present-day change at a variety of scales and in a range of Earth and other-worldly environments by constraining reservoir compositions, chemical drivers, and the timing of key events and/or transformation rates.

This special issue of Geochimica et Cosmochimica Acta brings together a number of contributions presented at the 4th International Workshop on Highly Siderophile Element Geochemistry (Durham, UK, 2016), and includes a modest number of related works from the wider community. This workshop was twice the size of the previous in its series, and represented the timely re-establishment of these 4-yearly meetings after a 10 year hiatus. This forum provided for the presentation of new findings pertinent to low- and high-temperature geochemical processes and allowed ample time for discussion so as to effectively integrate ideas from all corners of the HSE geochemistry community. To reflect emerging areas of interest and the capability of new instrumentation, emphasis was given to the application of HSEs in studying planetary processes, through both meteoritical studies and experimental petrology, and also to investigations of HSE systematics at mineral to atom-levels across the spectrum of scientific themes. The collection of original research contributed to this special issue is divided into three sections that are summarised below. The final portion of this volume includes a dedication to Professor Hazel Prichard who was a dedicated and influential scholar of HSE behaviour in the natural environment. Her attendance and valuable contributions to this HSE workshop and the discussions that took place there will be remembered and heartily appreciated by all who were present.

1.2 Understanding planetary processes and Solar System evolution

The opening section of this issue gathers a remarkable range of works of importance for constraining the building blocks, birth, and evolution of planets. These utilise Au-Cu abundances and long-lived radiogenic HSE isotope systems (e.g, Re-Os), appraise nucleosynthetic HSE compositions and corrections methodologies linked to cosmic ray exposure, take a close look at refractory metal nuggets in chondrites through synchrotron and traditional microscopy techniques, and include a pioneering study of palladium stable isotope compositions.

The first paper of the special issue is a study of coupled HSE systematics and high-precision Os isotope compositions of carbonaceous chondrites, principally those that are Karooda-like (CKs), by Goderis *et al*. These authors find that equilibrated bulk CKs, which exhibit thermal metamorphic grades across petrologic types 3 to 6 and are highly oxidised and record no resolvable nucleosynthetic Os isotope anomalies. Critically, the lack of Os isotopic anomalies in CKs is related to the destruction of nucleosynthetic carrier phases through oxidation during aqueous alteration and thermal metamorphism early in the history of the CK parent body. These authors argue that the absence of Os isotopic anomalies among ordinary, enstatite, these carbonaceous chondrites, and other meteorite groups (e.g., irons and a number of ureilites) support hypotheses in which s- and r-process carriers were effectively homogenised across chondrite forming region or even the entire protoplanetary disk. These findings contrast to siderophile Mo and some other HSEs, Ru and Pd, for which isotopic anomalies are preserved and must testify to differences in their chemical properties, host phases, and/or the nature of nebular and planetary processing. Yet, a solution to these differences remains enigmatic and warrants further study. Stable isotope compositions of the HSEs are useful in tracing planetary processes, such as core formation, as they can be sensitive recorders of the mechanisms of sulphide-silicate-metal partitioning at rock to planet scales, Creech *et al* pioneer a new approach that employs a double-spike correction and measurement by MC-ICP-MS to provide the first high-precision Pd stable isotope data for a suite of chondrite and ureilite meteorites. This study is important in showing that Pd stable isotopes are fractionated to a lesser extent than Pt during metal-silicate differentiation, and that Earth's Pd stable isotope composition is consistent with the addition of chondritic material during late-accretion (referred to also as the late veneer if strictly after core formation). However, it is important to note that these authors emphasise that variation in δ^{106}Pd among carbonaceous chondrites is not yet fully accounted for and is a promising avenue requiring more investigation. Two articles by Daly *et al* seek to identify inherited signatures of the proto-Solar molecular cloud by constraining the distribution and origin(s) of refractory metal nuggets (RMNs; >1 at. % HSEs and <1 µm in size) in carbonaceous chondrites. These authors apply a number of emerging microscopy approaches, some involving a synchrotron beamline, to show that RMNs are distributed in a range of locations within chondrites, not restricted to refractory calcium and aluminium rich inclusions (CAIs), and that crystallographic relationships and RMN elemental chemistries are consistent with these phases pre-dating their host chondrites. Critically, the compositions of these RMNs are interpreted to reflect their diverse pre-solar chemical signatures thereby providing a window into the ancestry of the giant molecular cloud parental to our Solar System for which further new and influential results are eagerly anticipated.

These studies of chondrites and their constituent parts (± ureilite meteorites) are followed by investigations of iron meteorites (Hunt *et al*), a broad-suite of martian meteorites (Wang and Becker), and two primitive achondrites suites (acapulcoite and lodranite meteorites; Dhaliwal *et al*). Hunt *et al* provide high-precision Pt isotope data, which includes data for ^{190}Pt that is a low abundance isotope that can be challenging to measure, for a range of iron meteorite types. Comparison of these new data to models of the effects of exposure to galactic cosmic rays (GCRs) confirms the utility of Pt isotopes as a neutron dosimeter able to unmask nucleosynthetic isotope variations and to correct for GCR effects on the short-lived ^{182}Hf-^{182}W and ^{107}Pd-^{107}Ag radiogenic decay systems. Crucially, homogeneity in s-, r-, and p-process Pt isotopes between iron meteorites and Earth is argued to support their homogeneous distribution in the inner Solar System during planet formation. Wang and Becker provide abundance data for Cu and Ag, and infer that this pair of elements do not fractionate with respect to one another during planetary magmatic differentiation. On this basis, these authors utilise the Cu-Ag ratios of martian meteorites to constrain the mantle composition of Mars and to compare this with carbonaceous, enstatite and ordinary chondrites and the mantle of Earth. Critically, it is found that Cu-Ag systematics support previous proposals in which siderophile element partitioning scales with the size of the planetary body, and that Cu and Ag undergo limited fractionation during the formation of metallic cores and the generation and crystallisation of silicate magmas at high temperature. Thus, these authors do not evoke a role for late accretion to account for the broadly chondrite-like Cu-Ag ratios of Mars and Earth. The HSE abundance and ^{187}Re-^{187}Os isotope data for acapulcoite, lodranite, and transitional acapulcoite-ladronite meteorites that is presented by Dhaliwal *et al* alongside triple O-isotope compositions, bulk- and mineral major- and trace-element chemistries, are considered to support the generation of these primitive achondrites from chondritic pre-cursors that have experienced very small degrees of silicate melt removal during inhomogeneous melting of a heterogeneous precursor on a single parent-body. Data modelling supports the proposal that the HSE and Re-Os isotope systematics reflect varying degrees of melt removal in the Fe-Ni-S system and/or ponding of HSE-rich metallic melt in a subset of the studied samples exhibiting high Pt/Os and low Pd/Os that could potentially sample a deeper region in proximity to a fledgling core. Thus, this study provides important constraints on the earliest stages of planetary evolution, at the point where a chondritic precursor undergoes small degrees of melting but before generating magma oceans and efficiently forming a single and - presumably - central Fe-Ni core. As such, these constraints on the characteristics of the first steps in the evolution of differentiated planetary bodies will be critically important to computer simulations of the growth of cores on bodies such as Earth and Mars.

1.3 Experimental constraints and relevance to Earth and planetary systems

The second portion of this volume compiles contributions that use experimental petrology methods to place constraints on HSE behaviour in magmatic systems over a range of temperatures and chemical conditions relevant to Earth and other silicate bodies. Helmy and Fonseca demonstrate that Ni and Pd activity is increased in a Se-sulphide system relative to a system devoid of Se, but that the Pt-Se activity coefficient in sulphide melt is lower than that of Pt-S. The presence of Se is shown to have no discernible effect on the inter-element partitioning of HSEs in the 700 ˚C to 1050 ˚C range. These authors also show that sulphide is able to accommodate wt. % levels of Se and that no discrete selenides form, consequently it is sulphides that are predicted to control Se behaviour in magmatic systems though Se is shown to behave as a volatile element and able to degas at the upper end of the experimental temperatures. These findings may negate the requirement for crustal contributions as a means of fractionating S/Se ratios. Canali *et al* provide an assessment of Pt-As association in magmas through a series of dedicated high-temperature experimental studies to investigate several parameters, including an evaluation of the solubility of Pt and Pt-arsenide phases such as sperrylite ($PtAs_2$). Critically, this work establishes the role that As plays in the appearance of a Pt-bearing phase at lower Pt-concentrations than would otherwise be possible, where the authors conclude that unusually high As concentrations are required and thus invoke crustal contamination as a requirement in natural magmatic systems that crystallise sperrylite. The final two experimental studies presented in this section address the complexing of HSE in As-bearing sulphide systems (Helmy and Bragagni) and As-free systems (Fonseca *et al*). Each of these authors discusses their results in terms of the sequence of HSE-bearing phases that are observed and the manner in which these fractionate HSE. Helmy and Bragagni conclude that mechanical segregation may play an important role in the inter-element HSE fractionation observed in natural sulphide systems. Fonseca *et al* focus on the consequences that their experimental findings have for our understanding of mineralogical controls on the Re-Os isotope system in Earth's silicate rocks (principally those of ophiolites and the spectrum of mantle peridotites). Two important conclusions of the latter study are that laurite is predicted to be the only phase with the potential to preserve the initial $^{187}Os/^{188}Os$ composition of the bulk assemblage from which it formed, and that large datasets for HSE and Os-isotope compositions (ideally for samples of significant mass) are needed to ensure Os-age records are robust.

1.4 Tracing Earth's secular changes and geochemical cycles

The concluding section of this special issue addresses low- and high-temperature changes in HSE over time and explores several aspects of the geochemical cycles on Earth through a variety of study methods. These approaches take advantage of HSE abundance systematics at bulk and mineral scales, exploit Re-Os-isotope compositions of rocks and their constituent phases, and use Monte Carlo calculations that seek to model whole Earth anthrobiogeochemical cycling of Pt, Pd and Rh. The final six articles in this section are included as a dedication to Prof. Hazel Prichard and these broadly represent the breadth of her research interests. The significance of Hazel's contributions to HSE research through her published works, awards, and her training of scholars is summarised by Hall, Maier and Barnes.

The first two articles of this section of the special issue assess the utility of HSEs in tracing Earth's palaeoenvironmental change. Gregory *et al* present an important study of pyrite trace-element chemistry along with multi-element and isotopic proxies for corresponding whole-rock data. Pyrite is a recently developed proxy for studying the metal systematics of ancient oceans, and as such this work provides a key test of this emerging tool that could prove robust to greenschist facies metamorphism and provides a means to see through potential hydrothermal overprints in the wider geological record. These authors explore the utility of their bulk-rock and pyrite data (chiefly Ag, Sb, Se, Pb, Cd, Te, Bi, Mo, Ni and Au abundances) in tracing perturbations among redox sensitive elements in response to marine oxygenation events during dominantly O_2-poor conditions in the Ediacaran and their impact on the availability of bioessential elements. Critically, this work explores the promise of pyrite chemistry, in partnership with complementary data, to placing more quantitative constraints on ancient ocean chemistry and pore-water compositions than have been possible through previously available methods alone. This approach, therefore, offers potential to not only advance the means by which ocean compositions are probed over deep-time, but also scope to investigate records of the deep biosphere that may be of interest to astrobiologists as analogues of other-worldly environments. Lu *et al* provide a review of the record of ^{192}Os (representing non-radiogenic osmium) concentrations and initial $^{187}Os/^{188}Os$ isotope compositions in organic-rich mudrocks over 3 billion years of Earth history. These authors identify a long-term trend of increasing seawater $^{187}Os/^{188}Os$ compositions from the Archean to the Phanerozoic that is attributed to increased oxygenation of the atmosphere and ocean, and weathering of progressively more radiogenic crustal materials over time.

Superimposed fluctuations on this long-term trend are variously ascribed to changes to ocean chemistries in response to catastrophic events with global impact such as bolide impacts and massive outpourings of basaltic lavas associated with large igneous provinces. In addition, periods of significant mountain building or tectonic reconfiguration, changes in seafloor spreading rates, and changes to the nature of locally exposed and eroded crust are also linked to these perturbations to Earth's long-term record of change in ocean chemistry. Yet, these authors emphasize the critical need to improve our understanding of the behaviour of Os in the modern environment that is subject to anthropogenic stresses and rapid climate change of societal concern.

With the exception of the final article in this special issue, which provides models giving a quantitative understanding of the anthrobiogeochemical cycles of three of the HSE, Pt, Pd, and Rd (Mitra and Sen), the other remaining contributions relate to records of Earth's high-temperature geochemical processes and histories of deep-Earth reservoirs. van der Meer *et al* assess the HSE and Re-Os isotope systematics of a suite of xenoliths from Venetia's diamondiferous mantle situated in the Limpopo Mobile Belt, which is sandwiched between the Kaapvaal and Zimbabwe Cratons. An important finding of this study is that a subset of the studied samples define a virtually isochronous relationship that gives a ~3.28 Ga age, which overlaps with the time at which the overlying Limpopo crust forms, and is linked to rapid crustal recycling of the mantle lithosphere within ~100 Myrs of the melt extraction event. Significantly, the broadly isochronous age is in excess of the range of calculated Re-depletion ages (T_{RD}) for the suite of mantle xenoliths, including the most depleted samples. This finding emphasizes the fact that Re-depletion model ages are minimums, can significantly underestimate the time of major mantle differentiation events, and may result in spurious overlap with the timing of crustal events. A careful assessment of the complex nature of unequilibrated ^{187}Os/^{188}Os records among sulphides of a limited number of mantle xenoliths of Somerset Island, Rae Craton, Arctic Canada (Bragagni *et al*) provides further reason to treat whole-rock T_{RD} ages with great caution, and emphasizes the utility of integrated HSE abundance and petrologic studies in assessing the long and complex histories of these types of deeply derived samples. Despite these challenges, the authors link peaks among their sulphide T_{RD} age populations to regional events of geodynamic importance at ~2.8 Ga (craton building), ~2.2 Ga (rifting), and ~1.9 Ga (orogenesis). A study of Eoarchean tectonically-emplaced mantle rocks and metakomatiites by Ishikawa *et al* provides HSE abundance and Re-Os isotope data that is considered to testify to their derivation from a mantle with broadly-chondritic relative abundances of HSE but at concentrations ~10 to 20 % lower than Earth's present-day upper mantle. This provides tantalizing evidence that late accretion added broadly chondritic materials over a prolonged period extending from the Hadean through into the Archean, the early mantle of which may have been distinct to the modern mantle at a global scale.

Two articles present new methods of investigation that record the textural context of phases subject to chemical analyses. Prichard *et al* present an important and pioneering study that integrates 3D X-ray tomography with the *in situ* analyses of platinum group minerals (PGM) sequentially exposed at polished surfaces. This novel approach provides a means of relating ^{187}Os/^{188}Os compositions of individual phases to their crystallographic relations. A study such as this, which targets a statistically meaningful number of grains, also provides for robust assessments of the magmatic and/or exsolution processes potentially responsible for specific populations of PGM while also enabling isotopic constraints to be placed on the composition and inherent variability of the source reservoir. McDonald *et al* use X-ray computed microtomography in combination with compositional analyses via scanning electron microscope analyses and laser ablation ICP-MS to assess their new method for the homogenisation of sulphide inclusions in diamond. This innovation provides for advances in the means by which HSE abundances, Os-isotope compositions, and other multi-element isotope compositions can be determined for these phases captured at great depths in Earth's mantle. Potentially, this new method overcomes challenges encountered during prior studies in which pre-existing Os isotopic heterogeneity required the efficient separation and digestion of the entire sulphide to obtain geologically meaningful data. These conisderations also prohibited the collection of multi-element isotopic data for the same sulphide in earlier work. The advances reported here thereby open new avenues to address a range of hypotheses concerning Earth's interior chemical evolution and deep carbon cycle.

Three of the concluding articles of this special issue explore topics linked to shallow-level volcanics and are of broad relevance to the exploration of precious metals. The HSE abundance systematics of kimberlites from the Karelian and Kaapvaal Cratons are utilised by Maier *et al* to constrain the portion of fragmented and partially digested mantle material present and mixed with a modelled melt composition. These authors infer that the metasomatised component of the Karelian and Kaapvaal Cratons is relatively poor in HSE and that the prospectivity of large igneous province magmas for HSEs (with the exception of Au) is not controlled by their interaction with lithospheric mantle during ascent. The processes influencing the Cu and Au fertility of felsic rocks is assessed by Hao *et al* through a multi-element study that utilised the platinum group elements to constrain the relative timing of sulphide- and volatile-saturation in relation to the tenor of associated hydrothermal mineralisation. The authors' principal findings are that the ore-grade suites result from a wetter magma that experienced relatively late sulphide saturation followed shortly thereafter by volatile saturation. With respect to ores and their grade, Rayleigh fractionation is inferred to be at least as important as the initial concentration of the chalcophile elements in the parent magma. In contrast to the felsic ore bodies, the barren suites reflect a relatively dry magma in which sulphide saturation was reached early and locked away the Cu and Au in a cumulus pile at depth. To constrain the factors responsible for the well-known enrichment of a sub-set of HSEs in Cr-spinel, and to understand the influence that the fractionation of this phase exerts on the HSE chemistry of primitive magmas, Park *et al* provide new *in situ* data with which to assess the compositional systematics of Cr-spinel phases in a number of volcanic suites that were generated in a range of tectonic settings. These authors identify systematic differences between Cr-spinels of different tectonic settings and show that enrichment of Rh, Ir, Os, and Ru is a function of the parental melt composition and the magnetite (Fe^{3+}) component of the spinel. In addition, the relatively low temperature of arc magmas in comparison to intra-plate and MORB melts permits arc-group Cr-spinels to have more octahedral sites at equivalent magnetite components, and this could account for the significantly higher partition coefficient of Ru for this suite of spinels. Collectively, the characteristics and fractional crystallisation of Cr-spinel in arc magmas are argued to account for the highly-fractionated HSE systematics of arc basalts.

1.5 Concluding remarks

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