

Preface to

Highly-Siderophile-Element Constraints on Earth and Planetary Processes

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 volumes 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 attended.

The enormous efforts of the assembled guest editorial team made this special issue possible. These include - Dr Anat Shahar (Geophysical Laboratory, Carnegie Institution of Washington), Prof. Laurie Reisberg (CPRG-CNRS Nancy), Dr. Marc-Alban Millet (Cardiff University), Dr Brian Kendall (University of Waterloo), Prof. Al Brandon (University of Houston), Dr. Chris W. Dale (University of Durham), Prof. James Brennan (Dalhousie University/University of Toronto), Prof. Harry Becker (Frei University, Berlin), Prof. Ian H Campbell (Australia National University), Prof. Nicola Dauphas (University of Chicago), Dr. Raul Fonseca (Universität Bonn), Dr. Chi Ma (California Institute of Technology), Prof. Fred Moynier (Institut de Physique du Globe de Paris), Dr. Iain McDonald (Cardiff University), and Prof. Holly Stein (Colorado State University/University of Oslo). Prof. Mark Rehkamper tirelessly advised this team and supported editorial processing as supervising associate editor.

1.2 Understanding planetary processes and Solar System evolution through the highly-siderophile-elements

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, long-lived radiogenic HSE isotope systems (e.g, Re-Os), appraise nucleosynthetic HSE compositions

45 and corrections methodologies linked to cosmic-ray-exposure, take a close-look at refractory metal
46 nuggets in chondrites through synchrotron and traditional microscopy techniques, and include a
47 pioneering study of palladium stable isotope compositions.

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

81 These studies of chondrites and their constituent parts (\pm ureilite meteorites) are followed by
82 investigations of iron meteorites ([Hunt *et al.*](#)), a broad-suite of martian meteorites ([Wang and Becker](#)),
83 and two primitive achondrites suites (acapulcoite and lodranite meteorites; [Dhaliwal *et al.*](#)). [Hunt *et al.*](#)
84 provide high-precision Pt-isotope data, which includes data for ^{190}Pt that is a low abundance
85 isotope that can be challenging to measure, for a range of iron meteorite types. Comparison of this
86 new data to models of the effects of exposure to galactic cosmic rays (GCRs) confirms the utility of
87 Pt-isotopes as a neutron dosimeter able to unmask nucleosynthetic isotope variations and to correct
88 for GCR effects on the short-lived ^{182}Hf - ^{182}W and ^{107}Pd - ^{107}Ag radiogenic decay systems. Crucially,
89 homogeneity in s-, r-, and p-process Pt-isotopes between iron meteorites and Earth is argued to
90 support their homogeneous distribution in the inner Solar System during planet formation. [Wang and
91 Becker](#) provide abundance data for Cu and Ag, and infer that this pair of elements do not significantly
92 fractionate from one another during planetary magmatic differentiation. On this basis, these authors
93 utilise the Cu-Ag ratios of martian meteorites to constrain the mantle composition of Mars and to
94 compare this with carbonaceous, enstatite and ordinary chondrites and the mantle of Earth. Critically,

95 it is found that Cu-Ag systematics support theories that siderophile element partitioning scales with
96 the size of the planetary body and that Cu and Ag undergo limited fractionation during the formation
97 of metallic cores and the generation and crystallisation of silicate magmas at high-temperature. Thus,
98 these authors do not evoke a role for late-accretion to account for the broadly chondrite-like Cu-Ag
99 ratios of Mars and Earth. The HSE abundance and ^{187}Re - ^{187}Os isotope data for acapulcoite, lodranite,
100 and transitional acapulcoite-ladronite meteorites that is presented by [Dhaliwal *et al.*](#), alongside triple
101 O-isotope compositions, bulk- and mineral major- and trace-element chemistries, are considered to
102 support the generation of these primitive achondrites from chondritic pre-cursors that have
103 experienced very small degrees of silicate melt removal during inhomogeneous melting of a
104 heterogeneous precursor on a single parent-body. Data modelling supports the theory that the HSE
105 and Re-Os isotope systematics reflect varying degrees of melt removal in the Fe-Ni-S system and/or
106 ponding of HSE-rich metallic melt in a subset of the studied samples exhibiting high Pt/Os and low
107 Pd/Os that could potentially sample a deeper region in proximity to a fledgling core. Thus, this study
108 provides important constraints on the earliest stages of planetary evolution, at the point where a
109 chondritic precursor undergoes small degrees of melting but before generating magma oceans and
110 efficiently forming a single and - presumably - central Fe-Ni core. As such, these constraints on the
111 characteristics of the first-steps in the evolution of differentiated planetary bodies will be critically
112 important to computer simulations of the growth of cores on bodies such as Earth and Mars.

113 1.3 Experimental constraints on the behaviour of highly-siderophile-elements and 114 their relevance to Earth and planetary systems

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

144 1.4 Tracing Earth's secular changes and geochemical cycles through highly-
145 siderophile-elements

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

155 The first two articles of this section of the special issue assess the utility of HSE in tracing Earth's
156 palaeoenvironmental change. [Gregory *et al.*](#), present an important study of pyrite trace-element
157 chemistry along with multi-element and isotopic proxies for corresponding whole-rock data. Pyrite is
158 a recently developed proxy for studying the metal systematics of ancient oceans, and as such this
159 work provides an important test of this emerging tool that could prove robust to greenschist facies
160 metamorphism and provides a means to see-through potential hydrothermal overprints in the wider
161 geological record. These authors explore the utility of their bulk-rock and pyrite data (chiefly Ag, Sb,
162 Se, Pb, Cd, Te, Bi, Mo, Ni and Au abundances) in tracing perturbations among redox sensitive
163 elements in response to marine oxygenation events during dominantly O₂-poor conditions in the
164 Ediacaran and their impact on the availability of bioessential elements. Critically, this work explores
165 the promise of pyrite chemistry, in partnership with complementary data, to placing more quantitative
166 constraints on ancient ocean chemistry and pore-water compositions than have been possible through
167 previously available methods alone. This, approach, therefore offers potential to not only advance the
168 means by which ocean compositions are probed over deep-time, but also scope to investigate records
169 of the deep biosphere that may be of potential interest to astrobiologists as analogues of other-worldly
170 environments. [Lu *et al.*](#), provide a review of the record of ¹⁹²Os (representing non-radiogenic osmium)
171 concentrations and initial ¹⁸⁷Os/¹⁸⁸Os isotope compositions in organic-rich mudrocks over 3 billion
172 years of Earth history. These authors identify a long-term trend of increasing seawater ¹⁸⁷Os/¹⁸⁸Os
173 compositions from the Archean to the Phanerozoic that is attributed to increased oxygenation of the
174 atmosphere and ocean, and weathering of progressively more radiogenic crustal materials over time.
175 Superimposed fluctuations on this long-term trend are variously ascribed to changes to ocean
176 chemistries in response to catastrophic events with global impact such as bolide impacts and massive
177 outpourings of basaltic lavas associated with large igneous provinces. In addition periods of
178 significant mountain building or tectonic reconfiguration, changes in seafloor spreading rates, and
179 changes to the nature of locally exposed and eroded crust are also linked to these perturbations to
180 Earth's long-term record of change in ocean chemistry. Yet, these authors emphasize the critical need
181 to improve our understanding of the behaviour of Os in the modern environment that is subject to
182 anthropogenic stresses and rapid climate change of societal concern.

183 With the exception of the final article in this special issue, which provides models giving a
184 quantitative understanding of the anthropiogeochimical cycles of three of the HSE, Pt, Pd, and Rd
185 ([Mitra and Sen](#)), the other remaining contributions relate to records of Earth's high-temperature
186 geochemical processes and histories of deep-Earth reservoirs. [Van der Meer *et al.*](#), assess the HSE and
187 Re-Os isotope systematics of a suite of xenoliths from Venetia's diamondiferous mantle situated in
188 the Limpopo Mobile Belt, which is sandwiched between the Kaapvaal and Zimbabwe Cratons. An
189 important finding of this study is that a sub-set of the studied samples define a virtually isochronous
190 relationship that gives a ~3.28 Ga age, which overlaps with the time at which the overlying Limpopo
191 crust forms, and is linked to rapid crustal recycling of the mantle lithosphere within ~100 Myrs of the
192 melt extraction event. Significantly, the broadly isochronous age is in excess of the range of

193 calculated Re-depletion ages (T_{RD}) for the suite of mantle xenoliths – including the most depleted
194 samples. This finding emphasizes the fact that Re-depletion model ages are minimums, can
195 significantly underestimate the time of major mantle differentiation events, and may result in spurious
196 overlap with the time of other crustal events. A careful assessment of the complex nature of
197 unequilibrated $^{187}\text{Os}/^{188}\text{Os}$ records among sulphides of a limited number of mantle xenoliths of
198 Somerset Island, Rae Craton, Arctic Canada (Bragagni *et al*) provides further reason to treat whole-
199 rock T_{RD} ages with great caution, and emphasizes the utility of integrated HSE-abundance and
200 petrologic studies in assessing the long and complex histories of these types of deeply derived
201 samples. Despite these challenges, the authors link peaks among sulphide T_{RD} age populations to
202 regional events of geodynamic importance at ~2.8 Ga (craton building), ~2.2 Ga (rifting), and ~1.9
203 Ga (orogenesis). A study of Eoarchean tectonically-emplaced mantle and metakomatiites by Ishikawa
204 *et al*. provides HSE-abundance and Re-Os isotope data that is considered to testify to their derivation
205 from a mantle with broadly-chondritic relative abundances of HSE but at concentrations ~10-20 %
206 lower than Earth's present-day upper mantle. This provides tantalizing evidence that late-accretion
207 added broadly-chondritic materials over a prolonged period extending from the Hadean through into
208 the Archean, the early mantle of which may have been distinct to the modern mantle at a global-scale.

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

228 Three of the concluding articles of this special issue explore topics linked to shallow-level volcanics
229 and are of broad relevance to the exploration of precious metals. The HSE-abundance systematics of
230 kimberlites from the Karelian and Kaapvaal Cratons are utilised by Maier *et al* to constrain the
231 portion of fragmented and partially digested mantle material present and mixed with a modelled melt
232 composition. These authors infer that the metasomatised component of the Karelian and Kaapvaal
233 Cratons is relatively poor in HSE and that the prospectivity of large igneous province magmas for
234 HSEs (with the exception of Au) is not controlled by their interaction with lithospheric mantle during
235 ascent. The processes influencing the Cu and Au fertility of felsic rocks is assessed by Hao *et al*
236 through a multi-element study that utilised the platinum-group-elements to constrain the relative
237 timing of sulphide- and volatile-saturation in relation to the tenor of associated hydrothermal
238 mineralisation. The authors' principal findings are that the ore-grade suites result from a wetter
239 magma that experienced relatively late sulphide saturation followed shortly thereafter by volatile
240 saturation. With respect to ores and their grade, Rayleigh fractionation is inferred to be at least as
241 important as the initial concentration of the chalcophile elements in the parent magma. In contrast to
242 the felsic ore bodies, the barren suites reflect a relatively dry magma in which sulphide saturation was

243 reached early and locked-away the Cu and Au in a cumulus pile at depth. To constrain the factors
244 responsible for the well-known enrichment of a sub-set of HSEs in Cr-spinel, and to understand the
245 influence that the fractionation of this phase exerts on the HSE chemistry of primitive magmas, [Park](#)
246 *et al* provide new *in situ* data with which to assess the compositional systematics of Cr-spinel phases
247 in a number of volcanic suites that were generated in a range of tectonic settings. These authors
248 identify systematic differences between Cr-spinels of different tectonic settings and show that
249 enrichment of Rh, Ir, Os, and Ru is a function of the parental melt composition and the magnetite
250 (Fe^{3+}) component of the spinel. In addition, the relatively low temperature of arc magmas in
251 comparison to intra-plate and MORB melts permits arc-group Cr-spinels to have more octahedral sites
252 at equivalent magnetite components, and this could account for the significantly higher partition
253 coefficient of Ru for this suite of spinels. Collectively, the characteristics and fractional crystallisation
254 of Cr-spinel in arc magmas are argued to account for the highly-fractionated HSE systematics of arc
255 basalts.

256 1.5 Concluding remarks

257 On behalf of the guest editorial team I would like to thank all of the authors for their contributions to
258 this special issue. This gratitude is offered to those authors that were able to adhere to the relatively
259 tight schedule and also to those that have ultimately opted to allow additional time to deliberate and
260 further develop their research. I would also like to acknowledge the important input provided by all
261 participants of the 4th International Workshop on HSE Geochemistry who contributed immeasurably
262 to the discussion of presented works. The wider-community is acknowledged for the engagement with
263 these recent efforts to foster exchange among HSE scientists. The amassed body of reviewers around
264 the globe is also offered particular thanks for their heroic efforts to critically evaluate submitted
265 articles in a timely fashion. The staff of the editorial office of *Geochimica et Cosmochimica Acta* and
266 the Executive Editor, Marc Norman, provided valuable assistance for which all involved in the
267 production of this special issue are grateful. The 4th International Workshop on Highly Siderophile
268 Element Geochemistry was sponsored by generous awards granted by The Meteoritical Society
269 Endowment Fund, The Geochemical Society's Meeting Assistance Programme, the European
270 Association of Geochemistry, Engineering Design Plastics (UK), ThermoFisher Scientific, Nu
271 Instruments, the UK's Geochemistry Group, the Applied Mineralogy Group, the UK Mineral Deposits
272 Studies Group, and the Volcanic and Magmatic Studies Group.

273

274

275 Amy J. V. Riches

276 Marie Curie Fellow

277 Department of Earth Sciences

278 University of Durham

279 Durham, UK

280

281

282 Acknowledgement:

283 AJVR is supported on an Independent Fellowship thanks to funding from the European Union's
284 Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant
285 agreement No 653066.