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Highly Siderophile Element and Os Isotope Systematics of Volcanic Rocks at Divergent and Convergent Plate Boundaries and in Intraplate Settings

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2 **Highly siderophile element and Os isotope systematics of**
3 **volcanic rocks at divergent and convergent plate**
4 **boundaries and in intraplate settings**
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6

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41 INTRODUCTION

42

43 Terrestrial magmatism is dominated by basaltic compositions. This definition encompasses
44 mid-ocean ridge basalts (MORB), which account for more than eighty percent of Earth's volcanic
45 products and which are formed at divergent oceanic plate margins; intraplate volcanic rocks such as
46 ocean island basalts (OIB), continental flood basalts (CFB) and continental rift-related basalts, and
47 highly magnesian ultramafic volcanic rocks that dominantly occur in Archean terranes, termed
48 komatiites. All of these broadly basaltic rocks are considered to form by partial melting of the upper
49 mantle, followed by extraction from their source regions and emplacement at the Earth's surface. For
50 these reasons, basalts can be used to examine the nature and extent of partial melting in the mantle,
51 the compositions of mantle sources, and the interactions between Earth's crust and mantle. Because
52 much of Earth's mantle is inaccessible, basalts offer some of the best 'proxies' for examining mantle
53 composition, mantle convection and crust-mantle interactions. By contrast, at arcs, volcanism is
54 dominated by andesitic rock compositions. While some arcs do have basaltic and picritic magmatism,
55 these magma types are rare in convergent plate margin settings and reflect the complex fractional
56 crystallization and often associated concomitant assimilation processes occurring in arc settings.
57 Despite the limited occurrence of high MgO magmas in arc volcanics, magmas from this tectonic
58 setting are also important for elucidating the behavior of the HSE from creation of basaltic
59 compositions at mid-ocean ridges to the subduction of this crust beneath arcs at convergent plate
60 margins.

61 The highly siderophile elements (HSE; comprising Re and Au, along with the six platinum-
62 group elements [PGE] Os, Ir, Ru, Rh, Pt and Pd) combined with the ^{187}Re - ^{188}Os and ^{190}Pt - ^{186}Os
63 systems that are embedded within these elements, have found significant utility in the study of
64 basaltic rocks (e.g., [Shirey & Walker, 1998](#); [Carlson, 2005](#); [Day, 2013](#)). The greatest strengths of the
65 HSE lie in the fact that they strongly partition into metal or sulfide phases, and so record evidence for
66 processes that are not revealed from other isotope systems commonly used in high-temperature
67 geochemical studies (e.g., He-O-Sr-Nd-Hf-Pb). Partial melting over much of Earth's geological
68 history has resulted in significant fractionation of the HSE between the mantle and the crust (oceanic
69 and continental). The HSE show contrasting behavior during melting, with the platinum-PGE (PPGE;
70 Pt, Pd), Re and Au usually behaving as moderately compatible to moderately incompatible elements
71 during melting and crystallisation, and the iridium-PGE (IPGE; Os, Ir and Ru) acting as highly
72 compatible elements ([Barnes et al., 1985](#)). The differential response of the HSE to partial melting is
73 demonstrated by differences in both the absolute and relative abundances of the HSE in mantle-

74 derived melts and in residual mantle rocks themselves. High degree melts, such as komatiites (e.g.
75 [Puchtel et al., 2009](#)) show a smaller enrichment of PPGE over IPGE than relatively lower degree
76 melts, such as MORB (e.g. [Rehkämper et al., 1999](#); [Bezous et al., 2005](#)) (**Figure 1a**). Mantle
77 peridotites often show a complementary depletion of PPGE relative to the IPGE that reflects the
78 degree of melt depletion (**Figure 1b**), consistent with preferential removal of $\text{Re} > \text{Au} > \text{Pd} > \text{Pt} > \text{Rh}$
79 $> \text{Ir} \geq \text{Ru} \geq \text{Os}$ ([Pearson et al., 2004](#); [Becker et al., 2006](#); [Fischer-Gödde et al., 2011](#)). In the broadest
80 sense, these observations suggest that the HSE in mantle and mantle-derived melts are controlled by
81 both: (i) the degree of melting and; (ii) the mineralogy of mantle rocks. The IPGE are preferentially
82 retained in mantle rocks at low-degrees of melting, consequently, moderate- to low-degree melts such
83 as MORB have relatively low IPGE abundances.

84 Furthermore, because Pt is moderately compatible, Re is moderately incompatible and Os is
85 highly compatible during melt generation, the Re-Os and Pt-Os isotope systems differ significantly
86 from other geologically useful long-lived radiometric systems (e.g., Rb-Sr, Sm-Nd, Lu-Hf, U-Th-Pb),
87 where both the parent and the daughter elements are preferentially concentrated into the melt. In this
88 chapter, we review the distribution of the HSE amongst mantle minerals and their behavior during
89 melting, the HSE abundances and Os isotope compositions preserved at mid-oceanic ridge settings
90 (divergent plate boundaries), intraplate settings and of magmas formed at arcs (convergent plate
91 boundaries), to examine the behavior of these elements in a range of tectonic settings.

92

93 **HIGHLY SIDEROPHILE ELEMENT DISTRIBUTION AND BEHAVIOR IN**

94 **THE UPPER MANTLE**

95

96 **Core formation and the late accretion of impactor material.**

97

98 The HSE have high affinity for both Fe-metal and sulfide over coexisting silicate minerals or
99 silicate melt. Low-pressure metal-silicate partition coefficients determined experimentally are
100 extremely high (between 10^4 and 10^{15}) ([Kimura et al., 1974](#); [Jones and Drake, 1986](#); [Peach et al.,](#)
101 [1990, 1994](#); [Fleet et al., 1991, 1996](#); [Borisov et al., 1994](#); [O'Neill et al., 1995](#); [Holzheid et al., 2000](#);
102 [Ertel et al., 2001](#); [Fortenfant et al., 2003](#); [Yokoyama et al., 2009](#); [Mann et al., 2012](#); [Brenan et al.,](#)
103 [2015, this volume](#)). Consequently, these elements should have been substantially partitioned into
104 Earth's metallic core, leaving the silicate mantles effectively stripped of the HSE. Yet, HSE
105 concentrations in Earth's upper mantle are much greater than predicted from low-pressure
106 experimental data (see [Day et al., 2015, this volume](#)). Moreover, their relative abundances display a

107 broadly chondritic pattern, rather than reflecting differences in their respective metal-silicate partition
108 coefficient (**Figure 2**). However, the siderophile behavior of some HSE may be greatly reduced at
109 high pressure-temperature conditions, and on this basis it has been suggested that high-pressure
110 equilibration at the base of a deep molten silicate layer or ‘magma ocean’ on the early Earth, may
111 account for their abundances in the upper mantle ([Murthy, 1991](#)). High-pressure experiments that
112 simulate the conditions of core formation do indeed indicate that the HSE are less siderophile under
113 these conditions (e.g. [Mann et al., 2012](#)). However, the range of HSE partition coefficients, even at
114 elevated P-T conditions, cannot account for either the absolute or relative abundances in the
115 terrestrial mantle, suggesting that high-pressure equilibration was not the dominant process
116 controlling their present distribution. Therefore, mantle HSE abundances have long been taken to
117 suggest that between 0.5% and 0.8% by mass of ‘late accreted’ broadly-chondritic material was
118 added to Earth after core formation was complete (e.g., [Kimura et al., 1974](#); [Chou, 1978](#)). Differing
119 absolute abundances, but similar chondrite-relative HSE abundances have also been inferred for the
120 Moon, Mars and other meteorite parent-bodies ([Day et al., 2007, 2010a, 2012, 2015 this volume](#); [Day
& Walker, 2015](#); [Brandon et al., 2012](#); [Dale et al., 2012a](#); [Riches et al., 2012](#)), suggesting that late
122 accretion was a phenomenon common to all terrestrial planets, setting the HSE abundances in
123 planetary mantles. In this way, core formation and late addition of meteorite material are thought to
124 have established the HSE abundance in Earth’s silicate mantle, providing a framework for
125 understanding the long-term effects of mantle melting.

126

127

128 **Highly siderophile elements in mantle minerals**

129

130 The behavior of the HSE during partial melting of the mantle is controlled by their
131 distribution amongst sulfides, platinum group minerals (PGM) and coexisting silicates and oxides in
132 mantle rocks (see also [Lorand and Luguet, 2015, this volume](#); [O’Driscoll and González-Jiménez,
2015, this volume](#); [Harvey et al., 2015, this volume](#); [Becker and Dale, 2015, this volume](#)).

134

135 **Sulfide:** In addition to their strongly siderophile behavior the HSEs are also known to be
136 highly chalcophile (sulfur-loving) hence it has long been known that sulfide in mantle rocks exerts a
137 dominant control over the behavior of HSE (e.g. [Mitchell and Keys, 1981](#)) despite its extremely low
138 abundance (the proportion of sulfide in mantle rocks is thought to be in the range 0.0014 to 0.008%,
139 [Luguet et al., 2003](#)). The exact magnitude of partitioning of the HSE between sulfide and silicate,
140 however, remains poorly constrained with values ranging from 1000 to $>10^8$ (**Figure 3**) ([Peach et al.,](#)

141 1990; 1994; Fleet et al., 1996; Crocket et al., 1997; Andrews and Brenan, 2002a; Gannoun et al.,
142 2004, 2007; Fonseca et al., 2009; Mungall and Brenan, 2014). At least some of this variation is likely
143 to relate to compositional variations of sulfide and silicate, or the conditions under which
144 equilibration occurred. Values at the low end of the range are usually found in natural occurrences of
145 glass and sulfide (e.g. Gannoun et al., 2004, 2007), while the highest values are indirect estimates
146 based on alloy-sulfide and alloy-silicate partitioning (e.g. Fonseca et al., 2009). A particular problem
147 with the “indirect” estimates of alloy-silicate partitioning (Fonseca et al., 2009) is that they were
148 determined for Fe and S-free compositions, precluding the possible formation metal-sulfide
149 complexes (e.g. Gaetani and Grove, 1997). Moreover, the solubility of at least some HSE in silicate
150 melts is enhanced in sulfur-bearing experiments, relative to sulfur-free (Laurenz et al., 2013) bringing
151 partition coefficients into the range of other experimental estimates (Andrews and Brenan, 2002a;
152 Mungall and Brenan, 2014). While the differences in partition coefficient that remain still span up to
153 three orders of magnitude, estimates based on individual experiments or natural coexisting sulfide-
154 silicate show significantly less variation. These data indicate that the PGE (Os, Ir, Ru, Pt and Pd)
155 partition similarly into sulfide, with only Re showing a significant difference to the other HSE.

156
157 During mantle melting, sulfide will be removed in the silicate melt, as a function of
158 temperature, pressure, oxygen fugacity and the iron content of the melt (Wallace and Carmichael,
159 1992; Mavrogenes and O’Neill, 1999; O’Neill and Mavrogenes, 2002). Given the estimated sulfur
160 content of both the primitive mantle ($\sim 250 \pm 50 \mu\text{g g}^{-1} \text{ S}$; Lorand 1990; O’Neill 1991; Palme and
161 O’Neill 2003) and the depleted mantle ($\sim 120\text{-}150 \mu\text{g g}^{-1} \text{ S}$; Salters and Stracke, 2004), and the
162 relatively low degrees of partial melting required to produce most basalts, it is likely that they leave
163 their source sulfide saturated (that is, sulfide remains as a stable mantle mineral). For example, the
164 low HSE content of some low-degree alkali basalt partial melts can be explained by the presence of
165 residual sulfide in the mantle source, while the high HSE content of high-degree mantle melts, such
166 as komatiites, can be explained by exhaustion of sulfide in the source. However, sulfide behavior
167 alone cannot account for the systematic depletion of HSE seen in mantle rocks, or the variable HSE
168 content and very high Re abundances seen in MORB.

169
170
171 **Silicate and oxides:** Rhenium not only partitions into sulfide, but also into other mantle phases
172 including clinopyroxene, orthopyroxene, garnet and spinel (Hart and Ravizza, 1996; Mallman and
173 O’Neill, 2007; Righter and Hauri, 1998, Burton et al., 1999, 2000, 2002), particularly under reducing
174 conditions (Mallman and O’Neill, 2007). The relatively low partition coefficients for Re between

175 silicate phases and melt, and the much lower coefficient for its partitioning between sulfide and
176 silicate melt compared to other HSE, makes this element moderately incompatible during partial
177 melting (Figure 3). The partitioning of Re into silicate then raises the question of to what degree the
178 HSE may also be incorporated into silicates or oxides in mantle rocks. Overall, natural and
179 experimental data suggest that silicate or oxide phases in the mantle do not exert a strong control on
180 the behavior of HSE during partial melting. Taking estimates of the proportion of silicate phases
181 present in the upper mantle (e.g. [Workman and Hart, 2005](#)), partial melting of a sulfide-free mantle
182 would yield melts that are slightly depleted in Os, Ir and Ru, relative to their source. Such a pattern is
183 consistent with that seen for high-degree melts, such as komatiites. Nevertheless, silicate and oxide
184 behavior cannot account for the fractionation of the HSE, and in particular the low Os, Ir and Ru
185 contents, seen in MORB basaltic rocks from all tectonic settings.

186
187 Spinel: Empirical estimates of partitioning derived from mineral separates suggest that Os, Ru and Ir
188 are highly compatible in Cr-bearing spinel with partition coefficients of up to 150, while Pt and Pd
189 are moderately compatible ([Hart and Ravizza, 1996](#); [Puchtel and Humayun, 2001](#)). Experimental
190 work on spinel-silicate melt partitioning at moderate to high oxygen fugacity suggests that for Fe-
191 bearing spinels Ru, Rh and Ir are all highly compatible with partition coefficients of 20 to > 1000
192 (**Figure 4**), whereas Pd is barely compatible ([Capobianco and Drake, 1990](#); [Capobianco et al., 1994](#),
193 [Richter et al., 2004](#)). More recently it has been shown that the partition coefficients for Ir, Rh, and Ru
194 are strongly controlled by the ferric-iron content of the spinels. For Cr-bearing spinels, in which Fe^{3+}
195 is replaced by Cr^{3+} , partition coefficients for Ir and Rh are much lower than for Fe-rich compositions,
196 and Pt and Pd are highly incompatible ([Brenan et al., 2012](#)).

197
198 Olivine: Some of the first empirical data for olivine mineral separates were taken to indicate that Os
199 may be compatible in olivine with an inferred olivine-silicate partition coefficient of ~20 (**Figure 4**),
200 ([Hart and Ravizza, 1996](#)). However, other work on separated olivine suggested that Os is highly
201 incompatible ([Walker et al., 1999](#); [Burton et al., 1999, 2000, 2002](#)). At this stage it is not clear
202 whether these variations reflect compositional differences between samples, or simply the presence
203 of micro-nuggets of sulfide or PGMs in the separated silicate phase. Experimental work, however,
204 suggests that many HSE are weakly compatible or only slightly incompatible in olivine, particularly
205 under reducing conditions ([Brenan et al., 2003, 2005](#)).

206
207 Orthopyroxene and clinopyroxene: Empirical constraints from [Hart and Ravizza \(1996\)](#) suggest that
208 Os may be compatible in orthopyroxene and clinopyroxene (**Figure 4**),, but other studies yield much

209 lower Os concentrations for these phases (relative to coexisting sulfide or olivine) (e.g. [Burton et al.,](#)
210 [1999, 2000](#)). Experimental work indicates that Re may be mildly compatible in ortho- and
211 clinopyroxene under reducing conditions (e.g. [Mallman and O'Neill, 2007](#)), but is incompatible
212 under more oxidizing conditions (e.g. [Watson et al., 1987](#); [Righter and Hauri, 1998](#); [Righter et al.,](#)
213 [2004](#); [Mallman and O'Neill, 2007](#)). While Pt and Pd appear to be mildly compatible in clinopyroxene
214 ([Hill et al., 2000](#); [Righter et al., 2004](#)).

215
216 Overall, natural and experimental data suggest that silicate or oxide phases in the mantle do not exert
217 a strong control on the behavior of HSEs during partial melting. Taking estimates of the proportion of
218 silicate phases present in the upper mantle (e.g. [Workman and Hart, 2005](#)) partial melting of a
219 sulfide-free mantle would yield melts that are slightly depleted in Os, Ir and Ru, relative to their
220 source. Such a pattern is consistent with that seen for high-degree melts, such as komatiites (**Figure**
221 **1a**). Nevertheless, silicate and oxide behavior cannot account for the fractionation of HSEs, and in
222 particular the low Os, Ir and Ru contents, seen in basaltic rocks from all tectonic settings (**Figure 1a**).
223

224 **Refractory mantle sulfide:** For natural magmatic and experimentally produced sulfide the
225 data suggests that while the HSEs are strongly partitioned into this phase there is little fractionation
226 between the elements (with the exception of Re). Mantle sulfides, however, dominantly comprise
227 refractory monosulfide solid solution (MSS) and Cu-rich sulfides, which together control much of the
228 HSE budget of the upper mantle (e.g. [Alard et al., 2000](#)). Petrographic observations suggest that MSS
229 often occurs as inclusions trapped in silicate phases, and is characterized by high Os, Ir and Ru
230 abundances, whereas the interstitial Cu-rich sulfides possess lower Os, Ir and Ru contents (**Figure 5**).
231 The silicate hosted MSS sulfides were interpreted to be the refractory residues of partial melting, and
232 the interstitial sulfides as having crystallised from a sulfide-bearing melt. On the basis of these
233 observations it has been argued that the fractionation of HSE during mantle melting might be
234 accomplished by partitioning between refractory “solid” MSS and liquid sulfide ([Bockrath et al.,](#)
235 [2004a](#)). However, at mantle temperatures of 1300-1400°C and pressures of 5-16 kbar, that is, those
236 appropriate for the generation of MORB (e.g. [Klein and Langmuir, 1987](#)) any refractory sulfide is
237 likely to be completely molten well before the peridotitic silicate and oxide phases start to melt
238 ([Rhyzenko and Kennedy, 1973](#); [Hart and Gaetani, 2006](#)). Consequently, two phases of sulfide are
239 unlikely to be stable during the melting that produces MORB, consistent with modeled depletion of
240 mantle peridotites where MSS-sulfide melt partitioning cannot explain the observed variations in Pd,
241 Pt and Au ([Fisher-Godde et al., 2011](#)). However, under conditions of melting at lower temperatures,
242 for example, due to the presence of volatiles such as H₂O and at fO₂ lower than that at which sulfide

243 is oxidized to sulfate, MSS fractionation may play a role in generating melts with low Os, Ir and Ru
244 contents (Mungall, 2002, Mungall et al., 2006; Dale et al. 2012b; Botcharnikov et al., 2013)

245
246 **Os-Ir-Ru metallic alloys:** Osmium, Ir and Ru (the IPGE) are not only strongly concentrated in
247 refractory monosulfide solid solution, but also in platinum-group minerals (PGM), which encompass
248 alloys and sulfides where Ru, Os and/or Ir are the major metallic elements. It is clear from the
249 distribution and absolute concentrations of IPGE in PGM (**Figure 6**) that precipitation and
250 accumulation of such phases should have a profound effect on IPGE/PPGE fractionation (Brenan and
251 Andrews, 2001). In addition, Pt-rich PGM, such as Pt-Ir alloys, have also been found in upper mantle
252 lithologies (Luguet et al., 2007; Lorand et al., 2010). Palladium-rich PGM also exist, which also may
253 contain Pt, but typically Pd combines with bismuth and/or tellurium to form bismuthotellurides
254 which are thought to be indicators of refertilisation rather than residual to melting (e.g. Lorand et al.,
255 2010). Thus, Os-Ir-Ru and, to a lesser extent, Pt can all be retained by PGM during melting, while
256 Pd is not.

257 Some have argued that PGE-alloys may represent material that was once part of the core, either as a
258 result of incomplete segregation of metal to the core, or due to the entrainment of outer core material
259 into the mantle at the core-mantle boundary (Bird and Weathers, 1975; Bird and Bassett, 1980; Bird
260 et al., 1999). However, recent experimental data suggests that metal originating in the outer core
261 would possess similar concentrations of Os, Pt and Re, rather than show an enrichment in Ru-Os and
262 Ir (van Orman et al., 2008; Hayashi et al., 2009) likewise any metal trapped in the mantle during core
263 formation (e.g. Mann et al., 2012). The solubility of Os, Ir and Ru is extremely low in silicate melts
264 (e.g. Borisov and Palme, 2000; Brenan et al., 2005). Therefore, it has been argued that Os-Ir-Ru-rich
265 PGM may precipitate directly from a silicate melt, through nucleation on nanoclusters of HSE
266 molecules (Tredoux et al., 1995). Furthermore, on the basis of the high solubility of Ir and Ru in
267 sulfide melts it has been proposed that crystallisation of Ru-Ir-Os alloys in the presence of a sulfide
268 liquid is unlikely (Brenan and Andrews, 2001). Rather it has been argued that such alloys can only
269 precipitate from a melt that is sulfide-undersaturated (Brenan and Andrews, 2001; Andrews and
270 Brenan 20002b; Bockrath et al., 2004b; Barnes and Fiorentini, 2008).

271
272 Together, these observations have been taken to suggest that the relationship between Os-Ir-Ru alloys
273 and refractory sulfides in the mantle is key to understanding the behavior of the HSE during higher
274 degrees of partial melting (e.g. Fonseca et al., 2012), where the removal of sulfur in silicate melts
275 leads to a decrease in the proportion of sulfide in the source. All the while that sulfide remains
276 present the HSE are quantitatively retained, and can reach wt. % levels in sulfide. However, as soon

277 as sulfide has been completely dissolved, Os-Ir-Ru-Pt alloys form in response to lowering of fS_2 and
278 diminished metal-sulfide complexation in the silicate melt (Fonseca et al., 2012). Effectively, much
279 of the HSE budget of the mantle, with the exception of Re, remains in the mantle until sulfide has
280 been completely removed, after which time Os-Ir-Ru and Pt are hosted by PGM phases rather than
281 being liberated in a silicate melt. This model is consistent with an increasing number of petrographic
282 observations indicating the presence of PGM phases in melt-depleted mantle peridotite (Luguet et al.,
283 2003, 2007; Pearson et al., 2004; Brandon et al., 2006; Kogiso et al., 2008, Lorand et al., 2010, 2013;
284 Fisher-Gödde et al., 2012).

285 The degree of partial melting needed to trigger PGM formation will depend on how much
286 sulfur there is in the mantle source at the onset of melting, and is also a result of the solubility of S
287 being inversely proportional to pressure (Mavrogenes and O'Neill, 1999). The mantle that melts to
288 produce MORB is already significantly depleted (e.g. Hofmann, 1997), and the melting occurs at
289 relatively shallow levels (e.g. Klein and Langmuir, 1987). However, there is considerable uncertainty
290 as to the amount of sulfur in the depleted mantle, with estimates ranging down to $\sim 120 \mu\text{g g}^{-1}$ (Salters
291 and Stracke, 2004) compared to the concentration in primitive “fertile” (unmelted) mantle at $250 \mu\text{g}$
292 g^{-1} (Lorand, 1990; O'Neill, 1991; Palme and O'Neill, 2003). Taking the S content of the MORB
293 source mantle to be $120 \mu\text{g g}^{-1}$, then 15% melt extraction is needed to exhaust sulfide from the
294 source, and thereby allow the generation of PGM in the mantle residue (Fonseca et al., 2011, 2012;
295 Mungall and Brenan, 2014). While these calculations indicate that even the depleted mantle requires
296 significant degrees of melting to remove sulfide, such melt proportions are well within the range of
297 estimates for the generation of MORB (e.g. Klein and Langmuir, 1987). In this case PGM formation
298 in the upper mantle may be a potential cause for the characteristic depletion of Os, Ir Ru and Rh,
299 relative to Pt and Pd observed in MORB (Figure 7). The absence of significant fractionation of the
300 HSE in komatiites, considered to represent higher-degrees of melting than MORB, suggests that
301 alloys are not stable at the higher pressures and temperatures conditions required for the generation of
302 such melts (cf. Mungall and Brenan, 2014).

303 Overall, the natural and experimental data for mantle minerals indicates that whenever sulfide
304 is present in the mantle, the HSE are largely retained during partial melting, the exception being Re
305 that is not as strongly incorporated into sulfide, and is relatively soluble in silicate melts. However, if
306 base metal sulfide is removed from the system during high degrees of melting, at the pressure
307 temperature conditions appropriate for MORB melting, then this will result in the formation of Os-Ir-
308 Ru alloys and/or sulfides.

309
310

311 **Highly siderophile element behavior accompanying fractional crystallisation**

312
313 The major and trace element variations preserved in mid-ocean ridge basalts indicates that their
314 composition has been extensively modified by fractional crystallisation, prior to eruption on the
315 ocean floor (e.g. [Klein and Langmuir, 1987](#)). The principal silicate phases involved in the fractional
316 crystallisation that generates MORB are olivine, plagioclase and clinopyroxene (e.g. [Klein and](#)
317 [Langmuir, 1987](#); [Grove et al., 1993](#)). In general, the more evolved MORB (that is, those with lower
318 MgO and Ni contents, due to the crystallisation and removal of olivine) possess lower HSE contents
319 (**Figure 7**). On the basis of early empirical estimates for the partitioning of Os into olivine, this
320 relationship has led some to suggest that the HSE are compatible in this phase and removed from the
321 silicate melt. However, as discussed previously, with the exception of Re, there is little evidence to
322 suggest that the HSE are strongly partitioned into olivine, plagioclase or clinopyroxene (**Figure 4**).

323
324 Most MORB are thought to be sulfur saturated ([Wallace and Carmichael, 1992](#)) and sulfide is a
325 ubiquitous phase. Nevertheless, even if MORB melts are sulfur saturated at their source, they are
326 likely to arrive at the surface undersaturated, because the sulfur content at sulfide saturation increases
327 dramatically at lower pressures (e.g. [Mavrogenes and O'Neill, 1999](#)). In this case the only viable
328 mechanism by which MORB melts can become sulfur saturated is through extensive fractional
329 crystallisation, driving the residual melt to higher S contents. Therefore, it seems most likely that it is
330 the fractional crystallisation of olivine, plagioclase and clinopyroxene that drives the melt to sulfur
331 saturation, resulting in the precipitation of sulfide. Hence, the relationship between Ni (concentrated
332 in olivine) and HSE (concentrated in sulfide) can be attributed to the coupled crystallisation of
333 silicates and sulfide.

334
335 Sulfide may be present at relatively high proportions in MORB (up to ~0.23% by mode, [Kiseeva and](#)
336 [Wood, 2015](#)), and it strongly incorporates most HSE (section 2.3, **Figure 3**) with partition
337 coefficients between 10^4 - 10^6 . In contrast, Re, while still being compatible in sulfide, has a
338 sulfide-silicate melt partition coefficient, at least, two orders of magnitude lower than that of the
339 other HSE ($D_{Re} \sim 10^{-3}$). Consequently, MORB sulfides have high Os (and other HSE) contents, and
340 low Re/Os relative to their parental melt, and the effect of sulfur saturation and sulfide crystallisation
341 will be to decrease absolute HSE abundances, and to raise the Re/Os ratio in the residual melt.

342
343

344 THE ^{187}Re - ^{187}Os ISOTOPE SYSTEM AND THE FORMATION OF MID-OCEAN RIDGE
345 BASALTS

346 **Introduction**

347
348 Mid-ocean ridge basalts form by partial melting of the Earth's upper mantle, and variations in their
349 radiogenic isotope compositions or concentration ratios of incompatible elements are considered to
350 reflect compositional heterogeneity in the mantle source (Tatsumoto, 1966; O'Nions et al., 1977;
351 Kay, 1985; Hofmann, 1997). These compositional variations occur on a variety of scales and tectonic
352 settings, ranging from the global-scale of the so-called DUPAL anomaly (centred on the Indian
353 ocean) (Dupré & Allègre, 1983; Hart, 1984; Hamelin & Allègre, 1985; Hamelin et al., 1986; Michard
354 et al., 1986; Price et al., 1986; Dosso et al., 1988; Mahoney et al., 1989, 1992; Rehkamper &
355 Hofmann, 1997; Escrig et al., 2004); to those associated with ocean-island volcanics or near-ridge
356 seamounts (White & Schilling 1978; Zindler et al., 1984; Brandl et al., 2012); to minor pervasive
357 variations within ridge segments of normal MORB (e.g. Hofmann, 1997; Agranier et al., 2005). A
358 number of processes have been put forward to account for these compositional variations including
359 variable degrees of mantle depletion by prior partial melting (e.g. DePaolo & Wasserburg, 1976;
360 Zindler et al., 1984), the infiltration of silicate melts or fluids (e.g. Green, 1971), or recycling of
361 lithospheric material into the mantle (e.g. Hofmann, 1997).

362
363 The ^{187}Re - ^{187}Os isotope system, based on the long-lived β decay of ^{187}Re to ^{187}Os , potentially
364 provides an exceptional tracer of recycled lithosphere in Earth's mantle. This is because both oceanic
365 and continental crust possess exceptionally high Re/Os (parent/daughter ratios), and develop
366 radiogenic Os isotope compositions over time (e.g. Pegram & Allègre, 1992; Shirey & Walker, 1998;
367 Hauri, 2002). In contrast, portions of the lithosphere have low Re/Os, and evolve to unradiogenic Os
368 isotope compositions relative to that of the primitive upper mantle (PUM) (Walker et al., 1989;
369 Pearson et al., 1995). These distinctive isotope signatures can be readily traced as recycled material if
370 mixed back into the convective mantle. For example, the $^{187}\text{Os}/^{188}\text{Os}$ variations seen in HIMU (=
371 high μ = elevated $^{238}\text{U}/^{206}\text{Pb}$) ocean island basalts indicate the presence of material that has evolved
372 over a long-time period with high Re/Os, consistent with models indicating recycled oceanic
373 lithosphere in the source of these volcanic rocks (Zindler and Hart, 1986; Day et al., 2010b; Day,
374 2013).

375
376 Some of the earliest measurements of $^{187}\text{Os}/^{188}\text{Os}$ in MORB also yielded isotope compositions more
377 radiogenic than estimates for the primitive upper mantle (e.g. Martin, 1991; Roy-Barman and

378 [Allègre, 1994](#)) and these were attributed either to contamination by seawater derived Os or melting of
379 a heterogeneous mantle (e.g. [Martin, 1991](#); [Roy-Barman and Allègre, 1994](#)). The work of [Schiano et](#)
380 [al \(1997\)](#) on normal MORB, however, not only indicated relatively radiogenic Os isotope
381 compositions but also that these compositions appeared to covary with the Sr-Nd and Pb isotopes of
382 the same samples. For the DUPAL anomaly, radiogenic Os isotope compositions were taken to
383 indicate the presence of mafic continental crust in the mantle source ([Escrìg et al., 2004](#)). While
384 radiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotope compositions for MORB from the south Atlantic were attributed to
385 metasomatism of the asthenospheric mantle, and local effects from plume-ridge interaction ([Escrìg et](#)
386 [al., 2005](#)). At first sight the data from these studies might be taken to suggest that the Os isotope
387 variations reflect those of the MORB mantle source, rather than a secondary process, and that Os
388 isotopes do indeed act as a sensitive tracer of different recycled or enriched material in the mantle.

389 However, these data also indicate a covariation between the Os isotope composition and the
390 Os elemental abundance in these samples ([Schiano et al., 1997](#); [Escrìg et al., 2005](#)). Covariations
391 between Os, Ni and Mg contents in MORB are most readily explained by fractional crystallisation
392 (e.g. [Burton et al., 2002](#)) but in this case it is then difficult to attribute the Os isotope variations to a
393 mantle source, leading some to propose that the radiogenic Os isotope ratios reported by these studies
394 must result from seawater derived contamination (e.g. [Shirey and Walker, 1998](#); [Hart et al., 1999](#);
395 [Standish et al., 2002](#); [Peucker-Ehrenbrink et al., 2003](#)). Subsequent work demonstrated that many of
396 the MORB previously analysed ([Schiano et al., 1997](#); [Escrìg et al., 2004, 2005](#)) had been affected by
397 an analytical artefact ([Gannoun et al., 2007](#)), nevertheless a number of samples still possess relatively
398 radiogenic isotope compositions ([Gannoun et al., 2004, 2007](#); [Yang et al., 2013](#), [Burton et al., 2015](#)).

400 Despite the potential utility of this isotope system, in particular, for tracing the presence of
401 recycled material in MORB, these studies highlight the particular difficulties of both the
402 measurement and the interpretation of ^{187}Re - ^{187}Os isotope data in MORB. Mid-ocean ridge basalts
403 possess extremely low Os concentrations, usually less than 10 parts per trillion (pg g^{-1}) which, not
404 only makes their accurate measurement exceptionally challenging, but also renders MORB highly
405 susceptible to effects that are rarely seen in lithophile elements isotope systems (such as Rb-Sr or
406 Sm-Nd). Such effects include; (i) Radiogenic ingrowth of ^{187}Os , produced from the decay of ^{187}Re
407 over very short periods of time, (ii) seawater contamination, both direct on the sea floor or indirect in
408 the magmatic plumbing system, and (iii) sample heterogeneity, due to variable contamination in glass
409 or amongst coexisting magmatic phases or through sulfide nugget effects.

410
411

412 **Analytical techniques.**

413

414 Osmium has seven naturally occurring isotopes, two of which ^{187}Os and ^{186}Os are the decay
415 products of long lived radioactive isotopes, ^{187}Re and ^{190}Pt . Of these two decay systems, the Re-Os
416 method has been used as a dating tool and geochemical tracer for over four decades (Shirey and
417 Walker, 1998). Despite its great potential as a geochemical tool, analytical difficulties initially
418 limited the application of the osmium isotope method, mainly because of the high ionization potential
419 of Os (ca. 9eV). The discovery that a solid Os sample could yield negative molecular ions by
420 conventional thermal ionisation (Creaser et al., 1991; Volkening et al., 1991) rendered largely
421 obsolete all the excitation methods for atomic osmium used before (Hirt et al., 1963; Luck and
422 Allègre, 1982; Walker and Fasset, 1986). In the N-TIMS method Os is measured as osmium trioxide
423 (OsO_3^-) via heating on platinum filaments with an electron donor. A Ba–Na emitter solution is
424 employed to lower the work function of the filament, which enhances the emission of negative ions.
425 The formation of the Os oxide species is also advantaged by bleeding oxygen into the source
426 (Walczyk et al., 1991). The ionisation efficiency increases significantly with decreasing Os loads and
427 can reach above 30% at the pg Os level (Birck, 2001; Gannoun and Burton, 2014).

428 Another major problem with Re-Os isotopic analysis has been the chemical behavior of Os in
429 solution because of the numerous oxidation states including the volatile tetroxide species (OsO_4). At
430 present, no single technique is equally applicable to all matrices particularly when organic matter
431 and/or refractory mineral phases are present because the variable oxidation states may inhibit the
432 complete homogenisation of Os between sample and spike.

433 High temperature ($\sim 250^\circ\text{C}$) oxidising digestions using either Carius tubes (Shirey and
434 Walker, 1995) or high-pressure asher (HPA) digestion vessels (Meisel et al., 2003) have the merit of
435 dissolving acid-resistant phases such as chromite and HSE alloys. These methods have been
436 supplemented by employing HF digestion after Carius tube/HPA digestion (e.g., Ishikawa et al.,
437 2014), but with mixed results (Day et al., 2015). However, such techniques can potentially yield high
438 Os blanks ($> 1\text{pg}$) that can contaminate low Os ($\pm\text{PGE}$ and Re) abundance samples, such as MORB.
439 Mid-ocean ridge basalt glass possesses low Os abundances, with some samples in the range of 0.2
440 and 3 pg g^{-1} , in which refractory minerals are usually absent. For these reasons low-temperature
441 digestion techniques have been used in preference to other approaches when analysing Os in MORB.
442 These use HF and HBr in sealed Teflon vessels at temperature of $\leq 140^\circ\text{C}$, followed by extraction of
443 Os in liquid bromine (Birck et al., 1997). Extremely low blanks of $<50\text{ fg}$ of Os have been achieved
444 with this method (Gannoun et al., 2004; 2007). Furthermore, MORB glasses are likely to be
445 completely dissolved in HF-HBr acids mixtures even at room temperature.

446 Mid-ocean ridge basalt sulfide grains can be extracted directly using a magnet and handpicked
447 under a binocular microscope (Gannoun et al., 2004; 2007; Harvey et al., 2006) or removed from
448 hand-polished slabs using a diamond scribe to etch around and under the grains (Warren and Shirey,
449 2012). The grains are weighed, spiked with ^{185}Re - ^{190}Os and dissolved with high purity HBr. The Os
450 fraction is then purified using microdistillation (Birck et al., 1997; Gannoun et al., 2007, Harvey et
451 al., 2006). It is also possible to undertake dissolution simultaneously with microdistillation (Pearson
452 et al., 1998). The purified Re and Os are analysed by NTIMS following the method described by
453 Pearson et al. (1998). Osmium analysis in sulfides can also be achieved using in situ laser ablation
454 techniques. The strength of this technique lies in the ability to relate Os isotope information from
455 individual sulfide to their precise spatial and textural setting in the rock (Pearson et al., 2002).
456 However single sulfide Os data analysed by the N-TIMS technique are typically of a much higher
457 precision than in situ analysis (cf. Gannoun et al., 2007; Harvey et al., 2006; Pearson et al., 1998)
458 even for sulfide with low Os contents (i.e. less than $10\ \mu\text{g g}^{-1}$). Moreover, for in situ analysis, because
459 of the isobaric interference of ^{187}Re on ^{187}Os accurate measurement of $^{187}\text{Os}/^{188}\text{Os}$ is only possible for
460 sulfides with low $^{187}\text{Re}/^{188}\text{Os}$ (Pearson et al., 2002). Such conditions are only met in the case of
461 mantle sulfides.

462

463 **Rhenium-Osmium elemental variations in MORB glass.**

464

465 The fractionation of Re and Os accompanying the generation of MORB is one of the key
466 processes controlling the distribution of these elements between Earth's mantle and crust. Osmium
467 behaves as a highly compatible element during partial melting, and is preferentially retained in the
468 residual mantle. Consequently, MORB have much lower concentrations, ranging from 0.18 to 170 pg
469 g^{-1} (with a mean of $10\ \text{pg g}^{-1}$) than mantle peridotite, ranging from 800 to 13000 pg g^{-1} (with a mean
470 of $3900\ \text{ng g}^{-1}$). In contrast, Re is moderately incompatible during partial melting and preferentially
471 enters the melt. Accordingly, MORB have high Re concentrations, ranging from 480 to 3000 pg g^{-1}
472 (with a mean of $1023\ \text{pg g}^{-1}$) compared to 10 to 450 pg g^{-1} in mantle peridotite (with a mean of 200
473 pg g^{-1}) (**Figure 8**).

474 By comparison, komatiites have generally much higher Os concentrations, up to $10,000\ \text{pg g}^{-1}$,
475 with a similar range of Re concentrations as MORB. These high Re and Os concentrations are
476 generally attributed to higher degrees of melting. Ocean island basalts (OIB) have Os concentrations
477 that range from 1 to $500\ \text{pg g}^{-1}$, and arc lavas from 0.1 to $>10\ \text{pg g}^{-1}$. The low Os concentration of
478 many arc lavas is likely due to extensive removal during fractional crystallization and indeed in cases
479 where basaltic compositions have been sampled Os concentrations can be greater than $50\ \text{pg g}^{-1}$ (Dale

480 [et al., 2012b](#)). The relatively low Re concentration of many arc lavas and OIB was originally thought
481 to reflect differences in the mineralogy of the mantle source or the extent of melting, but it is likely
482 that for many of these samples the low Re concentrations result from volatile behaviour during sub-
483 aerial eruption (e.g. [Lassiter, 2003](#); [Day et al., 2010b](#); [Gannoun et al., 2015b](#)). As outlined previously,
484 the low Os concentration of MORB is likely to result, in part, from preferential partitioning into
485 residual mantle sulfide and/or PGM phases and, in part, to the low solubility of Os in silicate melts.
486 In addition, the Os composition of primitive MORB melts will be further reduced by sulfide
487 segregation during fractional crystallisation. In contrast, the relatively high Re concentrations result,
488 in part from Re being much less strongly incorporated in mantle sulfide and PGM phases and, in part,
489 from much of the Re budget being controlled by silicate phases, and having a much higher solubility
490 in silicate melts. Rhenium, is removed into both silicates and sulfide during fractional crystallisation.

491 A remarkable feature of MORB, and indeed all other terrestrial basalts, is the relatively
492 constantly increasing fractionation of Re/Os with decreasing Os content. The values range from
493 mantle Re/Os values of around 0.01 for Os concentrations of 2-7 ng g⁻¹, to Re/Os values of ~1000 for
494 lavas with concentrations of 0.1 pg g⁻¹ (**Figure 9**). The systematic nature of this fractionation,
495 suggests either that it is dominantly controlled by a single process, such as mantle melting or
496 fractional crystallisation, or else that several process act to have the same effect, for example,
497 fractionation by refractory mantle sulfide and also by sulfide segregation during fractional
498 crystallisation.

499 Rhenium shows a broad positive covariation with Al₂O₃ and sulfur consistent with the
500 incompatibility of all these elements during mantle melting (**Figure 10**). The positive Re–S
501 covariation might be explained by the fact that both elements will be removed into sulfide during
502 fractional crystallization, resulting in a decreasing S and MgO content during the differentiation of S-
503 saturated MORB ([Mathez, 1976](#); [Bezos et al., 2005](#); [Ballhaus et al., 2006](#)). Despite significant scatter,
504 Os broadly covaries with Ni in MORB (**Figure 11**), consistent with a role for olivine crystallisation
505 in Os partitioning. Although previous studies have attributed the Os–Ni covariation directly to the
506 compatibility of Os in olivine ([Brügmann et al., 1987](#); [Hart and Ravizza, 1995](#)), natural samples and
507 experiments indicate that Os is much less compatible. [Burton et al., \(2002\)](#) have shown that Os is in
508 fact extremely incompatible in olivine. Rather it is the crystallisation of olivine that drives the melt to
509 sulfur saturation, which in turn results in sulfide precipitation (in which Os is highly compatible) that
510 is trapped within the olivine as ‘melt inclusions’ ([Walker et al., 1999](#); [Burton et al., 2002](#), [Brenan et](#)
511 [al., 2003, 2005](#)). In summary, Re and Os display similar overall behaviour in MORB from the three
512 major ocean basins. Osmium is highly compatible during melting and fractional crystallisation,
513 whereas Re is moderately incompatible.

514 **The $^{187}\text{Os}/^{188}\text{Os}$ isotope variations in MORB glass.**

515
516 The $^{187}\text{Os}/^{188}\text{Os}$ isotope compositions for MORB from the Pacific, Atlantic and Indian Oceans
517 are shown against the reciprocal of the concentration in **Figure 12**. Mid-ocean ridge basalts from the
518 three major oceans show a similar range of $^{187}\text{Os}/^{188}\text{Os}$ isotope compositions, ranging from 0.126 to
519 0.148 with a mean value of 0.133 ± 0.009 (2σ st. dev.) (Gannoun et al., 2004, 2007; Yang et al., 2013;
520 K W Burton, unpublished data). There is no overall correlation with Os concentration (cf. Schiano et
521 al., 1997; Escrig et al., 2004), however, in general MORB glasses have Os concentrations in the
522 following order: Indian > Atlantic > Pacific, and those samples with a higher Os concentration have a
523 tendency to possess more radiogenic $^{187}\text{Os}/^{188}\text{Os}$ compositions. Comparison of $^{187}\text{Os}/^{188}\text{Os}$ radiogenic
524 ratios with the parent/daughter ratio, $^{187}\text{Re}/^{188}\text{Os}$, on a conventional isotope evolution diagram
525 (**Figure 13**) indicates that there is no systematic covariation. The data do, nevertheless, indicate that
526 MORB glasses with lower $^{187}\text{Re}/^{188}\text{Os}$ are generally found in the Indian > Atlantic > Pacific. In
527 addition, those samples with the lowest $^{187}\text{Re}/^{188}\text{Os}$ tend to possess the most radiogenic isotope
528 compositions.

529 With regard to the long-lived radiogenic isotopes of Sr, Nd and Pb, while the cross-linked
530 data are limited, there are no systematic variations between $^{187}\text{Os}/^{188}\text{Os}$ and $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$,
531 and $^{206}\text{Pb}/^{204}\text{Pb}$ (**Figure 14**). Similarly, there is no correlation between $^{187}\text{Os}/^{188}\text{Os}$ composition and
532 ridge bathymetry or spreading rate (**Figure 15**) (using data compilation of DeMets et al., 2010 and
533 Argus et al., 2011).

534

535

536 **Analytical issues associated with MORB**

537

538 Several studies have reported $^{187}\text{Os}/^{188}\text{Os}$ data for MORB glass (Schiano et al., 1997; Escrig
539 et al., 2004) that could not be reproduced elsewhere, using lower blank techniques (Gannoun et al.,
540 2007; K.W. Burton unpublished data). Comparison of these data shows that for many of the
541 relatively unradiogenic samples there is reasonably good agreement between studies (**Figures 16 and**
542 **17**) but notably none of the very radiogenic values previously reported were reproduced for the same
543 samples. Such a difference might be attributed either to the nature of the samples or the methods
544 involved in their preparation for chemistry. The earlier studies used leaching techniques to remove
545 any Fe-Mn oxyhydroxides that may have accumulated on the glass while on the sea floor. Iron-
546 manganese precipitates, if present, are likely to possess a radiogenic Os isotope composition acquired
547 from seawater ($^{187}\text{Os}/^{188}\text{Os} = \sim 1$), therefore if present they might shift the measured $^{187}\text{Os}/^{188}\text{Os}$ to

548 more radiogenic values. However, experiments on some of the same glasses indicate that extensive
549 leaching, with oxalic acid and HBr, yields indistinguishable results to those for the same glass
550 samples simply rinsed in dilute HCl, ethanol and water. Another possibility is that because of the
551 large sample sizes used in the earlier studies, between 1 and 5 g (Schiano et al., 1997; Escrig et al.,
552 2004) compared to 300 to 500 mg (e.g. Gannoun et al., 2007), phenocrysts possessing radiogenic
553 isotope compositions may have been inadvertently included in the material measured. Likewise,
554 entrainment of included sulfides possessing very radiogenic compositions may have the same effect.
555 If the radiogenic $^{187}\text{Os}/^{188}\text{Os}$ were due to the presence of entrained silicates or sulfides, then some
556 variation in the parent/daughter ratio might be expected (cf. Figure 9 of Day 2013). Such
557 heterogeneity is spectacularly displayed in two samples from the same locality in the Indian Ocean,
558 where significant variations in the isotope and elemental composition of MORB glass can be
559 attributed to the variable presence of sulfide inclusions. However, duplicate and triplicate
560 measurement of eleven of the samples showed no resolvable variation, and there is no evidence for
561 isotope and elemental heterogeneity in any of these glass samples. Therefore, it seems more likely
562 that the difference in measured $^{187}\text{Os}/^{188}\text{Os}$ composition is an analytical artefact. One possibility is
563 that this is due to interference from $^{187}\text{ReO}_3^-$ on the measured $^{187}\text{OsO}_3^-$, although this can be carefully
564 monitored during N-TIMS analysis through the direct measurement of $^{185}\text{ReO}_3^-$. More likely is that
565 the earlier data were under-corrected for the total procedural blank during chemical purification. The
566 blanks of the original studies possessed a radiogenic $^{187}\text{Os}/^{188}\text{Os}$ composition, and the difference
567 between the earlier data (Schiano et al., 1997; Escrig et al., 2004) and those samples that were re-
568 analysed increases with decreasing Os concentration in the sample, consistent with increasing
569 contribution from the blank (Figure 17). Overall, these studies highlight the analytical difficulties of
570 obtaining accurate $^{187}\text{Os}/^{188}\text{Os}$ data for MORB glass many of which possess low Os concentrations
571 (i.e. between 0.2 and 5 pg g^{-1}).

572

573

574 **The origin of the Os isotope variations in MORB glass**

575

576 Notwithstanding any shifts that arise from analytical problems, the data obtained thus far, for
577 all the major oceans, indicates a resolvable variation in the $^{187}\text{Os}/^{188}\text{Os}$ isotope composition of
578 MORB, ranging from values similar to those expected for the primitive upper mantle (e.g. Meisel et
579 al., 1996) to radiogenic compositions akin to those found in ocean island basalts (e.g. Day, 2013). It
580 is unlikely that these data have also been compromised by analytical problems; first, because there is
581 no covariation between the corrected $^{187}\text{Os}/^{188}\text{Os}$ and the Os concentration, as might be expected if

582 the blank concentration was not correctly determined. Second, replicates with differing sample
583 weights and subject to different dissolution technique yield indistinguishable $^{187}\text{Os}/^{188}\text{Os}$ values
584 (Gannoun et al., 2007; Yang et al., 2013, Burton et al., 2015). Moreover, those samples with
585 radiogenic $^{187}\text{Os}/^{188}\text{Os}$ compositions are actually those with the highest Os concentrations, and
586 therefore would be less susceptible to any blank effect. Finally there is no significant covariation
587 between Os and Sr, Nd or Pb isotopes, as might be expected if the variations were due to
588 compositional heterogeneity in the mantle source.

589
590 **Radiogenic growth of ^{187}Os since MORB eruption.** For lithophile elements, such as Sr or Nd,
591 parent/daughter ratios in MORB glass and coexisting silicates are relatively low, consequently shifts
592 in their radiogenic isotope composition are unlikely to have a measurable effect for timescales less
593 than 10^3 million years (e.g. Hofmann, 1997). Therefore variations in Sr or Nd isotope composition
594 preserved in MORB can be attributed to compositional heterogeneity in the upper mantle source (e.g.
595 Hofmann, 1997). For the ^{187}Re - ^{187}Os system however, silicate phases and glass possess exceptionally
596 high $^{187}\text{Re}/^{188}\text{Os}$ (parent/daughter). This then raises the possibility that radiogenic ^{187}Os could be
597 produced in situ from the decay of ^{187}Re over relatively short periods of time (that is a few hundred
598 thousand years or less; e.g. Hauri et al., 2002, Gannoun et al., 2004, 2007). For example, MORB
599 glass possesses $^{187}\text{Re}/^{188}\text{Os}$ with values ranging from 30 to 8000 (Gannoun et al., 2007; Yang et al.,
600 2013), and a glass with $^{187}\text{Re}/^{188}\text{Os} = 4000$ would produce a shift in $^{187}\text{Os}/^{188}\text{Os}$ from mantle values
601 of 0.1296 to a value of 0.14 in less than 250 thousand years (Gannoun et al., 2007). This effect is
602 illustrated in **Figure 13**, where timescales of between 50 ka and > 1 Ma could produce the range of
603 $^{187}\text{Os}/^{188}\text{Os}$ preserved in the MORB glasses if they were simply due to the decay of Re.

604 One approach to determining the age of crystallisation of the MORB glasses is the
605 measurement of short-lived isotopes of Th-U and Ra in the same samples. Such Th-U-Ra data were
606 obtained for a few MORB glasses spanning much of the observed range of $^{187}\text{Os}/^{188}\text{Os}$ compositions
607 for the datasets in Gannoun et al. (2004, 2007). Of those samples measured, if it is assumed that they
608 initially possessed a PUM-like composition at the time of crystallization, then between 700 kyr and
609 1.25 Myr would be required to generate their given $^{187}\text{Os}/^{188}\text{Os}$ isotope compositions. However, the
610 same samples possess $^{230}\text{Th}/^{232}\text{Th}$ activity ratios greater than 1, suggesting that they must be ≤ 350
611 kyr old (that is, the maximum time available before all ^{230}Th has decayed). Moreover, all but one
612 sample has a $^{226}\text{Ra}/^{230}\text{Th}$ activity ratio that is also greater than 1, suggesting those samples must be \leq
613 8 kyr old. Therefore, for these samples, at least, the radiogenic $^{187}\text{Os}/^{188}\text{Os}$ compositions cannot be
614 explained solely as a result of in situ decay of ^{187}Re subsequent to igneous crystallisation (Gannoun
615 et al., 2004, 2007).

616
617 An alternative approach that can be used with phenocryst-bearing MORB samples is to obtain
618 Re-Os isotope data for the constituent phases in MORB, including sulfide, glass, spinel, olivine,
619 clinopyroxene and spinel (Gannoun et al., 2004). If these coexisting phases are in Os isotope
620 equilibrium, then they may yield an isochron that will give the age of crystallisation, and the initial
621 Os isotope composition defined by the best-fit line will correspond to that of the mantle source.
622 However, if some of the phases were assimilated from previously crystallised basalts, gabbro (from
623 deeper in the oceanic crust), or contaminated by seawater, then they may possess different isotope
624 information to that of the host glass or other minerals (Gannoun et al., 2004). ^{187}Re - ^{187}Os data were
625 obtained for coexisting phases from two MORB samples from the FAMOUS region on the mid-
626 Atlantic ridge (Figures 18 and 19). These results illustrate the age information that can be obtained
627 from MORB glass and coexisting phases, some of the processes involved in MORB genesis, and the
628 $^{187}\text{Os}/^{188}\text{Os}$ composition of the MORB source. Sample ARP1974-011-018 (36.85°N; 33.25°W) is an
629 olivine basalt containing olivine (Fo₉₀–Fo₈₀), plagioclase (An₉₁–An₉₅), and clinopyroxene
630 (Wo₄₄En₁₅Fs₅–Wo₄₀En₁₅Fs₉) phenocrysts (up to 1 to 2 mm in diameter) and microphenocrysts in a
631 hyalocrystalline matrix, and, in places, a glassy pillow rim (e.g. Le Roex et al., 1981). The ^{187}Re -
632 ^{187}Os isotope data for matrix, glass, plagioclase, and olivine yield a best-fit line corresponding to an
633 age of 565 ±336 ky and an initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.1265 ±0.0046 (Figure 18). The data for
634 clinopyroxene are distinct from this best-fit line, suggesting either an older age or a different and
635 more radiogenic source for this phase. Sample ARP1973-010-003 (36.8372°N; 33.2482°W; 2760-m
636 water depth) is a porphyritic, picritic basalt with abundant olivine phenocrysts (Fo₉₁–Fo₈₉; up to 5
637 mm in diameter) set in a glassy to hyalocrystalline matrix. Cr-spinel [Cr/(Cr + Al) = 48.01]
638 phenocrysts and sulfide [~14 weight percent (wt %) Ni] blebs (up to 1 mm in diameter) occur as
639 inclusions in olivine or discrete crystals in the groundmass. Plagioclase (An₈₀) microlites are also
640 common (Le Roex et al., 1981, Su and Langmuir, 2003). The ^{187}Re - ^{187}Os data for olivine,
641 plagioclase, glass, and sulfide yield a best-fit line corresponding to an age of 2.53 ±0.15 My and an
642 initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.129 ±0.002 (Figure 19). Spinel, which is relatively Os-rich (Table 1 of
643 Gannoun et al., 2004), possesses a distinct isotope composition from this best-fit line and is probably
644 the phase responsible for the displacement of the matrix from the same line.

645 The simplest interpretation of these data is that the ages represent the time of igneous
646 crystallization and the initial Os isotope composition represents that of the mantle source. The
647 crystallization ages are, however, much older than might be expected from age-distance relations
648 with the ridge axis that suggest ages of 5 to 10 kyr (Selo and Storzer, 1979). They are also different
649 to the ages inferred from the Th-U-Ra isotope composition of the glass. Glass from sample

650 ARP1974-011-018 gives a $^{226}\text{Ra}/^{230}\text{Th}$ activity ratio close to 1, suggesting that the sample is ≤ 8 ky
651 old, whereas the $^{230}\text{Th}/^{232}\text{Th}$ activity ratio is 1.273, suggesting that the sample is ≤ 350 ky old,
652 consistent with previous ^{230}Th data for the same sample (Condomines et al., 1981). Arguably the
653 ^{187}Re - ^{187}Os age of 565 ± 336 kyr is indistinguishable from the ^{230}Th age constraints. Glass from
654 sample ARP1973-010-003 gives $^{226}\text{Ra}/^{230}\text{Th}$ ratio of 1.3, which might at first be taken to indicate that
655 the sample is less than 8 ky old. However, the same sample has a $^{234}\text{U}/^{238}\text{U}$ ratio of 1.043, and such
656 elevated values are often taken to indicate seawater contamination, consistent with previously
657 published data for this sample (Condomines et al., 1981), which raises the possibility that Ra has also
658 been affected by the same seawater contamination. It might be argued that the best-fit lines are due to
659 contamination by radiogenic Os from seawater, rather than having some age significance. This would
660 require that the contamination occurred during mineral crystallization and has affected phases such as
661 olivine and plagioclase in a systematic manner; otherwise, it is difficult to imagine how different
662 phases would align to yield the correlations observed.

663 Alternatively, the data may indicate that few if any of the constituent phases crystallized in
664 their present basalt host (i.e., they are xenocrysts not phenocrysts). There is evidence for assimilation
665 of xenocrystic phases in samples from the FAMOUS region (e.g. Clocchiati, 1977; le Roex et al.,
666 1981; Shimizu, 1998). For example, in this sample high-Al spinel is considered to be a relict from
667 high-pressure crystallization (Sigurdsson and Schilling, 1976), which suggests that spinel is not in Os
668 isotopic equilibrium with the other phases. However, if most of the phases lie on the same best-fit
669 line, then this interpretation demands that all such minerals are xenocrysts. For the picritic basalt, if
670 eruption occurred about 5 to 10 kyr ago, then the Re–Os isotopic data indicate that original
671 crystallization of the minerals occurred about 2.5 Myr prior to this event. In this case, the xenocrysts
672 were assimilated from previously solidified “olivine–plagioclase” basalts, or cumulates through
673 which the present host basalts have ascended.

674 Taken together, these results demonstrate that the radiogenic $^{187}\text{Os}/^{188}\text{Os}$ composition of
675 MORB glass can be readily generated from the decay of ^{187}Re over very short timescales (that is, a
676 few hundred thousand years or less). Nevertheless, the ages obtained for the samples from the
677 FAMOUS region on the mid-Atlantic ridge are much older than might be expected on the basis of
678 their distance from the ridge axis, and this can only be explained either by seawater contamination
679 (that occurred during the crystallisation of magmatic minerals) or by the entrainment of crystals (i.e.
680 xenocrysts) from older oceanic crust.

681
682

683 **Extreme $^{187}\text{Os}/^{188}\text{Os}$ heterogeneity in MORB glass.** Occasionally MORB itself shows
684 significant Os isotope and elemental heterogeneity. For example, replicate measurements of the
685 MORB sample EN026 10D-3 show significant heterogeneity, with $^{187}\text{Os}/^{188}\text{Os}$ isotope compositions
686 that range from 0.128 to > 0.15 (Day et al., 2010b). For MORB glass this is exemplified by two
687 samples from the same locality on the central Indian ridge, MD57 D9-1 and D9-6 (8.01°S; 68.07°E)
688 which show $^{187}\text{Os}/^{188}\text{Os}$ compositions ranging from 0.126 to 0.254, with covariations in Os
689 concentration (**Figure 20**). Those samples with the least radiogenic $^{187}\text{Os}/^{188}\text{Os}$ composition possess
690 unusually high Os concentrations (up to 220 pg g^{-1}). Sulfides from the same samples possess
691 $^{187}\text{Os}/^{188}\text{Os}$ between 0.126 to 0.132, and concentrations between 136 and 246 ng g^{-1} . Given the
692 presence of Os-rich sulfides in these samples, it seems most likely that this heterogeneity is due to the
693 entrainment of this phase. If the radiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotope composition of the glass is simply due
694 to the radiogenic growth of ^{187}Os from the decay of ^{187}Re , since the time of igneous crystallization,
695 then the initial ratio determined from elemental or parent/daughter ratios may reflect the composition
696 of the source (cf. Day, 2013). Alternatively, if the radiogenic composition of the glass is due to
697 seawater contamination or altered oceanic crust then the initial $^{187}\text{Os}/^{188}\text{Os}$ isotope composition
698 determined from such covariations may have little relationship with that of the mantle source.

699
700 **Seawater contamination or assimilation of altered oceanic crust.** The age constraints from
701 spreading rates, Th-U-Ra disequilibria and ^{187}Re - ^{187}Os isotope data for MORB glass and coexisting
702 minerals suggest that the radiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotope compositions of MORB glass cannot be
703 solely explained by an age effect following igneous crystallisation. An alternative possibility is that
704 these radiogenic compositions could be due to seawater contamination, either occurring directly
705 during quenching of the glass on the ocean floor or through the assimilation of hydrothermally
706 altered oceanic crust in the magmatic plumbing system. Seawater possesses a very radiogenic
707 $^{187}\text{Os}/^{188}\text{Os}$ composition (~ 1.026 - 1.046) (e.g. Sharma et al., 2012, Gannoun and Burton, 2014) and a
708 $^{187}\text{Re}/^{188}\text{Os}$ ratio of ~ 3400 , (calculated using the Os concentrations from Sharma et al., 2012,
709 Gannoun and Burton, 2014 and Re from Anbar et al., 1992, Colodner et al., 1993). In this case,
710 seawater contamination could account for both the radiogenic Os isotope composition and the
711 tendency of such samples to possess relatively low $^{187}\text{Re}/^{188}\text{Os}$.

712 Trace elements that are enriched in seawater, such as Cl or B could potentially be used as
713 indicators of seawater contamination. At first sight, however, there is no apparent covariation of
714 either B or Cl with $^{187}\text{Os}/^{188}\text{Os}$ in the MORB glasses. Rather the variations that do exist indicate that
715 many of the samples with radiogenic Os compositions possess low Cl and B concentrations,
716 inconsistent with seawater contamination (**Figure 21**). The difficulty in interpreting Cl and B is that

717 both are highly incompatible elements, and therefore they are strongly affected by partial melting and
718 fractional crystallisation (Michael and Schilling, 1989; Chaussidon and Jambon, 1994; Jambon et al.,
719 1995; Michael and Cornell, 1998). Indeed, Cl and B for the same MORB glasses show a negative
720 covariation with MgO suggesting that fractional crystallisation has strongly influenced their
721 abundances, thereby masking any subtle effects from seawater contamination. Like Cl and B, K also
722 behaves as a highly incompatible element during melting and crystallisation, in this case an
723 alternative approach is to use incompatible element ratios such as B/K or Cl/K that are not
724 significantly fractionated during crystallisation to place some constraints on potential contamination
725 by seawater. For example, mantle Cl/K ratios are lower than 0.08, whereas altered oceanic crust has a
726 Cl/K ratio ~0.1, and seawater ~50 (Michael and Schilling, 1989; Jambon et al., 1995; Michael and
727 Cornell, 1998). However, again there is no clear co-variation of Cl/K with $^{187}\text{Os}/^{188}\text{Os}$, rather the
728 radiogenic Os values appear to possess low Cl/K (Gannoun et al., 2007).

729 A more robust tracer of seawater interaction is provided by $^{11}\text{B}/^{10}\text{B}$ of the MORB glasses. The
730 upper mantle is thought to possess a $\delta^{11}\text{B}$ value (Chaussidon and Marty, 1995) of -10‰ , (where $\delta^{11}\text{B}$
731 $= 1000 \times [(^{11}\text{B}/^{10}\text{B})_{\text{sample}} / (^{11}\text{B}/^{10}\text{B})_{\text{standard}}] - 1$) relative to the borate standard NBS 951 with an $^{11}\text{B}/^{10}\text{B}$
732 ratio of 4.04558). In contrast, for altered oceanic crust $\delta^{11}\text{B}$ ranges from $+2$ to $+9\text{‰}$, seawater has a
733 $\delta^{11}\text{B} = +39.5\text{‰}$ (e.g., Spivak and Edmond, 1987; Smith et al., 1995) and serpentinized oceanic
734 mantle samples can range from $+9\text{‰}$ to $+39\text{‰}$ (Boschi et al., 2008; Vils et al., 2009; Harvey et al.,
735 2014a). While melting and crystallisation processes are unable to significantly fractionate boron
736 isotopes, mixing with altered oceanic crust and mantle can account for the $\delta^{11}\text{B}$ range of -7 to -1‰
737 observed in MORB (Chaussidon and Jambon, 1994).

738 The $\delta^{11}\text{B}$ values of MORB glasses for which $^{187}\text{Os}/^{188}\text{Os}$ data are available range from -9 to
739 $+2\text{‰}$, and those samples with high $\delta^{11}\text{B}$ values also possess radiogenic $^{187}\text{Os}/^{188}\text{Os}$ compositions
740 (Figure 22). The B concentration of seawater is $\sim 4.6 \mu\text{g g}^{-1}$ which is some 5–10 times higher than
741 that of unaltered MORB ($< 1 \mu\text{g g}^{-1}$), whereas the Os concentration in seawater of 10^{-2}pg g^{-1} is some
742 3 orders of magnitude less than that of average MORB. Direct mixing of seawater would be
743 dominated by B at the low mixing proportions suggested in Figure 22 (that is, a horizontal vector in
744 Os versus $\delta^{11}\text{B}$) indicating that the radiogenic $^{187}\text{Os}/^{188}\text{Os}$ and high $\delta^{11}\text{B}$ values cannot be easily
745 explained by direct contamination from seawater. Conversely, contamination from Fe-Mn crust with
746 a seawater Os isotope composition would produce far greater shifts in $^{187}\text{Os}/^{188}\text{Os}$ than B. Rather, the
747 co-variations are entirely consistent with the assimilation of between 5-10% of altered oceanic crust
748 with a variable $^{187}\text{Os}/^{188}\text{Os}$ composition.

749 It might be argued that the relatively heavy $\delta^{11}\text{B}$ values ($> -5\text{‰}$), and the radiogenic
750 $^{187}\text{Os}/^{188}\text{Os}$ could be due to the presence of recycled oceanic crust (present as pyroxenite) in the

751 MORB mantle source. Recycled oceanic crust can lose substantial amounts of Re during subduction
752 (~50% or more, [Becker, 2000](#); [Dale et al., 2007](#)) but Re/Os ratios are still sufficiently elevated to
753 produce radiogenic $^{187}\text{Os}/^{188}\text{Os}$ values with time. However, recent studies suggest that during
754 dehydration of the subducting slab, B is preferentially partitioned into the released fluids, leaving a
755 depleted residue ([Moran et al., 1992](#); [Bebout et al., 1993](#); [Peacock and Hervig, 1999](#); [Nakano and](#)
756 [Nakamura, 2001](#); [Harvey et al., 2014b](#)). Furthermore, boron isotope fractionation occurs during such
757 dehydration and the residue becomes increasingly enriched in the light B isotope (^{10}B) generating
758 light $\delta^{11}\text{B}$ values ([You et al., 1996](#); [Ishikawa et al., 2001](#); [Leeman et al., 2004](#)), rather than the heavy
759 values required to generate the ranges observed in MORB.

760 Notwithstanding analytical difficulties, the Os isotope and elemental variations in MORB
761 glass, the mismatch in age constraints and measured $^{187}\text{Os}/^{188}\text{Os}$ compositions, and the covariations
762 with B isotopes suggest that assimilation of seawater-altered oceanic crust is likely to be the
763 dominant process responsible for the radiogenic Os isotope signal seen in many of the MORB glasses
764 studied thus far.

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766

767 **SULFIDES IN MID-OCEAN RIDGE BASALTS**

768

769 **Petrology and chemistry**

770 Sulfide is a ubiquitous phase in MORB glass, indicating that these melts were sulfur saturated
771 ([Wallace and Carmichael, 1992](#)). Because decompression will drive the melt away from sulfide
772 saturation (e.g. [Mavrogenes and O'Neill, 1999](#)) it might be expected that most MORB would be
773 undersaturated when transported to lower pressures during eruption. The presence of sulfide globules
774 in early crystallising phases, however, clearly indicates that MORB are sulfur saturated during the
775 initial stages of magmatic evolution ([Mathez and Yeats, 1976](#); [Patten et al., 2012](#); [Yang et al., 2014](#))
776 and, as previously suggested for MORB, this sulfur saturation is most likely to result from fractional
777 crystallisation itself. In addition, MORB contain more sulfur than subaerially erupted basalt, because
778 degassing is impaired by the overlying pressure of seawater.

779 Sulfides occur as spherules embedded in the walls of large vesicles ([Moore and Calk, 1971](#);
780 [Moore and Schilling, 1973](#)), as small irregular grains in microcrystalline aggregates of plagioclase
781 and olivine ([Mathez and Yeats, 1976](#)) and as well-developed spherical globules, in glass or in
782 phenocrysts ([Mathez and Yeats, 1976](#); [Czamanske and Moore, 1977](#); [Patten et al., 2012](#); [Roy-Barman](#)
783 [et al., 1998](#)) (**Figures 23a and 23b**). The globules, which range from 5 to 600 μm in diameter, have

784 different textures that can be divided into three groups (Moore and Calk, 1971; Mathez, 1976;
785 Mathez and Yeats, 1976; Czamanske and Moore, 1977; Peach et al., 1990; Roy-Barman et al., 1998;
786 Patten et al., 2012; 2013). The first, comprise a fine grained micrometric intergrowth of Fe-Ni-rich
787 and Cu-Fe-rich sulfide phases that represent quenched monosulfide solid solution (MSS) and
788 intermediate solid solution (ISS). The second, comprise globules of coarser grained intergrowth of
789 MSS and ISS with pentlandite and oxide (Mathez, 1976; Czamanske and Moore, 1977; Patten et al.,
790 2012) and the third group comprise zoned globules that consist of two massive and distinct grains of
791 MSS and ISS, first identified recently by Patten et al. (2012).

792 Pentlandite and oxide occur to a lesser extent in all types of textures. Sulfide droplets with
793 different sizes and textures may coexist in the same MORB sample. Patten et al. (2012) have shown
794 that sulfide droplets exhibiting all three textures may be present in the same sample separated by only
795 few millimetres, (cf. Czamanske and Moore, 1977). Patten et al. (2012) also observed a relationship
796 between the size of the droplets and their textures. Below 30 μm , over 90% of the droplets have a
797 fine grained texture and between 30 and 50 μm , 60% of the sulfide droplets are coarse-grained. In
798 contrast, above 50 μm all the droplets are zoned.

799 Sulfide globules usually comprise fine-grained exsolution of Fe-Ni and Cu-rich sulfide
800 phases. When the bulk compositions of sulfide are calculated to 100%, in order to estimate liquidus
801 temperature of the MSS using the Ebel and Naldrett (1997) approach for O-free systems, they
802 showed low variability in S content, moderate variability in Fe contents and high variability in Cu
803 and Ni contents (Patten et al., 2012). **Figure 24** shows the bulk composition of sulfide globules in the
804 Fe-Ni-Cu system. The limited field of such bulk compositions confirms the agreement between
805 different studies (Czamanske and Moore, 1977; Roy-Barman et al., 1998; Patten et al., 2012). The
806 dashed lines in **Figure 24** indicate the sulfide liquid at crystallisation temperatures of the MSS at
807 1100, 1050 and 1000°C from Ebel and Naldrett (1997). The liquidus temperature of the sulfide
808 globules from MORB determined in this way, range from slightly above 1100°C to 1030°C where
809 globules are randomly distributed over this temperature interval irrespective of their size or textures
810 (cf. Patten et al., 2012).

811 Pentlandite occurs to a lesser extent than MSS and ISS in all textures of sulfides. Oxide also
812 occurs either inside MSS, inside ISS or at their interface, comprising up to 7% of some sulfide
813 globules. Oxides are best developed in zoned droplets and electron probe analyses reveal that they
814 are Ti-free magnetite (Patten et al., 2012) in agreement with Czamanske and Moore (1977), who
815 suggested that a few percent of magnetite is common in sulfide globules in MORB.

816
817

818 ¹⁸⁷Re-¹⁸⁷Os behaviour in MORB sulfide

819

820 If present, sulfide dominates the Os budget in MORB, where sulfide-silicate partition
821 coefficients for Os in basaltic system are in the range $\sim 10^4$ – 10^6 (Roy-Barman et al., 1998; Gannoun
822 et al., 2004, 2007). In contrast, Re while still being highly compatible in sulfide, has a partition
823 coefficient at least two orders of magnitude lower than that of Os ($\sim 10^1$ – 10^3 ; Roy-Barman et al.,
824 1998; Gannoun et al., 2004, 2007) similar to that of Cu (Peach et al., 1990; Gaetani and Grove,
825 1997). As a result of the difference in partitioning of Re and Os, MORB sulfides have high Os
826 concentrations (tens to a few hundreds of ng g⁻¹) and a low Re/Os relative to their coexisting glass
827 (some 3 orders of magnitude lower). Consequently, sulfide is much less susceptible to the effects of
828 seawater assimilation, or radiogenic in-growth, than coexisting silicate minerals or glass (Roy-
829 Barman et al., 1998; Gannoun et al., 2004, 2007).

830 For those sulfides for which Os isotope and elemental abundances have been measured thus
831 far, there is a clear covariation between ¹⁸⁷Os/¹⁸⁸Os and the Os concentration (**Figure 25**). Where
832 those sulfides with low Os concentrations (i.e. ≤ 10 ng g⁻¹) possess ¹⁸⁷Os/¹⁸⁸Os compositions > 0.15 ,
833 and those with high Os concentrations (i.e. ≥ 100 ng g⁻¹) possess ¹⁸⁷Os/¹⁸⁸Os compositions around
834 ~ 0.13 or less. At first sight, this relationship might be taken to indicate that the sulfide globules, like
835 their host glass have been systematically affected by contamination with material derived from
836 altered oceanic crust. There is no clear relationship between the Os concentration of the sulfide and
837 that of the host glass. However, with one exception, sulfides possess ¹⁸⁷Os/¹⁸⁸Os values that are less
838 radiogenic than their glass host, where in general, the more radiogenic the host glass the greater the
839 difference in ¹⁸⁷Os/¹⁸⁸Os with coexisting sulfide (**Figure 26**). It is difficult to explain such a
840 difference between sulfide and glass simply by radiogenic decay of ¹⁸⁷Re, rather it suggests that the
841 ¹⁸⁷Os/¹⁸⁸Os composition of the glass has been more significantly affected by the assimilation of older
842 oceanic crustal material than the coexisting sulfide.

843 If MORB sulfides preserve ¹⁸⁷Os/¹⁸⁸Os compositions that are systematically less radiogenic
844 than their host silicate glass then this has some important implications for the timing of
845 contamination relative to crystallisation. If contamination of the silicate melt occurred before sulfide
846 precipitation then the sulfide should possess an Os isotope composition that is indistinguishable from
847 that of the melt. Therefore, the contrasting Os isotope composition of the glass and sulfide suggests
848 that the silicate melt experienced contamination after the segregation of sulfide in the melt.

849 At the high temperatures of MORB eruption ($\sim 1200^\circ\text{C}$) most sulfides will be present as liquid
850 globules rather than as a solid phase, and diffusional equilibration between silicate and sulfide liquids
851 is likely to be rapid. The time in which a sulfide globule will equilibrate its Os isotope composition

852 with a melt can be assessed using simple diffusion calculations. Using an implicit finite difference
853 model (Crank, 1975) and assuming a sulfide globule radius of 250 μm and a silicate-sulfide melt
854 diffusion coefficient of $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ the sulfide will equilibrate with the melt in ~ 12 h (Gannoun et
855 al., 2007). This is a relatively conservative estimate because cation diffusion in most basaltic melts is
856 10^{-5} to $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (Watson and Baker, 1975), whereas diffusion rates in pyrrhotite are likely to be
857 faster than $10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at magmatic temperatures (Brenan et al., 2000). Therefore, under normal
858 circumstances, complete equilibration between sulfide and glass would be expected, with both
859 possessing an indistinguishable $^{187}\text{Os}/^{188}\text{Os}$ composition. However, because of the large
860 concentration difference between the sulfide and the silicate liquid, a large amount of melt has to
861 exchange with a small sulfide bleb before the sulfide reaches Os isotope equilibrium with the glass. It
862 is possible to calculate the volume (and mass) of melt that is needed to equilibrate the sulfide using
863 simple mass balance equations and the concentration and isotopic data for the glass and sulfides
864 obtained here. Assuming initial $^{187}\text{Os}/^{188}\text{Os}$ for the sulfides of 0.125 and a sulfide globule radius of
865 250 μm , then sulfides will have only equilibrated with $<0.5 \text{ cm}^3$ of melt (or less if the sulfide blebs
866 were smaller). This suggests that the sulfides have only exchanged with the immediate melt
867 surrounding the sulfide. Furthermore, a sulfide that contains $>200 \text{ ng g}^{-1}$ Os would have to exchange
868 with $<50 \text{ cm}^3$ of melt in order to completely equilibrate with that melt. Thus, the absence of any Os
869 isotope or elemental covariation between the sulfides and their host glass suggests that Os isotope
870 exchange is likely to have been limited. These observations are consistent with Pd elemental data for
871 MORB from the SouthWest Indian Ridge taken to suggest that segregated sulfides were poorly
872 equilibrated with their host silicate magmas (Yang et al., 2013).

873 Nevertheless, many, if not all of the sulfides analysed thus far are likely to have been
874 modified by contamination, depending on their Os concentration. The sulfides with $^{187}\text{Os}/^{188}\text{Os}$
875 compositions > 0.13 have most likely been significantly modified through partial exchange with the
876 contaminated silicate melt. Although those sulfides with a high Os concentration ($>20 \text{ ng g}^{-1}$) may
877 have also been affected by such exchange they do, however, yield the least radiogenic compositions
878 yet observed in normal MORB samples.

879

880 **The $^{187}\text{Os}/^{188}\text{Os}$ isotope composition of the MORB mantle source**

881

882 The MORB glass measured thus far preserves variations in $^{187}\text{Os}/^{188}\text{Os}$ extending from
883 unradiogenic values as low as 0.125, comparable to estimates for the primitive upper mantle, to
884 radiogenic values up to 0.25. There are no clear covariations with lithophile element isotopes, such as
885 Sr or Nd, as might be expected from Os isotopic heterogeneity inherited for a mantle source. Rather,

886 the radiogenic Os isotope compositions show a relationship with B isotopes that is most simply
887 attributed to seawater-derived contamination that occurs during magma ascent. In this case, to a
888 greater or lesser extent all MORB glass has been affected by seawater contamination. Individual
889 sulfide grains appear to provide a much more robust record of the primary Os isotope signature (Roy-
890 Barman et al., 1998; Gannoun et al., 2004; 2007, Burton et al., 2015) although even this phase
891 appears to be susceptible to seawater-derived contamination. In this case it is difficult to assess the
892 extent to which any radiogenic signal, preserved in either glass or sulfide, is due to an age effect
893 caused by ^{187}Re decay following igneous crystallisation, or the presence of Re-enriched material,
894 such as recycled oceanic crust in the MORB source.

895 Assuming that the Os isotope information preserved by high-Os sulfide grains has been
896 minimally affected by seawater contamination then they potentially provide some unique constraints
897 on the nature of the MORB source. A fundamental assumption underlying the use of radiogenic
898 isotopes, such as Sr, Nd and Os, in mantle derived basalts is that they are in equilibrium with their
899 mantle source (e.g., Hofmann and Hart, 1978). Abyssal peridotites are ultramafic rocks thought to
900 represent the residue of the melting responsible for generating MORB (Dick et al., 1984; Johnson and
901 Dick, 1992; Brenan et al., 2000). Consequently during melting and basalt genesis the composition of
902 long-lived isotopes of heavy elements in both MORB and residual abyssal peridotites should be the
903 same. The average $^{187}\text{Os}/^{188}\text{Os}$ composition of abyssal peridotites is 0.127 ± 0.015 ($n = 129$) (**Figure**
904 **27**), however, like MORB, abyssal peridotites are also susceptible to seawater alteration during their
905 exhumation on the sea floor, which may shift the composition towards radiogenic values. In this case
906 individual abyssal peridotite sulfides are likely to yield a more reliable indication of their primary Os
907 isotope composition, and these yield an average $^{187}\text{Os}/^{188}\text{Os}$ composition of 0.125 ± 0.021 ($n = 63$).
908 The best estimate for the $^{187}\text{Os}/^{188}\text{Os}$ composition of the primitive upper mantle, that is a theoretical
909 mantle composition with high Al_2O_3 that is considered to have experienced no depletion through
910 melting, is 0.1296 ± 0.009 (2σ ; $n = 117$) (Meisel et al., 2001). By comparison, the high-Os ($>20 \text{ ng g}^{-1}$)
911 sulfides from MORB yield an average composition of 0.129 ± 0.005 ($n = 31$) with values as low as
912 0.1236 (**Figure 27**). Therefore, these high-Os sulfides show no evidence for significant Re
913 enrichment in the MORB source that might accompany the presence of recycled oceanic crust.
914 Rather they indicate that the upper mantle source of these samples has experienced a long-term
915 depletion of Re, similar to that observed in abyssal peridotites, and consistent with the incompatible
916 nature of this element during mantle melting.

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919

LOWER OCEANIC CRUST

920
921
922 The oceanic crust comprises some 1-1.5 km of basalt and dolerite that is underlain by 4-5 km of
923 gabbro. Therefore, mid-ocean ridge basalts are thought to be evolved lavas formed by fractional
924 crystallisation in the lower oceanic crust, that itself comprises plutonic rocks and cumulates, from
925 primitive magmas. Given that Re is moderately incompatible while Os is compatible during mantle
926 melting, one might expect that gabbros in the lower crust would have higher Os and lower Re
927 concentration and accordingly low Re/Os ratios than evolved MORB assuming that the phases that
928 control solid/liquid partitioning of Re and Os during crystallization are similar to those involved
929 during partial melting. Gabbroic lower oceanic crust should therefore dominate the PGE budget of
930 the oceanic crust as whole.

931
932 However, the first reported siderophile element data for gabbros from Ocean Drilling Program (ODP)
933 Site 735 (Blusztajn et al., 2000) yielded rather low PGE concentrations (**Figure 28**), even lower than
934 average MORB (Bezous et al., 2005; Gannoun et al., 2007) pointing to their evolved compositions.
935 Indeed, Dick et al. (2000) and Hart et al. (1999) noted that the average composition of gabbro from
936 ODP Site 735B is closer to that of average MORB (on the basis of major and trace element
937 systematics). Consequently, the gabbro recovered at this site cannot be considered as the primitive
938 complement to typical evolved MORB. More recently, Peucker-Ehrenbrink et al. (2012) have argued
939 that all prior geochemical work on in situ upper oceanic crust such as DSDP-ODP sites 417, 418 and
940 504 (Bach et al., 2003; Peucker-Ehrenbrink et al., 2003), and 801 (Reisberg et al., 2008), and evolved
941 gabbros at ODP 735 (Hart et al., 1999; Blusztajn et al., 2000), and site 894 (Lecuyer and Reynard,
942 1996) failed to reproduce the true average for the complementary crustal reservoir to MORB lavas
943 and therefore needs to be complemented with more detailed geochemical and petrologic studies of
944 primitive gabbroic material from the lower crust.

945
946 In order to more accurately assess the global HSE chemistry of the whole oceanic crust Peucker-
947 Ehrenbrink et al. (2012) obtained data for an oceanic crust section from the Oman ophiolite that
948 includes the crust-mantle transition. The mean weighted composition of the 4680 m Oman section
949 yielded Re 427 pg/g, Os 55pg/g, Ir 182 pg/g, Pd 2846 pg/g, Pt 4151 pg/g and initial $^{187}\text{Os}/^{188}\text{Os}$ of
950 0.142, indicating higher PGE concentration and lower Re concentration than all data previously
951 reported on partial sections of ocean crust that lack cumulate lower crust. Assuming that these data
952 are truly representative of the lower oceanic crust then they suggest that these rocks are the main

953 PGE reservoir in the oceanic crust as a whole and that the average Re in these gabbros is much lower
954 than in MORB lavas (Re ~1070 pg/g; [Hauri and Hart, 1997](#); [Gannoun et al., 2007](#); [This chapter](#)). The
955 Oman gabbros are characterised by a distinct subchondritic average Os/Ir ratio of ~ 0.3 which is
956 significantly different from the chondritic ratio or the primitive upper mantle value of ~ 1.1 ([Becker
957 et al., 2006](#); [Lodders et al., 2009](#)). This difference is surprising because Ir is generally viewed as a
958 geochemical analogue of Os during magmatic processes ([Becker et al., 2006](#); [Puchtel and Humayun,
959 2000](#)). The Os/Ir fractionation observed in the Oman gabbros, while within the range observed in
960 MORB (0.2-1.4 average 0.6), is the opposite of that observed in the upper crustal part from DSDP
961 504B (average Os/Ir of ~2.4; [Peucker-Ehrenbrink et al., 2003](#)). However the Os/Ir of abyssal
962 peridotites in general and in the harzburgitic mantle section of Oman in particular, remains chondritic
963 ([Hanghoj et al., 2010](#)). If such harzburgites are representative of the mantle source then the
964 subchondritic Os/Ir ratio in Oman gabbros cannot reflect a source signature. [Hanghoj et al. \(2010\)](#)
965 report both superchondritic and subchondritic Os/Ir ratios in Oman dunites (0.5 - 8.3). As Os and Ir
966 alloys included in chromites have been observed in Oman dunites ([Ahmed and Arai, 2002](#); [Ahmed et
967 al., 2006](#)), [Peucker-Ehrenbrink et al. \(2012\)](#) suggested that such a phase may be responsible for the
968 fractionation of Os from Ir during melting, melt extraction or crystal fractionation.

969
970 Estimating the HSE inventory of the whole ocean crust remains challenging because of the
971 discontinuous nature of the field sampling and the question of how representative are the samples that
972 have been analysed thus far. [Peucker-Ehrenbrink et al. \(2012\)](#) used data from Site 504B for the upper
973 oceanic crust ([Peucker-Ehrenbrink et al., 2003](#)) combined that for the Oman ophiolite for the lower
974 oceanic crust ([Peucker-Ehrenbrink et al., 2012](#)). The weighted chemical and isotope characteristics of
975 this “composite” oceanic crust (**Figure 28**), corrected for Re decay since emplacement, are 736 pg/g
976 Re, 45 pg/g Os, 133 pg/g Ir, 2122 pg/g Pd, 2072 pg/g Pt, $^{187}\text{Re}/^{188}\text{Os}$: 80 and $^{187}\text{Os}/^{188}\text{Os}$: 0.144. Such
977 crust is more enriched in Re and less depleted in PGE than observed in average gabbros from ODP
978 Hole 735D. Therefore, unless fundamentally altered during subduction, subducted oceanic crust will
979 evolve to form a PGE-depleted, Re-rich mantle component that over time will evolve to radiogenic
980 $^{187}\text{Os}/^{188}\text{Os}$ isotope compositions. However, the projected ingrowth of radiogenic $^{187}\text{Os}/^{188}\text{Os}$ may be
981 inhibited by the loss of Re from the basaltic upper part of the crust during eclogite-facies
982 metamorphism ([Becker et al., 2000](#); [Dale et al., 2007](#)) but not the gabbroic lower part of the crust
983 ([Dale et al., 2007](#)).

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987 **Assimilation of gabbroic lower crust**

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989 Recent work has shown that the crystallization of gabbros, troctolites and other plutonic rocks of the
990 lower oceanic crust may be protracted, and that these rocks sometimes possess ages that are several
991 million years older than predicted from the magnetic ages of the overlying basaltic crust (e.g.
992 [Schwartz et al., 2005](#); [Grimes et al., 2008](#)). This extended timescale for the growth of the lower
993 oceanic crust has been attributed to the crystallisation of gabbros in the mantle followed by uplift to
994 lower crustal depths ([Schwartz et al., 2005](#); [Grimes et al., 2008](#)). Such uplift may relate to unroofing
995 by low-angle detachment faults, typical of asymmetrical spreading ridge segments (e.g. [Lissenburg et](#)
996 [al., 2009](#)).

997

998 Over a timescale of several million years gabbros and troctolites, and their constituent phases, in the
999 lower oceanic crust will rapidly evolve to radiogenic Os isotope compositions. This raises the
1000 possibility that younger melts passing through older lower crust may acquire a radiogenic Os isotope
1001 composition, either by remelting and assimilation of older material or through the physical
1002 entrainment of older crystals. Primitive xenocrysts are commonly found in MORB (e.g. [Dungan and](#)
1003 [Rhodes, 1978](#); [Coogan, 2014](#)) with evidence for mixing shortly before eruption (e.g. [Moore et al.,](#)
1004 [2014](#)). Indeed, as discussed previously, the old ages of phenocryst phases in basalts that are thought
1005 to have been erupted just 5 to 10 ka (**Figures 18 and 19**), may indicate that these are rather
1006 xenocrysts physically entrained from previously solidified “olivine–plagioclase” bearing plutonic
1007 rocks through which the present host basalts have ascended. In this case, it is possible that some
1008 MORB glass may acquire a radiogenic Os isotope composition without interaction with seawater
1009 altered oceanic crust, or the presence of a radiogenic mantle source. For MORB glass such a
1010 signature might be distinguished by the absence of any covariation with Cl abundance or B isotopes.

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1019 HSE ABUNDANCES AND RE-OS ISOTOPE SYSTEMATICS OF INTRAPLATE VOLCANISM

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1021 The HSE and Re-Os systematics of intraplate volcanism were reviewed recently by Day
1022 (2013). The purpose of this section is to briefly summarize the likely origins of intraplate volcanism,
1023 based specifically upon HSE abundance and Re-Os isotope constraints, and to provide a brief update
1024 of developments in the field since 2013. In particular, and mostly as a function of the difficulties
1025 associated with producing precise $^{186}\text{Os}/^{188}\text{Os}$ data (e.g., Chatterjee and Lassiter, 2015), there has
1026 been no significant advances in the application of the Pt-Os isotope system to intraplate volcanism
1027 since Day (2013); the interested reader is referred to this earlier review article for an up to date
1028 appraisal of Pt-Os systematics.

1029 The origin of intraplate volcanism has been variously attributed to (i) mantle plumes (Wilson,
1030 1963; Morgan, 1971), (ii) plumes which are not particularly “hot” (e.g., Falloon et al., 2007; Putirka
1031 et al., 2007), (iii) stress-driven processes (Anguita and Hernan, 1975) or (iv) chemical heterogeneities
1032 preserved in the upper mantle (e.g., Courtillot et al., 2003; Arndt, 2012). The occurrence of intraplate
1033 volcanism does not appear to be related to proximity to plate boundaries (cf. Hawaii; Wilson, 1963
1034 versus the Canary Islands; Morgan, 1971) and does not occur systematically on either the continents
1035 or within oceanic basins, even spanning continental–oceanic margins (i.e., the Cameroon Line;
1036 Rehkämper et al., 1997; Gannoun et al., 2015a). Intraplate volcanism can be associated with
1037 convergent (e.g. Samoa; Wright and White, 1987) and divergent (e.g. Iceland; Morgan, 1971)
1038 tectonic settings.

1039 In general, intraplate volcanism is controlled by anomalous thermo-chemical and/or tectonic
1040 conditions capable of producing large volumes of extrusive products. Many investigations into the
1041 HSE of intraplate volcanic rocks have predominantly featured primitive, high-MgO rocks, e.g.,
1042 komatiites and picrites (e.g. Connolly et al., 2011; Ireland et al., 2009, respectively), because of the
1043 compatibility of the HSE during fractional crystallisation, and the sensitivity of $^{187}\text{Os}/^{188}\text{Os}$ to crustal
1044 assimilation processes in more evolved magmas (e.g., Chu et al., 2013). However, evolved potassic
1045 and sodic mafic-alkaline volcanic rocks and phonolites, trachytes and rhyolites, which may have
1046 experienced extensive fractional crystallisation, are also observed and have recently been
1047 investigated for their HSE abundance and Re-Os isotope systematics (e.g., Chu et al., 2013; Li et al.,
1048 2014; Wang et al., 2014). For this reason, we adopt the same definition used by Day (2013) for
1049 intraplate ‘hotspot’ volcanism, i.e., “*Volcanic rocks that are unassociated with conventional plate*
1050 *tectonic boundary magmatic processes and that may require anomalous thermo-chemical and/or*
1051 *tectonic conditions to induce small- to large-scale melting”.*

1052

1053 **Mantle melting processes**

1054

1055 The composition of the mantle source may be expressed by a variety of end-member
1056 compositions based upon its history of prior melt depletion i.e., depleted versus fertile peridotite
1057 (e.g., [Niu, 2004](#); [Godard et al., 2008](#)) and overall lithology, i.e., peridotite versus pyroxenite
1058 ([Hirschmann and Stolper 1996](#); [Yaxley, 2000](#); [Kogiso et al., 2004](#); [Lambart et al., 2012, 2013](#)). In
1059 addition, fertile heterogeneities in the mantle nucleate magmatic channels that focus melts up to the
1060 surface and hinder their re-equilibration with ambient peridotite ([Katz and Weatherley, 2012](#)).
1061 Therefore, the chemical signature of hybrid melts of peridotite and pyroxenite can be retained in the
1062 composition of mantle-derived basalts. [Day \(2013\)](#) discussed the significance of the ‘shape’ that a
1063 melting regime can have, discussing two end-member geometries; (i) batch melting of a columnar
1064 (cylindrical) region (e.g., [Rehkämper et al., 1999](#)), and (ii) regions of adiabatic melting in triangular
1065 or corner-flow melting regime (e.g., [Plank and Langmuir, 1992](#)). Each of these melting regimes
1066 aggregate melt pooled from over the melting volume, accounting for the overall composition of the
1067 magma generated.

1068 Briefly, model (i) is most consistent with an upwelling ‘mantle plume-like’ melting regime. It
1069 assumes uniform melting throughout the source region and that HSE-rich sulfide is completely
1070 exhausted at 20–25% partial melting. This cylindrical melting model reproduces the HSE abundances
1071 of low-degree alkali basalts (e.g., Canary Island lavas; e.g., [Day et al., 2009](#)) and high-degree partial
1072 melts (e.g., komatiites; e.g., [Rehkämper et al., 1999](#)), but the HSE signature of some tholeiitic
1073 magmas generated by low degrees of partial melting are not predicted using this cylindrical melt
1074 volume (e.g., [Momme et al., 2003, 2006](#)). The triangular melting regime (model ii) assumes near-
1075 fractional melting in 1% increments with decreasing pressure, i.e., through adiabatic ascent (e.g.
1076 [Rehkämper et al., 1999](#); [Momme et al., 2003](#)). In this melting regime, S-saturated low-degree partial
1077 melts with low HSE-concentrations mix with shallower, higher-degree (and potentially S-
1078 undersaturated) partial melt. Refinements to the two general classes of models described above have
1079 allowed distinct melt regimes in some continental flood basalt (CFB) provinces to be determined
1080 ([Momme et al., 2006](#)), whereas in the Icelandic rift zones depleted versus enriched mantle
1081 components have also been identified ([Momme et al., 2003](#)). Moreover, the use of these models has
1082 permitted the detection of a pyroxenitic component in primitive lavas from the Canary Islands ([Day
1083 et al., 2009](#)), and a similar component has been implicated in the generation of some Hawaiian lavas
1084 ([Lassiter et al., 2000](#); [Sobolev et al., 2007](#)).

1085 Source compositional estimates become increasingly complicated when the necessity arises to
1086 account for the contributions from mixtures of source lithologies (e.g., peridotite and recycled
1087 sediment or basalt) and the complex interplay of the HSE that each of these source reservoirs may
1088 contribute to a pooled melt (e.g., [Hirschmann and Stolper, 1996](#)).

1089

1090 **Osmium isotopes as tracers of hotspot sources**

1091

1092 **Ocean island basalts.** Many intraplate basalts retain HSE signatures of their mantle source
1093 region and osmium isotopes, when compared to lithophile element-based radiogenic isotopes, can
1094 offer a unique perspective on the petrogenesis of intraplate lavas. The large Re/Os fractionations
1095 generated during crust-mantle partitioning make it possible to model $^{187}\text{Os}/^{188}\text{Os}$ variations in OIB in
1096 the context of variably aged recycled crust and lithosphere (e.g., [Hauri and Hart, 1993](#); [Marcantonio
1097 et al., 1995](#); [Widom et al., 1999](#); [Day et al., 2009](#); [Day, 2013](#)). For example, ancient oceanic mantle
1098 lithosphere or SCLM has been implicated in the genesis of lavas from the Azores, Iceland and Jan
1099 Mayen ([Skovgaard et al., 2001](#); [Schaefer et al., 2002](#); [Debaille et al., 2009](#)), where measured
1100 unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ values cannot be explained by melting exclusively of modern oceanic
1101 lithospheric material and thus require a mantle source or sources that have evolved in a low Re/Os
1102 environment (cf. unradiogenic abyssal peridotites reported by [Snow and Reisberg, 1995](#); [Alard et al.,
1103 2005](#); [Harvey et al., 2006](#); [Liu et al., 2008](#); [Warren and Shirey, 2012](#); [Lassiter et al., 2014](#)). Intraplate
1104 basalts and specifically ocean island basalts (OIB), are generated from mantle sources with distinct
1105 long-term time-integrated parent-daughter fractionations of Sr-Nd-Pb-Hf isotopes (e.g., [Zindler and
1106 Hart, 1986](#); [Hofmann, 2003](#); [White, 2010](#)), and also preserve a large range of $^{187}\text{Os}/^{188}\text{Os}$
1107 compositions (e.g., [Pegram and Allègre, 1992](#); [Hauri and Hart, 1993](#); [Reisberg et al., 1993](#);
1108 [Marcantonio et al., 1995](#); [Roy-Barman and Allègre, 1995](#); [Widom and Shirey, 1996](#); [Lassiter and
1109 Hauri, 1998](#); [Brandon et al., 1999, 2007](#); [Widom et al., 1999](#); [Schiano et al., 2001](#); [Eisele et al., 2002](#);
1110 [Schaefer et al., 2002](#); [Lassiter et al., 2003](#); [Workman et al., 2004](#); [Escrig et al., 2005b](#); [Class et al.,
1111 2009](#); [Day et al., 2009, 2010b](#); [Debaille et al., 2009](#); [Ireland et al., 2009](#); [Jackson and Shirey, 2011](#)).
1112 These signatures are only retained in instances where the melt produced at depth, albeit with ancient
1113 time-integrated compositions, and reflecting the recycling of material back into the convecting
1114 mantle (e.g., [Zindler and Hart, 1986](#)), are not significantly contaminated or overprinted though
1115 interaction with the lithosphere through which these basalts necessarily transit en route to the surface.
1116 For example, in a recent study of the Louisville Seamount Chain, [Tejada et al. \(2015\)](#) demonstrated
1117 that OIB erupted along this chain of oceanic volcanoes reach the surface with negligible chemical
1118 interaction with the lithospheric mantle that underlies the South Pacific. Moreover, unlike the

1119 Hawaiian-Emperor Seamount chain, whose compositions are readily explained by heterogeneous
1120 mantle sources (see following section), Os isotope signatures of these basalts have a very narrow
1121 range, consistent with their derivation from a primitive mantle source (cf. Meisel et al., 2001; Becker
1122 et al., 2006). Age corrected $^{187}\text{Os}/^{188}\text{Os}$ of the Louisville Seamount basalts range from 0.1245–
1123 0.1314, similar to other Pacific OIB, such as Rarotonga (0.125–0.129, Hauri and Hart (1993); 0.124–
1124 0.139, Hanyu et al. (2011) and some Samoan basalts (0.1230–0.1313, Hauri and Hart (1993);
1125 Jackson and Shirey (2011)). The age corrected $^{187}\text{Os}/^{188}\text{Os}$ for two aggregates of olivine phenocrysts
1126 separated from Louisville Seamount basalts (0.1272 and 0.1271–0.1275) agree with whole rocks
1127 from the same seamount (0.1253–0.1274; Tejada et al., 2015), supporting the hypothesis that early-
1128 crystallising olivine can preserve the pristine magmatic Os isotopic compositions of their source (cf.
1129 Jackson and Shirey, 2011; Hanyu et al., 2011) (**Figure 29**).

1130 Studies of HSE abundance complement and extend the knowledge of intraplate magma
1131 petrogenesis gleaned from Os isotope systematics. Only lavas with high-MgO contents and >0.05 ng
1132 g^{-1} Os should be considered as potentially being representative of the true HSE characteristics of
1133 intraplate magma and its mantle source. Such restrictions on the analysis of intraplate magmas mean
1134 that there is still a dearth of high quality HSE data on OIB. Much of what has been elucidated from
1135 HSE abundances in OIB comes from studies of Hawaiian lavas (Bennett et al., 2000; Crocket, 2002;
1136 Jamais et al., 2008; Ireland et al., 2009; Pitcher et al., 2009). These studies support the hypothesis
1137 that, in general, high-MgO lavas preserve early-formed Os-rich (+ HSE) phases that become
1138 incorporated in early forming phenocrysts such as olivine (e.g., Brandon et al., 1999; Ireland et al.,
1139 2009). Removing the effects of mineral fractionation on HSE abundances allowed Day (2013) to
1140 directly compare the absolute and relative HSE abundances and calculated Re/Os of parent melts in
1141 addition to $^{187}\text{Os}/^{188}\text{Os}$, of Hawaiian, Canary Island and Samoan lavas. Combined with the HIMU
1142 type $^{206}\text{Pb}/^{204}\text{Pb}$ compositions of Canary Island lavas, this led to the conclusion that, in contrast to
1143 Hawaiian and Samoan OIB, and komatiites, whose compositions suggest a relatively high proportion
1144 of peridotite in their parental melts, lavas from the Canary Islands, and specifically El Hierro and La
1145 Palma, contain recycled oceanic crust in their mantle source. Osmium isotope studies of HIMU-type
1146 OIB support and enhance Sr-Nd-Pb isotope and trace element arguments for a recycled oceanic
1147 lithosphere component in their mantle source (Hauri and Hart, 1993; Marcantonio et al., 1995;
1148 Widom et al., 1999; Eisele et al., 2002; Day et al., 2010b). The observed range of $^{187}\text{Os}/^{188}\text{Os}$ and
1149 $^{206}\text{Pb}/^{204}\text{Pb}$ of HIMU basalts (e.g., Becker et al., 2000; Dale et al., 2009a; van Acken et al., 2010)
1150 could be produced by direct melting (~50% to 90%) of recycled oceanic crust, but would result in
1151 melts that contain too much silica and too little magnesium (e.g., Yaxley and Green, 1998). Although
1152 field evidence suggests that pyroxenites account for $\leq 10\%$ of mantle lithologies (e.g., Reisberg et al.,

1153 1991; Pearson et al., 1991), they melt disproportionately to peridotite under any P-T conditions (only
1154 1 to 2% pyroxenite may generate up to 50% of the melt at low degrees of partial melting), thus
1155 producing silica-undersaturated, iron-rich melts with high MgO (e.g., Hirschmann et al., 2003). This
1156 means that direct melting of recycled oceanic crust and lithosphere is not necessary to produce HIMU
1157 OIB.

1158 Spinel websterites have been suggested to be geochemically analogous to pyroxenites, at least
1159 in terms of their HSE systematics (Marchesi et al., 2014). The Re-Os fractionation generated as a
1160 result of peridotite versus pyroxenite (and/or spinel websterites) has been suggested as a likely
1161 contributor to the observed ^{186}Os - ^{187}Os -rich compositions of some plume basalts (Luguet et al., 2008)
1162 previously attributed to interaction between the mantle and outer core (e.g., Brandon et al. 1998,
1163 2003; Puchtel et al., 2005; Walker et al., 1997). Subsequent studies (e.g., Baker and Jensen, 2004;
1164 Luguet et al., 2008; Scherstén et al., 2004) and, more recently, Marchesi et al. (2014) suggest that
1165 such enrichments could be attributed to processes requiring no input from the outer core. However,
1166 these models may require unreasonably high contributions from pyroxenitic / spinel websteritic
1167 lithologies in the mantle (as high as 90% in some cases, but potentially as low as 50%; van Acken et
1168 al., 2010; Marchesi et al., 2014), as a result of the comparatively low Os concentrations in pyroxene-
1169 rich lithologies.

1170 The enriched mantle (EM) signatures of other OIB have been attributed to the addition of
1171 subducted sediment or metasomatised lithosphere into their mantle sources (e.g., Workman et al.,
1172 2004). EM-type OIB span a range of compositions in Sr-Nd-Pb isotope space, varying from EMI
1173 (e.g., Pitcairn; Woodhead and McCulloch, 1998; and the Comores; Class et al., 2009), which exhibit
1174 a wide range of Os and Pb isotope compositions, but more restricted Sr isotope compositions, to
1175 EMII OIB (e.g., Samoa; Wright and White, 1987; Workman et al., 2004; Jackson and Shirey, 2011).
1176 These compositions are consistent with sediment, recycled oceanic crust and peridotite producing
1177 EMI-flavoured compositions with more radiogenic $^{187}\text{Os}/^{188}\text{Os}$ (Roy-Barman and Allègre, 1995;
1178 Class et al., 2009), while subducted sediment mixed with ambient peridotite produces enriched EMII
1179 compositions with lower $^{187}\text{Os}/^{188}\text{Os}$. Therefore, lithological variations in the mantle source play a
1180 key role in the composition of OIB, and HSE abundances combined with Re-Os systematics are
1181 critical in the identification of the various components mixed with variably depleted asthenospheric
1182 mantle.

1183
1184 **Continental intraplate volcanism.** The heterogeneous mantle sources described above are not
1185 restricted to OIB, or oceanic settings in general. These modifiers of magma composition also
1186 influence intraplate volcanism associated with continental regions. The main differences between

1187 oceanic and continentally erupted intraplate magmas is the greater potential for the latter to be
1188 influenced by interaction with the thicker and older overlying sub-continental lithospheric mantle
1189 (SCLM) and continental crust, in addition to the potential compositional heterogeneities within the
1190 asthenospheric mantle. Recently, [Sun et al. \(2014\)](#) reported Re-Os systematics of ultrapotassic (>7
1191 wt. % K₂O) basalts from the Xiaogulihe area of western Heilongjiang Province, NE China. The
1192 relatively unradiogenic Os isotope ratios (¹⁸⁷Os/¹⁸⁸Os = 0.119 to 0.143) contrasted with the similarly
1193 potassic basalts from NE China reported by [Chu et al. \(2013\)](#) (¹⁸⁷Os/¹⁸⁸Os = 0.13–0.17) and were
1194 attributed by [Sun et al. \(2014\)](#) to a dominantly peridotitic source, but one that required an unusually
1195 high K₂O content. In this particular setting, phlogopite-bearing garnet peridotite hosted within the
1196 lower part of the SCLM was implicated; its derivation being potassium-rich silicate melts produced
1197 by the subduction of ancient continent-derived sediments (>1.5 Ga). The observation that lherzolite
1198 xenoliths from Keluo and Wudalianchi contain phlogopite ([Zhang et al., 2000, 2011](#)) supports the
1199 hypothesis that SCLM, metasomatized by potassium-rich melts, is present beneath the WEK volcanic
1200 field and contributes to the basalts from Xiaogulihe.

1201

1202 **Crustal and lithospheric mantle assimilation/contamination**

1203

1204 Oceanic intraplate volcanism is often assumed to be immune to lithospheric contamination.
1205 Compared to continental intraplate eruptions, OIB do not interact with thermo-chemically complex
1206 SCLM. The low Os contents in OIB (typically <1 ng g⁻¹) makes the Re-Os isotope system a
1207 particularly sensitive indicator of lithospheric contamination, and the relatively unradiogenic
1208 ¹⁸⁷Os/¹⁸⁸Os compositions (<0.18) of OIB relative to local oceanic crustal reservoirs (typically
1209 ¹⁸⁷Os/¹⁸⁸Os >0.4; [Reisberg et al., 1993](#); [Marcantonio et al., 1995](#); [Peucker-Ehrenbrink et al., 1995](#);
1210 [Widom et al., 1999](#)) make the tracing of assimilation of crustal or lithospheric mantle materials in
1211 OIB a straightforward process (e.g., [Reisberg et al., 1993](#); [Marcantonio et al., 1995](#); [Lassiter and](#)
1212 [Hauri, 1998](#); [Skovgaard et al., 2001](#); [Gaffney et al., 2005](#)). In particular, at the lowest levels of Os
1213 content, OIB are even more vulnerable to crustal contamination ([Reisberg et al. 1993](#)), while OIB
1214 with Os contents greater than 30 to 50 pg g⁻¹ are typically assumed to be less susceptible to
1215 assimilation of lithospheric components (e.g., [Reisberg et al., 1993](#); [Eisele et al., 2002](#); [Class et al.,](#)
1216 [2009](#)). Crustal contamination thus rapidly drives Os isotope ratios to more radiogenic values resulting
1217 from the assimilation of oceanic crust with high Re/Os and ¹⁸⁷Os/¹⁸⁸Os.

1218 A consequence of the low HSE abundances of crustal material is that the addition of crust to a
1219 primitive melt should result in the dilution of HSE abundances in the resultant magma. [Ireland et al.](#)
1220 [\(2009\)](#) presented such a model, illustrating the effect of crustal contamination on Hawaiian picrites.

1221 Briefly, three end-member scenarios are considered; (i) continental crust addition to komatiite; (ii)
1222 oceanic crust addition to tholeiite and, (iii) abyssal peridotite addition to alkali basalt. These models
1223 demonstrate that crustal contamination dilutes OIB HSE abundances at $\leq 20\%$ crustal or lithospheric
1224 assimilation. However, both $^{187}\text{Os}/^{188}\text{Os}$ and Re/Os can change dramatically in the evolving liquid,
1225 which has implications for the time integrated Os isotope ratio of such contaminated magmas and the
1226 effectiveness of using $^{187}\text{Os}/^{188}\text{Os}$ as a tracer for the mantle source of the magma. The effects of
1227 assimilation on HSE abundances (absolute or relative) in general, are less well-defined and where
1228 this issue has been addressed in the literature the consensus appears to be that fractional
1229 crystallisation exerts a stronger influence on HSE distributions than contamination factors (e.g.,
1230 [Chazey and Neal, 2005](#); [Ireland et al., 2009](#)). However, crustal contamination of continental flood
1231 basalts (CFB) can lead to a significant augmentation in the S content of a magma, sometimes
1232 resulting in S-saturation and significant HSE fractionation (e.g., [Keays and Lightfoot, 2007](#); [Lorand
1233 and Alard, 2010](#)). This may also elevate concentrations of Re and the PPGE relative to Os, Ir and Ru.
1234 Assimilation of mantle lithosphere also has pronounced effects on Re/Os, but requires large additions
1235 to generate significant effects on magma HSE abundances. Conversely, [Widom et al. \(1999\)](#)
1236 demonstrated that unusually unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ in some Canary Island lavas was most likely
1237 the result of the assimilation of peridotite xenoliths with sub-chondritic $^{187}\text{Os}/^{188}\text{Os}$ and $>1 \text{ ng g}^{-1}$ Os,
1238 prior to the eruption of the basalt at the surface. More recently, a similar process was described by
1239 [Gannoun et al \(2015a\)](#) to account for particularly unradiogenic Os concentrations in basalts from the
1240 Cameroon Line (**Figure 30**).

1241 These simple crustal contamination models can be greatly complicated by the inclusion of
1242 fractional crystallisation processes, which are often intimately associated with crustal contamination.
1243 The combination of these processes will almost inevitably result in the generation of elevated Re, Pt
1244 and Pd abundances compared to Os, Ir and Ru in melts and crustal rocks, compared with their
1245 corresponding mantle residues. However, direct measurement of $^{187}\text{Os}/^{188}\text{Os}$ in early formed mineral
1246 phases handpicked from intraplate magmas, such as olivine ([Debaille et al., 2009](#); [Jackson and
1247 Shirey, 2011](#)), generally yield more restricted ranges in $^{187}\text{Os}/^{188}\text{Os}$ than their associated whole-rocks,
1248 and may provide a means of seeing past bulk-rock contamination of OIB. As a result of these
1249 potential complications, a common sense approach, based upon a rigorous assessment of local
1250 potential contaminants and melt products was advocated by [Day \(2013\)](#) when applying thresholds for
1251 “contaminated” versus “uncontaminated” OIB. Both crustal and SCLM contamination of primitive
1252 melts have been reported in the literature (e.g., [Ellam et al., 1992](#); [Horan et al., 1995](#); [Molzahn et al.,
1253 1996](#); [Chesley and Ruiz, 1998](#); [Keays and Lightfoot, 2007](#); [Li et al., 2010](#); [Chu et al., 2013](#)).
1254 Successful modelling of SCLM or crustal assimilation is dependent upon the accurate determination

1255 of likely end-member compositions, ranging from the parental primitive melt to its possible
1256 assimilants. Day (2013) successfully demonstrated the effect of contamination of primitive parent
1257 melts using North Atlantic Igneous Province (NAIP) picrites (Schaefer et al., 2000; Kent et al., 2004;
1258 Dale et al., 2009b) and intrusive rocks from the Rum Intrusion (O'Driscoll et al., 2009).

1259

1260 **The origin of Continental Flood basalts (CFB) and Large Igneous Provinces (LIP)**

1261

1262 Volcanic rocks from some CFB have been interpreted to have survived the transit from their
1263 asthenospheric source to eruption at the surface without any significant interaction with the SCLM or
1264 the crust (e.g., Schaefer et al., 2000; Zhang et al., 2008; Dale et al., 2009b; Rogers et al., 2010; Day et
1265 al., 2013). Many of these lavas are picritic in composition, have high-MgO (>13.5 wt. %), high Os
1266 concentrations, and $^{187}\text{Os}/^{188}\text{Os}$ ratios which are, in general, unradiogenic; consistent with their
1267 derivation from primitive mantle or a depleted mantle source (e.g., Schaefer et al., 2000; Dale et al.,
1268 2009b; Rogers et al., 2010). This chemical and isotopic signature has, in turn, been used to suggest
1269 that such CFB may be modern-day equivalents of uncontaminated Archaean komatiites, albeit from a
1270 cooler mantle, (cf., Brüggemann et al., 1987; Wilson et al., 2003; Puchtel et al., 2009; Connolly et al.,
1271 2011).

1272 In contrast, several studies have highlighted the importance of an interaction between
1273 asthenosphere-derived melts, SCLM and the crust to produce the observed spectrum of CFB
1274 compositions (e.g., Ellam et al., 1992; Horan et al., 1995; Molzahn et al., 1996; Chesley and Ruiz,
1275 1998; Xu et al., 2007; Li et al., 2010; Heinonen et al., 2014) and the HSE fingerprint of some
1276 komatiites (Foster et al., 1996). Osmium isotope systematics, combined with other radiogenic isotope
1277 tracers in CFB demonstrate that the interplay between a primary magma and its potential lithospheric
1278 contaminants can be complex, as illustrated in a number of localities (e.g., Siberia - Horan et al.,
1279 1995; Ethiopia - Rogers et al., 2010; Emeishan, China, - Zhang et al., 2008). Correlations between
1280 $^{187}\text{Os}/^{188}\text{Os}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ (Molzahn et al., 1996), $^{206}\text{Pb}/^{204}\text{Pb}$ (Xu et al., 2007), and possibly even
1281 $^3\text{He}/^4\text{He}$ (Dale et al., 2009b) illustrate the effects of lithospheric contamination on primary,
1282 asthenosphere-derived melts. However, observed variations in Os isotopes are not wholly consistent
1283 with SCLM or crustal contamination alone, suggesting that, like many OIB, some inherent
1284 heterogeneity within the asthenospheric source is present. For example, the 260 Ma Emeishan
1285 province (e.g., Li et al., 2010) requires a more depleted mantle source than 190 Ma Karoo CFB
1286 (Ellam et al., 1992). Some CFB provinces may therefore tap mantle sources that contain recycled
1287 material, similar to the source of some HIMU and EM flavoured OIB (e.g., Shirey, 1997; Dale et al.,
1288 2009b), while others are derived from an essentially primitive mantle (see review in Day, 2013).

1289 Heterogeneity in the composition and distribution of sulfide types within a magma source
1290 region in the mantle (e.g., interstitial versus enclosed sulfides; [Alard et al., 2002](#); see also [Harvey et](#)
1291 [al., 2015, this volume](#)) can have a profound influence on the composition of a basaltic melt (e.g.
1292 [Harvey et al., 2010, 2011](#)). The combination of source heterogeneity and degree of partial melting
1293 can therefore account for the observed differences in initial Os isotopic and HSE abundance
1294 variations in CFB provinces, that range from depleted DMM-like mantle compositions (e.g., [Rogers](#)
1295 [et al., 2010](#)) through undepleted basalts (e.g., [Schaefer et al., 2000](#)), to more radiogenic compositions,
1296 which provide strong evidence for recycled components in some CFB provinces ([Shirey, 1997](#)).

1297 Coupled with the effects of adding subducted oceanic lithosphere back into the convecting
1298 mantle, i.e. the source of CFB and LIP, and the combinations of pelagic / terrigenous sediments,
1299 variably altered oceanic crust and serpentinized peridotite ([Allègre and Turcotte, 1986](#)), unravelling
1300 the sources of voluminous basaltic magmatism has sometimes been demonstrated to be problematic,
1301 often requiring both HSE and Re-Os isotope evidence used in concert with more traditional lithophile
1302 element-based isotope systems. For example, [Heinonen et al. \(2014\)](#) invoked a mixture of depleted
1303 Os-rich peridotite with ~10–30% of seawater-altered and subduction-modified MORB (with a
1304 recycling age of less than 1.0 Ga) as the likely source of the distinctive isotopic fingerprint found in
1305 CFB from the Antarctic Karoo province. A specific mixed peridotite-pyroxenite-like source was
1306 required to explain the unusual combination of elevated initial $^{87}\text{Sr}/^{86}\text{Sr}$ and Pb isotopic ratios, and
1307 low initial $^{187}\text{Os}/^{188}\text{Os}$ observed in the dykes sampled from around Ahlmannryggen, western
1308 Dronning Maud Land. In other words, simple, two-component mixing is often not consistent with the
1309 observed chemical and isotopic composition of CFB. In the example described by [Heinonen et al.](#)
1310 [\(2014\)](#), not only was a combination of mixed lithologies in the source, in addition to the inherent
1311 differences in their HSE and $^{187}\text{Os}/^{188}\text{Os}$ fingerprints required to account for the composition of the
1312 Ahlmannryggen dykes, but also a contribution from a seawater-altered subducted component was
1313 required.

1314 A similar investigation into the nature of the Eastern North America (ENA) Central Atlantic
1315 Magmatic Province (CAMP) by [Merle et al. \(2014\)](#) also revealed the complex combination of
1316 chemical and isotopic fingerprints that can be preserved in large-volume basaltic eruptions. Although
1317 CAMP magmatism in general may have been produced as a result of either heat incubation under
1318 thick continental lithosphere ([McHone, 2000](#); [De Min et al., 2003](#); [Puffer, 2003](#); [McHone et al.,](#)
1319 [2005](#); [Verati et al., 2005](#); [Coltice et al., 2007](#)), or by a plume head under the continental lithosphere
1320 ([May, 1971](#); [Morgan, 1983](#); [White & McKenzie, 1989](#); [Hill, 1991](#); [Wilson, 1997](#); [Courtilot et al.,](#)
1321 [1999](#); [Ernst & Buchan, 2002](#); [Cebria et al., 2003](#)), [Merle et al. \(2014\)](#) proposed several increasingly
1322 complex scenarios to account for the chemical and isotopic signatures preserved in the ENA CAMP

1323 basalts, including (i) direct derivation from a mantle plume (Wilson, 1997) or oceanic plateau basalt-
1324 type melts (e.g. Kerr & Mahoney, 2007); (ii) magmas derived from a mantle plume but contaminated
1325 by continental crust en route to the surface (Arndt et al., 1993); (iii) mixing between asthenospheric and
1326 ultra-alkaline mafic (lamproite, kimberlite, and kamfugite) melts (Arndt & Christensen, 1992; Gibson
1327 et al., 2006; Heinonen et al., 2010), possibly followed by crustal contamination; (iv) ternary mixing
1328 between OIB, MORB and SCLM-related melts, possibly followed by crustal contamination; (v)
1329 direct melting of a shallow source enriched in incompatible elements such as metasomatized SCLM
1330 or the mantle wedge above subduction zones (Puffer, 2001; De Min et al., 2003; Deckart et al. 2005;
1331 Dorais & Tubrett, 2008). Unfeasibly large degrees of crustal contamination would be required to
1332 produce the observed $^{143}\text{Nd}/^{144}\text{Nd}$, $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ isotopic compositions of the ENA
1333 CAMP basalts, and crustal contamination, assimilation (of continental crust) with fractional
1334 crystallization (DePaolo, 1981) and assimilation through turbulent ascent were discounted on the
1335 strength of the Re-Os and $^{187}\text{Os}/^{188}\text{Os}$ systematics i.e., initial $^{187}\text{Os}/^{188}\text{Os}$ ratios higher than 0.15 at Os
1336 concentrations lower than 50 ng g^{-1} (e.g., Widom, 1997).

1337 Merle et al. (2014) determined that mixing involving either OIB or MORB-like parental
1338 melts, followed by crustal contamination, partially reproduces the compositions of the ENA CAMP
1339 basalts, but the trends observed in the Nd-Pb and Os-Nd isotopic diagrams require the addition of up
1340 to 35% continental crust, yet the assimilation of more than 20% of continental crust is
1341 thermodynamically unrealistic (Spera & Bohrsen, 2001). Consequently, the hypothesis of a magma
1342 originating from mixing between OIB and SCLM-related melts and further contaminated by the
1343 continental crust was deemed unlikely. Therefore, the continental crust-like characteristics of the
1344 ENA CAMP were inferred to be present in the mantle source itself. Recent studies have suggested
1345 that such contrasting chemical characteristics may be derived from a metasomatized SCLM-type
1346 source (cf. Chu et al., 2013; Sun et al., 2014; Wang et al., 2014), where phlogopite in the SCLM was
1347 thought to be derived from the melting of subducted terrigenous sediments. To account for the
1348 measured Os isotope compositions of the ENA CAMP basalts, the Os isotopic composition of the
1349 source needed to be within the range of $^{187}\text{Os}/^{188}\text{Os}$ for off-cratonic SCLM (0.1180 to 0.1290;
1350 Carlson, 2005), therefore the model favored by Merle et al. (2014) to explain the multi-isotope
1351 system fingerprint of the ENA CAMP basalts required a reservoir that experienced progressive
1352 incorporation of subducted sediments derived from the local continental crust into a depleted sub-arc
1353 mantle wedge above a subduction zone.

1354 Recent work has revealed that HSE abundances can be broadly modelled as a function of
1355 fractional crystallization in CFB. Day et al. (2013) studied the 1.27 Ga Coppermine CFB in northern
1356 Canada, which represents the extrusive manifestation of the Mackenzie large igneous province (LIP),

1357 which includes the Mackenzie dyke swarm and the Muskox layered intrusion. These authors reported
1358 new HSE abundance and Re-Os isotope data for picrites and basalts from the CFB, as well as a
1359 highly unusual andesite glass flow. The glass contained high HSE contents (e.g., 3.8 ng g⁻¹ Os) and
1360 mantle-like initial ¹⁸⁷Os/¹⁸⁸Os ($\gamma_{1270\text{Ma}} \text{ Os} = +2.2$), but $\delta^{18}\text{O}$, ϵNd_i , and trace element abundances
1361 consistent with extensive crustal contamination, implicating a potential origin for sample CM19 as a
1362 magma mingling product formed within the Muskox Intrusion during chromitite genesis (cf. [Day et](#)
1363 [al., 2008](#)) and direct evidence for the processing of some CFB within upper-crustal magma chambers.
1364 These authors also modelled absolute and relative HSE abundances in CFB from the Coppermine,
1365 Parana and West Greenland, revealing that HSE concentrations decrease with increasing
1366 fractionation for melts with $<8 \pm 1$ wt.% MgO (**Figure 31**). The models reveal that significant inter-
1367 element fractionation between (Re+Pt+Pd)/(Os+Ir+Ru) are generated during magmatic
1368 differentiation in response to strongly contrasting partitioning of these two groups of elements into
1369 sulfides and/or HSE-rich alloys. Furthermore, fractional crystallization has a greater role on absolute
1370 and relative HSE abundances than crustal contamination under conditions of CFB petrogenesis due to
1371 the dilution effect of low total HSE continental crust. [Day et al. \(2013\)](#) found that picrites
1372 (>13.5 wt.% MgO) from CFB ($n = 98$; 1.97 ± 1.77 ng g⁻¹) having higher Os abundances than OIB
1373 picrites ($n = 75$; 0.95 ± 0.86 ng g⁻¹) and interpreted these differences to reflect either higher degrees of
1374 partial melting to form CFB, or incorporation of trace sulfide in CFB picrites from magmas that
1375 reached S-saturation in shallow-level magma chambers.

1376

1377 **Continental intraplate alkaline volcanism**

1378

1379 Continental intraplate alkaline volcanic rocks (CIAV) comprise a wide spectrum of sodic and
1380 potassic compositions ranging from alkali basalts, picrites and basanites through to more evolved
1381 eruptive products that include nephelinites, carbonatites, melilitites, and kimberlites. The origin of
1382 some of these rock types are not unequivocal, with petrogenetic models ranging from pure incipient
1383 rift-related sources (e.g., [Thompson et al., 2005](#)), to ‘hotspot’ or ‘plume’ related origins (e.g.,
1384 [Haggerty, 1999](#)). Finding a likely source for these volcanic rocks is not made any less ambiguous
1385 when experimental and geochemical data are considered as many of these lavas are thought to derive
1386 from close to the boundary layer that separates the convecting and conducting mantle (e.g., [Foley,](#)
1387 [1992](#); [Day et al., 2005](#)), i.e. both the asthenosphere and SCLM can be implicated in the genesis of
1388 these magmas. Re-Os isotope data are limited for these types of lavas, and instances where this is
1389 combined with HSE abundance data are comparatively rare. Examples from the literature when HSE
1390 and / or Re-Os isotope data are available are summarized in [Day \(2013\)](#).

1391 When elevated osmium contents in basalts clearly exclude the influence of crustal
1392 contamination, radiogenic $^{187}\text{Os}/^{188}\text{Os}$ (e.g., >0.15) is often interpreted as being derived from olivine-
1393 poor mantle heterogeneities, such as clinopyroxenites (Carlson et al., 1996; Carlson and Nowell,
1394 2001; Janney et al., 2002), primarily as a result of their time-integrated ingrowths to high $^{187}\text{Os}/^{188}\text{Os}$
1395 (Reisberg et al., 1991; Reisberg and Lorand, 1995; Kumar et al., 1996). At the onset of S-saturated
1396 melting at depth, these fertile heterogeneities with radiogenic Os isotopic compositions melt
1397 preferentially (Hirschmann et al., 2003; Rosenthal et al., 2009). Combined with the Os isotope and
1398 HSE signature associated with pyroxenite-dominated melts, high NiO and low MnO concentrations
1399 in olivine phenocrysts are also diagnostic of olivine-poor mantle domains such as phlogopite-rich
1400 pyroxenites (Prelević et al., 2013). These phlogopite-bearing pyroxenites can be derived from the
1401 reaction of peridotitic mantle wedge with melts derived from terrigenous sediments, possibly from
1402 the uppermost regions of the subducting slab (Prelević et al., 2015). As such, many CIAV appear to
1403 have non-peridotitic sources, with some sodic mafic-alkali magmas possessing radiogenic $^{187}\text{Os}/^{188}\text{Os}$
1404 compositions, but moderately high Os contents ($>0.5 \text{ ng g}^{-1} \text{ Os}$). Extreme Os isotopic compositions
1405 could reflect low degrees of partial melting and preferential sampling of more fusible mafic
1406 components, such as pyroxenite, in the asthenospheric mantle (cf. CFB above). Alternatively, melting
1407 of metasomatised lithosphere during rifting events (e.g., Carlson and Nowell, 2001; Thompson et al.,
1408 2005) may also be responsible for the PGE abundances and Re-Os systematics of some CIAV, such
1409 as the Newer volcanic rocks, Australia (Vogel and Keays, 1997). Similarly, carbonatites may also
1410 ultimately originate from mafic as opposed to ultramafic sources due to their close association with
1411 other ultrapotassic rocks (e.g., Gudfinnsson and Presnall, 2005). For example, young ($>20 \text{ Ma}$)
1412 carbonatites from Fuerteventura, Canary Islands, possess low Os abundances (5 to 15 pg g^{-1}) and
1413 highly radiogenic $^{187}\text{Os}/^{188}\text{Os}$ that extend to values in excess of 0.6 (Widom et al., 1999). Conversely,
1414 the high Os abundance and unradiogenic Os isotope signatures of some kimberlites and katungites
1415 are consistent with a petrogenesis involving the assimilation or derivation from the SCLM (Pearson
1416 et al., 1995; Carlson et al., 1996; Araujo et al., 2001; Carlson and Nowell, 2001; Pearson et al.,
1417 2008). More recently, Chalapathi Rao et al (2013) provided strong evidence for contrasting mantle
1418 sources for kimberlites and lamproites in the Eastern Dharwar craton, southern India. Re–Os isotope
1419 of orangeites from the Bastar craton and Mesoproterozoic kimberlites and lamproites contrasted with
1420 an unradiogenic Re-depleted kimberlite sample with present-day $^{187}\text{Os}/^{188}\text{Os}$ (0.1109) and a Re-Os
1421 isotopic fingerprint characteristic of Proterozoic lithosphere, with the positive γOs (2.9 to 3.6) of two
1422 kimberlites from Raichur and Narayanpet (Eastern Dharwar craton) that retained both both plume
1423 and subduction-related source signatures (cf. Heinonen et al. 2014 for the petrogenesis of continental
1424 flood basalts from the Antarctic province of the Karoo). The enriched Re–Os mantle sources for the

1425 nearby Kodomali orangeite ($\gamma_{Os} = +3$) and the Krishna lamproites, with very radiogenic ($\gamma_{Os} 56 +$
1426 355), similar to those displayed by the lamproites of the Italian peninsula (Conticelli et al., 2007),
1427 suggest a subducted component for the latter ultra-potassic rocks, demonstrating the complex
1428 interplay of likely sources contributing to magma genesis around the Eastern Dharwar craton in both
1429 time and space (Chalapathi Rao et al., 2013).

1430 The low Os concentrations of primary low-degree potassic and sodic mafic-alkali volcanic
1431 rocks, combined with the high Os abundance of mantle and crustal xenoliths in some kimberlites,
1432 alnoites and melnoites make these volcanic rocks highly susceptible to contamination as they pass
1433 through and interact with the SCLM and overlying crust. Evolved magmas of this type may also be
1434 susceptible to the effects of S-saturation prior to eruption (Vogel and Keays, 1997), i.e. they may
1435 have experienced the prior precipitation of sulfide and concomitant harvesting of HSE from the S-
1436 saturated magma. Despite these caveats, some continental intraplate magmas still retain unique
1437 information on the composition of their mantle source. In particular, early Cretaceous alkaline
1438 picrites and basalts from the North China craton have petrological and Os-Sr-Nd isotope
1439 compositions consistent with contributions from recycled and foundered eclogitic lower continental
1440 crust (Gao et al., 2008). More recently, Chu et al. (2013) examined a suite of highly potassic basalts
1441 from Wudalianchi-Erkeshan, NE China and, despite the incorporation of modest amounts of
1442 continental crust and the potential of sulfide contamination derived from the SCLM, traced the source
1443 of the basalts back to the asthenosphere. Their findings suggested a complex interaction between
1444 crust and SCLM with highly potassic melts generated at least partly from SCLM containing
1445 phlogopite, itself with an ancient terrigenous sediment signature (Sun et al., 2014). In contrast to a
1446 predominantly peridotitic phlogopite-bearing source for continental volcanism reported by Sun et al.
1447 (2014), Miocene ultrapotassic rocks within the Sailipu area of the western Lhasa terrane, southern
1448 Tibet, were variously attributed to the interaction of both spinel- and garnet-lherzolite derived melt
1449 with a phlogopite-bearing pyroxenite source (Wang et al. 2014). Although the latter study postulated
1450 that the observed chemistry of the ultramafic melts could be attributed to crustal contamination,
1451 unfeasibly large-scale assimilation of continental crust would be necessary to account for the nature
1452 of the Sailipu basalts. While the lithophile element-based isotope systems are relatively insensitive to
1453 crustal contamination, mixing calculations using HSE concentrations and $^{187}Os/^{188}Os$ of primitive arc
1454 compositions ($Os = 0.2 \text{ ng g}^{-1}$; $^{187}Os/^{188}Os = 0.125$; Shirey and Walker, 1998; Suzuki et al., 2011),
1455 continental crust ($Os = 0.01 \text{ ng g}^{-1}$; $^{187}Os/^{188}Os = 1.10$; Shirey and Walker, 1998) and depleted mantle
1456 material ($Os = 0.405 \text{ ng g}^{-1}$; $^{187}Os/^{188}Os = 0.108$; Shirey and Walker, 1998) demonstrated that the
1457 composition of the samples from western Lhasa (Wang et al., 2014) would require an unreasonably
1458 high degree of crustal contamination (>80%) (Figure 32). Two other studies of ultrapotassic rocks

1459 from Italy and the Balkans (Conticelli et al., 2007; Prelević et al., 2015, respectively) attributed a
1460 similar combination of mantle sources (as opposed to crustal contamination) as being primarily
1461 responsible for the observed chemical and isotopic compositions.

1462 The recent study of Chu et al. (2013) also discussed the complex chemical and isotopic
1463 signatures preserved in the Wudalianchi-Erkeshan highly potassic basalts in the context of crustal and
1464 lithospheric contamination. Here, the range of $^{187}\text{Os}/^{188}\text{Os}$ in basalts ($^{187}\text{Os}/^{188}\text{Os} = 0.1187\text{--}0.17$) was
1465 partially attributed to 2–8 % crustal contamination; a degree of assimilation that otherwise would be
1466 difficult to detect using lithophile element isotope systems. In fact, Gannoun et al. (2015a) suggested
1467 that degrees of crustal assimilation of up to 15 % would have no measureable effect on Nd and Pb
1468 isotope ratios of basalts, while Li et al. (2014) commented that lithophile element-based isotope
1469 systems may be opaque to as much as 18 % crustal contamination. In the latter study, high NiO and
1470 SiO_2 contents, but low MnO, CaO, MgO and Pb contents, in addition to radiogenic $^{187}\text{Os}/^{188}\text{Os}$, low
1471 Os abundances (5 to 43 ng g^{-1}) and high, but variable, Re/Os (3 to 126) of intra-continental OIB-like
1472 basalts from West Qinling, central China, were attributed to crustal contamination on the strength of
1473 the sensitivity of Os isotope systematics to the incorporation of continental crust.

1474 In contrast, the most unradiogenic Os isotope signatures observed in continental alkaline
1475 intraplate volcanism may have been affected by the assimilation of xenocryst-hosted primary sulfide.
1476 The often unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ and high ($> \mu\text{g g}^{-1}$) Os content of sulfides enclosed within olivine
1477 xenocrysts (Alard et al., 2002) are prime candidates for the source of a possible “nugget effect”. For
1478 example, a 20 μg mantle sulfide with an Os concentration of 20 $\mu\text{g g}^{-1}$ (see Alard et al., 2000, 2002;
1479 Pearson et al., 2002; Harvey et al., 2006, 2010, 2011; Lorand et al., 2013; Harvey et al., 2015, this
1480 volume for typical sulfides) contains twice as much Os as 2 g of basalt with an Os concentration of
1481 100 pg g^{-1} . This type of nugget effect was attributed by Chu et al. (2013) as being responsible for the
1482 poor reproducibility of $^{187}\text{Os}/^{188}\text{Os}$ in two Wudalianchi-Erkeshan basalts (LHS-6 and HSS-6). In this
1483 instance, the heterogeneous distribution of a component that contains anomalously high Os (+ PGE)
1484 abundances throughout the sampled rock powder could account for the observed heterogeneities in
1485 replicate basalt analyses. A similar source of heterogeneity was suggested by Gannoun et al. (2015a)
1486 to account for comparable unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ signatures in some Cameroon Line basalts.

1487

1488 **Processes affecting the HSE compositions of sub-aerial volcanism**

1489

1490 The previous sections demonstrate that it is essential to consider the many possible source and
1491 contamination factors that may influence the ultimate composition of intraplate magmas. Irrespective
1492 of the tectonic setting in which an erupted magma was generated, sub-aerially erupted lavas may be

1493 subject to an additional group of processes whose affects need to be assessed prior to interpretations
1494 concerning magma sources and potential contaminants. These processes, including post-emplacment
1495 alteration and magmatic degassing, were reviewed comprehensively in Day (2013). While there has
1496 been a dearth of new data in the intervening period, one study in particular merits attention; the
1497 recent examination of Os loss through magmatic degassing at Piton de la Fournaise, Réunion Island
1498 (Gannoun et al., 2015b).

1499 Oceanic island basalts have lower Re concentrations than MORB. This is anomalous
1500 considering the incompatible behavior of Re during basalt petrogenesis (Hauri and Hart, 1997). This
1501 apparent quirk has been attributed to two possible causes; (i) the presence of garnet and/or sulfide in
1502 their mantle source (Richter and Hauri, 1998), or (ii) magmatic degassing of Re (Bennett et al., 2000;
1503 Lassiter, 2003; Norman et al., 2004). Several lines of evidence support the idea that Re loss is a late
1504 and shallow stage process, which favors process (i) above. For example, an increase in oxygen
1505 fugacity promotes the loss of Re from Re metal (Borisov and Jones, 1999), suggesting that at the
1506 oxidation state relevant to OIB (FMQ), the rate of Re loss from a magma will increase by an order of
1507 magnitude per log unit of fO_2 increase. Sub-aerial eruptions from Réunion and Hawaii preserve
1508 evidence for an increase in fO_2 in the lavas during emplacement, from FMQ -1.8 close to eruption
1509 vents, to up to FMQ +3 in lava samples that have travelled several km and cooled slowly (Rhodes
1510 and Vollinger, 2005; Boivin and Bachéler, 2009).

1511 Although Re and Os have the highest elemental condensation temperature (1821 and 1812 K,
1512 respectively; Lodders, 2003), these elements are commonly enriched in volcanic gas sublimates and
1513 aerosols (Crocket, 2000; Yudovskaya et al., 2008; Mather et al., 2012). However, the relative and
1514 absolute volatilities of Re and Os, and hence the degree of degassing from sub-aerial lavas, are not
1515 well constrained. The propensity for an elemental species to be volatilized post-eruption can be
1516 described in terms of an emanation coefficient, (E_x), where $E_x = (C_i - C_f) / C_i$, (C_i = concentration of
1517 element x in the magma and C_f = concentration of element x in the magma after degassing; Gill et al.,
1518 1985; Lambert et al., 1986). The emanation coefficient of Re ranges from 0.12 (Rubin, 1997) to as
1519 high as 0.74 (Norman et al. 2004). The difficulties associated with the analysis of $pg\ g^{-1}$ quantities of
1520 Os in basalts make the emanation coefficient of Os even less well known.

1521 In their recent study, Gannoun et al. (2015b) investigated the Re–Os isotope and elemental
1522 systematics of basaltic lavas and gas condensates (a range of Na-K-Ca-Cu sulfates, Ca-Mg-Al-Fe
1523 fluorides, and native sulfur) produced during eruption and degassing at Piton de la Fournaise,
1524 Réunion Island, in order to examine the geochemical behavior of these two elements during magma
1525 degassing. High temperature ($>350\ ^\circ C$) deposits were enriched in Re (24 to $79\ ng\ g^{-1}$), almost two
1526 order of magnitude higher than the corresponding lavas (0.2 to $0.8\ ng\ g^{-1}$), while the Os abundances

1527 of the high temperature condensates were similar to those of the lavas (14 to 132 pg g⁻¹). The highest
1528 temperature condensates (Na–K sulfates; 384 to 400 °C), yielded ¹⁸⁷Os/¹⁸⁸Os that were significantly
1529 lower (i.e. 0.124–0.129) than their corresponding lava. These unradiogenic osmium isotope ratios
1530 were attributed by [Gannoun et al. \(2015b\)](#) to the volatilization of Os originally contained in old,
1531 unradiogenic mantle sulfides. Sulfides associated with earlier volcanic eruptions at Réunion Island
1532 (<7 Ma) were deemed too young to provide the distinctive unradiogenic Os fingerprint of the
1533 volcanic gas, leading [Gannoun et al. \(2015b\)](#) to infer that the observed unradiogenic Os was
1534 ultimately derived from a mantle source. In the context of osmium mantle geochemistry, loss of
1535 unradiogenic Os during magmas degassing could help to explain osmium isotope disequilibrium
1536 between lavas and melting residues.

1537 This contrasted with the Re-Os systematics of the low-to-medium temperature condensates,
1538 which contained the highest Os abundances (13 to 77 ng g⁻¹) with unfractionated ¹⁸⁷Os/¹⁸⁸Os (0.130
1539 to 0.135), which are indistinguishable from the April 2007 lava flow and the historical lavas of Piton
1540 de la Fournaise (i.e. ¹⁸⁷Os/¹⁸⁸Os = 0.130 to 0.137; [Schiano et al., 2012](#)). In addition, very high
1541 concentrations of iridium (1 to 8 ng g⁻¹) reported for hieratite condensates (K₂SiF₆) suggested that Ir
1542 was also transported in volatile emissions as gaseous IrF₆ (cf. [Toutain and Meyer, 1989](#)). The
1543 selective enrichment of HSE demonstrates their potential for transport as metallic hexafluorides
1544 ([Molski and Seppelt 2009](#); [Craciun et al., 2010](#); [Gannoun et al., 2015b](#); see also review in [Day,](#)
1545 [2013](#)). The absence of isotopic fractionation between gas deposits and lavas also indicates that
1546 external components (such as seawater, rainwater or air), which all possess particularly radiogenic
1547 ¹⁸⁷Os/¹⁸⁸Os ([Levasseur et al., 1998, 1999](#); [Gannoun et al., 2006](#); [Chen et al., 2009](#)) have no significant
1548 influence on the Os budget of volcanic gases.

1549

1550 **HIGHLY SIDEROPHILE ELEMENT SYSTEMATICS OF ARCS**

1551

1552 Highly siderophile element abundance studies have been applied to arc volcanism to
1553 understand both subduction processes and the generation of economic deposits of precious metals
1554 within arc settings. A critical question has regarded the potential mobility of the HSE in subduction
1555 zone environments and the collateral effects such processes have regarding the siderophile element
1556 budget of the mantle. Fractionation of Re and Pt from Os in subduction zone environments could
1557 have a potentially significant effect both on Os isotope signatures at arcs (e.g., [Brandon et al., 1996](#)),
1558 but also on the long-term Re/Os and Pt/Os fractionations observed in OIB, MORB and mantle rocks.
1559 In addition, the potential mobility of HSE in subduction zone environments has important

1560 implications regarding the formation of economic PGE ore deposits such as major epithermal gold
1561 deposits associated with some volcanic arcs (e.g., [McInnes et al., 1999](#)). For the purpose of this
1562 review, we focus on the petrogenetic implications of arc volcanism.

1563 Arc magmatism includes tholeiitic to calc-alkaline compositions and dominantly involves the
1564 generation of basalt-andesites, andesites and more evolved magma-types. Only a limited number of
1565 arc volcanoes are known to erupt lavas approaching basaltic or picritic compositions. Because the
1566 HSE are typically compatible during mantle melting, as well as during fractional crystallization, this
1567 means that Os concentrations in arc volcanic rocks are typically very low, resulting in increased
1568 susceptibility of arc lavas to crustal contamination (e.g., [Richter et al., 2002](#); [Hart et al., 2002](#);
1569 [Lassiter & Luhr, 2001](#); [Turner et al., 2009](#); [Bezard et al., 2015](#)). High $^{187}\text{Os}/^{188}\text{Os}$ in arc lavas has
1570 therefore been attributed to assimilation of arc crust during magmatic ascent, but also due to
1571 enrichment in radiogenic Os due to contamination of the mantle wedge by slab-derived fluids/melts
1572 (e.g., [Borg et al., 2000](#); [Alves et al., 1999; 2002](#)), or a combination of these processes ([Suzuki et al.,](#)
1573 [2011](#)). In this section, we review the work done so far in arcs, using both lavas, as well as mantle-
1574 derived xenoliths erupted in association with active arcs. Since the behavior of the HSE are reviewed
1575 extensively elsewhere in this volume, the focus of this section is largely on the information that can
1576 be obtained from the HSE regarding arc processes.

1577

1578 **HSE and $^{187}\text{Os}/^{188}\text{Os}$ in arc lavas**

1579

1580 The majority of arc related volcanism is located around the Pacific ‘Ring of Fire’, extending
1581 from the southern tip of Chile, up much of South and North America, into the Aleutians and
1582 Kamchatka, through Japan and down as far as the Tonga Trench and New Zealand. Other significant
1583 arcs include the Lesser Antilles Arc and the Scotia Arc (**Figure 33**). Despite the extensive
1584 distribution of arc volcanoes, limited work has been conducted on Re-Os isotopes in arc volcanic
1585 rocks, primarily due to the limited availability of high MgO lavas, which are normally favored for
1586 study by Os isotope and HSE abundance studies. High MgO lavas do occur in some arc settings,
1587 most notably Grenada, south Lesser Antilles Arc, Tonga, and as boninite occurrences. These lavas
1588 are discussed in detail, below.

1589 Work on arcs has shown that arc volcanic rocks typically contain between 0.0001 and 1 ng g⁻¹
1590 Os and 0.01 to 1 ng g⁻¹ Re (**Figure 34**). Rhenium concentrations generally increase with decreasing
1591 MgO in arc lavas, consistent with moderate incompatibility of Re. However, Re can also behave as a
1592 volatile element during oxidizing conditions in arc lavas, and for this reason it is likely that low
1593 concentrations could reflect loss of Re by this process (e.g., [Richter et al., 2008](#)). Positive correlation

1594 between Os and MgO is consistent with strong compatibility of Os during fractional crystallization of
1595 arc lavas. The low MgO and HSE contents in arc lavas can make them potentially highly susceptible
1596 to crustal contamination effects (cf. [Lassiter & Luhr, 2001](#)). Osmium isotopic ratios in recently
1597 erupted arc lavas can span an extreme range, from high MgO lavas with $^{187}\text{Os}/^{188}\text{Os}$ (~0.127-0.128)
1598 similar to typical mantle estimates, to andesites, rhyolites and dacites with $^{187}\text{Os}/^{188}\text{Os} > 1$. There is an
1599 overall relationship of increasing $^{187}\text{Os}/^{188}\text{Os}$ with decreasing Os content, although more than one
1600 trend has been recognized in plots of reciprocal Os versus $^{187}\text{Os}/^{188}\text{Os}$ (**Figure 35**). [Alves et al.](#)
1601 ([2002](#)) pointed out that initial Os isotopic ratios are positively and systematically correlated on
1602 $^{187}\text{Os}/^{188}\text{Os}$ versus reciprocal Os plots, reflecting binary mixing processes, with a common end-
1603 member represented by upper mantle peridotite compositions.

1604 To date, no study has found clear associations of Re or Os contents and $^{187}\text{Os}/^{188}\text{Os}$ with arc
1605 basement type, convergence rate or sediment supply. This may be partly due to the lack of available
1606 high MgO rocks with which to make cross-comparison of ‘primary magmatic composition’. For
1607 example, Lassen Peak lavas with 8 to 11.1 wt.% MgO have up to 0.37 ng g⁻¹ Os and span a range of
1608 $^{187}\text{Os}/^{188}\text{Os}$ from 0.1289-0.235 ([Borg et al., 2002](#)). It has been suggested that these lavas contain a
1609 contribution of radiogenic Os from the subducting slab. Conversely, Grenada picrites and basalts
1610 (10.5-17.4 wt.% MgO) contain up to 0.36 ng g⁻¹ Os and have a slightly more restricted range of
1611 $^{187}\text{Os}/^{188}\text{Os}$ (0.1268-0.1644), yet these lavas are not considered to have a contribution from the slab,
1612 but instead have experienced various levels of crustal assimilation ([Woodland et al., 2002](#); [Bezard et](#)
1613 [al., 2015](#)). Likewise, boninite (13 wt. %) and some low MgO lavas (<1.5 wt. %) from the Tonga-
1614 Kermadec arc have $^{187}\text{Os}/^{188}\text{Os}$ of 0.1275-0.1283, indicating that more radiogenic values for lavas in
1615 this arc are consistent with localized arc contamination ([Turner et al., 2009](#)). Unique to that study is
1616 that the sample with the least radiogenic Os signature is a dacite, suggesting that evolved magmas
1617 can develop by fractionation from mantle-derived magma with minimal interaction with high Re/Os
1618 arc crust. High MgO (≥ 10 wt.%) volcanics from the central and northern Tonga arc, including some
1619 with boninitic affinity, possess a greater range of $^{187}\text{Os}/^{188}\text{Os}$ from 0.131-0.156, while lower MgO
1620 samples range up to $^{187}\text{Os}/^{188}\text{Os} = 0.4$, again largely illustrating the potential effects of localized arc
1621 contamination ([Dale et al., 2012b](#)).

1622 Contents of the HSE in arc-related lavas have been reported for Grenada basalts and picrites,
1623 Izu-Bonin lavas ([Woodland et al., 2002](#)) and Lihir lavas ([McInnes et al., 1999](#)) (**Figure 36**). These
1624 generally high MgO lavas show similar Re and PPGE enrichment over the IPGE, to many intraplate
1625 tholeiites and alkali basalts (e.g., [Day, 2013](#)). However, despite the picritic (MgO >13.5 wt. %) nature
1626 of Grenada lavas, they contain low concentrations of the HSE (<0.2 ng g⁻¹ Ir, 1–4 ng g⁻¹ Pd)
1627 compared with other lavas of similar MgO content. [Woodland et al. \(2002\)](#) argued that this was

1628 probably due to a combination of lower degrees of partial mantle melting and early removal of PGE
1629 with cumulus phases such as olivine, magnetite and sulfide. Comparison of alkali Grenada lavas with
1630 boninitic Izu–Bonin lavas illustrates that although the major element chemistries of Grenada and Izu–
1631 Bonin are different, relative and absolute abundances of the IPGE and PPGE are similar. Rhenium,
1632 however, is markedly depleted in the Grenada picrites compared with the Izu–Bonin boninites,
1633 suggesting either retention of Re by residual garnet in the Grenada sub-arc mantle wedge (Woodland
1634 et al., 2002) or volatile-loss of Re. In some of these cases, their generation above a subduction zone
1635 did not appear to have any significant systematic effect on the HSE signatures of resultant lavas.
1636 However, Grenada samples possess markedly high Pt/Ru ratios and significant PPGE/IPGE
1637 fractionation in general. This feature has also been observed in Tongan arc lavas and associated
1638 lavas from the Fonualei rifts (Dale et al. 2012b), which possess amongst the most extreme Pt/Ru
1639 ratios yet observed in terrestrial mantle-derived magmas (up to 300 in rocks with MgO >8 wt. %).
1640 This was attributed by Dale et al. (2012b) to the retention of IPGE in the mantle source by chromitite
1641 and/or IPGE-rich PGM, despite sulfide exhaustion. Sulfide exhaustion is consistent with the sulfide-
1642 undersaturated nature of the magmas and led to very high PPGE concentrations in the melts.

1643

1644 **HSE and $^{187}\text{Os}/^{188}\text{Os}$ in arc xenoliths**

1645

1646 HSE studies of mantle xenoliths from arc settings have provided the opportunity to document
1647 the behavior of these HSE during slab fluid-induced metasomatism of the mantle wedge, with spinel
1648 harzburgite, websterite and pyroxenite mantle xenoliths occurring in back-arc environments in a
1649 number of arcs. Relatively radiogenic Os isotope signatures in mantle xenoliths and mantle rocks
1650 from arc settings, including the Cascades, Canadian Cordillera, Japan, Lihir, Papua New Guinea,
1651 Kamchatka, and the Catalina Schist have been documented, and attributed to the mobility of Os in
1652 slab fluids (Brandon et al., 1996; 1999; McInnes et al., 1999; Peslier et al., 2000; Widom et al.,
1653 2003). For example Simcoe xenoliths, which represent fragments of mantle lithosphere from the
1654 back-arc of the Cascade arc front, have been metasomatised by silica-rich fluids or hydrous melts
1655 leading to higher $f\text{O}_2$ leading to radiogenic Os isotopic compositions being imparted to these
1656 peridotites (Brandon et al., 1996; 1999). These features are consistent with part or the entire
1657 metasomatic agent being derived from the Juan de Fuca slab. Studies of Kamchatka peridotites also
1658 indicate metasomatism of the Kamchatka sub-arc mantle wedge by radiogenic slab-derived fluids and
1659 melts (Widom et al., 2003).

1660 HSE patterns of the arc-related mantle xenoliths are broadly similar to typical oceanic mantle
1661 xenoliths (Figure 36), but the xenoliths can often exhibit elevated $^{187}\text{Os}/^{188}\text{Os}$, with Simcoe xenoliths

1662 ranging from 0.123-0.157 and Kamchatka xenoliths ranging from 0.123-0.148. The regional
1663 variations in Re–Os isotope signatures are consistent with previous petrographic and geochemical
1664 studies of the Kamchatka mantle xenoliths that reveal multistage metasomatic histories resulting
1665 from interaction of the mantle wedge with a variety of slab-derived fluids and melts, including silicic
1666 slab-melt metasomatism associated with subduction of relatively hot, young (~15–25 Ma) oceanic
1667 crust in the northern arc front, hydrous slab-fluid metasomatism associated with subduction of colder,
1668 old (~100 Ma) oceanic crust in the southern arc front, and carbonate-rich slab-melt metasomatism in
1669 the southern segment behind the arc front, where the slab is deeper. Similar ranges of Re–Os isotope
1670 signatures in peridotites from Avachinsky, Japan and Lihir, and from Valovayam and the Cascades,
1671 respectively, suggest that the age (temperature) and depth of subducting oceanic crust influences the
1672 Re–Os composition of metasomatized sub-arc mantle.

1673

1674 **Radiogenic Os from slab components or from crustal contamination**

1675

1676 A continuing debate exists over the influence of slab-derived $^{187}\text{Os}/^{188}\text{Os}$ to arcs, versus the
1677 potential for crustal or seawater contamination of magmas with low Os abundances. From Lassen
1678 lavas, [Borg et al. \(2000\)](#) showed that crustal contamination could only explain the Re–Os isotope
1679 systematics if distribution coefficients for Re in sulfide were ~40-1100 times higher than published
1680 estimates, and instead argued for contributions from a highly radiogenic Os slab component
1681 ($^{187}\text{Os}/^{188}\text{Os}$ up to 1.4). [Alves et al. \(2002\)](#) also favoured slab components adding radiogenic Os to
1682 arcs, citing evidence from arcs worldwide for different mixing systematics between mantle peridotite
1683 and variably radiogenic Os slab contributions. Conversely, [Bezard et al. \(2015\)](#) have shown that
1684 Grenada picrites with radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (0.705) have $^{187}\text{Os}/^{188}\text{Os}$ (0.127) that overlap with the
1685 mantle range and that assimilation and fractional crystallization can explain compositions of Lesser
1686 Antilles lavas, without the requirement of a slab input (**Figure 37**). [Dreher et al. \(2005\)](#) studied Os
1687 isotopes in Mindanao adakites, showing that the majority of these rocks had unradiogenic Os
1688 isotopes, inconsistent with the idea that adakites with high Sr/Y and low Y and heavy rare earth
1689 element concentrations, reflect melting of young subducted crust in subduction zones.

1690 On the other hand, the range in Os isotopes in Mexican Volcanic Belt rocks, which represent
1691 subduction-related calc-alkaline and lamprophyric rocks in which high $f\text{O}_2$ precludes sulfide
1692 fractionation, could be explained up to 12% assimilation and fractional crystallization ([Lassiter &
1693 Luhr, 2001](#)). To obviate potential issues of shallow-level crustal contamination, [Suzuki et al. \(2011\)](#)
1694 examined Cr-spinel from beach sands in the Bonin Islands, reasoning that Cr-spinel is an early-
1695 formed mineral in most magmas and an indicator of primitive magma Os compositions. They found

1696 unradiogenic Os in Cr-spinel with boninitic affinity, versus a potential slab component reflected in
1697 spinel with tholeiitic affinity. These authors also argued that oxidative conditions in the mantle can
1698 lead to radiogenic Os mobilization in the arc. Ultimately, the most convincing arguments for or
1699 against radiogenic Os from the slab comes from high-MgO Grenada picrites. These samples have
1700 been shown to have less-radiogenic Os signatures in more mafic lavas, with an increasing influence
1701 of crustal contamination in more evolved melts (Woodland et al., 2002; Bezard et al., 2015).
1702 Combined with evidence for the potential influence of subduction zone fluids on the composition of
1703 arc xenoliths, these results suggest that some contribution from the slab can be exhibited in arc lavas,
1704 but that the role of crustal contamination of melts within the arc itself can obfuscate original mantle-
1705 derived signatures.

1706

1707 **Mechanical mixing processes**

1708

1709 The debate as to whether slab-derived signatures are evident in HSE and Os isotopes within
1710 arc volcanic rocks has recently been enhanced by the recognition that mechanical mixing between
1711 peridotite mantle and recycled ocean rocks is likely an important process in modifying HSE contents
1712 at subduction zones. Studies of HSE contents and Os isotope compositions of *mélange* mafic
1713 metamorphic blocks at Catalina Island and the Franciscan Complex (California) and at the Samana
1714 Metamorphic Complex (Dominican Republic) have shown significant differences between block
1715 cores and block rims (Penniston-Dorland et al., 2012; 2014). In particular, while the cores of the
1716 blocks have enhanced PPGE compared with IPGE and radiogenic $^{187}\text{Os}/^{188}\text{Os}$, mimicking patterns for
1717 evolved basaltic rocks, or some sedimentary protoliths, the rims approach HSE contents expected in
1718 some mantle peridotites, with less radiogenic $^{187}\text{Os}/^{188}\text{Os}$ (**Figure 38**). Penniston-Dorland et al.
1719 (2014) have demonstrated that *mélange* mechanical mixing occurs across a range of temperatures
1720 ($\leq 200^\circ\text{C}$ to $\sim 600^\circ\text{C}$) during subduction leading to a hybrid rock composition of peridotite, basaltic
1721 materials and sediments. Measurements of the HSE in arc volcanics suggest variable amounts of
1722 peridotitic mantle with radiogenic Os components (e.g., Alves et al., 1999; 2002; Borg et al., 2000)
1723 and mechanical mixing may play a major role in this process.

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1729 CONCLUSIONS AND PERSPECTIVES

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1731 The highly siderophile elements are expected to be strongly incorporated into Earth's metallic
1732 core, but their abundance in the upper mantle appears to have been set by the late addition of
1733 meteoritic material after core formation was complete. Partial melting of the mantle since that time
1734 has resulted in a significant fractionation of the HSE. The platinum-PGE, Re and Au, can behave as
1735 moderately compatible or incompatible elements during melting, and may be variably enriched in
1736 melts, whereas the iridium-PGE behave as highly compatible elements. Sulfide is a major host for
1737 HSE in mantle rocks, despite its relatively low abundance (between 0.04 and 0.08%). However,
1738 sulfide cannot account for the fractionation of HSE that occurs during the melting that generates
1739 MORB, which generally possess very low Os-Ir-Ru contents, and relatively high Re-Pd and Pt.
1740 Rather this fractionation appears to result from the crystallisation of Os-Ir-Ru alloy phases in
1741 refractory mantle rocks, accompanying the exhaustion of sulfide by melting. The HSE content of
1742 MORB is further modified by the segregation of sulfide during fractional crystallisation in the
1743 magmatic environment, where the HSE are quantitatively removed into sulfide, leaving the residual
1744 melt depleted in these elements.

1745 The fractionation of Re and Os accompanying the generation of MORB, intraplate lavas and
1746 those produced at convergent margins is one of the key processes controlling the distribution of these
1747 elements between Earth's mantle and crust. Therefore, decay of ^{187}Re to ^{187}Os provides a potentially
1748 exceptional tracer of recycled crustal materials in Earth's mantle. This is because both oceanic and
1749 continental crust possess high Re/Os ratios, and develop radiogenic Os isotope compositions over
1750 time, which in turn can be readily traced as recycled material if mixed back into the convective
1751 mantle. However, while MORB glass commonly preserves a radiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotope
1752 composition, this is most readily explained by seawater-derived contamination of the melt that occurs
1753 during magma ascent through the oceanic crust. Although reliable data for MORB glass remain
1754 limited these observations suggest that to a greater or lesser extent all MORB glass has been affected
1755 by seawater-derived contamination. This then also implies that other elements may have been
1756 affected by such contamination, most likely dependent upon their relative concentration in MORB
1757 glass and seawater. Sulfide, although demonstrably affected by the same seawater contamination,
1758 provides a more reliable record of the primary $^{187}\text{Os}/^{188}\text{Os}$ isotope composition of MORB,
1759 particularly those sulfides with high Os concentrations (i.e. $> 100 \text{ ng g}^{-1}$). These high-Os sulfides
1760 preserve relatively unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotope compositions pointing to a mantle source that

1761 has experienced long term depletion of Re, similar to abyssal peridotites, with no evidence for the
1762 presence of recycled crust.

1763 In addition to the effects of seawater contamination observed in MORB, intraplate lavas and
1764 those generated at convergent margins may interact with sub-continental lithospheric mantle, itself
1765 variably contaminated by multiple metasomatic events since it became isolated from the convecting
1766 mantle, and incorporate additional complications from the overlying crust. At convergent margins
1767 there is the additional complication of fluxes generated as a result of the subduction of the down-
1768 going slab with the potential for overprinting pre-existing Re-Os isotope and HSE fingerprints. While
1769 the HSE and its isotope systems offer some unique perspectives on mantle processes and the
1770 generation of a wide range of magmas, their application needs to be exercised with care – the
1771 geochemical context provided by other isotope systems and trace element signatures should be
1772 considered and the specific set of local conditions, both physical and chemical, taken into account in
1773 addition to the use of these invaluable tools.

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Figure captions

Figure 1. CI-chondrite normalised PGE abundances in (a) mantle derived melts and (b) primitif upper mantle and residual mantle rocks. Due to extraction of the low melting temperature Cu-Ni sulfide melt, which concentrates Pt and Pd, the PGE patterns of residual mantle rocks are depleted in Re, Pd and Pt. The depletion factor increases with the degree of melting (10 to 40%), and therefore with the amount of magma extracted from the mantle column, due to the concentration of the PGE in monosulfide solid solution (mss) and also to the fact that an increase in the degree of melting decreases the amount of mss remaining in the residual mantle. Mantle derived rocks show the opposite behaviour. MORB are IPGE depleted (Ru, Ir, Os) relative to the mantle composition because base-metal sulfides are not exhausted. In contrast the very high degree of partial melting (>35%) needed to generate the archaean komatiite melts consumed all the base-metal sulfides in the mantle, generating PGE pattern close to the mantle. Data sources: MORB (Gannoun et al., 2007; Burton et al., 2015; Bézou et al., 2005; Yang et al., 2013; 2014; Jenner et al., 2012; Rehkämper et al., 1999); Komatiites (Connolly et al., 2011; Puchtel et al., 2004; 2005; 2009); Abyssal peridotites (Harvey et al., 2006; Luguet et al., 2007; Pearson et al., 2004; Reisberg and Lorand, 1995); Primitif mantle (Becker et al., 2006).

Figure 2. Highly siderophile elements concentrations, normalised to CI-chondrite (Lodders et al., 2009). Primitive Earth mantle composition are from Becker et al. (2006) and from McDonough and Sun (1995). Predicted composition of Earth's mantle as a result of metal-silicate partitioning at low pressure (1 atm) are from Borisov et al. (1994; 1995); Borisov and Plame (1997); Fortenfant et al. (2003; 2006); Ertel et al. (1999); Ertel et al. (2001) and at high pressure (20 GPa) are from Brenan & McDonough (2009); Cottrell and Walker (2006); Ertel et al. (2006); Holzheid et al. (2000); Righter et al. (2008); Ohtani and Yurimoto (1996). The Late veneer addition are using the average composition of all chondrite groups (Walker, 2009).

Figure 3. Summary of sulfide/silicate partition coefficients determined by experiment (Andrews and Brenan, 2002; Brenan, 2008; Crocket et al., 1997; Fleet et al., 1996; Mungall and Brenan, 2014) and from natural samples (Gannoun et al., 2004; 2007; Hart and Ravizza, 1996; Patten et al., 2013; Peach et al., 1990; Roy Barman et al., 1998)

Figure 4. Mineral-melt partition coefficients of HSE determined by experiment (Brenan et al., 2003; 2005; 2012; Chazey and Neal, 2005; Mallman and O'Neill, 2007; Righter et al., 2004) and from natural samples (Burton et al., 1999; 2000; 2002; Connolly et al., 2011; Debaille et al., 2009; Gannoun et al., 2004; Gao et al., 2008; Hart and Ravizza, 1996; Harvey et al., 2010; 2011; Jackson and Shirey, 2011; Puchtel and Humayun, 2001; Puchtel et al., 2009).

Figure 5. CI-chondrite-normalized PGE patterns for refractory mantle sulfides and intragranular Cu-rich sulfides. Reported patterns are a combination of different peridotites (Alard et al., 2000; 2005; Harvey et al., 2006; Lorand et al., 2001). Calculated mixture of residual included sulfide and an appropriate amount of intergranular sulfides produces a primitive mantle-like PGE pattern.

Figure 6. CI-chondrite normalized PGE abundances for Os-Ir-Ru alloys from ophiolite chromitites (Augé, 1985; 1988; González-Jiménez et al., 2009; 2011; Nakagawa and Franco, 1997).

2951
 2952
 2953 **Figure 7.** PGE vs. Ni plots of MORBs. The high-F (mostly MORBs from Kolbeinsey Ridge) and
 2954 low-F fields represent MORB suites produced by high and low degrees of partial melting defined by
 2955 Bézoz et al. (2005). Data sources: Jenner et al., 2012; Yang et al., 2014.
 2956
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 2958 **Figure 8.** Rhenium (pg.g^{-1}) against osmium (pg.g^{-1}) for terrestrial basalts. Literature data are from the
 2959 following references: MORB (Burton et al., 2015; Escrig et al., 2004; Gannoun et al., 2007; Schiano
 2960 et al., 1997; Yang et al., 2013). OIB (Class et al., 2009; Day et al., 2009; 2010b; Hauri and Hart,
 2961 1993; Ireland et al., 2009; 2011; Jackson et al., 2011; Schiano et al., 2001; Widom and Shirey, 1996);
 2962 Arc lavas (Alves et al., 2002; Chesley et al., 2002); Komatiites (Connolly et al., 2011; Puchtel et al.,
 2963 2004; 2005; 2009); Mantle rocks (Harvey et al., 2006; Pearson et al., 2004; Reisberg and Lorand,
 2964 1995); CI-chondrite (Becker et al., 2006).
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 2966
 2967 **Figure 9.** Re/Os ratio versus Os concentrations for terrestrial basalts. Data are from the same
 2968 references as for Figure 8
 2969
 2970
 2971 **Figure 10.** Rhenium concentrations (pg.g^{-1}) in MORB glass shown against (a) Aluminium (wt. %
 2972 Al_2O_3) and (b) sulfur ($\mu\text{g.g}^{-1}$). Plotted data for MORB are from the same references as in Figure 8.
 2973
 2974
 2975 **Figure 11.** Osmium concentrations (pg.g^{-1}) in MORB glass shown against Nickel ($\mu\text{g.g}^{-1}$). Plotted
 2976 data for MORB are from the same references as in Figure 8.
 2977
 2978
 2979 **Figure 12.** $^{187}\text{Os}/^{188}\text{Os}$ versus $1/^{188}\text{Os}$ ratios for MORB glasses. There is no covariation between Os
 2980 concentration and Os isotope composition, and hence no evidence for binary mixing (see text for
 2981 discussion). Plotted data are from Burton et al., 2015; Gannoun et al., 2004; 2007; Yang et al., 2013.
 2982
 2983
 2984 **Figure 13.** ^{187}Re - ^{187}Os isotope evolution diagram for MORB glasses. No covariation is observed
 2985 between $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$. MORB glass possesses high $^{187}\text{Re}/^{187}\text{Os}$ (parent/daughter) ratios
 2986 which raises the possibility that radiogenic ^{187}Os could be produced in very short periods of time
 2987 (Gannoun et al., 2004; 2007). However, those samples with the highest $^{187}\text{Re}/^{187}\text{Os}$ (>2000) possess
 2988 $^{187}\text{Os}/^{188}\text{Os}$ compositions close to the value expected for the primitive upper mantle.
 2989
 2990
 2991 **Figure 14.** $^{187}\text{Os}/^{188}\text{Os}$ isotope composition of MORB glasses (Burton et al., 2015; Gannoun et al.,
 2992 2004; 2007; Yang et al., 2013) shown against (a) $^{87}\text{Sr}/^{86}\text{Sr}$ (b) $^{143}\text{Nd}/^{144}\text{Nd}$ and (c) $^{206}\text{Pb}/^{204}\text{Pb}$ (see
 2993 text for discussion) (Sr, Nd and Pb data from Dosso et al., 1993; Escrig et al., 2004; Hamelin and
 2994 Allègre, 1985; Hamelin et al., 1984; 1986; Prinzhofer et al., 1989; Schiano et al., 1997; Vidal and
 2995 Clauer, 1981).
 2996
 2997
 2998 **Figure 15.** $^{187}\text{Os}/^{188}\text{Os}$ isotope composition of MORB glass shown against (a) ridge depth (metres
 2999 below sea level) and (b) spreading rate (cm/year) (calculated using Argus et al., 2011 and De Mets et
 3000 al., 2010).

3001
3002 **Figure 16.** Comparison of $^{187}\text{Os}/^{188}\text{Os}$ isotope ratios for MORB glass investigated previously
3003 (Schiano et al., 1997; Escrig et al., 2004) and re-analyzed in Gannoun et al. (2007) and Burton et al.
3004 (2015)
3005

3006
3007 **Figure 17.** Osmium abundance shown against the deviation of the measured $^{187}\text{Os}/^{188}\text{Os}$ (in %)
3008 between recent studies (Gannoun et al., 2007; Burton et al., 2015) and earlier work (Schiano et al.,
3009 1997; Escrig et al., 2004). The highest deviation in the reported $^{187}\text{Os}/^{188}\text{Os}$ is observed for the glass
3010 samples with the lowest Os contents.
3011

3012
3013 **Figure 18.** ^{187}Re – ^{188}Os isotope evolution diagram for coexisting phases from the olivine– basalt
3014 ARP1974-011-018 (Gannoun et al. 2004) . Olivine, plagioclase, glass, and matrix yield a best-fit line
3015 corresponding to an age of 565 ± 336 ky(2σ). Clinopyroxene (not shown) does not lie on this best-fit
3016 line, suggesting either an older age or a different and more radiogenic source for this phase.
3017

3018
3019 **Figure 19.** ^{187}Re – ^{188}Os isotope evolution diagram for coexisting phases from the picritic basalt
3020 ARP1973-010-003 (Gannoun et al. 2004). Olivine, plagioclase, glass, and sulfide lie on a best-fit line
3021 corresponding to an age of 2.53 ± 0.15 My (2σ). Spinel possesses a distinct isotope composition
3022 from this best-fit line and is probably the phase responsible for the displacement of the matrix from
3023 the same line.
3024

3025
3026 **Figure 20.** $^{187}\text{Os}/^{188}\text{Os}$ vs $1/[\text{Os}]$ for heterogeneous Indian MORB. Two samples from the central
3027 indian ridge, MD57 D9-1 and D9-6 show high range of $^{187}\text{Os}/^{188}\text{Os}$ ratios from 0.126 to 0.254 which
3028 covaries with Os concentrations (Burton et al., 2015).
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3031 **Figure 21.** $^{187}\text{Os}/^{188}\text{Os}$ vs (a) Cl and (b) B for MORB glass
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3034 **Figure 22.** $^{187}\text{Os}/^{188}\text{Os}$ isotope composition of MORB glass shown against $\delta^{11}\text{B}$ ratios in the same
3035 sample (symbols as in Fig. 2) illustrating a clear positive covariation between both isotope systems.
3036 MORB samples with radiogenic $^{187}\text{Os}/^{188}\text{Os}$ values also possess high $\delta^{11}\text{B}$ ratios. Mixing curves
3037 between uncontaminated MORB ($^{187}\text{Os}/^{188}\text{Os}$ of 0.125 and $\delta^{11}\text{B}$ of -10% with 7 pg.g^{-1} and $1\text{ }\mu\text{g.g}^{-1}$
3038 for Os and B concentrations respectively) and other sources are also shown. (1) Direct contamination
3039 by seawater with $^{187}\text{Os}/^{188}\text{Os}$ of 1.06, $\delta^{11}\text{B}$ of $+40\%$, $[\text{Os}] = 0.01\text{ pg.g}^{-1}$ and $[\text{B}] = 4.6\text{ }\mu\text{g.g}^{-1}$
3040 (Levasseuret al., 1998). (2) Assimilation of Fe–Mn oxyhydroxides or Os-rich sediments. The grey
3041 field in the left of the graph encompasses the potential mixing lines $^{187}\text{Os}/^{188}\text{Os} \sim 1$, $[\text{Os}] = 1\text{ pg.g}^{-1}$,
3042 $\delta^{11}\text{B} = +10\%$ and $[\text{B}] = 10\text{ }\mu\text{g.g}^{-1}$. (3) Assimilation of relatively old altered oceanic crust with variable
3043 $^{187}\text{Os}/^{188}\text{Os}$ ratios (0.15, 0.20 and 0.25 for a, b and c, respectively), $[\text{Os}] = 10\text{ pg.g}^{-1}$, $[\text{B}] = 8\text{ }\mu\text{g.g}^{-1}$ and
3044 $\delta^{11}\text{B} = +6\%$. Marks on the curves denote the weight percentage of assimilated altered oceanic crust
3045 (in 1% increments) present in the mixture.
3046

3047
3048 **Figure 23.** Backscattered-electron (BSE) images and chemical maps of typical MORB sulfides from
3049 the picritic basalt ARP1973-010-003 (Famous area, Mid-Atlantic ridge). Chemical maps were
3050 produced using a wavelength dispersive spectrometry (WDS) coupled to a CAMECA SX-100

3051 microprobe at Blaise Pascal University (Clermont-Ferrand, France). Shading indicates the relative
3052 abundance of a given element. MSS: monosulfide solid solution; ISS: intermediate solid solution; Pn:
3053 pentlandite. **a.** spherical sulfide globule inclusion in olivine. **b.** sulfide globule inclusion in basalt
3054 matrix. Both grains have coarse grained texture.

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3057 **Figure 24.** Bulk composition of sulfide droplets in the system Fe-Ni-Cu in weight fraction. The grey
3058 zone corresponds to the bulk composition of sulfide droplets from Czamanske & Moore (1977).
3059 Dashed line represents the composition of sulfide liquid composition at Mss crystallization at 1100,
3060 1050, and 1000 °C from Ebel & Naldrett (1997). Note that texture of sulfide droplets is not
3061 dependent on their composition. Droplet liquidus range between more than 1100 to 1050 °C.
3062 Modified from Czamanske and Moore (1977) and Patten et al. (2012).

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3065 **Figure 25.** $^{187}\text{Os}/^{188}\text{Os}$ isotope composition shown against Os concentration (ng g^{-1}) for individual
3066 sulfides from MORB. This indicates a negative covariation between $^{187}\text{Os}/^{188}\text{Os}$ and Os concentration
3067 in the sulfides, where low Os sulfides possess more radiogenic Os isotope compositions. These
3068 radiogenic values may indicate that such sulfides are more susceptible to seawater derived
3069 contamination. Data taken from Burton et al., 2015; Gannoun et al., 2004; 2007; Roy Barman et al.,
3070 1998. (see text for discussion).

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3072
3073 **Figure 26.** $^{187}\text{Os}/^{188}\text{Os}$ isotope composition of individual sulfides shown against the $^{187}\text{Os}/^{188}\text{Os}$ value
3074 of the glass host. In all cases, sulfide grains possess $^{187}\text{Os}/^{188}\text{Os}$ values that are less radiogenic than
3075 their glass host. Sulfides also show a much reduced range of Os isotope compositions compared to
3076 the corresponding host glass.

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3079 **Figure 27.** Histogram showing measured $^{187}\text{Os}/^{188}\text{Os}$ isotope ratios for (a) N-MORB glass data
3080 (Burton et al., 2015; Gannoun et al., 2004; 2007; Yang et al., 2013) (b) single grain sulfide data for
3081 MORB (Burton et al., 2015; Gannoun et al., 2004; 2007; unpublished data; Roy Barman et al., 1998)
3082 (c) abyssal peridotite whole-rock data (Alard et al., 2005; Brandon et al., 2000; Harvey et al., 2006;
3083 Martin, 1991; Snow and Reisberg, 1995; Standich et al., 2001) (d) single grain sulfide data for
3084 abyssal peridotites (Alard et al., 2005; Harvey et al., 2006; Warren and Shirey, 2012). The estimate
3085 for the primitive upper mantle (PUM; Meisel et al., 1996) is also shown. The average $^{187}\text{Os}/^{188}\text{Os}$
3086 isotope composition of abyssal peridotites is 0.127 ± 0.015 ($n = 129$) while individual sulfides yield an
3087 average $^{187}\text{Os}/^{188}\text{Os}$ composition of 0.125 ± 0.021 ($n = 63$). N-MORB analysed thus far show no
3088 evidence for a subchondritic source which may reflect local melting of abyssal peridotites (Brandon
3089 et al., 2000), resistance of depleted peridotites to remelting (Hirth and Kohlstedt, 1996; Mange, 1996)
3090 or that Os from undepleted (fertile) mantle dominates the MORB budget. However, the high-Os (>20
3091 ng g^{-1}) sulfides yield an average composition of 0.129 ± 0.005 ($n=31$) close to the PUM estimation
3092 with values as low as 0.1236. Therefore, these high-Os sulfides show no evidence no evidence for
3093 significant Re enrichment in the MORB source, as might be expected from the presence of recycled
3094 oceanic crust. Rather they indicate that the upper mantle source of these samples has experienced a
3095 long-term depletion of Re, similar to that observed in abyssal peridotites, and consistent with the
3096 incompatible nature of this element during mantle melting.

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3099 **Figure 28.** CI-chondrite normalised PGE abundance (Lodders et al., 2009). Open squares: average
3100 Deep Sea Drilling Project (DSDP) Sites 417/418; diamonds: DSDP Hole 504B (Peucker-Ehrenbrink

3101 et al., 2003); solid squares: Ocean Drilling Program Hole 735B (Blusztajn et al., 2000); open circles:
3102 Oman crustal section (Peucker-Ehrenbrink et al., 2012); solid circles: composite ocean crust
3103 (Peucker-Ehrenbrink et al., 2012). The pattern of average MORB (This chapter) and abyssal
3104 peridotites (Harvey et al., 2006; Lugué et al., 2007; Pearson et al., 2004; Reisberg and Lorand, 1995)
3105 are added for comparison.

3106 **Figure 29.** Plot of Os concentration versus Os isotope ratios for Louisville Seamount Chain basalts
3107 (age-corrected) and olivines (present-day). Pacific ocean island basalts (OIB), mid-ocean ridge
3108 basalts (MORB), and Ontong Java Plateau basalts (OJP) basalts are shown for comparison. Osmium
3109 abundances and isotopic signatures are limited compared to other Pacific OIB. Data sources: Schiano
3110 et al. (1997, 2001); Brandon et al. (1999); Eisele et al. (2002); Jackson and Shirey (2011); Hanyu et
3111 al. (2011); Tejada et al. (2013). Modified after Tejada et al. (2015).

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3113
3114 **Figure 30.** $^{187}\text{Os}/^{188}\text{Os}$ versus (a) $^{206}\text{Pb}/^{204}\text{Pb}$ and (b) $^{143}\text{Nd}/^{144}\text{Nd}$ diagrams for Cameroon Volcanic
3115 Line (CVL) basalts. Pb and Nd isotope data are from Barfod (1999) and Lee et al. (1996). HIMU,
3116 DMM, EM1, and BSE are shown for reference. The average $^{187}\text{Os}/^{188}\text{Os}$ ratio for sub-continental
3117 lithospheric mantle is from Shirey and Walker (1998). Ultramafic xenoliths beneath the continental
3118 part of the CVL are also shown. The increments in the curves are 2%. The grey shaded area indicates
3119 the possible compositions for crustally contaminated lavas. The most radiogenic samples from the
3120 continental sector can be explained by assimilation of 8 to 16% of continental crust. Assuming for the
3121 uncontaminated starting point $[\text{Os}] = 10 \text{ pg g}^{-1}$, $^{187}\text{Os}/^{188}\text{Os} = 0.156$, $^{206}\text{Pb}/^{204}\text{Pb} = 20.24$, $[\text{Pb}] = 2 \text{ }\mu\text{g}$
3122 g^{-1} ; for upper continental crust (UCC) $[\text{Os}] = 50 \text{ pg g}^{-1}$, $^{187}\text{Os}/^{188}\text{Os} = 1.4$, $^{206}\text{Pb}/^{204}\text{Pb} = 19.3$, $[\text{Pb}] = 8$
3123 $\mu\text{g g}^{-1}$; and for lower continental crust (LCC) $[\text{Os}] = 50 \text{ pg g}^{-1}$, $^{187}\text{Os}/^{188}\text{Os} = 0.8$ (Saal et al., 1998),
3124 $^{206}\text{Pb}/^{204}\text{Pb} = 17.5$, $[\text{Pb}] = 8 \text{ }\mu\text{g g}^{-1}$. Curves (1) and (2) describe the possible mixing trajectories
3125 between HIMU and DMM. (1) Assimilation of mantle xenocrysts and (2) mixing of lavas derived
3126 from DMM and HIMU sources. Modelling parameters are as follows: for (1) DMM mantle $[\text{Os}] = 3$
3127 ng g^{-1} , $^{187}\text{Os}/^{188}\text{Os} = 0.125$, $^{206}\text{Pb}/^{204}\text{Pb} = 18.5$, $[\text{Pb}] = 0.15 \text{ }\mu\text{g g}^{-1}$ and for (2) DMM melt $[\text{Os}] = 8 \text{ pg}$
3128 g^{-1} , $^{187}\text{Os}/^{188}\text{Os} = 0.127$, $^{206}\text{Pb}/^{204}\text{Pb} = 18.5$, $[\text{Pb}] = 0.45 \text{ }\mu\text{g g}^{-1}$. For Os–Nd modelling the starting
3129 point was chosen to be the closest to HIMU endmember, $^{143}\text{Nd}/^{144}\text{Nd} = 0.513$, $[\text{Nd}] = 40 \text{ }\mu\text{g g}^{-1}$,
3130 $^{187}\text{Os}/^{188}\text{Os} = 0.15$, $[\text{Os}] = 10 \text{ pg g}^{-1}$; for UCC $^{143}\text{Nd}/^{144}\text{Nd} = 0.512$, $[\text{Nd}] = 27 \text{ }\mu\text{g g}^{-1}$ (Rudnick and
3131 Fountain, 1995), $^{187}\text{Os}/^{188}\text{Os} = 1.4$, $[\text{Os}] = 50 \text{ pg g}^{-1}$; and for LCC $^{143}\text{Nd}/^{144}\text{Nd} = 0.512$, $[\text{Nd}] = 50 \text{ }\mu\text{g}$
3132 g^{-1} (Kwékam et al., 2013), $^{187}\text{Os}/^{188}\text{Os} = 0.8$, $[\text{Os}] = 30 \text{ pg g}^{-1}$ (Saal et al., 1998). Reproduced with
3133 permission of Elsevier BV from Gannoun A, Burton KW, Barfod DN, Schiano P, Vlastélic I,
3134 Halliday AN (2015a) Resolving mantle and magmatic processes in basalts from the Cameroon
3135 volcanic line using the Re–Os isotope system. *Lithos* 224–225:1–12.

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3138 **Figure 31.** HSE patterns for 1.27 Ga Coppermine CFB, ~130 Ma Parana basalts and ~61 Ma West
3139 Greenland picrites versus fractional crystallization models (grey-lines from 13 wt.% MgO, highest
3140 HSE concentrations to 4 wt.% MgO, lowest HSE concentrations) assuming an ‘average’ West
3141 Greenland picrite composition for model starting composition. Explanation of the model is provided
3142 in detail in Day et al. (2013). Data sources are: Woodland (2000), Rocha-Junior et al. (2012) and Day
3143 et al. (2013). CI-chondrite normalization from Horan et al. (2003).

3144
3145
3146 **Figure 32.** $^{187}\text{Os}/^{188}\text{Os}$ vs. $1/\text{Os}$ for the Wudalianchi-Erkeshan highly potassic basalts, NE China. The
3147 solid lines represent binary mixing lines modeled as follows: Fields of crust addition to the intraplate
3148 basalts of 2%, 3.5% and 8% lower continental crust are calculated using the values of Saal et al.
3149 (1988; $^{187}\text{Os}/^{188}\text{Os} = 0.8$ and Os concentration = 49 pg g^{-1}). Metasomatic compositions are based
3150 upon mean values from Alard et al. (2002) and Sen et al. (2011). Mean primary sulfide compositions

3151 are taken from Alard et al. (2000, 2002), Pearson et al. (2002), Harvey et al. (2006, 2010, 2011),
3152 Lorand et al. (2013) – see also the supplementary information from Harvey et al. (2015, this volume).
3153 Modified after Chu et al. (2013).

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3156 **Figure 33.** World map showing locations of major convergent margin settings (stippled lines) and
3157 divergent boundary settings (grey lines) mentioned in the text.

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3160 **Figure 34.** Plots of Os and Re versus MgO content for convergent margin picrites, basalts and
3161 evolved rocks. Data sources: Brandon et al. (1996); Alves et al. (1999; 2002); Borg et al. (2000),
3162 Woodland et al. (2002); Woodhead & Brauns (2004); Turner et al. (2009); Bezarid et al. (2015).

3163
3164
3165 **Figure 35.** Plots of Os and reciprocal Os ($1/Os$) versus $^{187}Os/^{188}Os$ for convergent margin picrites,
3166 basalts and evolved rocks. Data sources: Brandon et al. (1996); Alves et al. (1999; 2002); Borg et al.
3167 (2000), Woodland et al. (2002); Woodhead & Brauns (2004); Turner et al. (2009); Bezarid et al.
3168 (2015).

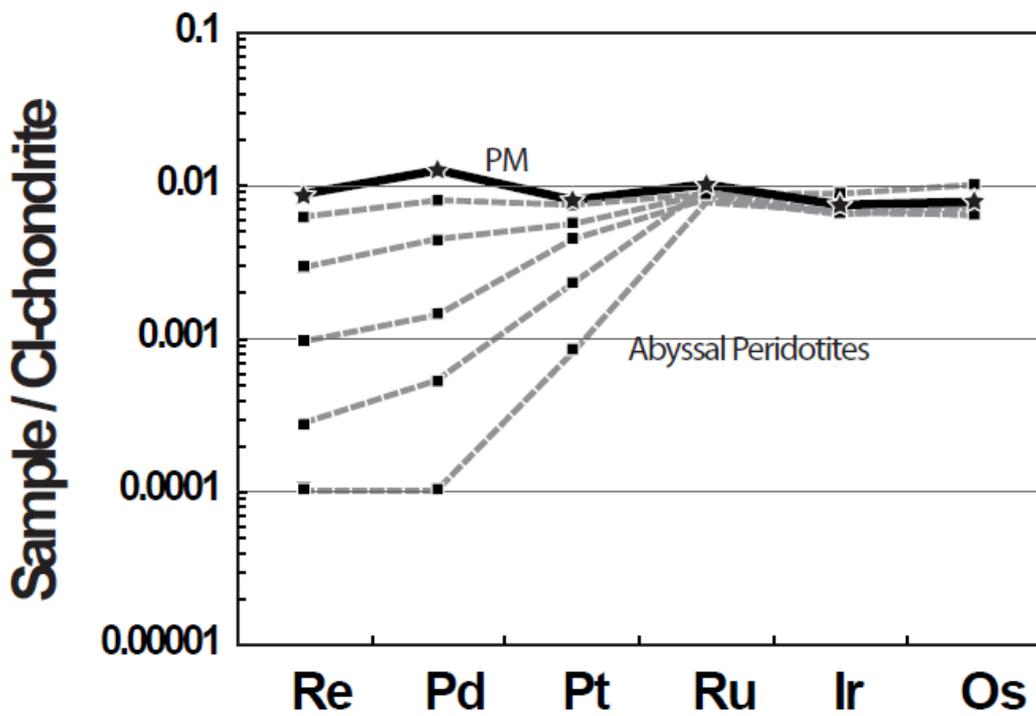
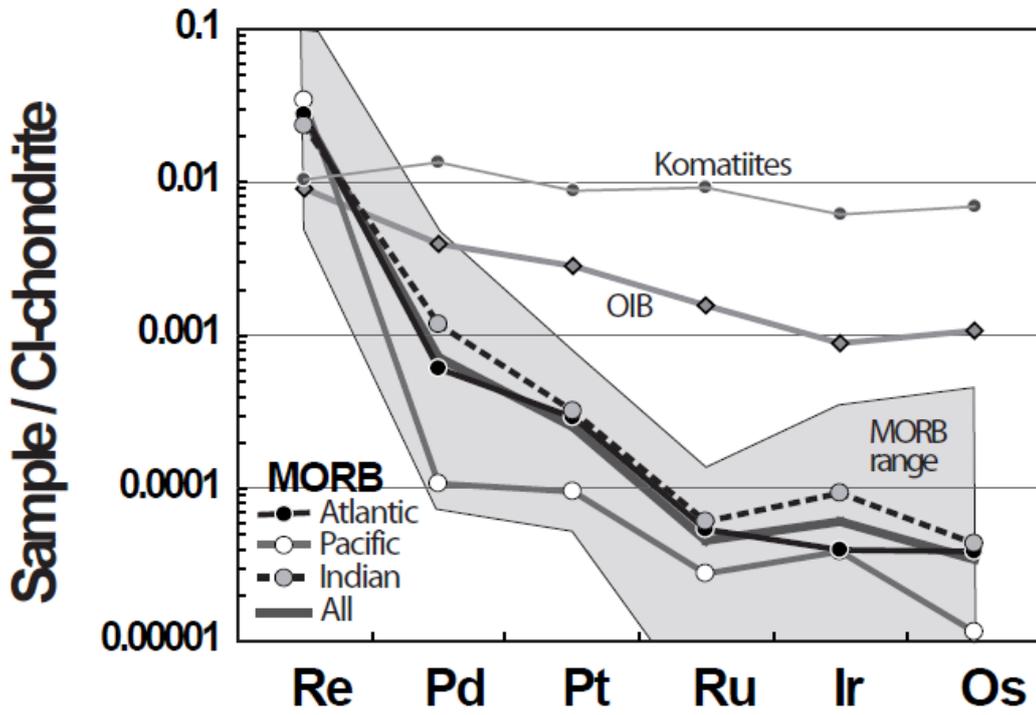
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3171 **Figure 36.** CI-chondrite normalized HSE diagrams for Lihir mantle xenoliths and lavas (McInnes et
3172 al., 1999), Grenada picrites and basalts and Izu-Bonin lavas (Woodland et al., 2000), and Kamchatka
3173 xenoliths (Widom et al., 2003). Note that PPGE > IPGE lavas from the Izu-Bonin and Grenada. CI
3174 chondrite normalization from Horan et al. (2003).

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3176
3177 **Figure 37.** Assimilation accompanied by fractional crystallization (AFC) models of $^{87}Sr/^{86}Sr$ versus
3178 $^{187}Os/^{188}Os$ for Lesser Antilles primitive lavas Parameters for Models 1 and 2 are shown in the figure
3179 and in Table 3 of Bezarid et al. (2015).

3180
3181
3182 **Figure 38.** Primitive mantle normalized HSE diagram for cores and rinds of Mèlange metamorphic
3183 magic blocks from the Catalina Schist, Franciscan Complex and Samana Metamorphic Complex.
3184 Cores are consistent with dominantly reflecting basaltic/sedimentary protoliths with radiogenic Os
3185 and rinds are can represent as 70% peridotite HSE contributions. Data are from Penniston-Dorland et
3186 al., 2012; 2014, with primitive mantle normalization from Becker et al. (2006).

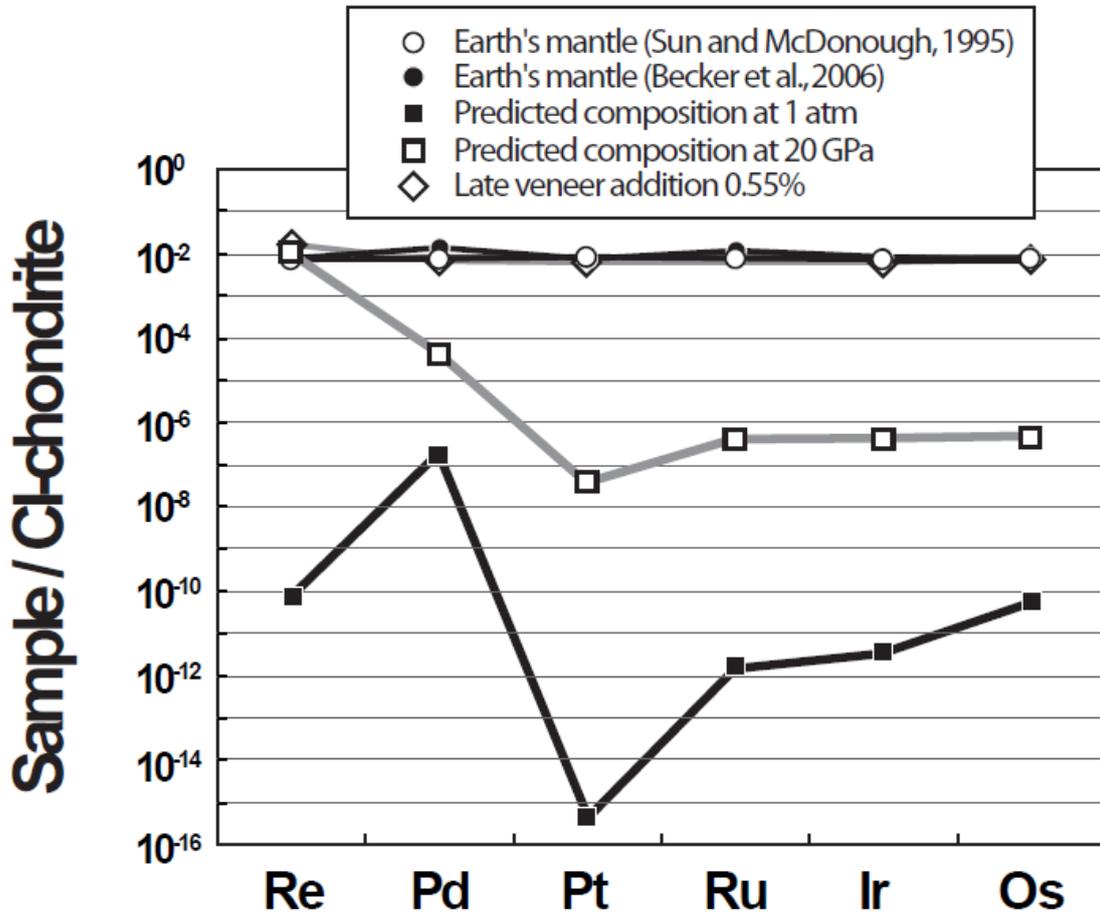
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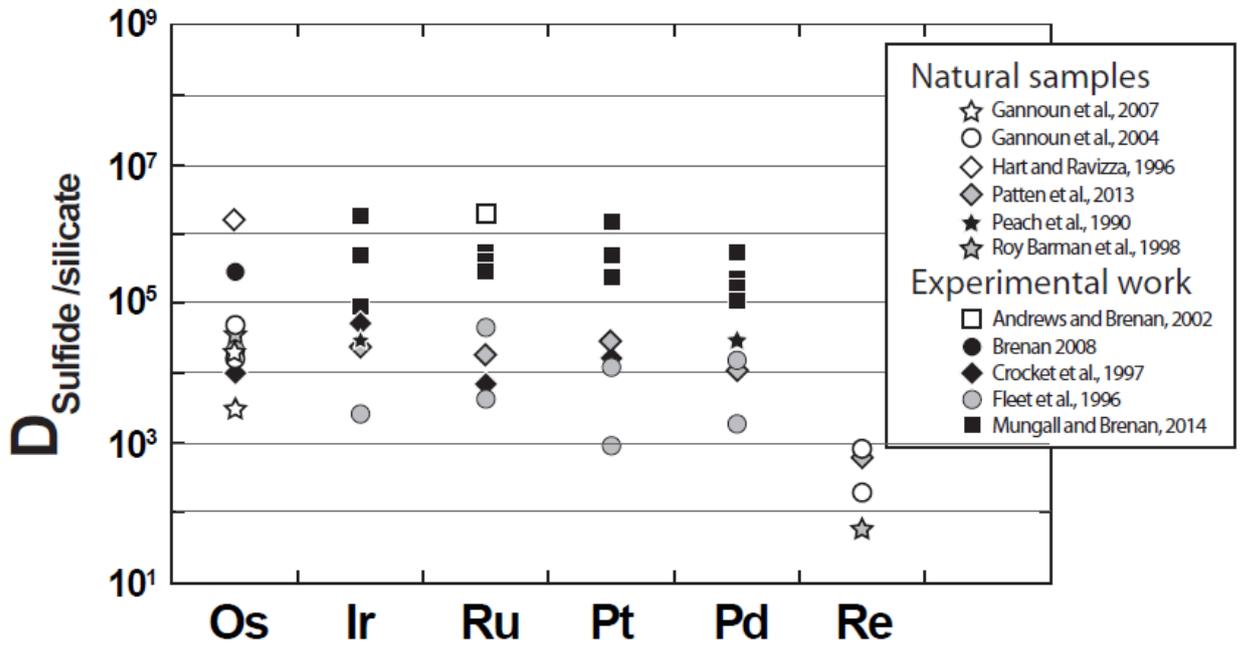
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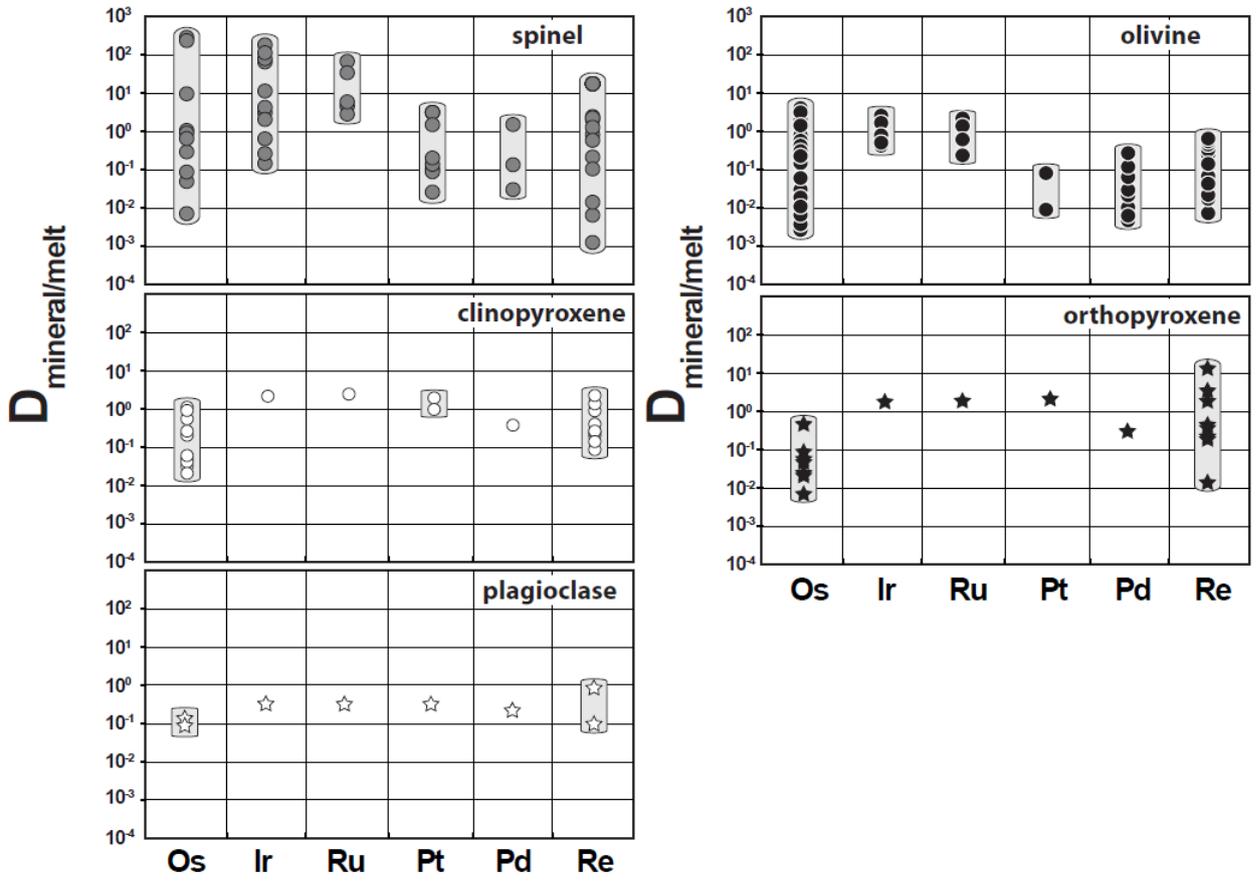
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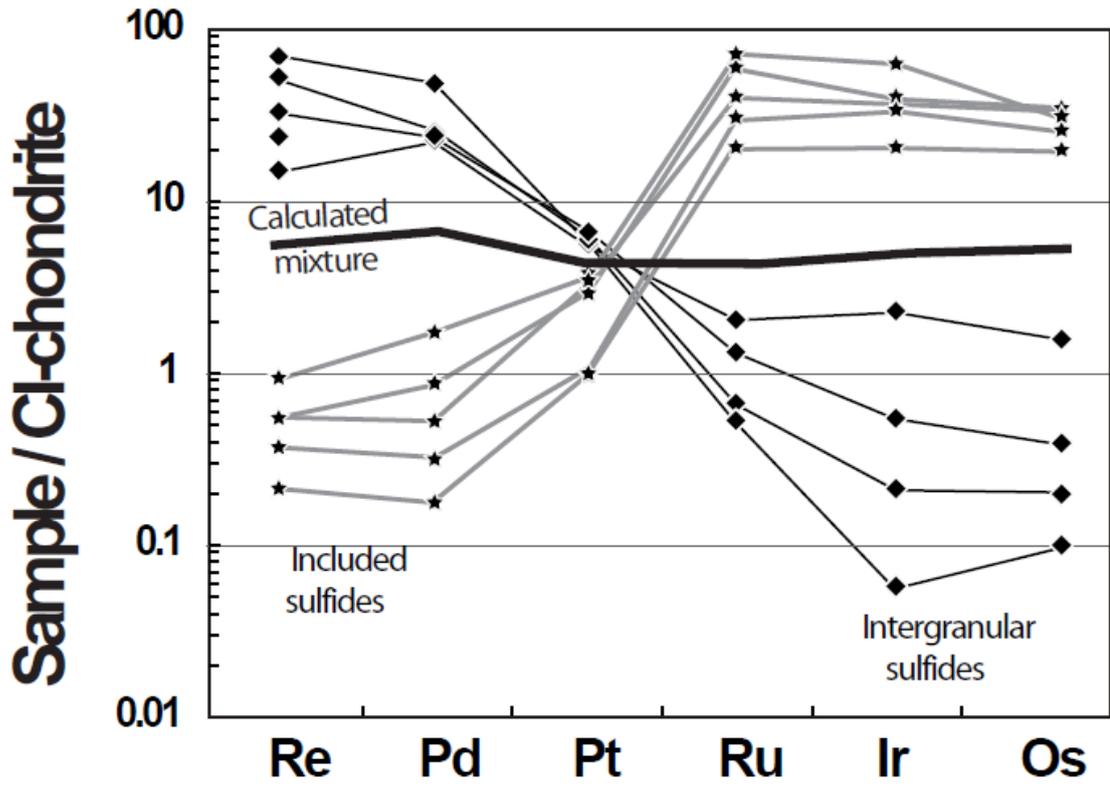


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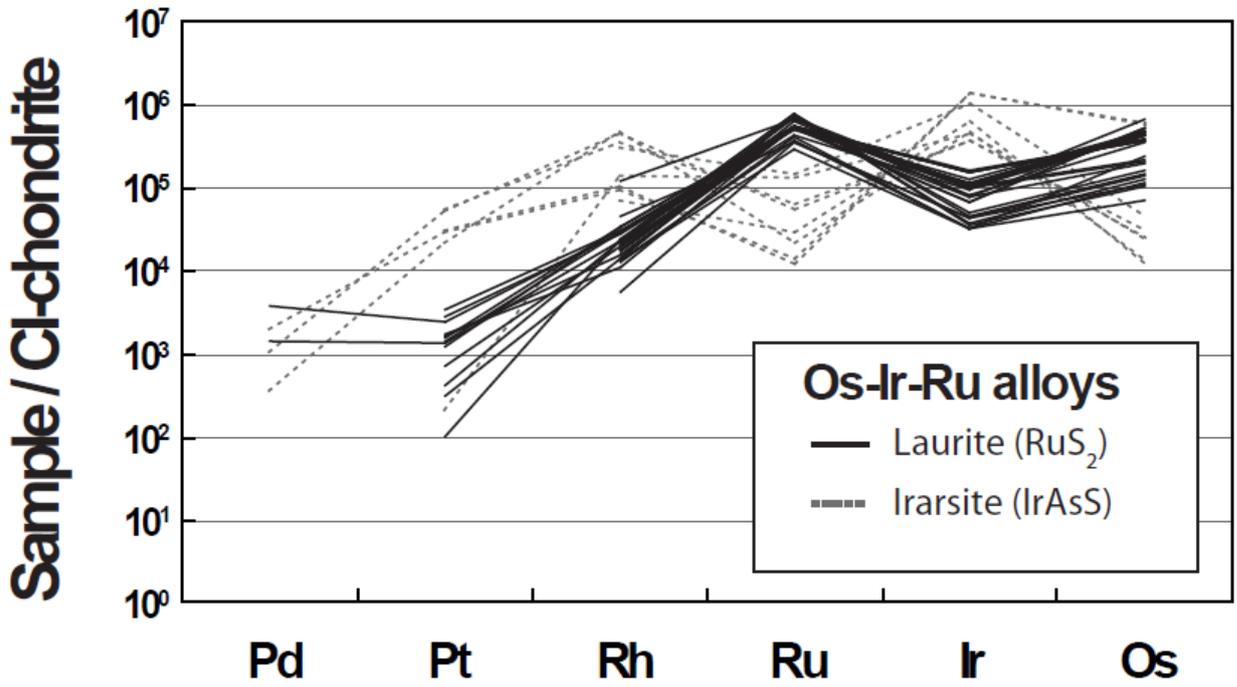


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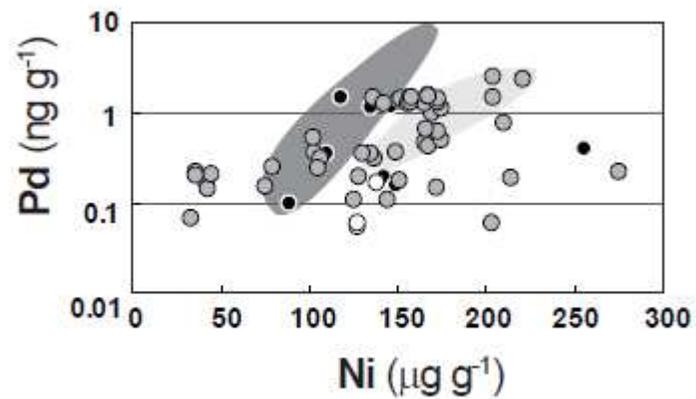
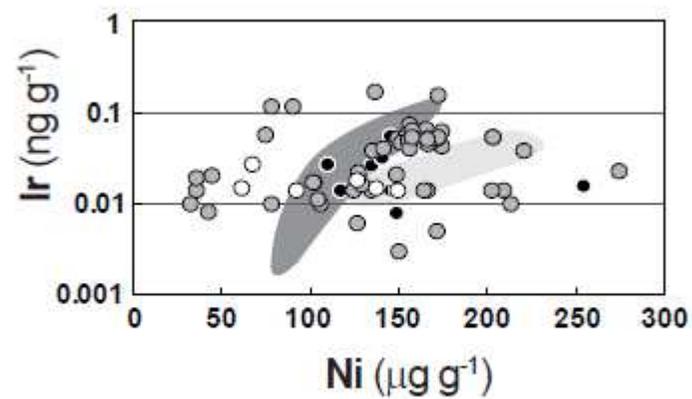
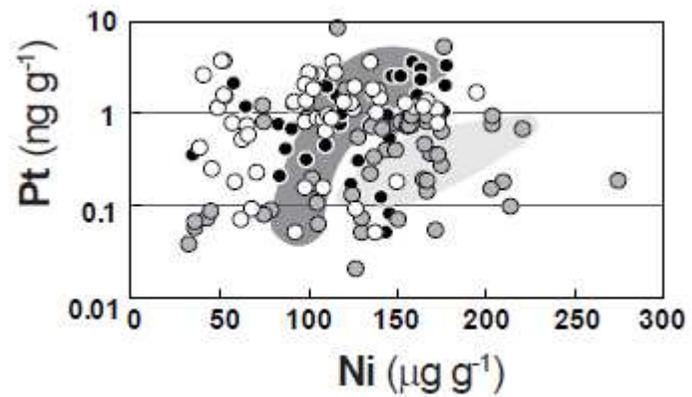
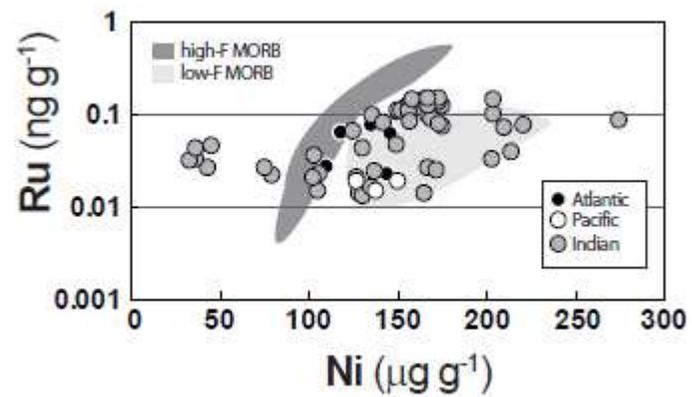
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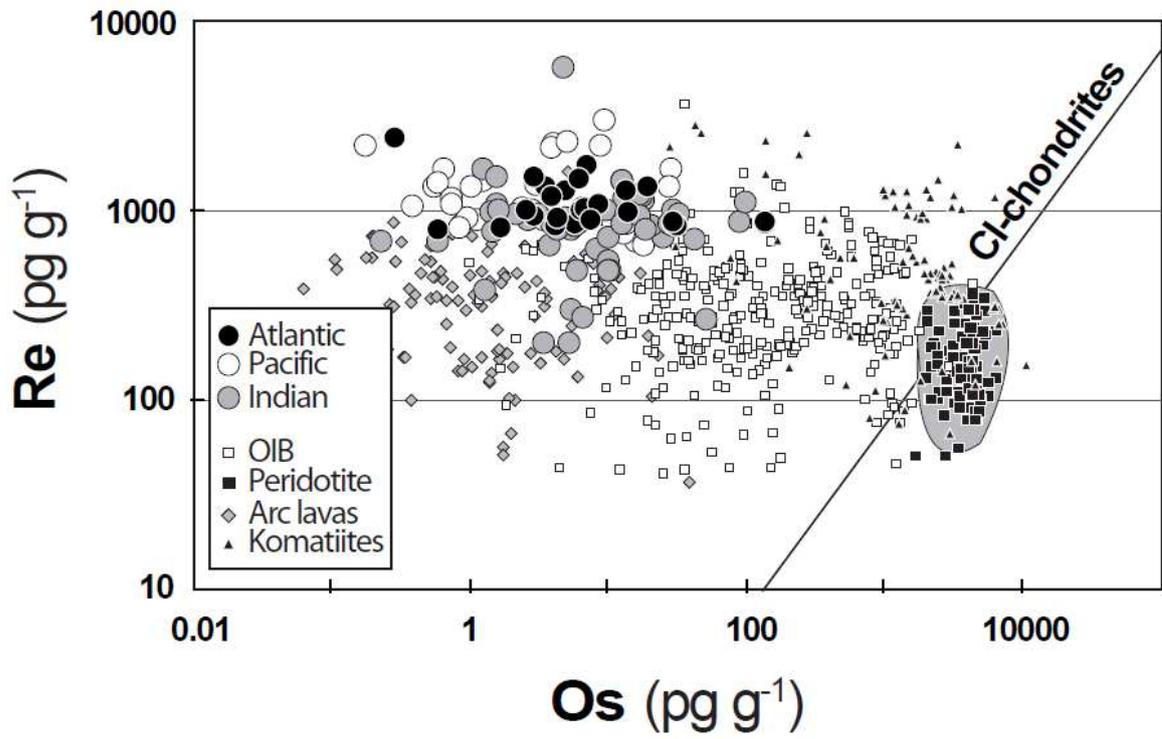
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Figure 7



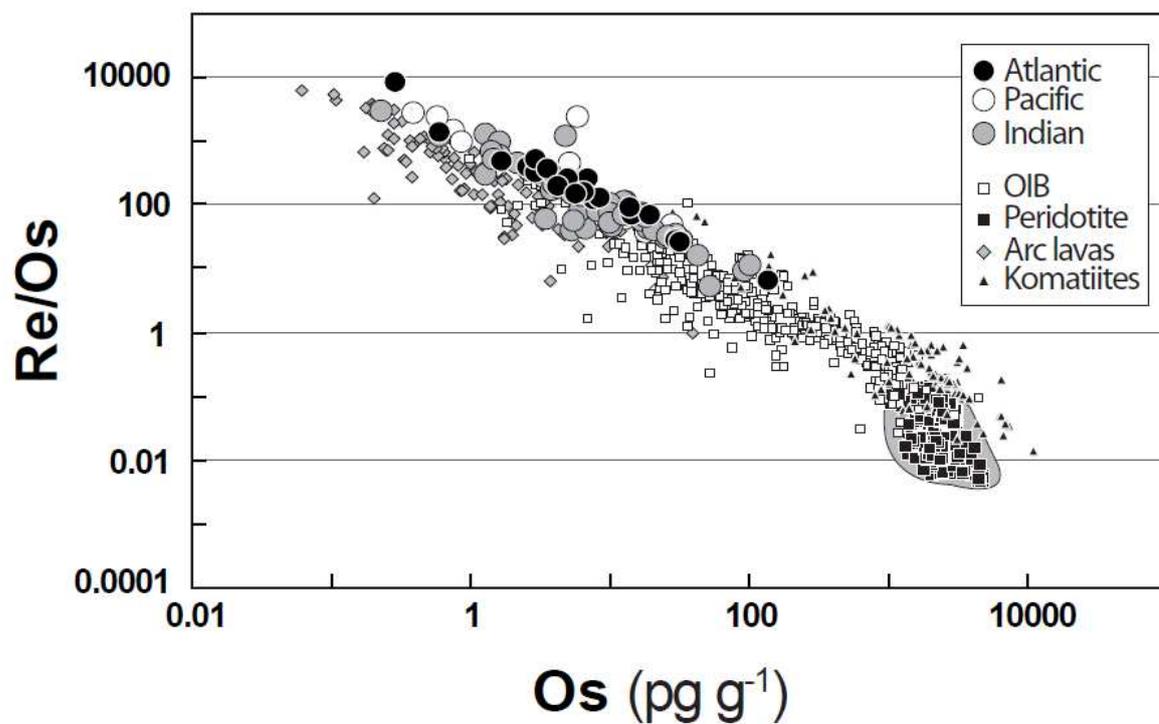
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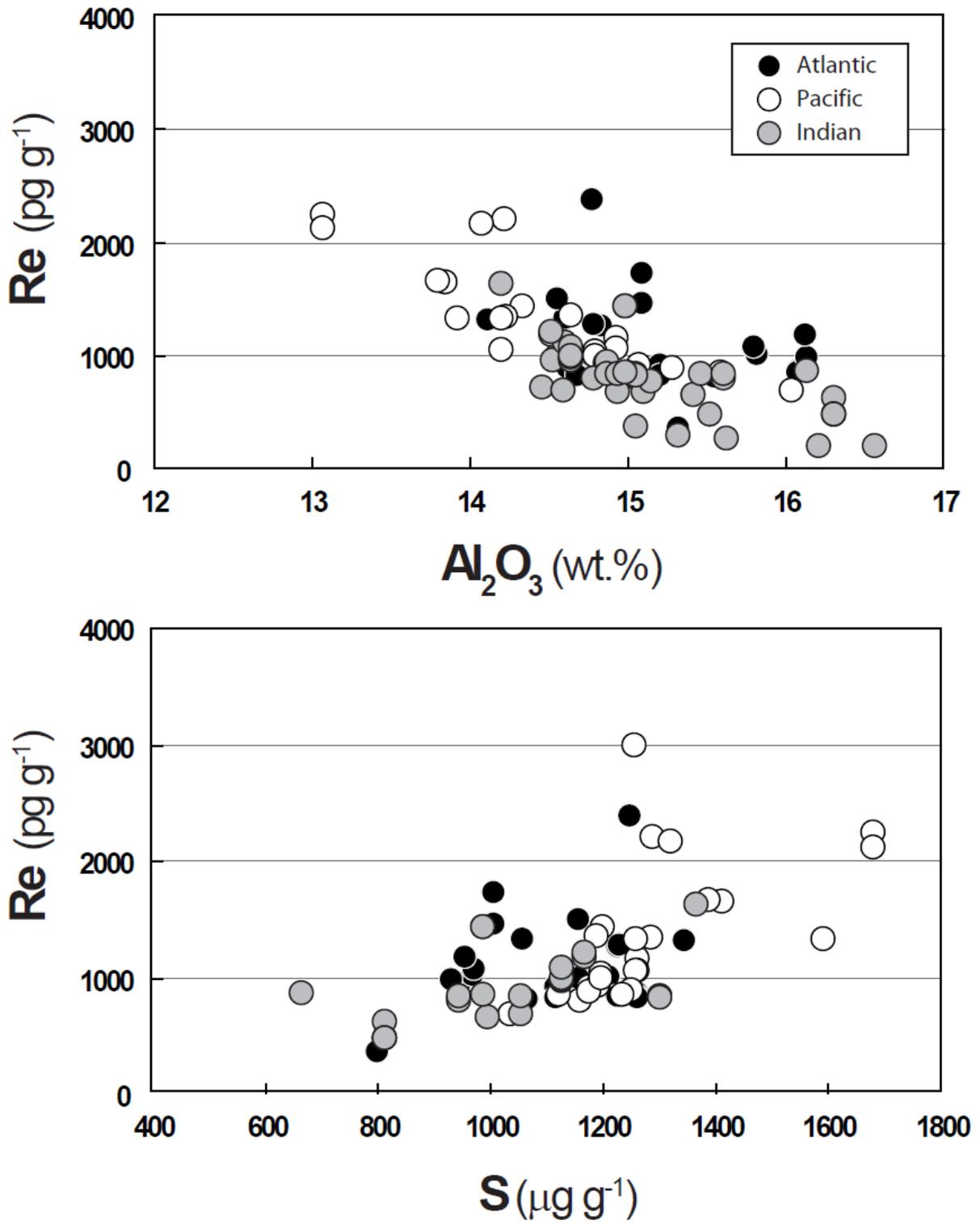
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3376 Figure 9
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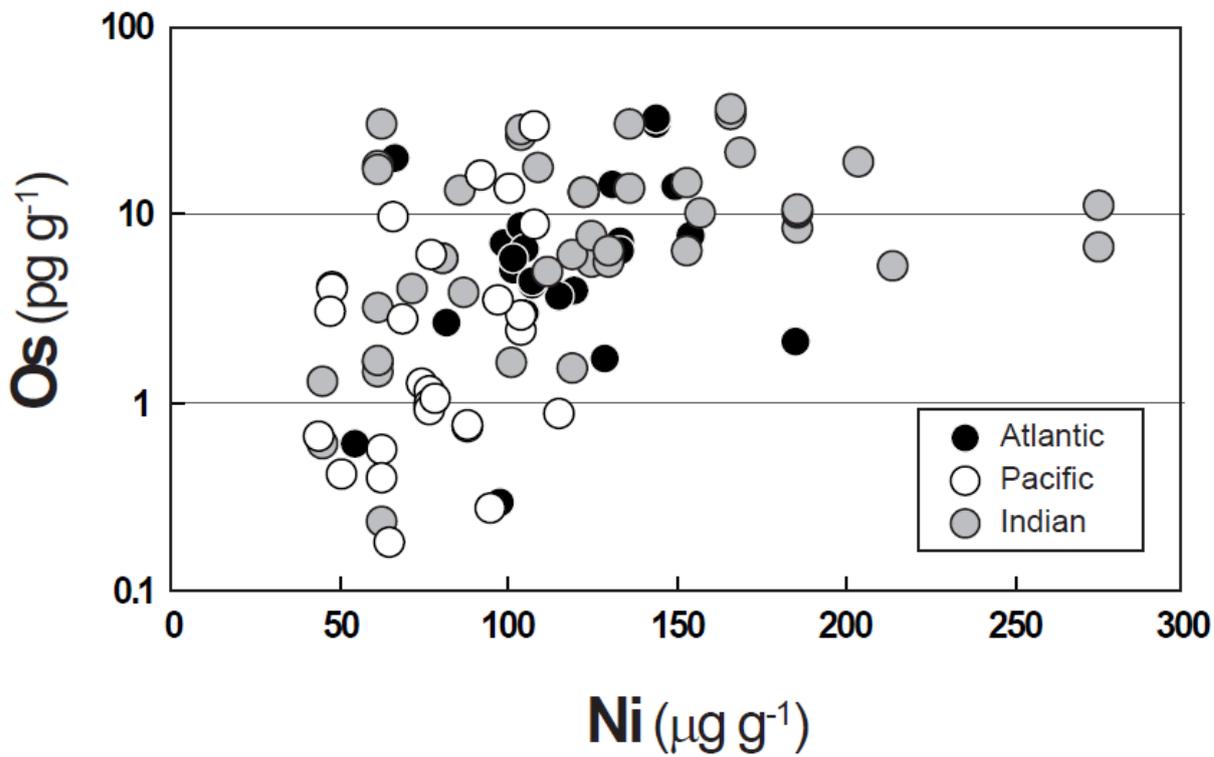
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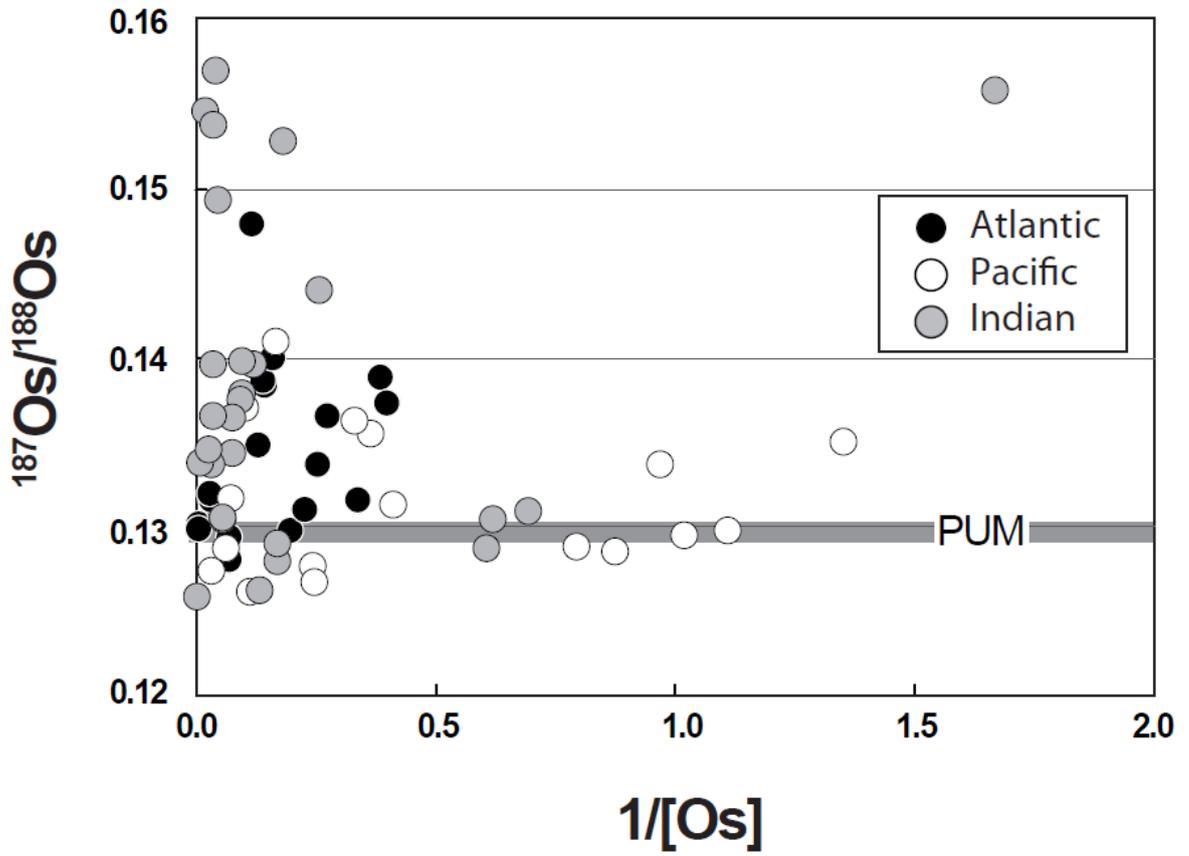
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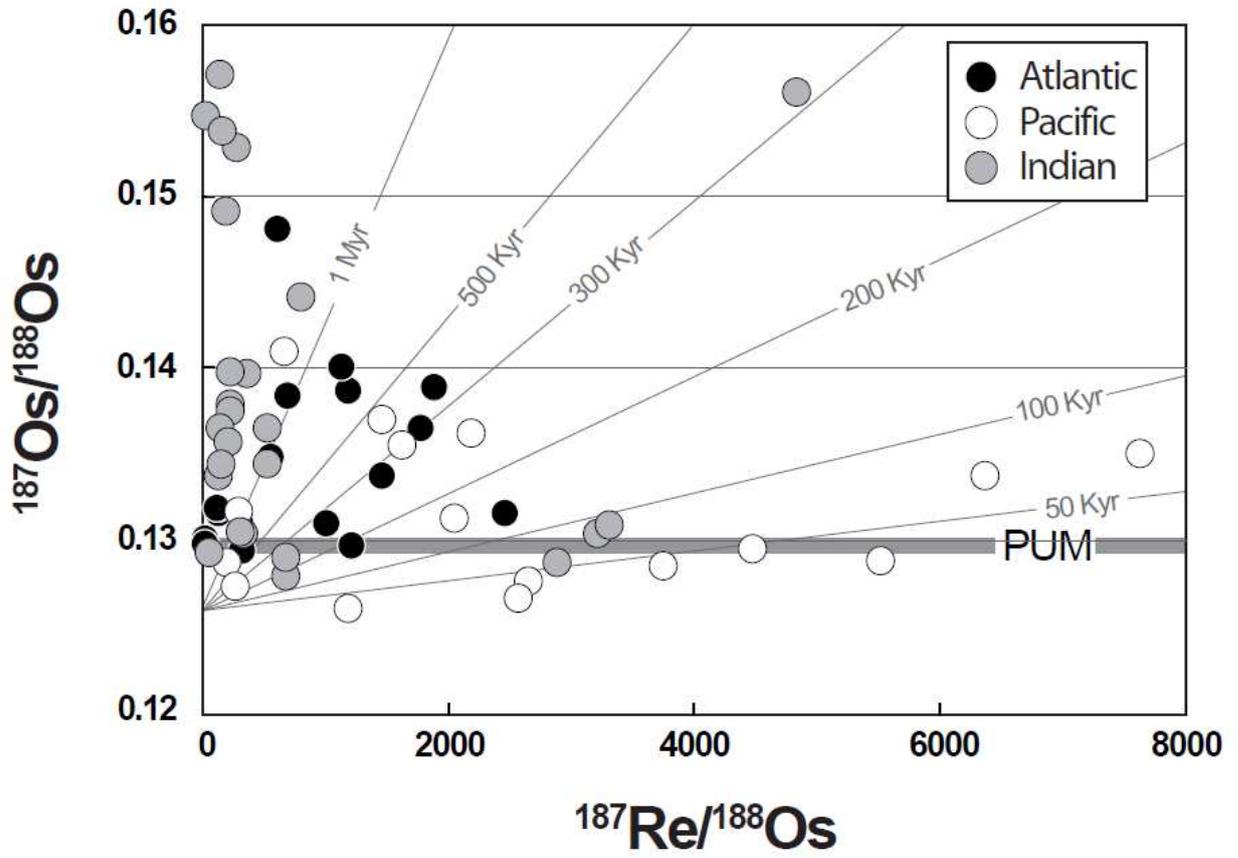
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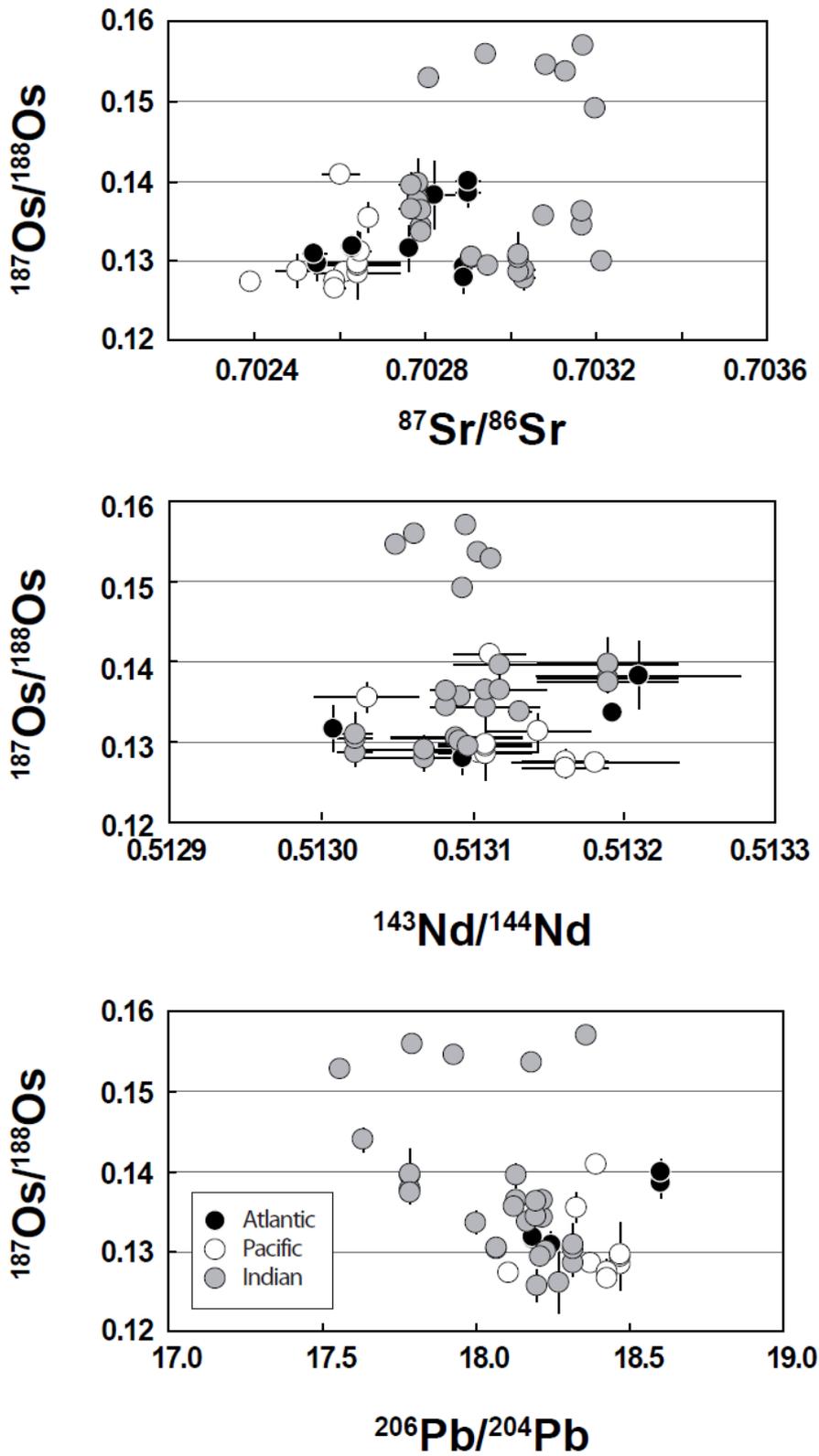
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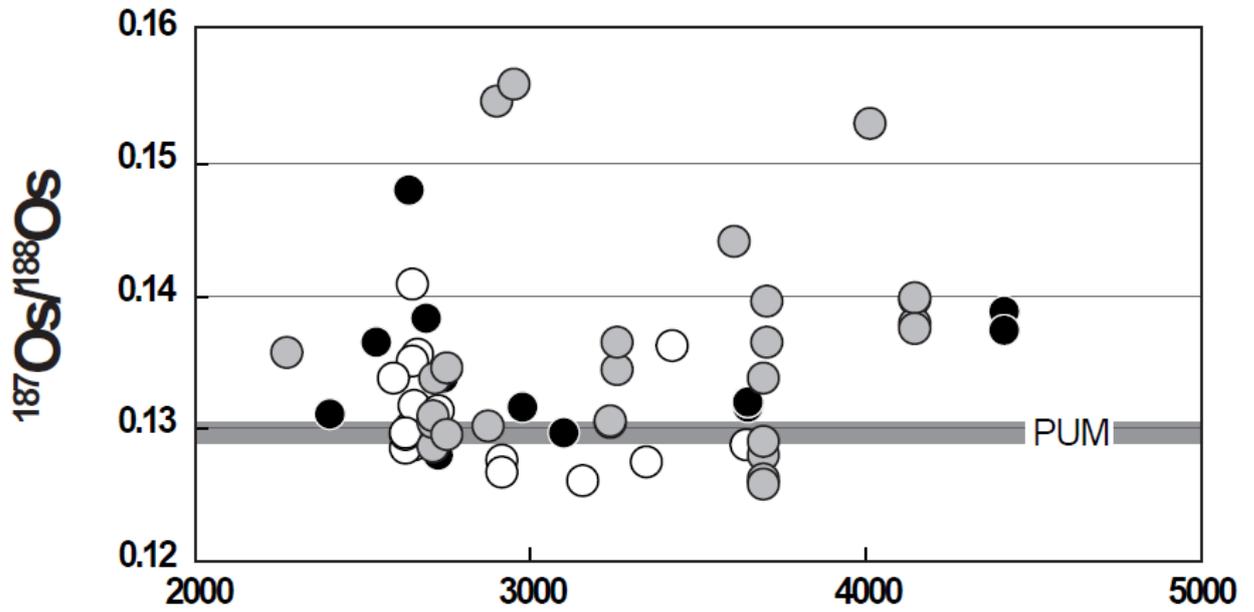
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3489 Figure 14
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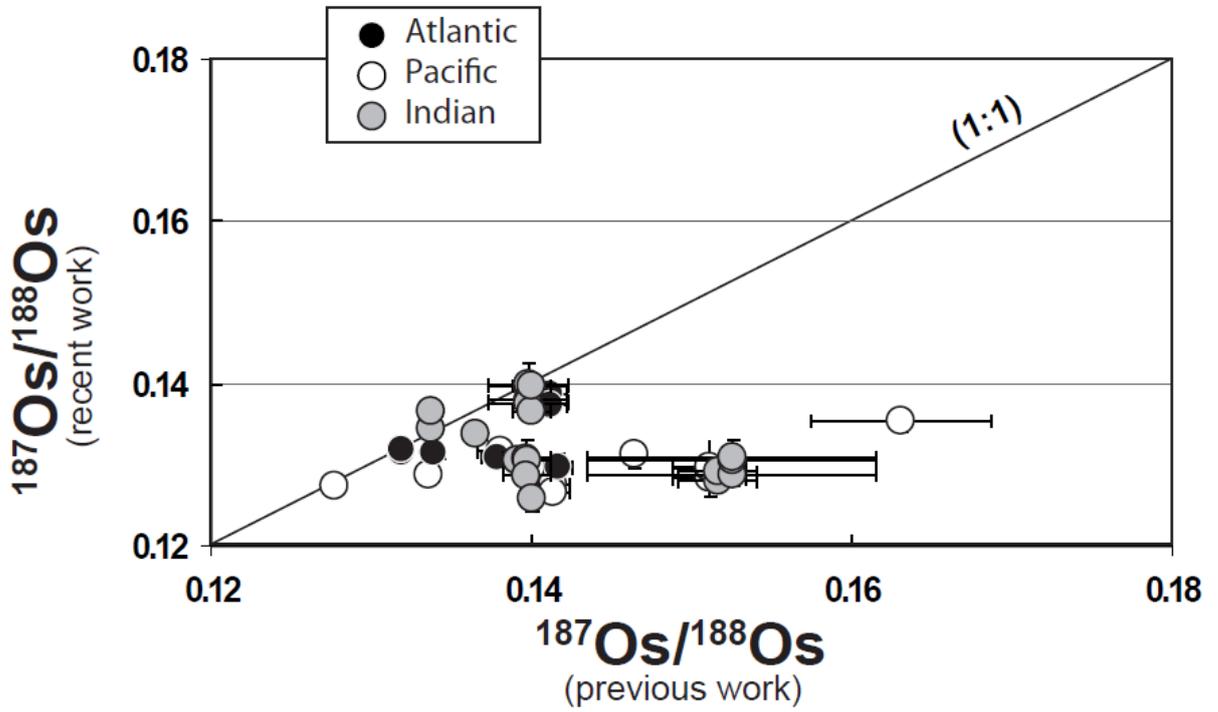
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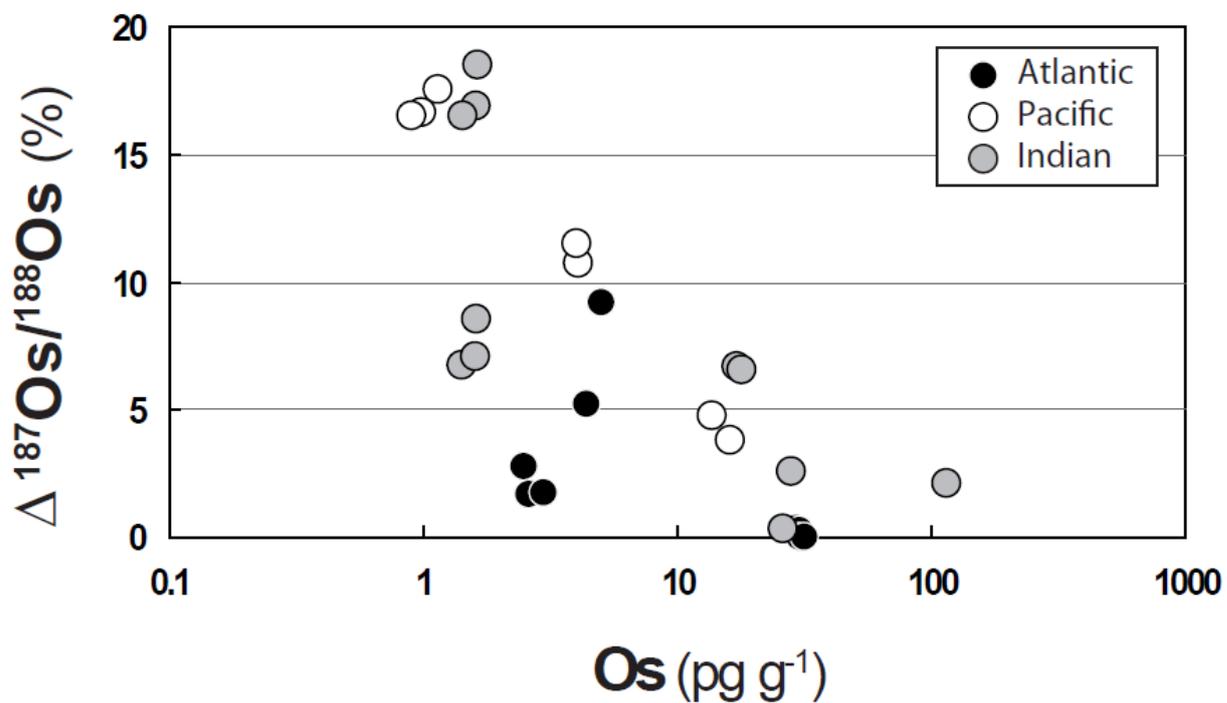
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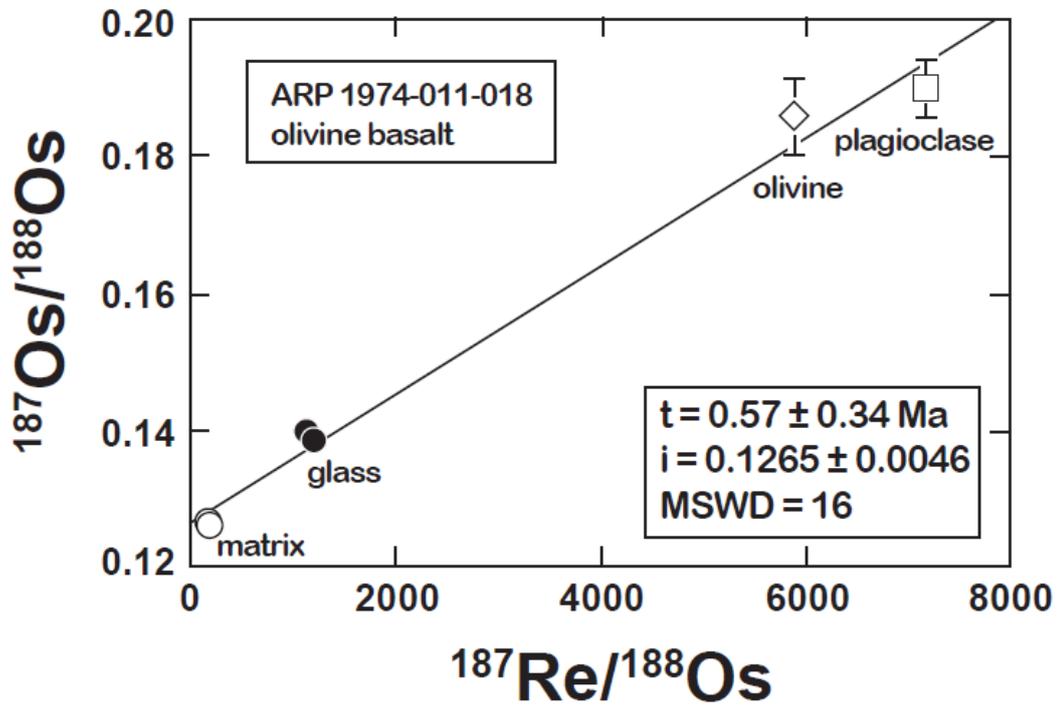
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3558 Figure 17
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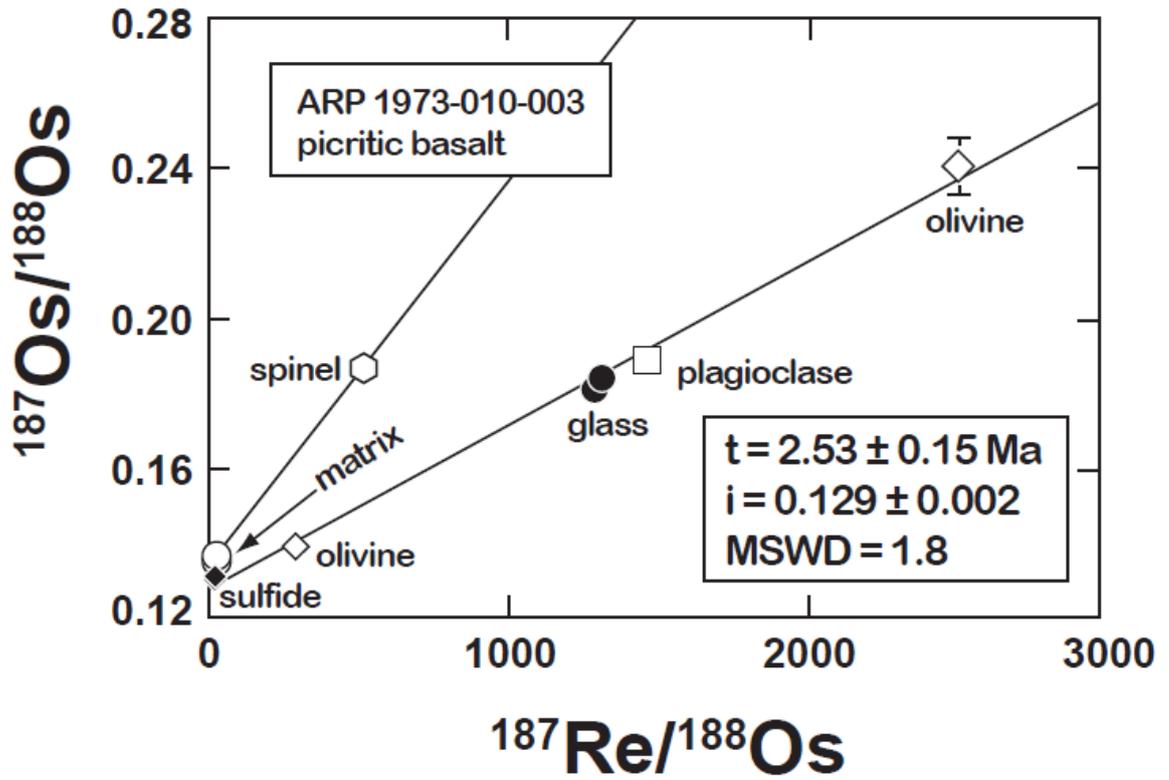
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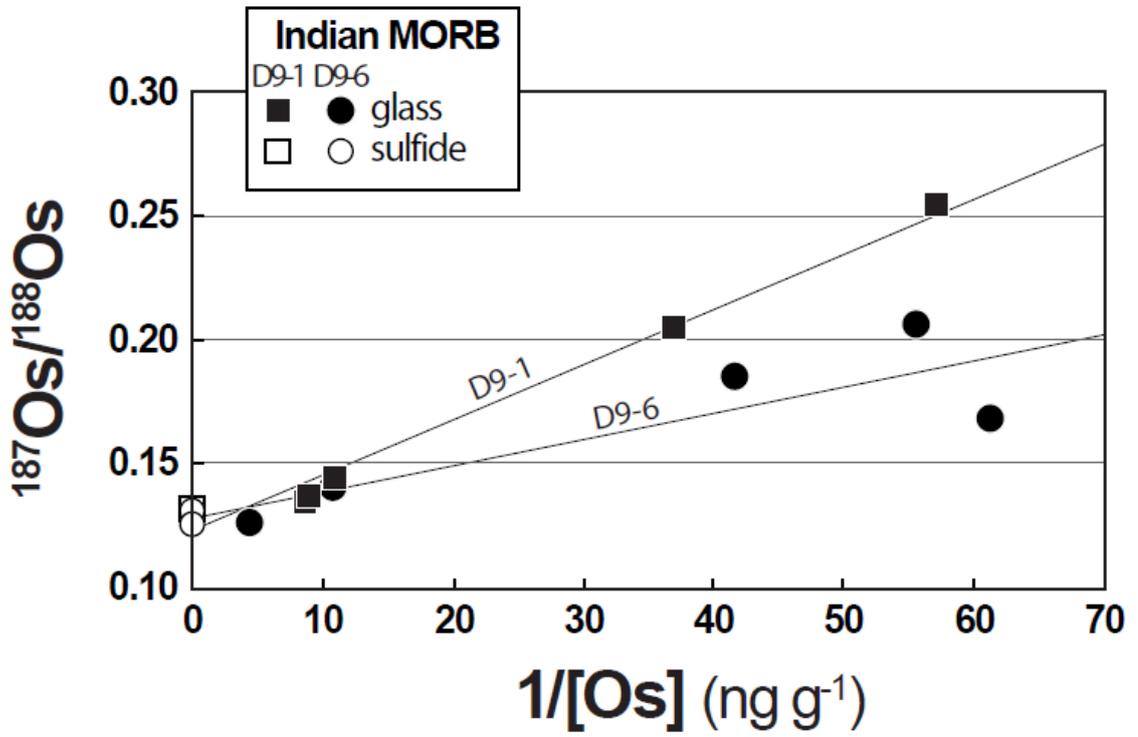
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3616 Figure 19
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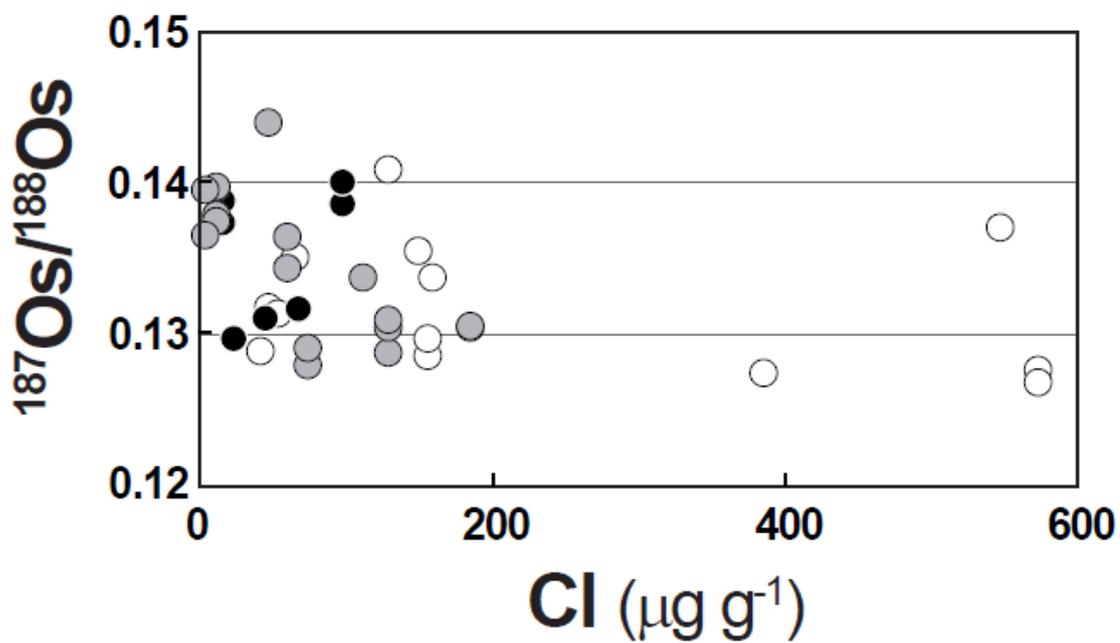
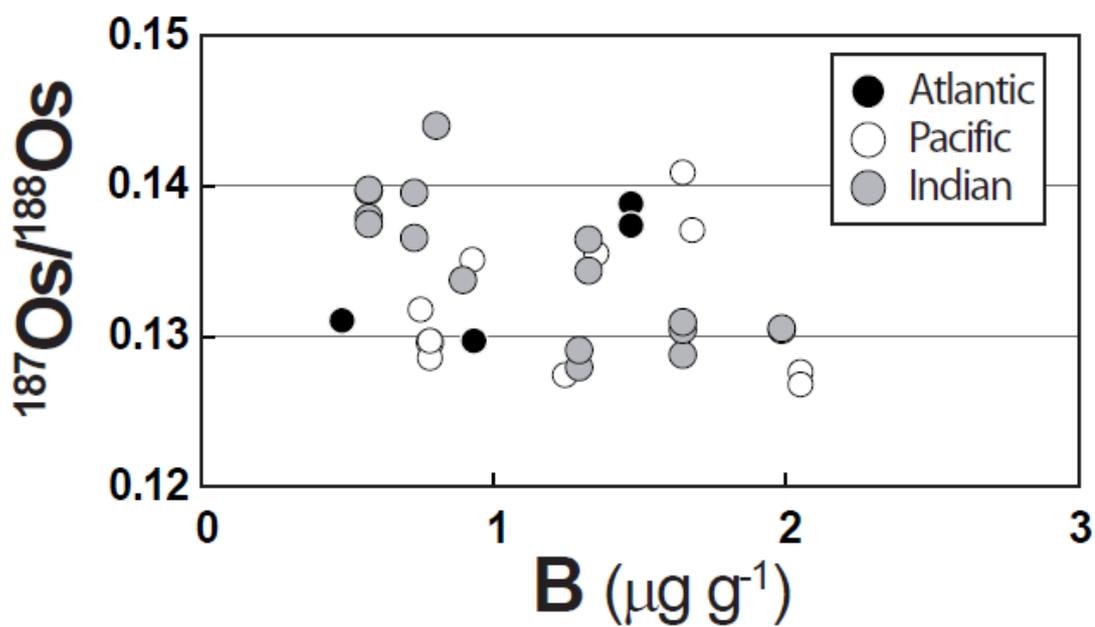
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3641 Figure 20
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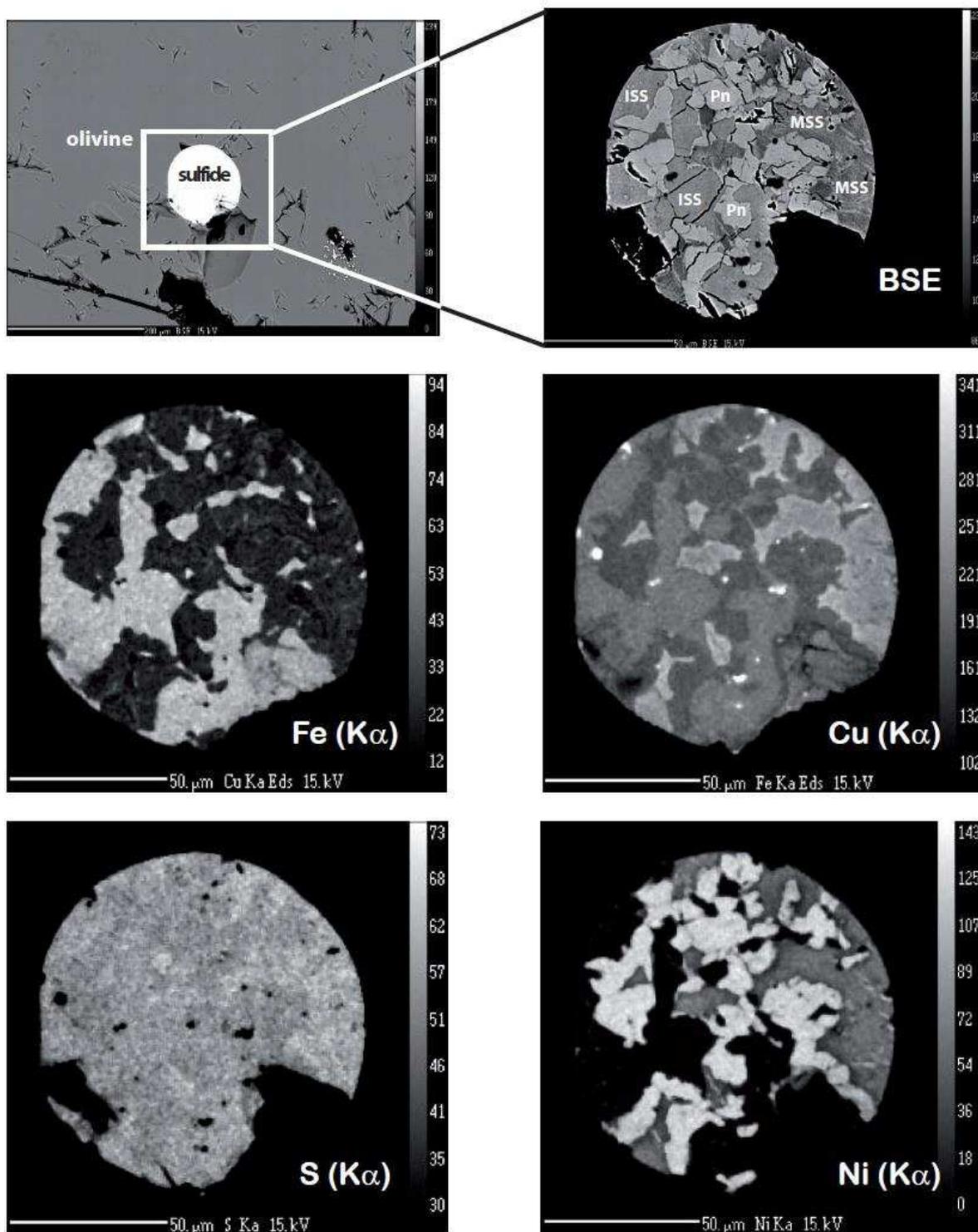
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3667 Figure 21
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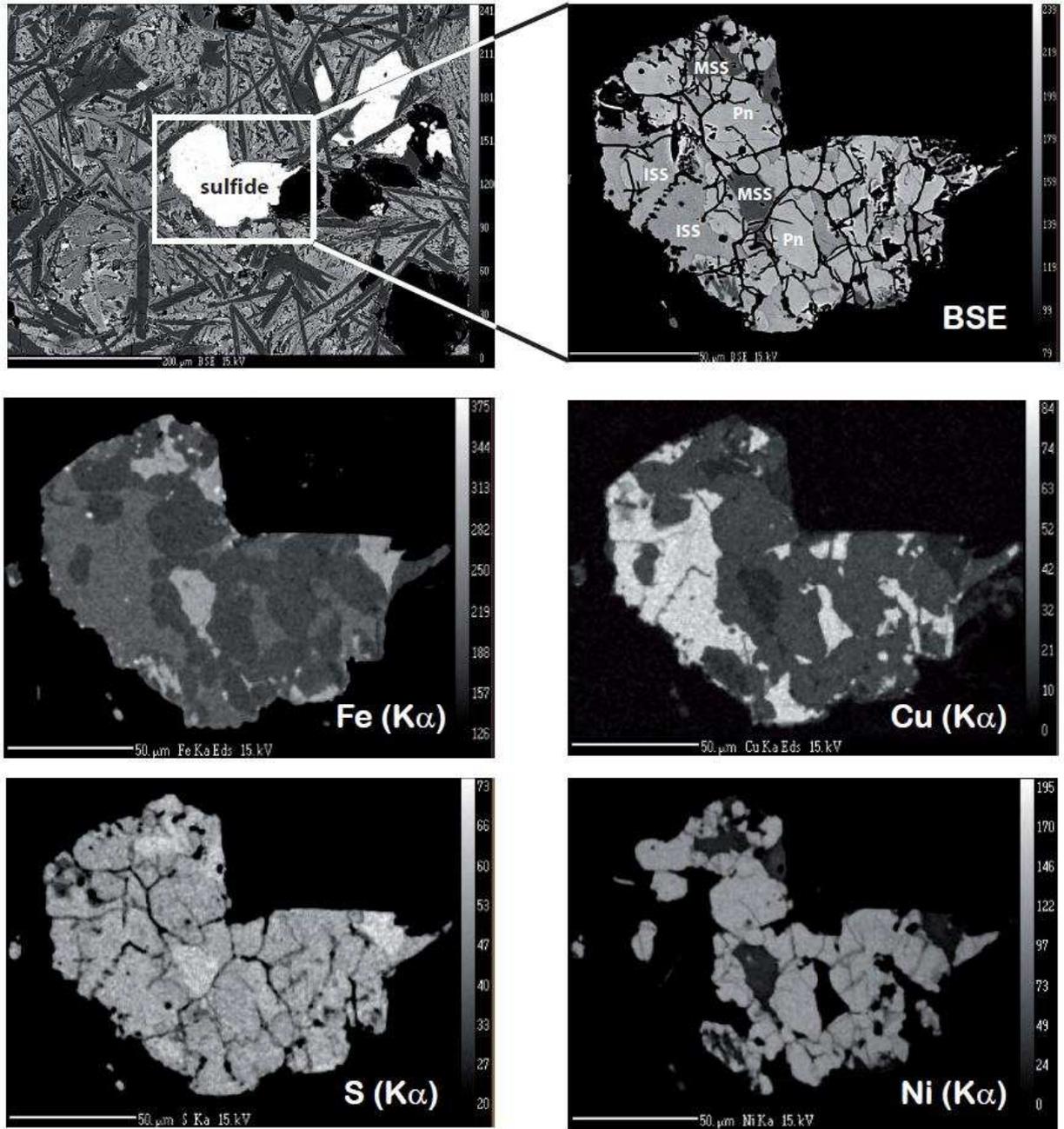
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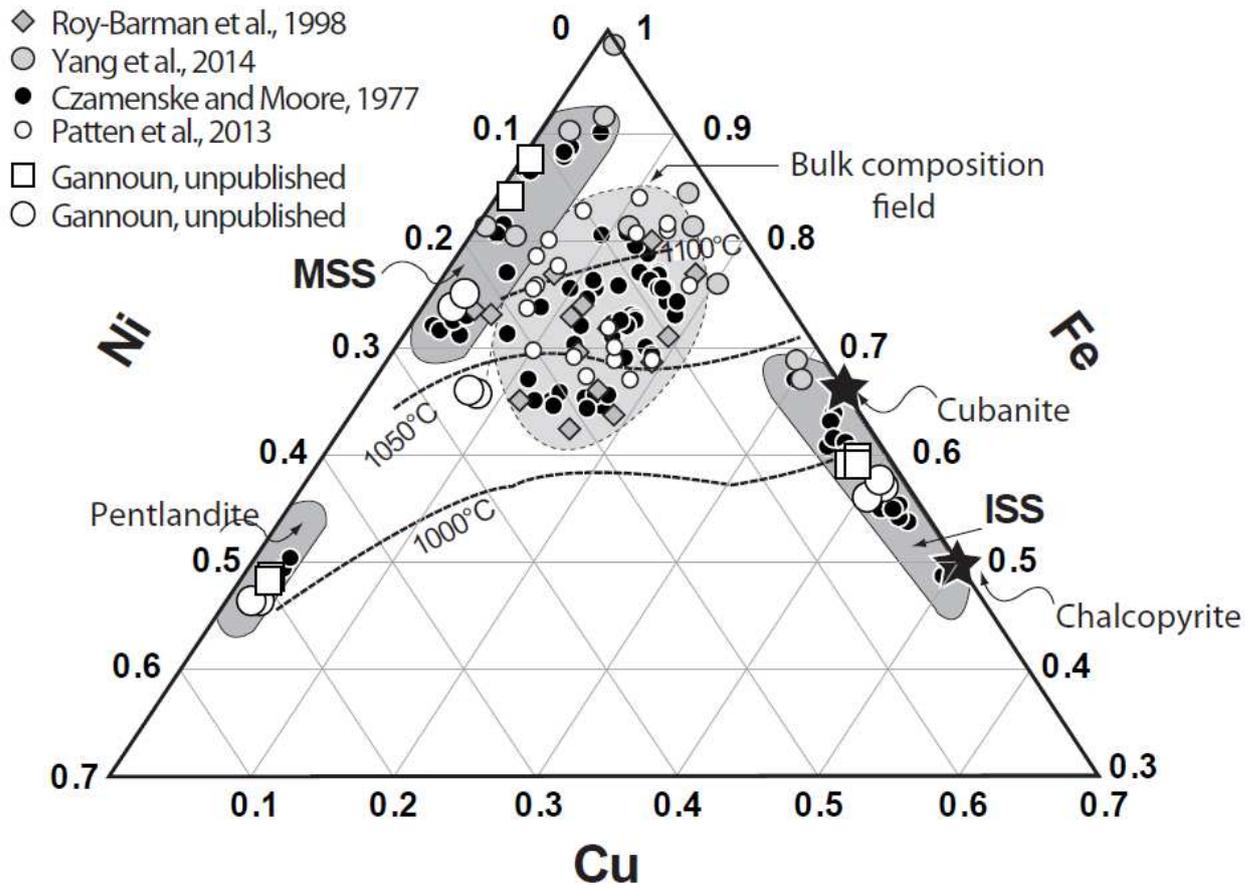
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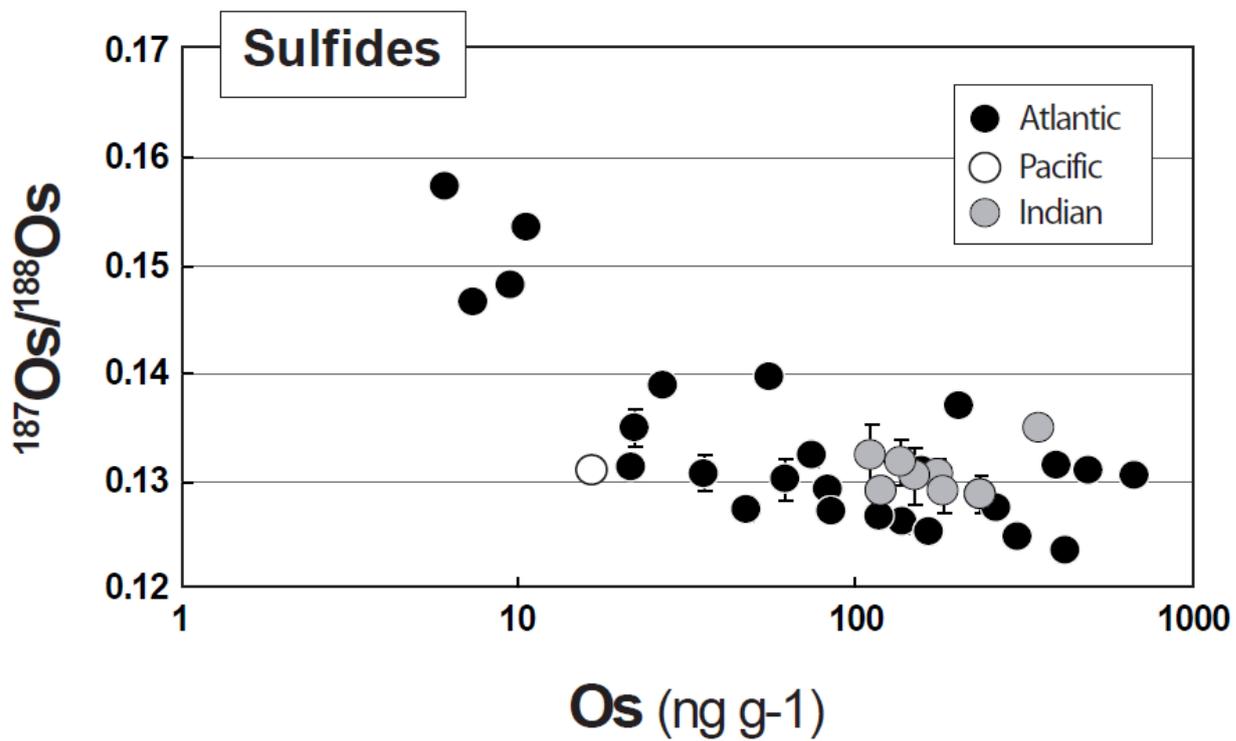
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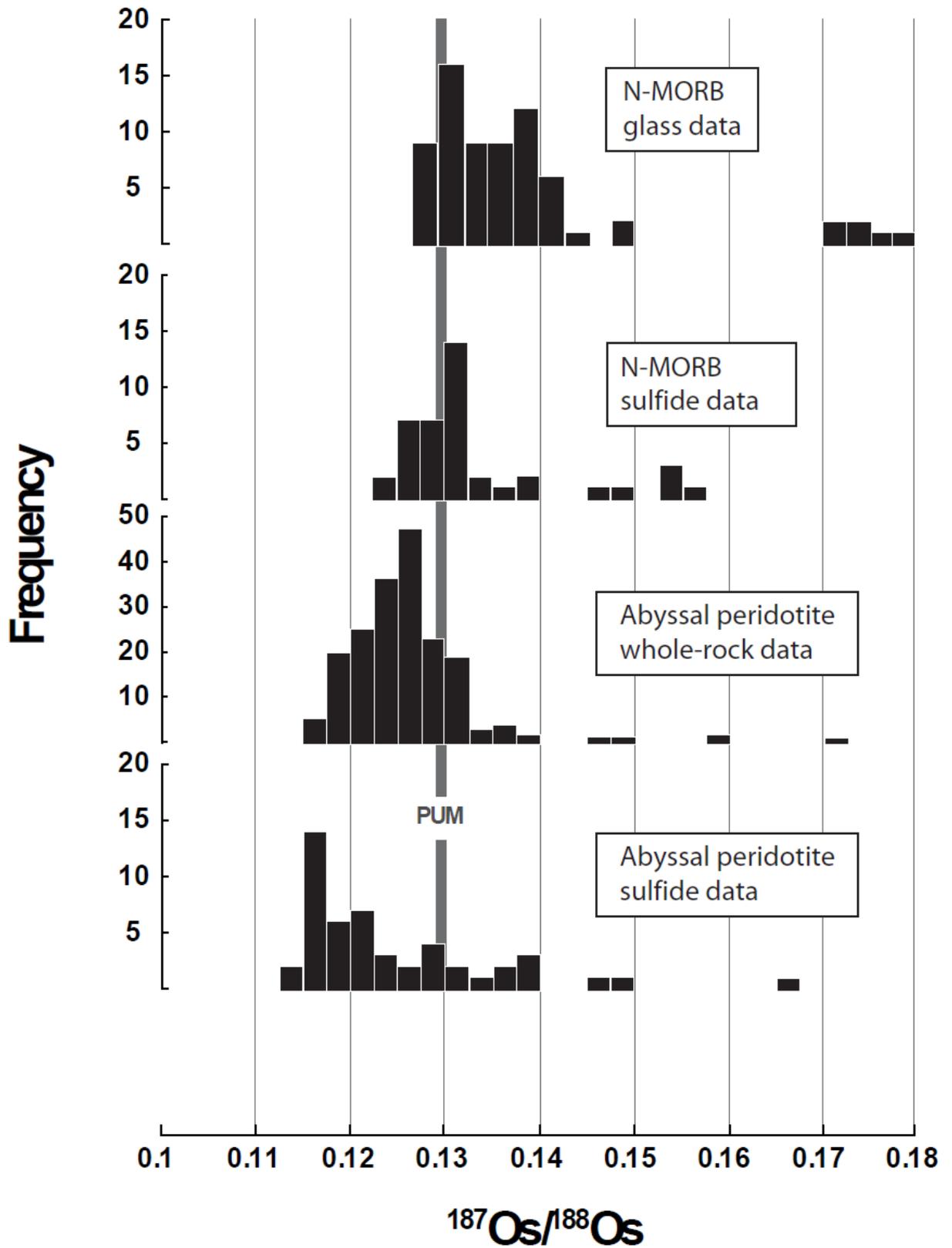
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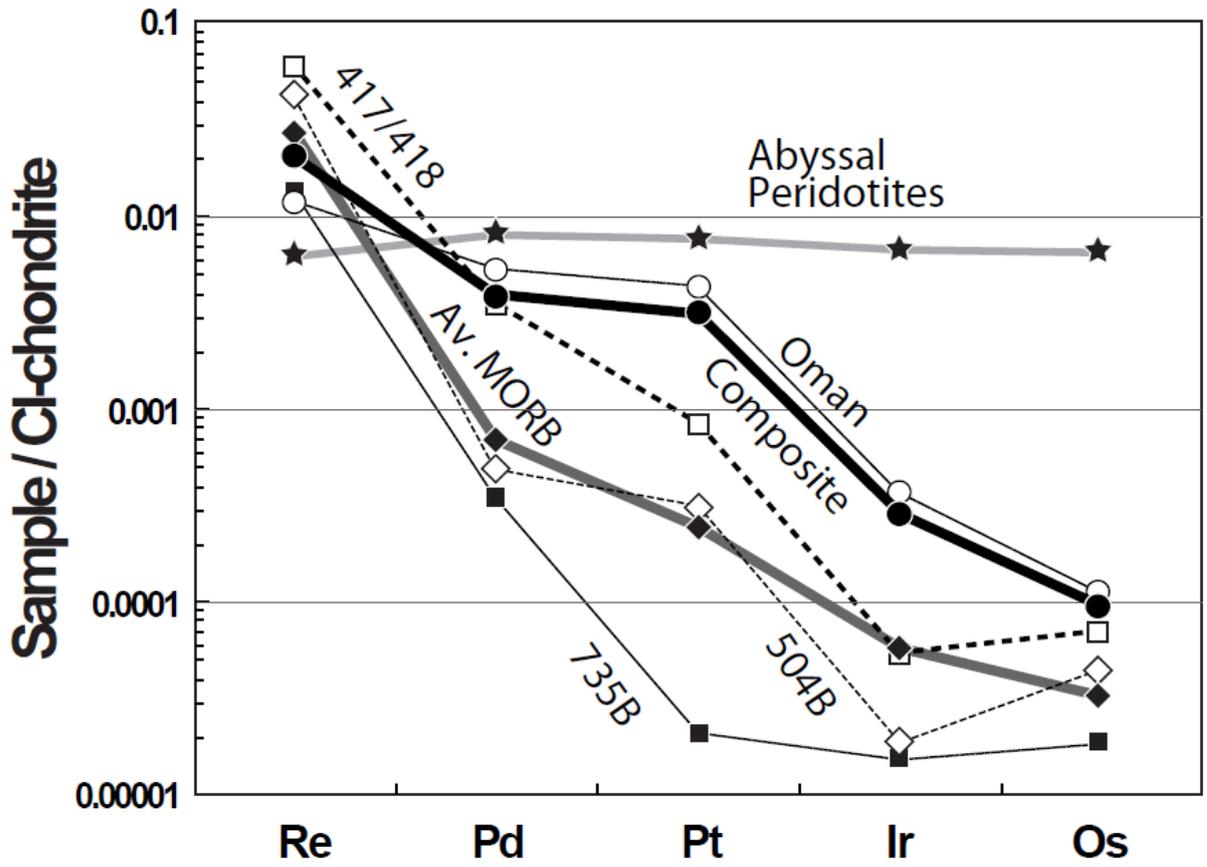
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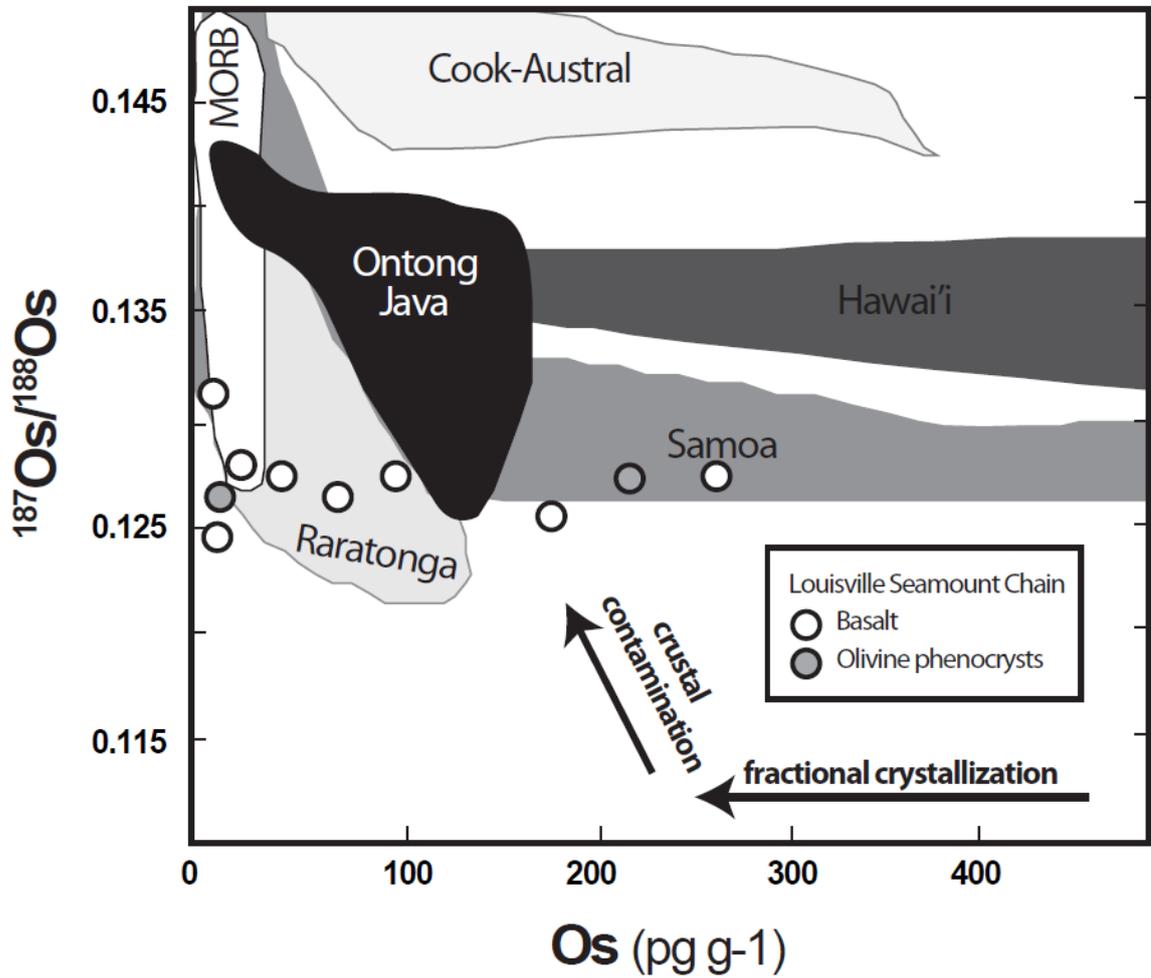
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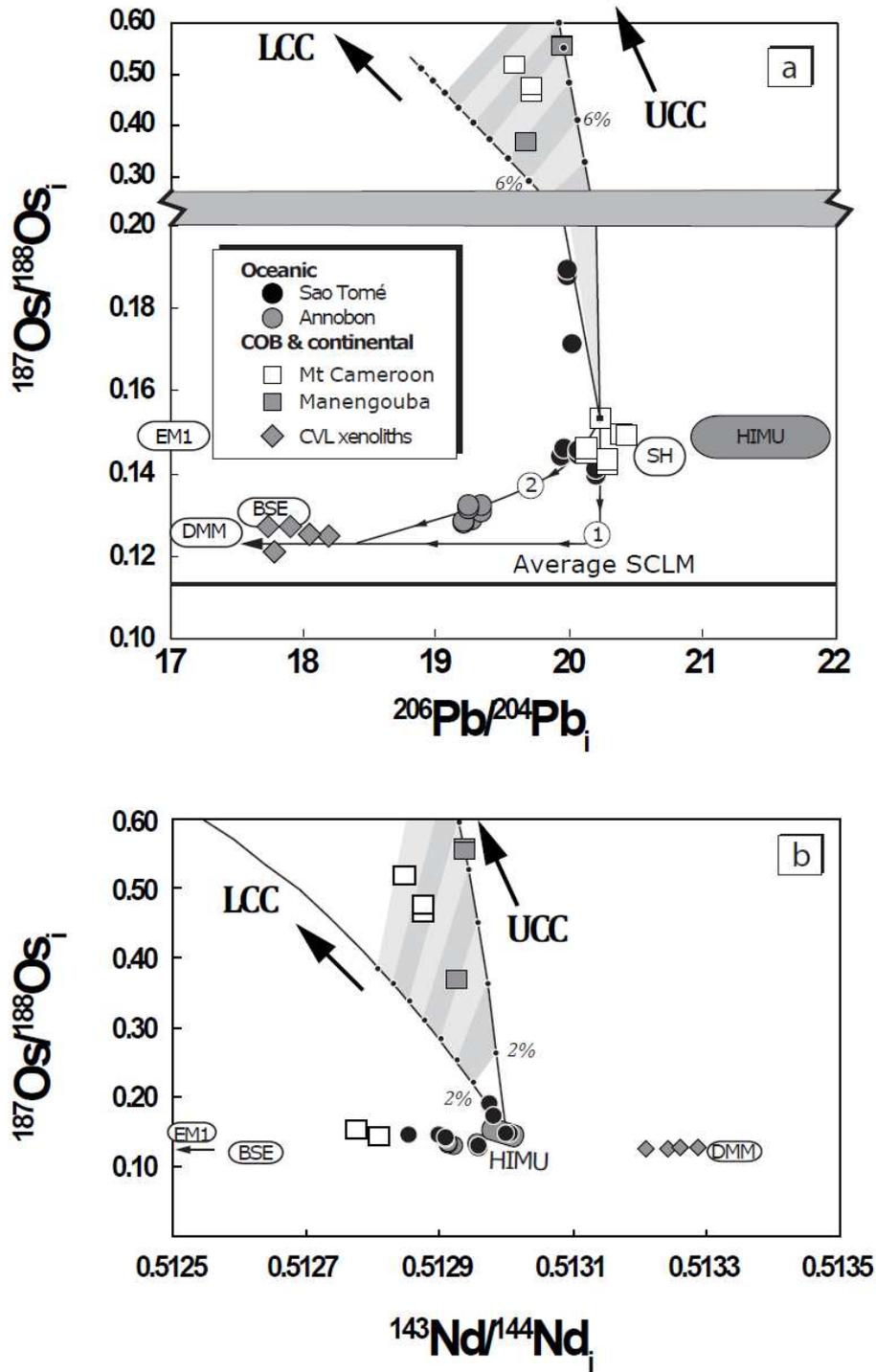
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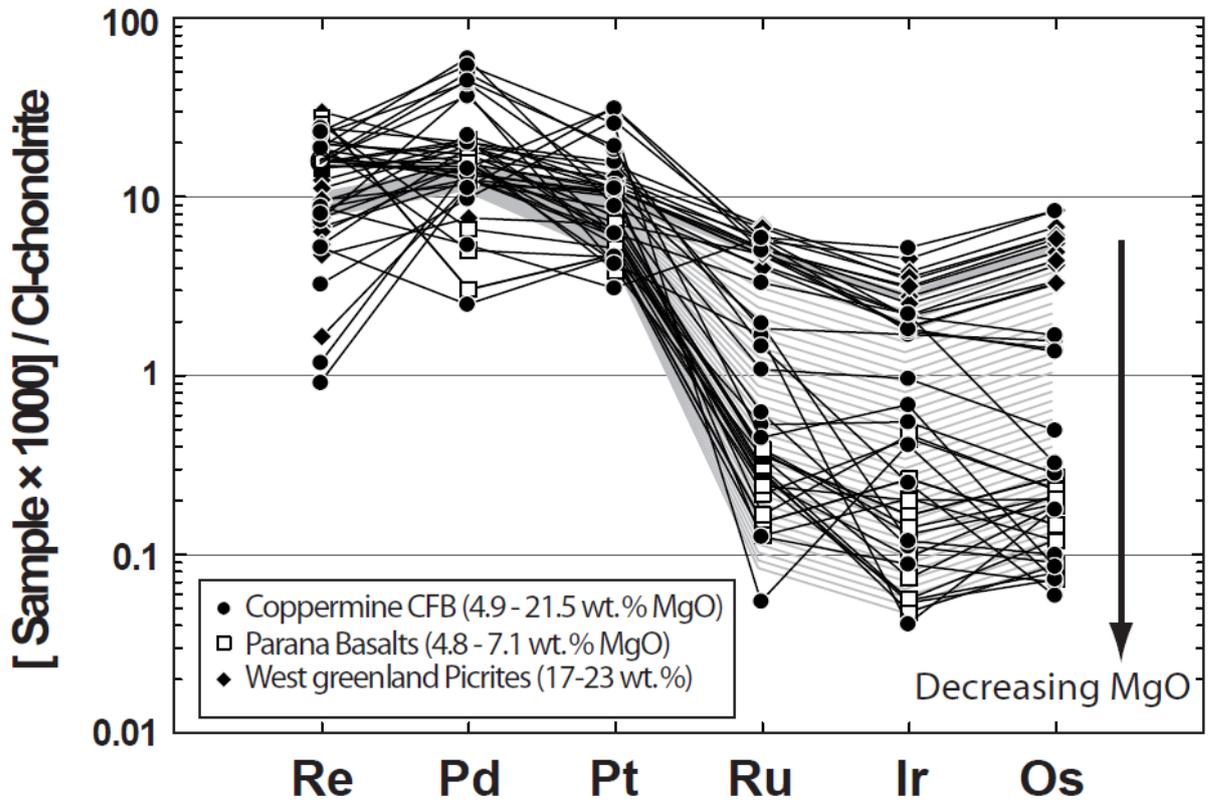
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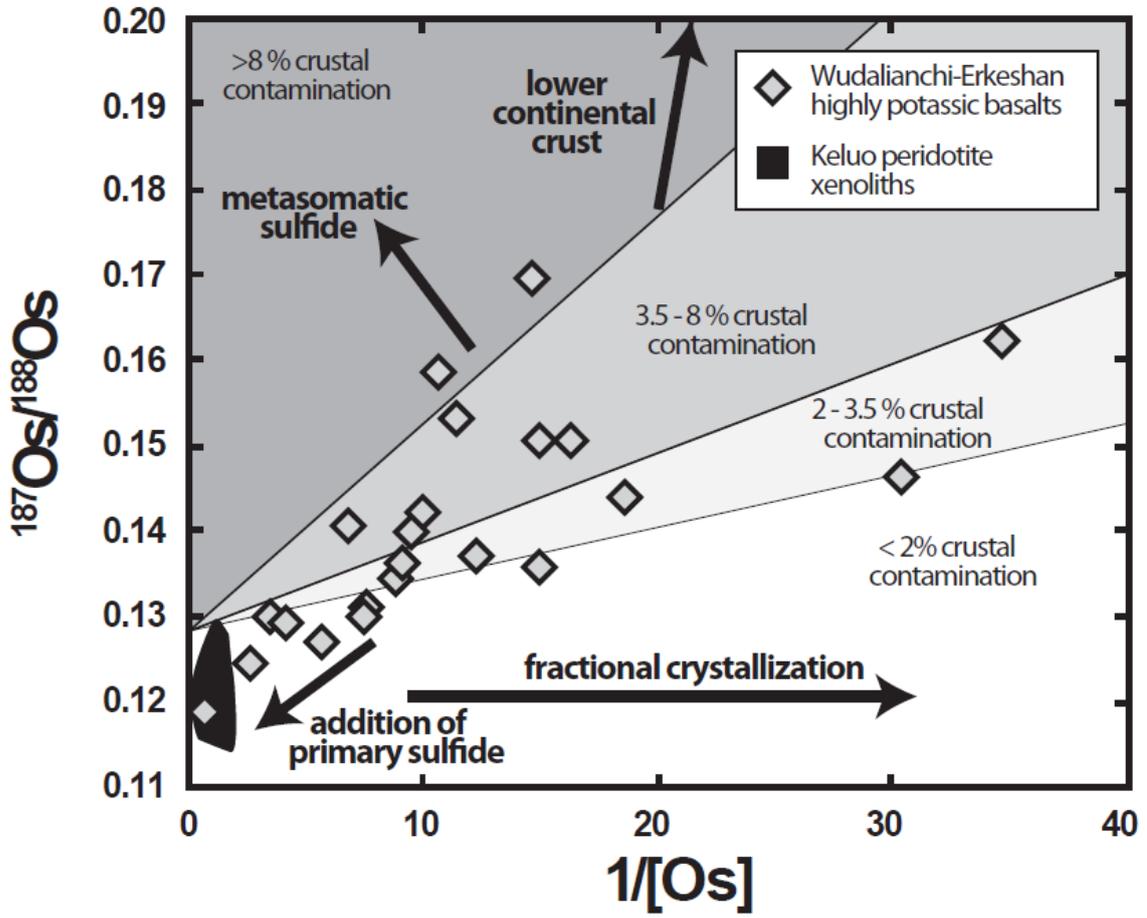
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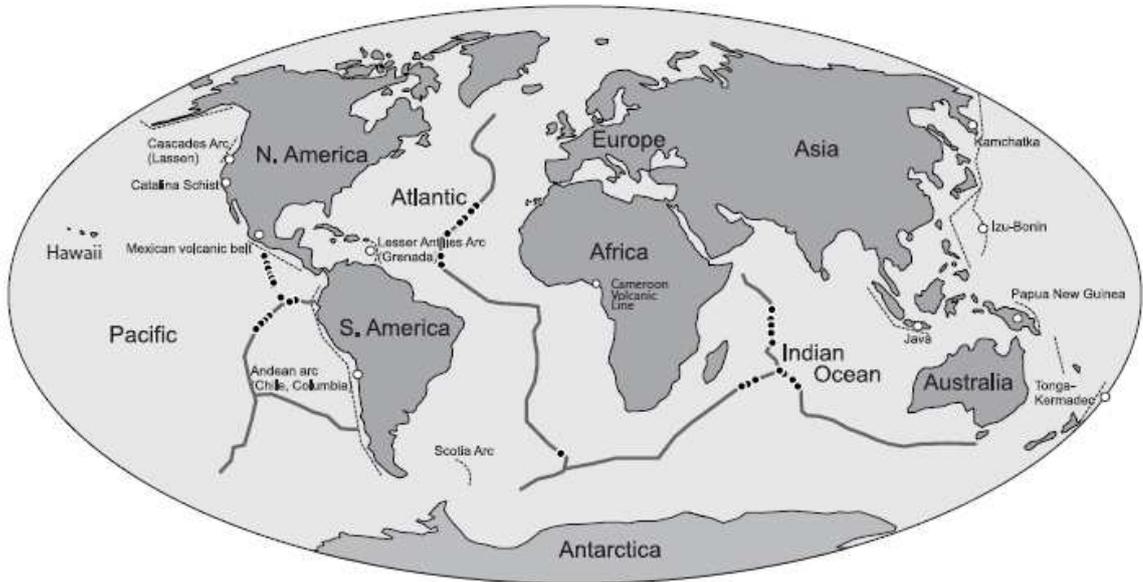
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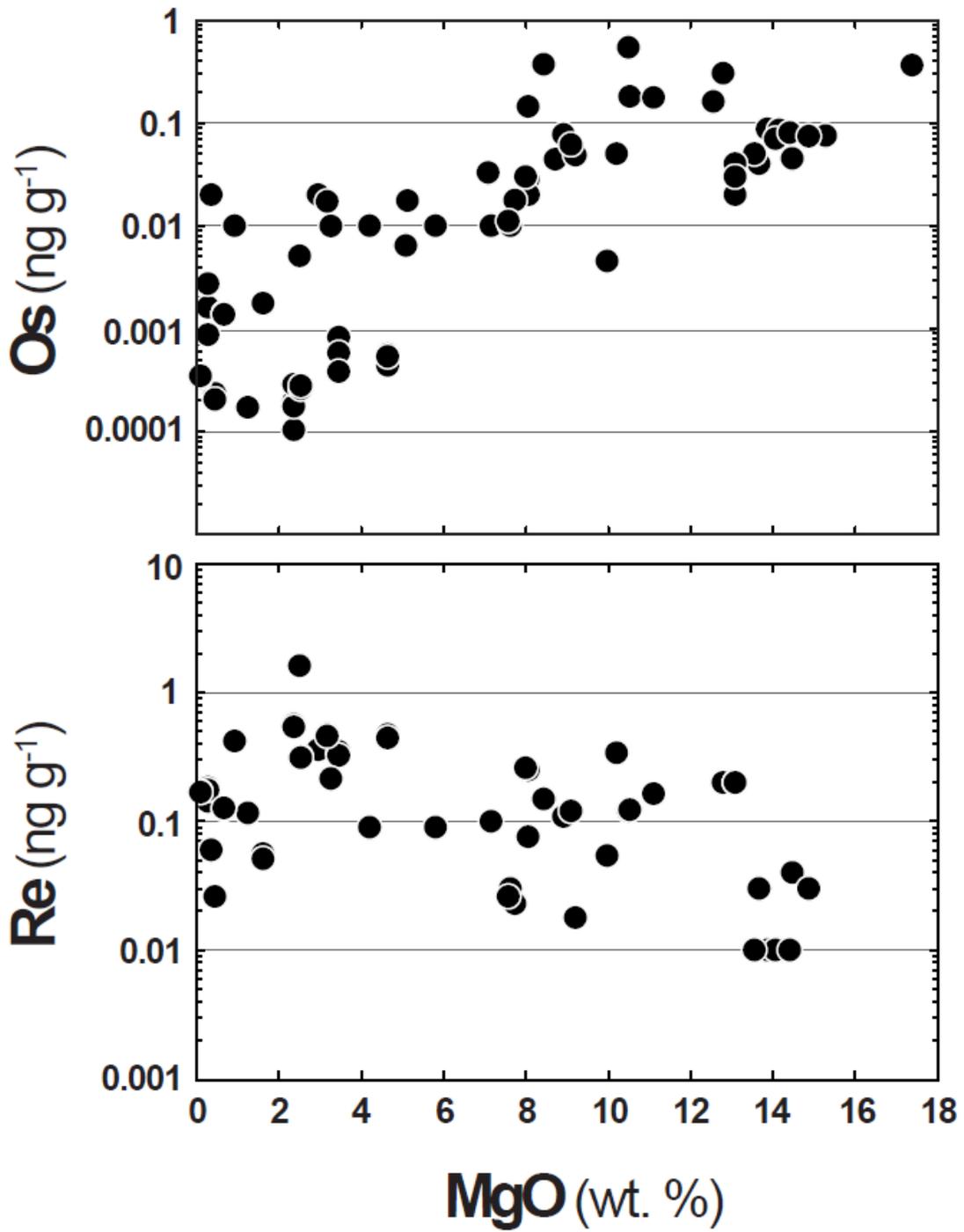
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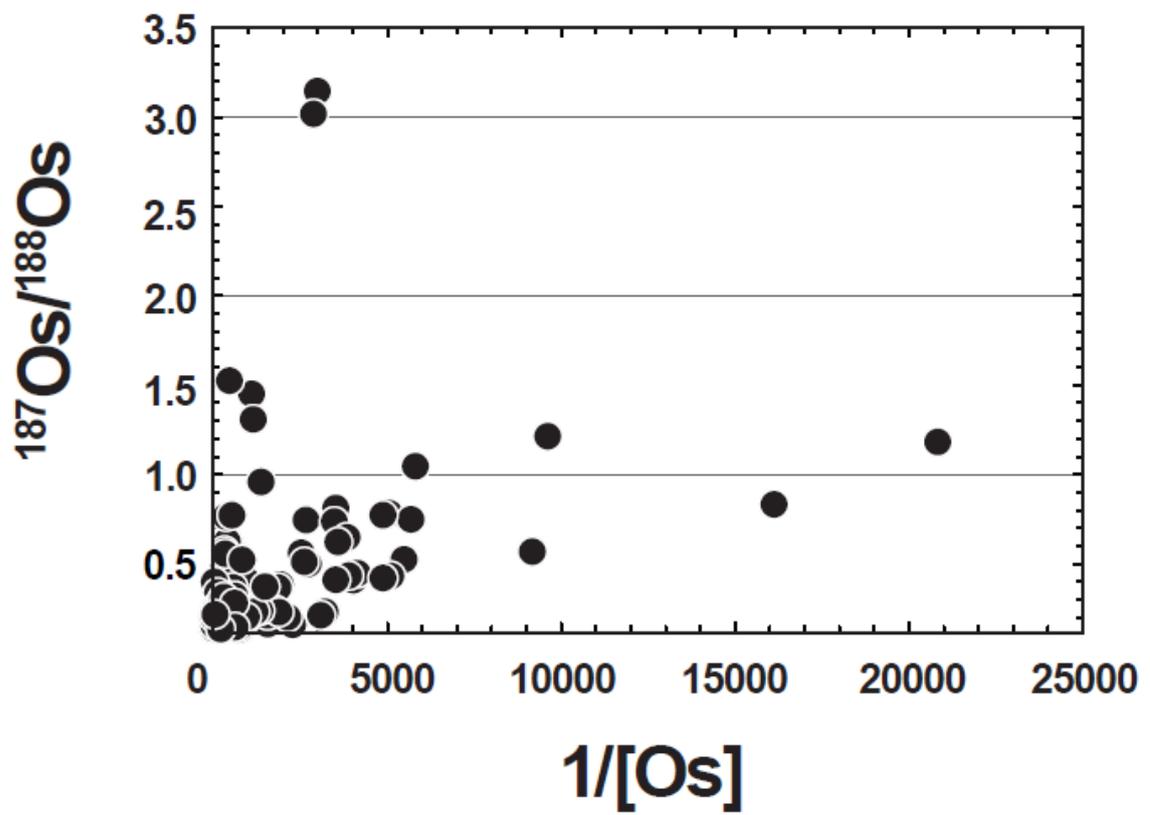
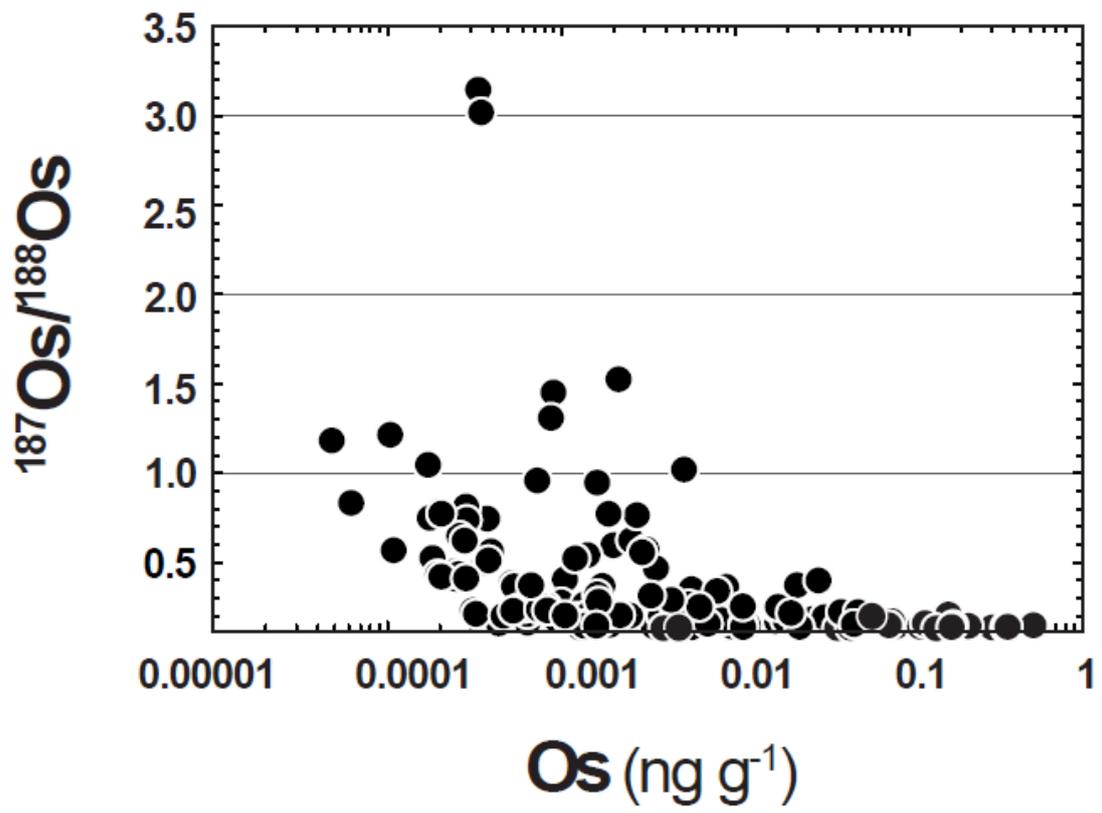
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3942 Figure 34
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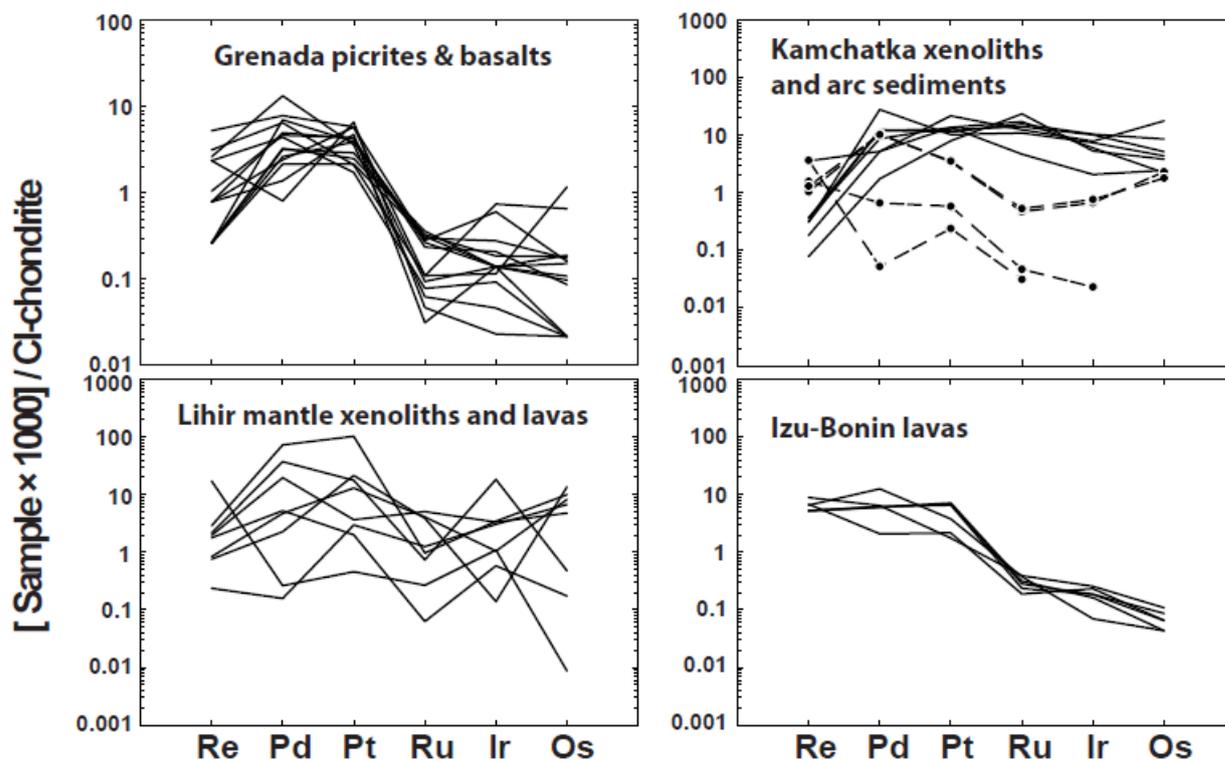


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3951 Figure 35
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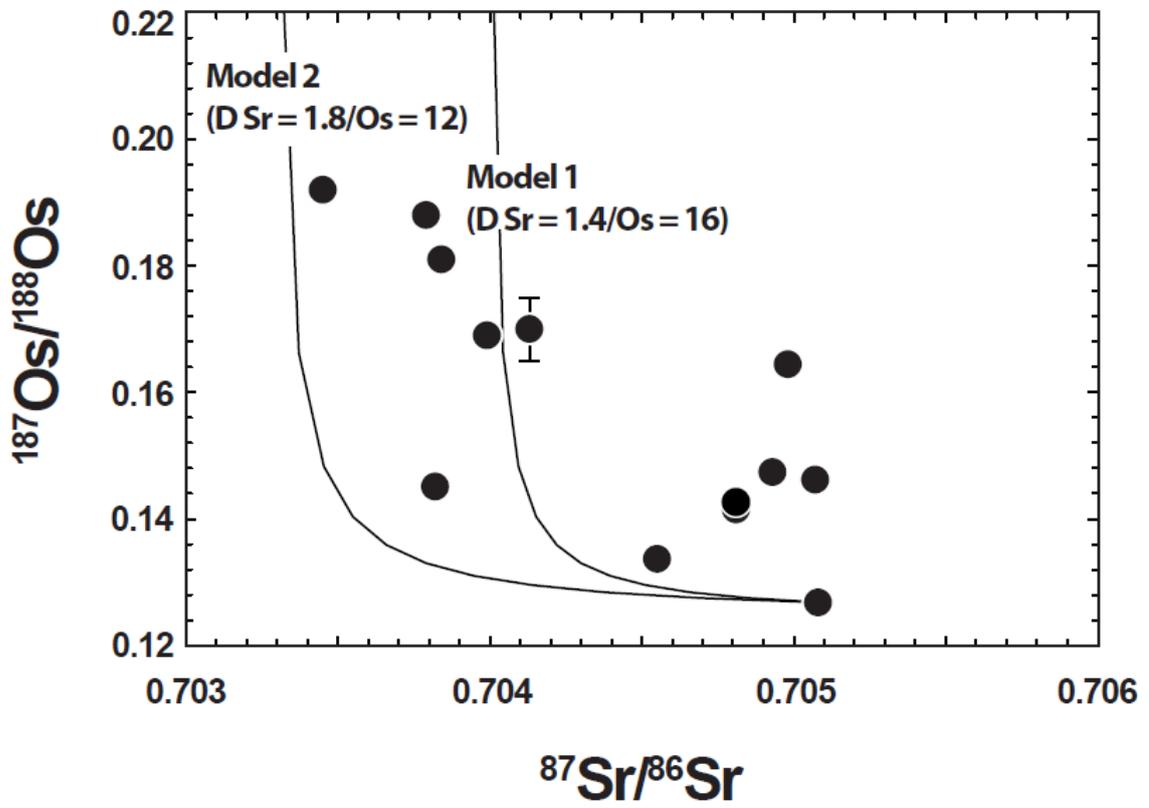


3954 Figure 36
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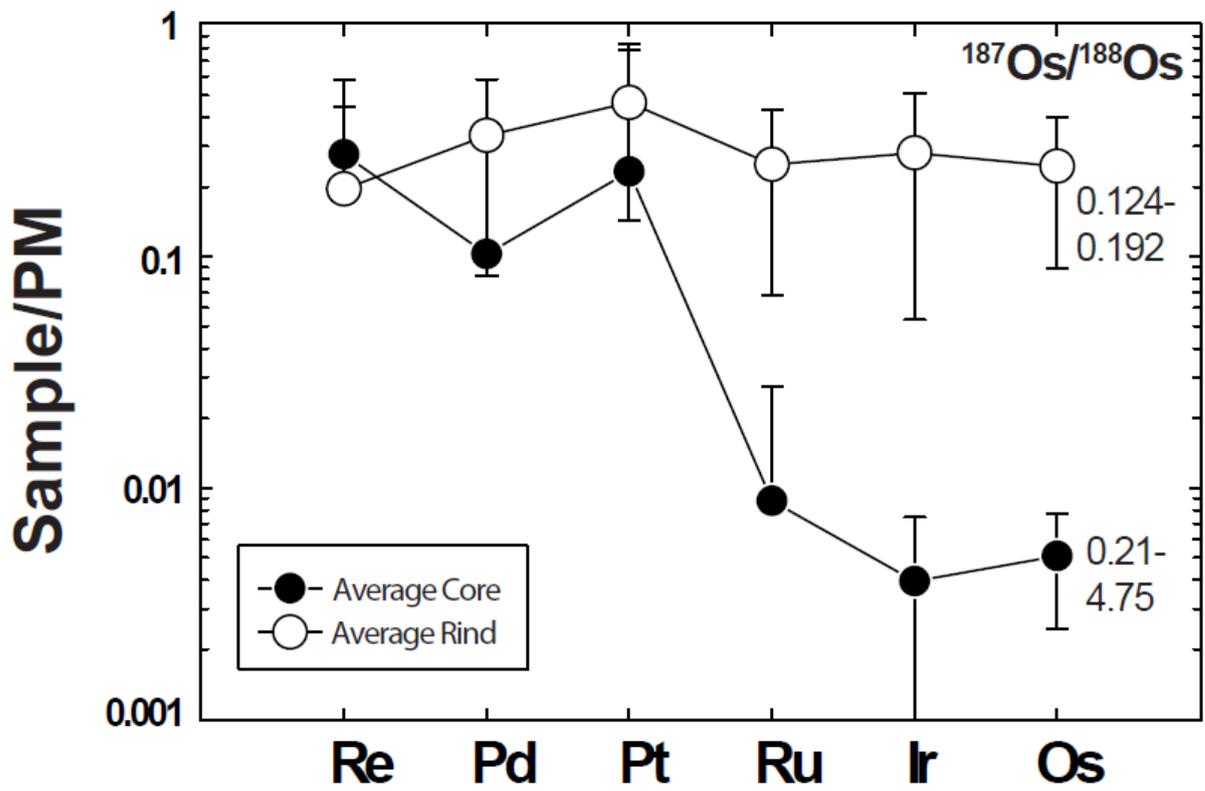
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3983 Figure 37
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4007 Figure 38
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