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Geochemistry of Molybdenum in the Continental Crust

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Abstract

The use of molybdenum as a quantitative paleo-atmosphere redox sensor is predicated on the assumption that Mo is hosted in sulfides in the upper continental crust (UCC). This assumption is tested here by determining the mineralogical hosts of Mo in typical Archean, Proterozoic, and Phanerozoic upper crustal igneous rocks, spanning a compositional range from basalt to granite. Common igneous sulfides such as pyrite and chalcopyrite contain very little Mo (commonly below detection limits of around 10 ~~ppb~~^{ppb}~~ng/g~~^{ng/g}) and are not a significant crustal Mo host. By contrast, volcanic glass and Ti-bearing phases such as titanite, ilmenite, magnetite, and rutile contain significantly higher Mo concentrations (e.g., up to 40 $\mu\text{g/g}$ in titanite), and can account for the whole-rock Mo budget in most rocks. However, mass balance between whole-rock and mineral data is not achieved in 4 out of 10 granites analyzed with *in-situ* methods, where Mo may be hosted in undetected trace molybdenite. Significant Mo depletion (i.e., UCC-

26 normalized Mo/Ce < 1) occurs in nearly every granitic rock analyzed here, but not in oceanic
27 basalts or their differentiates (Greaney et al., 2017; Jenner and O'Neill, 2012). On average,
28 granites are missing ~60% of their expected Mo contents. There are two possible reasons for
29 this: 1) Mo partitions into an aqueous magmatic vapor/fluid phase that is expelled from cooling
30 plutons, and/or 2) Mo is partitioned into titaniferous phases during partial melting and fractional
31 crystallization of an evolving magma. The first scenario is likely given the high solubility of
32 oxidized Mo. However, correlations between Mo/Ce and Nb/La in several plutonic suites suggest
33 fractionating phases such as rutile or Fe-Ti oxides may sequester Mo in lower crustal rocks or in
34 subducting slabs in arc settings.

35 **1. Introduction**

36 Molybdenum (Mo) geochemistry has emerged as a powerful tool for tracking early
37 atmospheric oxygenation (e.g., Anbar et al., 2007; Wille et al., 2007; Gaschnig et al., 2014),
38 redox conditions in ocean basins (e.g., Siebert et al., 2003; Arnold et al., 2004; Scott et al., 2008;
39 Dahl et al., 2011), and the influence of subducted sediments and fluids on arc magmas (Freymuth
40 et al., 2015; König et al., 2016). The interest in Mo stems from its geochemical properties: Mo is
41 a multi-valent element whose partitioning behavior depends on the redox state of its
42 environment. Despite the rapidly growing literature on the geochemical behavior of Mo at
43 Earth's surface, the behavior of Mo in igneous rocks is less well understood. Yet, such
44 knowledge is crucial for understanding how Mo will behave during crustal weathering and
45 processes that release Mo to sedimentary environments. Additionally, determining the
46 mineralogical hosts of Mo in evolving magmas will lead to a more accurate understanding of Mo
47 behavior during crust formation and differentiation, and the formation of molybdenite deposits in

48 various tectonic settings. This task was first undertaken by Kuroda and Sandell (1954) but, with
49 improved methodology, we aim to expand upon their dataset.

50 *1.1 Properties of Mo*

51 Molybdenum is a geochemically versatile element that displays siderophile (iron/metal-
52 loving; Kuroda and Sandell, 1954; Newsom and Palme, 1984; Lodders and Palme, 1991;
53 Walker, 2016), chalcophile (Goldschmidt, 1937; Kuroda and Sandell, 1954), and lithophile
54 behavior (rock/silicate-loving; Newsom and Palme, 1984; Greaney et al., 2017), depending on
55 the composition of the system of interest (including fO_2 and fS_2), the temperature, and the
56 pressure. Molybdenum's redox sensitivity plays a prominent role in its geochemical behavior
57 because its charge, size, and physical properties change depending on its oxidation state.

58 Molybdenum is insoluble in aqueous fluids when reduced to its tetravalent state, but when
59 oxidized to its hexavalent state it becomes soluble. This relationship between charge and
60 solubility is a key factor in determining the behavior of Mo in the crust and on the Earth's
61 surface.

62 In igneous systems, the transition from Mo^{4+} to Mo^{6+} occurs over a span of ~10 log units
63 fO_2 (O'Neill and Eggins, 2002), with Mo^{4+} being the dominant state at around three log units
64 below the IW buffer (iron-wüstite) and Mo^{6+} being the dominant state at around one log unit
65 below the FMQ buffer (fayalite-magnetite-quartz). Thus, Mo is expected to exist in its oxidized
66 state in mantle and crustal melts, which have oxygen fugacities near the fayalite-magnetite-
67 quartz (FMQ) or Ni-Ni-oxide (NNO) buffers. The work of Fitton (1995), Zack et al (2002), and
68 subsequent experimental studies suggest that Mo partitions into rutile in eclogites (eclogitic
69 rutile: 2-7 ~~µg/g ppm~~ Mo; Zack et al., 2002), and can be removed from melts generated in
70 subduction zones, even though Mo is found predominately as 6+ in oxidized experimental melts

71 (Holzheid et al., 1994; O'Neill and Eggins, 2002; Bali et al., 2012; Skora et al. 2017). Bali et al.
72 (2012) show that Mo is compatible in rutile in oxidized systems at the NNO buffer (nickel-nickel
73 oxide). This suggests that Mo may be incorporated into rutile even in its oxidized state.
74 Octahedrally-coordinated Mo^{6+} has a similar ionic radius to octahedrally-coordinated Ti^{4+} (59
75 and 60.5 pm, respectively; Shannon, 1976), so it can replace Ti in a coupled substitution to
76 maintain electrical neutrality. Alternatively, Mo may be locally reduced to Mo^{4+} (ionic radius =
77 60.5 pm) before exchanging for Ti^{4+} in an isovalent substitution (Zack et al., 2002; Skora et al.
78 2017). It has also been proposed that Mo is predominately hosted in biotite and amphibole in
79 igneous rocks (Voegelin et al., 2014; Yang et al., 2017), supporting the idea that it follows
80 similar substitution patterns as Ti. However, Mo can also be reduced and incorporated into
81 molybdenite (MoS_2) during oxidation-reduction reactions that occur in hydrothermal ore systems
82 (Stein, 1985).

83 On the surface of Earth and in oceans, 'free' Mo exists in its oxidized, soluble state given
84 the abundance of atmospheric O_2 . Unreactive molybdate (MoO_4^{2-}) is the most common form of
85 Mo in rivers and oceans today, where Mo has a residence time of around 440,000 years (Miller
86 et al., 2011). However, this was probably not the case on early Earth, which lacked or contained
87 only trace concentrations of atmospheric oxygen.

88 *1.2 Molybdenum as a redox proxy*

89 Throughout the first ~ 2 billion years of Earth's history, the atmosphere was far more
90 reducing than today, probably containing $< 10^{-5}$ times the present atmospheric level (PAL) of O_2
91 (Kasting, 2014 and references therein). Atmospheric oxygen did not accumulate to significant
92 levels until the Great Oxidation Event (GOE), which occurred between 2.4 Ga and 2.3 Ga, when

93 it likely rose to somewhere between 10^{-4} and 10^{-2} PAL (Lyons et al, 2014 and references
94 therein).

95 Many lines of evidence point to the rise of O_2 during the GOE. Arguably the most
96 important is the disappearance of sulfur-isotope mass-independent fractionation, caused by the
97 creation of an atmospheric ozone shield (Farquhar et al., 2000). Additionally, several redox-
98 sensitive metal proxies (Mo, U, Cr, Re) indicate that oxidative weathering of the continents
99 commenced at or just before the GOE, suggesting that atmospheric O_2 had become sufficiently
100 abundant to cause oxidative weathering of crustal rocks (Anbar et al, 2007; Wille et al., 2007;
101 Scott et al., 2008). These redox-sensitive metals are assumed to be concentrated in minerals that
102 will break down in the presence of atmospheric oxygen, *i.e.*, in sulfides in the case of Mo. Pyrite
103 and molybdenite are commonly invoked as the main Mo sources that contain reduced, insoluble
104 Mo (Anbar et al., 2007, Miller et al., 2011). When these sulfides break down in the presence of
105 atmospheric O_2 , the Mo becomes oxidized (and thereby soluble), and can be transported in
106 solution as molybdate (MoO_4^{2-}) in rivers, and eventually the oceans. Once in the ocean, Mo is
107 slowly removed through uptake by Fe-Mn oxides in oxygenated environments, or deposited in
108 black shales within euxinic (high-S, low- O_2) environments. Archean and Proterozoic black
109 shales have been analyzed for Mo and other redox-sensitive elements to track oxidative
110 continental weathering; enrichments suggest oxidative weathering and/or the development of
111 euxinic ocean basins (Turekian and Bertine, 1971; Helz, 1996; Erickson and Helz, 2000). High
112 sulfur concentrations are required in the water column for Mo to be reduced and incorporated
113 into Fe-Mo-S phases in reduced oceanic sediments (Helz, 1996; Erickson and Helz, 2000). Like
114 Mo, sulfur was probably not abundant in the Archean oceans until atmospheric oxygen caused
115 weathering of continental sulfides during the GOE (Canfield, 2005).

116 As observed by Gaschnig et al. (2014), Mo enrichments in black shales during and after
117 the GOE are accompanied by contemporaneous Mo depletions in the UCC. The UCC Mo
118 depletion, relative to the light rare earth elements of similar compatibility (Ce and Pr) first
119 appears in the Paleoproterozoic and continues to the present day. These observations support the
120 hypothesis that oxidative weathering of the continents played a role in removing Mo from the
121 weathered continental crust and transporting it into ocean basins after the GOE.

122 The use of Mo to trace atmospheric O₂ and infer Precambrian oceanic chemistry is
123 widely accepted in the paleo-atmospheric research community. However, using the Mo
124 concentrations in euxinic sediments to quantify the *p*O₂ is based on the assumption that Mo is
125 primarily concentrated in sulfides in the UCC, and that these sulfides will break down at a rate
126 that is proportional to *p*O₂ (Anbar et al., 2007; Williamson and Rimstidt, 1994). While Mo may
127 behave as a chalcophile element in euxinic sedimentary and low-temperature hydrothermal
128 environments, its behavior during igneous differentiation and crust formation is less well
129 understood. Newsom and Palme (1984) suggested that Mo will behave incompatibly during
130 mantle melting, like Ce and Pr, and this is corroborated by the observation that Mo is
131 significantly enriched in the UCC (1.1 $\mu\text{g/gppm}$; Rudnick and Gao, 2003) relative to the
132 primitive mantle (0.039 to 0.047 $\mu\text{g/gppm}$; Greber et al., 2015 and Palme and O'Neill, 2004,
133 respectively). Moreover, Mo is observed to behave incompatibly during differentiation of
134 intraplate basalt magmas (Yang et al., 2015; Greaney et al., 2017). Greaney et al. (2017) also
135 showed that while Mo is present in magmatic sulfides (average 2.6 $\mu\text{g/gppm}$), it is more
136 abundant in basaltic to andesitic volcanic glasses (average 5 $\mu\text{g/gppm}$) and Fe-Ti oxides (average
137 6.4 $\mu\text{g/gppm}$). However, the partitioning behavior of Mo in typical continental crustal igneous
138 rocks, such as granites, has not been systematically studied.

139 Here, we explore the partitioning of Mo in typical UCC granitic rocks, and incorporate
140 data published on Hawaiian basalts (Greaney et al., 2017), to determine whether Mo is
141 chalcophile, *i.e.*, concentrated primarily in sulfides in the igneous UCC. We present *in-situ* data
142 on Mo concentrations in various minerals as well as whole-rock data on Mo abundances in
143 granitic and basaltic rocks. Our goals are to determine the main mineralogical hosts of Mo in the
144 continental crust and to improve our understanding of the behavior of Mo during crust formation
145 and differentiation.

146 2. Samples

147 Granitic rocks are considered to be representative of the felsic UCC, so granitic rocks that
148 span Earth's history form the focus of this study. Since Mo is thought to be generally
149 incompatible during igneous differentiation (Newsom and Palme, 1984), it is expected to be
150 concentrated in more felsic rocks. Given the bimodal composition of the crust, and the
151 hypothesis that the Archean crust may have been significantly more mafic than present-day UCC
152 (e.g., Taylor and McLennan, 1985; Condie, 1993; Dhuime et al., 2015; Gaschnig et al., 2016;
153 Tang et al., 2016), partitioning data from Hawaiian basalts (Greaney et al., 2017) and MORB
154 (Jenner and O'Neill, 2012; Patten et al., 2013) are also considered. We were particularly
155 interested in sampling Archean crust, because its Mo residence and weathering behavior is
156 directly applicable to the GOE. When possible, we selected granitic rocks that retained igneous
157 textures and mineralogy, with an aim of studying previously well-characterized samples.
158 Archean and Proterozoic samples come from the Superior Province (Whalen et al., 2002;
159 Whalen et al., 2003), Baffin Island (Whalen et al. 2012), the Zimbabwe craton (Luais and
160 Hawkesworth, 1994), and the Barberton greenstone belt (Clemens et al. 2006). The majority of
161 these samples are TTGs (tonalite-trondjemite-granodiorite rocks) that contain higher sodium

162 contents than the more potassic granites that dominate the Proterozoic and Phanerozoic.

163 Additionally, due to the presence of residual rutile or ilmenite in lower-crustal residues and

164 amphibole in mid-crustal residues (Hoffmann et al. 2011), TTG's are generally characterized by

165 a depletion in the high field-strength elements (HFSE) Ti, Nb, and Ta. Complete sample

166 descriptions and photomicrographs can be found in the supplementary materials.

167 *2.1 Barberton TTGs (3.55 – 3.21 Ga)*

168 Powdered samples of TTGs from the Barberton Greenstone Terrane were analyzed here

169 for whole-rock compositions. No thin sections were available for *in-situ* work. Samples from

170 four generations of plutons that represent distinct tectono-magmatic events were studied: the

171 3.55-3.49 Ga Steynsdorp pluton; the 3.46-3.42 Ga Stolzberg, Doornhoek, Theespruit, and

172 Erstehoek plutons; the 3.29-3.24 Ga Badplaas pluton; and the 3.24-3.23 Ga Nelshoogte pluton

173 (Clemens et al., 2006; Moyen et al., 2007; Kröner et al., 1991). The Barberton Terrane is one of

174 the most intensively studied suites of Archean TTGs in the world, and several interpretations

175 have been developed to explain the petrogenesis of the TTGs and greenstone belts. A consensus

176 has developed around the hypothesis that these plutons were emplaced during accretion of an

177 exotic terrane and subsequent post-orogenic collapse (Clemens et al., 2006; Moyen et al., 2007).

178 *2.2 Superior Province TTGs (3.0 – 2.7 Ga)*

179 The TTGs from the Superior Province come from the North Caribou Terrane plutonic

180 complex (~3.0 Ga; Whalen et al., 2003) and the Central Wabigoon sub-province (~2.7 Ga;

181 Whalen et al., 2002). The North Caribou samples are mainly derived from the English Lake

182 Plutonic Suite and range in composition from felsic tonalites and trondhjemites to amphibolitic

183 and pyroxenitic xenolithic enclaves that may have originated as cumulates. Geochemical

184 modeling suggests a genetic link between the cumulate enclaves and the TTGs, and an overall

185 hydrous source for this suite. The younger Central Wabigoon samples are classified as granite to
186 granodiorite and have a higher K_2O/Na_2O ratios than the North Caribou TTGs. This suite is
187 thought to have formed from the partial melting of over-thickened lower crust during the
188 collision of arcs, such as the one that potentially produced the North Caribou samples. Both
189 whole-rock and *in-situ* data were collected for this suite. Three samples were sectioned for *in-*
190 *situ* analysis. These are composed of quartz, plagioclase, K-feldspar, biotite, amphibole
191 (primarily hornblende), titanite, Fe-Ti oxides, and minor muscovite and sulfides (Fig. 1), all of
192 which were analyzed for Mo concentration.

193 2.3 Zimbabwe Craton TTGs (2.9 – 2.6 Ga)

194 The samples from the Zimbabwe craton are mainly tonalites from the 2.9 Ga Mashaba
195 suite, as well as two samples from the 2.6 Ga Chibi Granite. The Zimbabwe craton is bounded by
196 three belts that accreted between the Neoproterozoic Limpopo Belt and the Neoproterozoic Zambezi
197 and Mozambique Belts. The craton itself is composed of 2.8 – 2.5 Ga greenstone sequences and
198 3.5 – 2.9 Ga TTGs. Luais and Hawkesworth (1994, 2002) outline a petrogenetic model that
199 involves partial melting of a garnet-bearing amphibolite and subsequent fractional crystallization
200 to produce the TTG suites. In this model, the Mashaba tonalite was formed by direct fusion
201 products of basaltic proto-lower crust leaving a garnet amphibolite residue. The late Chibi
202 granite is interpreted to have been derived through partial melting of greenstone mafic volcanic
203 rocks (Hawkesworth et al., 1979). Partial melting in the deeper part of a thick crust has been
204 invoked to explain the formation of these units (Hawkesworth et al., 1979; Luais and
205 Hawkesworth, 1994 and 2002). Whole-rock and *in-situ* data were collected for this suite, and
206 data for major and trace elements were previously published in Luais and Hawkesworth (1994).
207 The four samples selected for *in-situ* analysis are variably foliated and contain alteration

208 products such as chlorite, cummingtonite, epidote, and sericite. Common phases are quartz,
209 plagioclase, K-feldspar, biotite, hornblende, muscovite, titanite, Fe-Ti oxides, apatite, and zircon.

210 *2.4 Baffin Island (1.88 Ga)*

211 Whole-rock powders from the Qikiqtarjuaq Plutonic Suite (QPS) show the largest
212 compositional range of all suites studied here, varying from granodiorite/tonalite to gabbro
213 (Whalen et al., 2012). These intrusive bodies form a portion of the Cumberland batholithic
214 complex on Baffin Island. The origin of the QPS is uncertain, as it is a relatively newly
215 discovered and analyzed unit. However, U-Pb ages suggest that it is ~35 Myr older than the
216 Cumberland Batholith (Rayner et al., 2012), which has been interpreted to be a Trans-Hudson
217 Orogeny post-accretionary batholith, possibly resulting from a delamination event from the base
218 of over-thickened crust (Whalen et al., 2010). Thus, it can be inferred that the QPS was emplaced
219 at the initiation of an accretionary event, and may be arc-derived. Data for all major and trace
220 elements were previously published in Whalen et al. (2012), but Mo concentrations were re-
221 analyzed in this study using a more precise standard-addition technique. No thin sections were
222 analyzed.

223 *2.5 Phanerozoic Granites*

224 Mesozoic granitic rocks from the Western USA (Gaschnig et al., 2011; 2017) and a Silurian
225 granite from the Eastern US were analyzed as well. These include a garnet-bearing peraluminous
226 granite from the Idaho batholith, a metaluminous tonalite from the Lookout Mountain pluton in
227 the Blue Mountains (Oregon and Idaho, USA), and a Neo-Acadian epidote-bearing granodiorite
228 (Ellicott City Granodiorite, Maryland, USA). These samples consist of common granitic
229 minerals – abundant feldspar, quartz, biotite, and amphibole with accessory muscovite, titanite,
230 epidote, magnetite, ilmenite, apatite, allanite, zircon, and sulfides (Fig. 1, see supplementary

231 sample descriptions). Whole-rock and *in-situ* analyses of thin sections were carried out on these
232 samples.

233 2.6 Kilauea Iki lavas

234 Data from the Kilauea Iki lava lake, Hawaii, reported in Greaney et al. (2017), are
235 considered here for a more complete assessment of mineralogical hosts of Mo. The lava lake
236 erupted in 1959 and is considered a prime natural laboratory for studying basaltic magma
237 differentiation. Samples ranging through the entire differentiation suite from 43.7 to 57.1 wt%
238 SiO₂ were subjected to whole-rock and *in-situ* analysis. The rocks contain olivine, pyroxene
239 (augite), plagioclase, Fe-Ti oxides, glass, and minor apatite and sulfides (Fig. 1).

240 3. Methods

241 The methods follow those of Greaney et al. (2017) and Gaschnig et al. (2015), and are
242 reproduced here in detail in the supplementary material. Whole-rock trace element analyses were
243 carried out by standard-addition solution inductively coupled plasma mass spectrometry (ICP-
244 MS). Samples were dissolved in high pressure PTFE bombs using HF/HNO₃, then three aliquots
245 were spiked with variable known amounts of Mo using spikes created by Gaschnig et al. (2015).
246 This method produces a calibration curve from the sample itself, instead of having to extrapolate
247 a calibration curve from external standards, which could induce errors associated with the
248 extrapolation and improperly calibrated standards. The sample aliquots were analyzed on an
249 Element2 HR-ICP-MS at the University of Maryland in MR and LR mode for three isotopes of
250 Mo (95, 97, and 98). The limit of detection (LOD) ranged from 0.03 ~~μg/gppm~~ to 0.10 ~~μg/gppm~~
251 for most analytical sessions. However, it was as high as 0.16 ~~μg/gppm~~ during analyses of the
252 Barberton suite TTGs. The variable LOD is reflected in Table 1. The reported Mo abundances
253 for the three isotopes never varied by more than the reported RSD calculated from the counting

254 statistics. USGS standard reference rock powders AGV-2 and BHVO-1 were dissolved alongside
255 each batch of samples and run as secondary standards (Table 2). AGV-2's external
256 reproducibility results in a 2RSD of 7%. BHVO-1 (2RSD ~ 25%) is notoriously difficult to
257 reproduce (Willbold et al., 2016; Gaschnig et al. 2015), possibly due to heterogeneities in the
258 sample powder.

259 In addition, to demonstrate the robustness of measuring low-Mo abundances with the
260 standard addition method, three low-[Mo] TTGs from different suites were re-dissolved and
261 analyzed by isotope dilution at the Arizona State University Keck Biogeochemistry Lab. Two of
262 the three samples show excellent reproducibility, while the isotope-dilution data gave even lower
263 Mo abundances for the third sample, ZB89-10 (0.13 ~~μg/gppm~~ by ID vs. 0.25 ~~μg/g_ppm~~ by
264 standard addition). This discrepancy may reflect a slightly heterogeneous powder due to nuggets
265 of a Mo-rich phase, given that mass balance was not achieved for this sample (see section 4.1.3
266 and Table S4), and a Mo-rich phase was observed within magnetite of another sample from this
267 same TTG suite (see section 4.1.1). These replicate data are reported in the online supplement.
268 Additionally, for most plutonic suites, a full suite of trace elements were analyzed, including Ga,
269 Ge, Cd, In, Sn, Sb, W, Tl, and Bi. These data are provided in the supplementary materials.

270 *In-situ* mineral data were collected using electron probe microanalysis (EPMA) followed
271 by laser ablation ICP-MS using a New Wave UP-213 nm laser attached to an Element2 HR-ICP-
272 MS at the University of Maryland and a Photon Machines 193 nm laser attached to an Agilent
273 7700x Quadropole ICP-MS at the University of California Santa Barbara. NIST-610 was the
274 external standard, and the glasses BHVO-2g and NIST-612, as well as a synthetic Mo-bearing
275 sulfide produced by James Brenan (formerly at the University of Toronto, now at Dalhousie
276 University) were analyzed as secondary standards (Table 2). Spot-sizes ranged from 25 μm (for

277 smaller sulfides) to 80 μm (for silicates and larger sulfides). Three isotopes of Mo were
278 measured (95, 97, and 98), with all returning values that fell within the error calculated by
279 counting statistics, except when an obvious interference was present (e.g., $^{55}\text{Mn}^{40}\text{Ar}$ on ^{95}Mo in
280 garnet). Abundances of ^{98}Mo are therefore reported for the *in-situ* data. The LOD for *in-situ* Mo
281 analyses ranges were typically $\sim 0.01 \mu\text{g/gppm}$, however they occasionally ranged as high as 0.1
282 $\mu\text{g/gppm}$, depending on the analyte/background ratio of the instrument that day. The LA-ICP-
283 MS data were processed using Iolite (Paton et al. 2011).

284 4. Results

285 4.1 *In-situ* data

286 4.1.1 Sulfides

287 A total of 78 sulfide grains were analyzed from the Phanerozoic granites, TTGs, and several
288 evolved samples from the Kilauea Iki lava lake, Hawaii. Pyrite, chalcopyrite, and pyrrhotite are
289 present in the granitic samples while the sulfide blebs in the Kilauea Iki lavas form solid
290 solutions between isocubanite and bornite (see Greaney et al., 2017 for analyses). The sulfides
291 are volumetrically insignificant (<1 vol. %) in all of the analyzed samples, and, for most
292 samples, did not register in mineral modes determined by point counting (see the mass balance
293 table in the supplement).

294 Molybdenum concentrations (designated as [Mo]) in accessory sulfides vary by
295 approximately three orders of magnitude ($0.01 \mu\text{g/gppm}$ to $9.2 \mu\text{g/gppm}$). The maximum [Mo] is
296 found in the Kilauea Iki lava-hosted sulfides (mean [Mo]_{Kilauea sulfides} = $2.7 \mu\text{g/gppm}$, max = 9.2
297 $\mu\text{g/gppm}$) while the granite-hosted sulfides contain significantly less Mo than those from Kilauea
298 Iki (mean [Mo]_{granite sulfides} = $0.72 \mu\text{g/gppm}$, max = $8.0 \mu\text{g/gppm}$, Fig. 2), but have similar
299 concentrations to MORB-hosted sulfides (Patten et al., 2013). Molybdenite was not found as an

300 accessory phase in any sample, but one grain of magnetite in a TTG from the Zimbabwe craton
301 (ZB89-53) contains significant Mo (~1300 $\mu\text{g/gppm}$), along with Pb and other chalcophile
302 elements. This suggests that a small nugget of MoS_2 , or similar phase, may have been embedded
303 within or beneath the magnetite grain, but was not visible on the surface. This analysis was
304 excluded from the magnetite data presented in Fig. 2 and Table 3.

305 4.1.2 Silicates and Oxides

306 In addition to sulfides, quartz, K-feldspar, plagioclase, biotite, muscovite, hornblende,
307 titanite, garnet, allanite, zircon, epidote, chlorite, olivine, clinopyroxene (augite), volcanic glass,
308 magnetite, ilmenite, rutile, and the rare accessory phase columbite (also called niobite) were all
309 analyzed for their Mo abundances (Table 3). The mean data presented in this table also include
310 analyses that were below the LOD in plagioclase, K-feldspar, biotite, amphibole, muscovite,
311 sulfides, epidote, and quartz. In these cases, the lower LOD commonly calculated for these
312 analyses (0.01 $\mu\text{g/g} = \text{ppm}$) was used to calculate the mean [Mo] value. Thus, the average
313 concentrations for these phases should be considered maxima. Collectively, these data
314 encompass nearly every major mineral found in common igneous rocks. Most phases were
315 analyzed repeatedly across several rock types and localities except for columbite/niobite, which
316 is confined to a single crystal in a Phanerozoic granite (07RMG52).

317 Molybdenum concentrations are presented in box and whisker plots in Figure 2 with the
318 phases arranged from highest to lowest [Mo], as established by the median [Mo] value.

319 Molybdenum concentrations are considered to be significant if they are greater than 1 $\mu\text{g/gppm}$
320 (average UCC [Mo] = 1.1 $\mu\text{g/gppm}$; Rudnick and Gao, 2014). Titanite consistently contains
321 significant Mo, except for one sample from the Superior Province (WXP99-176), in which
322 titanite contained between 0.01 and 0.5 $\mu\text{g/gppm}$. Metamorphic rutile replaced part of the titanite

323 in that sample and may have preferentially incorporated Mo into its lattice, removing it from the
324 titanite. Excluding this sample, [Mo] in titanite is commonly $>30 \mu\text{g/gppm}$. Ilmenite and
325 magnetite are the other two common phases that routinely contained $\geq 1 \mu\text{g/gppm}$ Mo in both
326 granitic and basaltic samples. Rutile and columbite/niobite are less common upper crustal
327 minerals, but they were found as primary igneous and secondary metamorphic assemblages in
328 some samples and contain significant Mo. Volcanic glass was also found to be a significant host
329 of Mo in the Kilauea samples where the average Mo_{glass} concentration is $4.8 \mu\text{g/gppm}$. Glass data
330 from ~ 600 MORB samples (Jenner and O'Neill, 2012) are shown for comparison, and have an
331 average [Mo] of $0.62 \mu\text{g/gppm}$, which is significantly lower than KI glass because MORB has
332 lower whole-rock [Mo], and many of the KI lavas are more evolved than MORB. Most of the
333 minerals analyzed do not contain abundant ($>1 \mu\text{g/gppm}$) Mo, including the most common
334 minerals in granitic and basaltic rocks: quartz, feldspars, biotite, amphibole, olivine, and
335 pyroxenes. Sulfides are found near the middle or right-hand side of each plot in Fig. 2, reflecting
336 their generally low [Mo], relative to other minerals. Sulfide data from MORB (Patten et al.,
337 2013) are shown for comparison to OIB sulfides on the plot of basaltic minerals.

338 4.1.3 Mass Balance

339 Mineral modes were determined for the samples using a least-squares regression program,
340 MINSQ (Herrmann and Berry, 2002). Select samples were also point counted to ensure accuracy
341 of the MINSQ program (supplementary materials). The modal abundances are used together with
342 the measured Mo concentrations to calculate the primary location of Mo (Fig. 3; mass balance
343 provided in supplementary materials). Given their scarcity, sulfides were not registered in point
344 counting exercises, so they were assigned modal abundances of 0.01% to 0.1%, which are likely
345 to be overestimates in most samples. Nevertheless, in most samples the sulfide [Mo] contributes

346 less than 3% of the whole-rock [Mo]. The maximum sulfide Mo contribution occurs in the
347 Kilauea Iki volcanic rocks, where sulfides contain up to 6% of the total whole-rock [Mo]. By
348 contrast, titaniferous phases are the dominant hosts of Mo in granitic rocks. Silicates can also
349 contribute a significant portion of the total Mo budget (e.g., ~25% in one sample, Fig 3), given
350 their volumetric significance in granites. The calculated Mo distribution results in $[\text{Mo}]_{\text{whole rock, calculated}}$
351 that can be compared to measured whole rock data and $[\text{Mo}]_{\text{whole rock, measured}}$, to see if a
352 mass balance is attained.

353 Given analytical uncertainties on the standard addition, laser ablation, and modal mineralogy
354 measurements, we consider that mass balance is achieved if the calculated whole-rock
355 abundance is within 20% of the measured whole-rock value. Of the ten granitic samples
356 evaluated, mass balance is attained in only six. The remaining four are missing anywhere
357 between 60 and 80% of the expected Mo abundance, based-on the whole-rock [Mo] measured by
358 standard addition ICP-MS. All thin sections were carefully examined to ensure that no phase was
359 missing from *in-situ* analysis. The incomplete mass balance is probably a real phenomenon, and
360 is discussed further below.

361 4.2 Whole-rock data

362 Whole-rock [Mo] data are presented in Table 1 and a complete dataset, including major and
363 trace elements (including Ga, Ge, Cd, In, Sn, Sb, W, Tl, and Bi), is presented in the online
364 supplement. Almost all granitic rocks analyzed contain less than 1 $\mu\text{g/gppm}$ Mo, except for three
365 samples from Baffin Island. Several Kilauea Iki samples (data presented in Greaney et al., 2017)
366 contain more than 1 $\mu\text{g/gppm}$ because they are derived from an enriched mantle source and
367 evolved further than most MORB, without Mo fractionation on a whole-rock scale.

368 4.2.1 Data representation

369 During mantle melting and igneous differentiation, Mo is expected to have similar
370 partitioning behavior to the LREE, specifically Ce and Pr given their comparable ionic radii
371 (Newsom and Palme, 1984). Therefore, Mo concentrations are plotted between these two
372 elements on modified multi-element plots (Fig. 4) that have been normalized to the upper
373 continental crust values of Rudnick and Gao (2014). In addition to LREE, Nb is included to
374 indicate whether a sample has a Nb depletion (UCC normalized Nb/La < 1) that may be induced
375 by Ti-oxide fractionation in the subducting slab or during differentiation. The majority of
376 analyzed granitic rocks analyzed are depleted in Mo, relative to Ce and Pr. Only nine of the 45
377 samples show either a smooth LREE-Mo profile with no depletion, or are enriched in Mo. Given
378 the normalized values for Ce and Pr, an expected Mo value (Mo*) can be calculated as $([Ce]_n \times$
379 $[Pr]_n)^{0.5}$ where “n” means normalized to the UCC value of Rudnick and Gao (2015). The
380 percentage of Mo “missing” from a given sample can then be calculated as $100 \times (Mo^* -$
381 $Mo_{meas})/Mo^*$. Between 20 and 90% (with a mean of 60%) of Mo is missing from the 36 samples
382 that show Mo depletion, which equates to between 0.04 and 2.0 $\mu\text{g/gppm}$, depending on the
383 sample. Details regarding the Mo* calculation can be found in the supplement.

384 5. Discussion

385 5.1 Mineralogical Hosts of Mo

386 In igneous rocks, Mo is not primarily hosted in accessory sulfide minerals such as pyrite,
387 pyrrhotite, and chalcopyrite. This is most probably due to the relatively oxidized nature of
388 magmas, in which Mo exists in its hexavalent state (O'Neill and Eggins, 2012), making the
389 formation of MoS₂ rare. We conclude that Mo does not behave as a chalcophile element in
390 primary magmatic settings, because it is not sufficiently reduced to be incorporated into a sulfide
391 phase without the presence of abundant reduced sulfur. This contrasts with the behavior of Mo in

392 the low-T epithermal systems that are commonly associated with pluton cooling, in which Mo^{6+}
393 is reduced by H_2S in the exsolving fluids to form molybdenite (Hannah et al., 2007).

394 The most important Mo-bearing phases in the igneous rocks analyzed here are titanite
395 ([Mo]_{mean} = 15.9 $\mu\text{g/gppm}$), magnetite ([Mo]_{mean} = 5.83 $\mu\text{g/gppm}$), ilmenite ([Mo]_{mean} = 4.09
396 $\mu\text{g/gppm}$), and glass ([Mo]_{mean} = 4.83 $\mu\text{g/gppm}$) (Fig. 2). Columbite (FeNb_2O_6) is also a
397 significant Mo host in one sample from the Idaho batholith, but this is an uncommon mineral. As
398 pointed out above, octahedrally coordinated Mo^{6+} has a similar ionic radius to octahedrally
399 coordinated Ti^{4+} (73 and 74.5 pm, respectively; Shannon, 1976), which occurs in ilmenite,
400 titanite, and rutile. Likewise, the ionic radius of tetrahedral Mo^{6+} is similar to tetrahedral Ti^{4+} (55
401 and 56 pm, respectively), which occurs in pseudobrookite (a common oxide mineral in the KI
402 lavas) and other titaniferous spinel-group minerals. A coupled substitution with a divalent cation
403 is needed to maintain electrical neutrality when hexavalent Mo replaces tetravalent Ti. This
404 could be achieved by substitution of Fe^{2+} (ionic radius of 75 pm) into octahedrally coordinated
405 sites. In pseudobrookite, for example, an additional mole PFU of Fe^{2+} replacing Fe^{3+} for each
406 mole of Mo replacing Ti would satisfy charge balance.

407 Other minor Mo hosts include silicates such as garnet ([Mo]_{mean} = 0.33 $\mu\text{g/gppm}$) and
408 biotite ([Mo]_{mean} = 0.15 $\mu\text{g/gppm}$). These results generally agree with those of Voegelin et al.
409 (2014) who found that biotite has the highest Mo abundance of any silicate analyzed in their
410 study, which also included analyses of feldspars, hornblende, olivine, and pyroxenes
411 ([Mo]_{biotite, Voegelin} = 0.67 $\mu\text{g/gppm}$), while feldspars contained less than 0.1 $\mu\text{g/gppm}$. Although
412 these silicates have low Mo concentrations, their high volumetric abundances may contribute
413 significantly to total crustal Mo abundances, as up to 25% of the total whole-rock Mo is
414 attributed to silicates in one tonalite from the Superior Province (Fig. 3). Moreover, these phases

415 are relatively easily altered, compared to the titaniferous phases, and will act as a source of Mo
416 during continental weathering.

417 Molybdenite (MoS_2) was not observed in any of the samples analyzed here, but we propose
418 that very small grains of MoS_2 could complete the mass balance in some samples. While it is
419 relatively rare for it to occur as an accessory phase in granites, molybdenite, which contains 60%
420 Mo by weight, is a highly-concentrated source of Mo in the crust, and occurs as a fairly common
421 ore mineral that forms during epithermal processes associated with the emplacement of granitic
422 plutons. Since it is so Mo-rich, an exceedingly small ‘nugget’ of MoS_2 (e.g., <0.0004 vol. % of a
423 thin section) could complete the mass balance in samples that show deficits between calculated
424 and measured whole-rock [Mo]. While uncommon, MoS_2 inclusions in quartz have been
425 documented in felsic igneous rocks (Audétat et al., 2011). The role of MoS_2 in the overall Mo
426 budget of the crust, as well as the weathering properties of all Mo-bearing phases, are discussed
427 further in sections 5.2.2 and 5.2.3.

428 *5.2 Mo behavior during magmatic differentiation*

429 *5.2.1 Mo depletion in granites*

430 Depletion of Mo relative to Ce and Pr is observed in every granitic suite analyzed here, with
431 most of the samples (36 out of 45) exhibiting Mo depletion. The depletion is evident whether the
432 data are normalized to primitive mantle (McDonough and Sun, 1995) or UCC values (Rudnick
433 and Gao, 2014), and is especially stark when compared to MORB and Kilauea Iki data, in which
434 Mo has a similar or higher normalized abundance to the LREE (Fig. 4), as predicted by Newsom
435 and Palme (1984). Additionally, recently published Mo data for granites from the Lachlan Fold
436 Belt also show an UCC-normalized Mo depletion in the majority of samples for which published
437 Ce data could be located (Yang et al., 2017, and references therein). The widespread depletion of

438 Mo in granitic rocks may be due to the following two processes, which are not mutually
439 exclusive: a) Mo could be lost from an evolving magma to a fractionating titaniferous phase such
440 as rutile or Fe-Ti oxides (Kuroda and Sandell, 1954; Fitton, 1995; Audéat et al., 2011), or b) Mo
441 could be lost to a magmatic vapor phase (MVP) exsolved from a cooling pluton (Candela and
442 Holland, 1984; Audéat, 2010; Audéat et al., 2011). We also propose that S-type granites may
443 show Mo depletion because their source (detrital sediments from oxidatively weathered sources)
444 are depleted in Mo (per Gaschnig et al., 2014). However, with the exception of sample
445 07RMG52, the granitic rocks analyzed here are not proper S-type granites as determined by
446 mineralogy and Aluminum Saturation Index, so this hypothesis does not apply to our data. The
447 hypothesis that Mo is removed during crystal fractionation/accumulation in residual phases is
448 evaluated by determining whether Mo depletion correlates with Nb depletion in the pluton suites,
449 while MVP exsolution is evaluated by examining correlations between Mo and other fluid-
450 soluble elements.

451 5.2.2 Hypothesis 1: Loss of Mo due to partitioning into titaniferous phases

452 Within this first hypothesis, we propose two processes that may inhibit Mo from reaching the
453 upper crust: 1) Mo-loss could be due to fractionation of titaniferous phases (e.g., ilmenite,
454 magnetite, rutile, titanite) during igneous differentiation, and/or, 2) In arc settings, Mo could be
455 retained in residual rutile in a subducting slab, like Nb. These are both likely explanations for the
456 Mo depletion given the observed affinity that Mo has for rutile (Fitton, 1995; Zack et al., 2002)
457 and other Ti-bearing phases like ilmenite and magnetite (Arnorsson and Oskarsson, 2006;
458 Audéat, 2010; Greaney et al., 2017; this study), and they are not mutually exclusive. Titanite, a
459 major host of Mo in most of the titanite-bearing samples analyzed here, could also potentially
460 play a role in removing Mo and Nb as well (Marks et al., 2008), although it crystallizes relatively

461 late in a cooling magma. A correlation between Mo/Ce and Nb/La is observed in several of the
462 plutonic suites analyzed here (Fig. 5), suggesting that fractionation into Fe-Ti oxides during
463 differentiation may remove these elements from an evolving magma. This process may sequester
464 Mo and Nb in lower- or mid-crustal cumulates.

465 The Baffin Island Qikiqtarjuaq Plutonic Suite is an excellent example of differentiation from
466 gabbro to granite. It exhibits a strong correlation between Mo/Ce and Nb/La ($R^2 = 0.92$, Fig 5)
467 suggesting that Mo and Nb share the same geochemical behavior as the magma evolved. All
468 Baffin Island samples have an UCC-normalized Nb/La ratio <1 , suggesting that Nb was initially
469 sequestered in rutile during subduction and mantle melting. The differentiation suite also
470 displays a negative correlation between Nb and SiO_2 ($R^2 = 0.81$) and a negative correlation
471 between Mo/Ce and SiO_2 ($R^2 = 0.75$) over a range from 50.3 to 72.3 wt% SiO_2 , suggesting that
472 both elements were removed by crystal fractionation, instead of behaving incompatibly (Fig. S2).
473 In this plutonic suite, Nb was most likely held in residual rutile, and was then further sequestered
474 in fractionating Fe-Ti oxides, along with Mo, during differentiation (Figs. 4 and 5). The Mo
475 enrichments in the more mafic to intermediate samples may reflect an overabundance of these
476 Mo-bearing minerals relative to the more evolved rocks. This decrease in Mo with differentiation
477 contrasts with observations of Mo increase during differentiation at Hekla volcano, Iceland
478 (Yang et al., 2015) and at Kilauea Iki, Hawaii (Greaney et al., 2017). There appears to be a
479 correlation between Mo/Ce and Nb/La in the Superior Province samples as well (Fig. 5,
480 $R^2=0.89$), although this strong correlation is achieved by ignoring an apparent outlier in the data.
481 The Mashaba tonalities from the Zimbabwe Craton show a much weaker correlation between
482 Nb/La and Mo/Ce ($R^2=0.34$) and Ti/Gd and Mo/Ce ($R^2=0.42$). However, it should be noted that
483 the degree of differentiation in the Zimbabwe tonalites is much less than that observed in other

484 samples and that these samples have been interpreted to represent nearly pure partial melts of a
485 basaltic source without significant fractional crystallization (Luais and Hawkesworth, 1994).
486 Nevertheless, there is a strong correlation between Nb/Ta and SiO₂ in the Zimbabwe data,
487 suggesting that a Ti-bearing phase (e.g., titanite) is being removed from this system during
488 differentiation, but either is not taking Mo with it, or the fractionation signature is overprinted by
489 another process (Fig. S3). We have insufficient data on Phanerozoic granites to draw conclusions
490 about magmatic differentiation for those samples.

491 Molybdenum isotope studies also support the hypothesis that Mo is partitioned into
492 fractionating Ti-bearing phases. Based on the data in Voegelin et al. (2014), Yang et al. (2017)
493 propose that sequestration of Mo-bearing phases (they suggest biotite and hornblende) in the
494 lower crust may explain the heavy $\delta^{98}\text{Mo}$ isotope signature observed in UCC rocks relative to
495 basalts. Additionally, Wille et al. (2018) suggest that Mo isotopes may be fractionated during
496 crystallization of amphibole or clinopyroxene in arc settings. Overall, a net isotope fractionation
497 is observed between average UCC felsic rocks ($\sim +0.15\%$; Willbold and Elliott, 2017) and
498 MORB ($\sim 0.0\%$; Liang et al., 2017; Bezard et al., 2016) and OIB ($\sim -0.14\%$; Liang et al., 2017),
499 suggesting that not only [Mo] but also Mo isotopes may be fractionated during igneous
500 differentiation (Voegelin et al., 2014; Yang et al., 2017; Liang et al., 2017; Greber et al., 2015;
501 Wille et al., 2018). By contrast, other studies show that Mo abundances and isotopes are not
502 significantly fractionated by differentiation processes in intraplate and arc settings (Yang et al.
503 2015; Gaschnig et al., 2017).

504 Alternatively, many researchers have proposed that Mo abundances (Fitton, 1995) and
505 isotopes may be fractionated during dehydration and partial melting of the subducting slab in arc
506 settings (Willbold and Elliott, 2017; König et al., 2008). Specifically, Fitton (1995) observed that

507 a coupled Mo and Nb depletion in arc magmas may represent sequestration of these elements in
508 rutile in the subducting slab. Experimental work of Bali et al. (2012) found that at the Ni-NiO
509 buffer, Mo is retained in rutile relative to slab fluids, adding credence to this hypothesis. While
510 sulfides are not found to be major hosts of Mo in granites, Skora et al. (2017) demonstrated
511 experimentally that sulfides and rutile can fractionate Mo during sediment/slab melting in a
512 subduction zone, given sufficiently reducing conditions. This study did not measure Mo
513 abundances in the sulfides or rutile, so partition coefficients are unknown. However, Zack et al.
514 (2002) found that Mo is significantly enriched in rutile relative to sulfide minerals in eclogites
515 and therefore conclude that sulfides contribute less than 5% of the total eclogite Mo budget.
516 Audétat (2010) suggested that Mo may be sequestered in monosulfide solid solution (MSS)
517 during partial melting (e.g., of slab/sediment) and igneous differentiation, given the measured
518 $D^{\text{MSS/melt}} \sim 80$. However, a recent study of sulfide-saturated arc lavas found no Mo depletion after
519 the onset of sulfide saturation during differentiation (Jenner, 2017). Instead, Mo is seemingly
520 enriched in the resulting sulfide-depleted magmas. Further studies of Mo in magmatic
521 differentiation suites and in subduction zones are needed to determine which exact phase/s, if
522 any, is/are responsible for elemental and isotopic fractionation.

523 5.2.3 Hypothesis 2: Mo loss during fluid exsolution

524 As outlined by Audétat (2010) and Audétat et al. (2011), it is likely that Mo is lost from
525 granites due to exsolution of aqueous magmatic fluids or vapor phases, because experimental
526 studies show that Mo is partitioned into these phases (Candela and Holland, 1984; Zajacz et al.,
527 2017). Partition coefficients ($D^{\text{fluid/melt}}$) vary due to the nature of different ligands (e.g., Cl, F) and
528 salinity, but typically range from $D = 1$ to $D = 20$ (Zajacz et al., 2008). Molybdenum loss during
529 aqueous fluid exsolution would probably lead to the saturation of molybdenite (MoS_2) in

530 epithermal veins surrounding the plutons and, on larger scales, formation of economically viable
531 Mo porphyry deposits.

532 Some TTG suites show only a weak (e.g., Zimbabwe, Fig. 5) or no correlation (e.g.,
533 Barberton) between Mo and Nb or Mo and Ti, which suggests that fractionation of Mo by Ti- or
534 Nb-bearing phases did not play a dominant role in the evolution of the Mo budgets of these
535 magmas. Alternatively, fractionation may not be captured by the limited differentiation range in
536 these TTGs. Nevertheless, these plutonic suites (except for one set of Barberton TTGs) still show
537 significant Mo depletion. In the Zimbabwe suite, Mo is variably correlated with Cs ($R^2 = 0.84$),
538 Sb ($R^2 = 0.73$), Pb ($R^2 = 0.56$), and As ($R^2 = 0.46$) (Fig. S4) all of which are moderately
539 compatible in a low-salinity fluid phases (Zajacz et al., 2008), and these elements are known to
540 be expelled from granitic plutons. However, several of these correlations hinge on a single data
541 point (Fig. S4). There is no correlation between these fluid-mobile elements and incompatible,
542 less-fluid mobile elements such as the LREE, implying that the fluid-mobile element
543 concentrations are dominated by processes other than crystal-melt differentiation. Indeed, Mo is
544 more strongly depleted relative to Ce in this suite of TTGs relative to other locales (lower Mo/Ce
545 ratio in Fig. 5), so a vapor phase may have preferentially removed Mo from the Zimbabwe
546 TTGs. In contrast to the Zimbabwe samples, no individual pluton suite displays convincing ($R^2 >$
547 0.4) multi-element correlations in the Barberton TTGs. Correlations between Mo and fluid-
548 soluble elements are also not found for the Superior Province or Baffin Island samples. Thus, we
549 suggest that different processes of Mo-loss from plutons (fluid exsolution v. crystal
550 fractionation) may be acting on different plutonic suites, and these processes are not mutually
551 exclusive.

552 If we explore the hypothetical end-member case in which the effects of crystal fractionation
553 are assumed to be negligible, and Mo behaves as an incompatible element in all systems, then
554 loss through fluid exsolution to form MoS₂ could account for all calculated Mo depletions. In
555 this scenario, it can be inferred that approximately 60% (average Mo lost from a pluton – see
556 supplement information on Mo* calculation) of the Mo in un-weathered UCC granites is hosted
557 in MoS₂. This is a maximum estimate, because it is likely that Mo loss from the magma during
558 partial melting or crystal fractionation also occurs.

559 A simple calculation can be used to estimate the maximum amount of Mo released from
560 plutons to form molybdenite. We start with the following parameters and assumptions: the
561 continental crust covers 210x10⁶ km² of the Earth's surface (Cawood et al., 2013) and, to a depth
562 of 10 km, 40% of that area is granitic rock that initially contains 0.5 ~~ug/gppm~~ Mo (the average
563 interpolated Mo abundance, Mo*, of this study). Mean Mo loss from the granites in this study is
564 60%, and we initially assume that all Mo 'lost' is due to vapor-phase partitioning. With these
565 assumptions, a maximum 10¹⁴ kg of Mo would have been released from UCC granitic plutons to
566 form MoS₂. If we instead assume that granite only composes 20% of the upper 10 km of the
567 crust, and only 10% of the Mo missing from a pluton is a result of MoS₂ formation, then
568 approximately 10¹³ kg of Mo would have been released from UCC granitic rocks to form MoS₂.
569 Thus, we conclude that a maximum of 10¹³ kg to 10¹⁴ kg of Mo may be hosted in MoS₂ in the
570 upper 10 km of the continental crust. The USGS has identified ~10¹⁰ kg of Mo resources
571 available for mining (rounding to the nearest order of magnitude) (USGS, 2009). This suggests
572 that up to three to four orders of magnitude more Mo may lie inaccessible beneath the surface of
573 the continental crust.

574 In summary, a combination of fractionation during differentiation and loss via vapor phase
575 exsolution probably contributes to the total Mo loss recorded in granites. This would explain
576 discrepancies between plutonic suites – among which some show strong Ti-mineral fractionation
577 signatures and others do not – yet, nearly all of the samples studied here show depletions in total
578 [Mo]. Further studies of magmatic suites formed by partial melting with Fe-Ti oxides in the
579 residue, or differentiation involving fractionation of Fe-Ti oxides are needed to test these
580 hypotheses.

581 *5.3 Release of Mo during oxidative weathering of the UCC*

582 Mo enrichments in black shales that form in euxinic (S-rich) ocean basins are first
583 observed in the rock record at around 2.5 Ga and persist through the Phanerozoic, with a second
584 period of increased Mo abundances beginning at the end of the Proterozoic (Anbar et al. 2007;
585 Scott et al., 2008; Wille et al., 2007). These enrichments are interpreted to reflect changing
586 atmospheric and oceanic oxidation states due to the GOE and the Neoproterozoic Oxidation
587 Event. However, before Mo concentrations in black shales can be calibrated as a paleo-
588 atmospheric oxybarometer, one must first know which O₂ sensitive mineral phases host Mo in
589 the continental crust (Anbar et al., 2007). We have shown here that molybdenite, specifically, is
590 the predominant sulfide host of Mo in the UCC, while other common magmatic sulfides and
591 their subsolidus exsolution products (pyrite, chalcopyrite, etc.) do not contain significant Mo.
592 Based on our findings, it is likely that Mo released from MoS₂ during oxidative weathering is the
593 source of Mo enrichment observed in oceanic sediments since the GOE. Thus, experimentally-
594 determined oxidation rates of MoS₂ at low *p*O₂ are needed to derive the *p*O₂ of the atmosphere
595 during the GOE (e.g., Greber et al., 2015). While authigenic pyrite may host some Mo in
596 sedimentary rocks (e.g., Gregory et al., 2017), Mo must first be removed from the primary

597 igneous crust before it can be concentrated in these phases. If Mo was not released significantly
598 from the igneous UCC prior to the GOE – which is likely given the lack of Mo depletion in pre-
599 GOE diamictites (Gaschnig et al., 2014) – then authigenic sulfides were probably not a
600 weatherable source of Mo from the continental crust at the time of the GOE.

601 Given the strength of the Ti-O bond, titaniferous phases are fairly resistant to weathering, so
602 Mo will not be easily released from them, irrespective of pO_2 . It is very likely that Mo remains in
603 these minerals as the source rocks are weathered and the titaniferous minerals are incorporated
604 into sediments as detrital minerals. However, Mo is also highly enriched in volcanic glass – a
605 phase that is susceptible to weathering in anoxic and oxic environments. Therefore, we propose
606 that weathering of volcanic glass may have released Mo from the crust before the rise of
607 atmospheric oxygen. As no Mo depletion is observed in the UCC before the GOE (Gaschnig et
608 al., 2014), this process was probably not widespread on the continents. However, soluble Mo^{6+}
609 may have been released into the pre-GOE oceans from submarine weathering of glassy basalt.
610 This Mo might have been immediately reduced and sequestered if sufficient S, or another
611 reductant, existed in the water column. Alternatively, if there was insufficient S in the water
612 column to reduce Mo prior to the GOE (as suggested by Canfield, 2005), Mo might have
613 remained in solution in pre-GOE oceans and is therefore not recorded in the marine rock record.
614 This hypothesis has implications for the timing of the evolution of Mo-co-factored enzymes that
615 fix nitrogen, as sufficient Mo must be present in the water column for it to be incorporated into
616 these enzymes (Stüeken et al., 2015). However, this assumes that Mo is not immediately reduced
617 once it is weathered out of volcanic glass, and that Mo is not hosted in secondary alteration
618 phases. Both of these assumptions need to be tested with weathering models and analyses of Mo
619 in altered basalts.

620 *5.4 Molybdenum enrichments in rift-related magmas*

621 The Barberton Terrane is composed of TTGs, greenstones (metamorphosed Archean basaltic
622 rocks), and sedimentary units that were formed between 3.5 and 3.2 Ga. The samples studied
623 here span 300 Myr in age and were formed during three to four distinct tectono-magmatic events
624 at 3.5 Ga, 3.46 Ga, 3.29 Ga and 3.24 Ga (Clemens et al., 2006, Kröner et al., 1991). On the basis
625 of field relationships and pluton geochemistry, Moyen et al. (2006) interpreted the terrane to
626 have formed during collision of exotic blocks (3.55 – 3.42 Ga plutons) followed by a main
627 orogenic event (3.25 – 3.21 Ga) during which the Badplaas pluton was emplaced. This was
628 followed by post-orogenic collapse at 3.22 – 3.21 Ga, contemporaneous with emplacement of the
629 Nelshoogte pluton in an extensional setting. The plutonic suites emplaced during accretion and
630 the main orogenic stage exhibit Mo depletions relative to LREE (with the exception of one
631 sample from the Stolzberg pluton, STZ), while the Nelshoogte (NLG) pluton, which is
632 associated with post-orogenic collapse, is not depleted in Mo (Fig. 6). The concentrations of
633 REE do not change significantly between the different suites, but the NLG plutonic suite is less
634 enriched in LREE relative to HREE, and is slightly more magnesian. This observation that Mo is
635 enriched in ~3.2 Ga rift-related magmas is similar to Mo-enrichments observed in rift-related
636 magmas today.

637 Similarly, while many economic Mo deposits are associated with arc-derived, calc-alkaline
638 magmas (Westra and Keith, 1981; Whalen et al., 2001), the highest-grade Mo-porphyry deposits
639 are associated with rift settings (e.g., Climax-type deposits; Ludington and Plumlee, 2009), and
640 alkaline magmas from continental rifts show significant Mo enrichments (Audétat, 2010;
641 Audétat et al., 2011). The source of Mo in these rift-related magmas is unclear; both the
642 lithospheric mantle and the continental crust have been suggested as sources. Sun et al. (2016)

643 propose that assimilation of sedimentary rocks enriched in Mo (e.g., black shales) may be the
644 source of Mo. Other researchers have suggested that the Mo may ultimately be sourced from
645 Mo-enriched mantle melts that undergo fractional crystallization (Audétat, 2010; Pettke et al.,
646 2010). Pettke et al. (2010) proposed that the lithospheric mantle may be re-enriched in Mo
647 through subduction-related metasomatism, and that alkaline magmas may be generated from this
648 Mo-rich reservoir during rifting events.

649 The observation that Mo is enriched in the ~3.2 Ga rift-related NLG pluton can be used to
650 test these hypotheses. Significant Mo enrichments in black shales only occur after the onset of
651 widespread oxidative weathering at ~2.4 Ga (Scott et al., 2008; Anbar et al., 2007). Thus, the
652 hypothesis that rift magmas assimilate Mo-rich sediments, proposed by Sun et al. (2016) does
653 not hold for these Archean magmas. There is evidence for subduction-related magmatism in the
654 Barberton suite (Moyen et al., 2006; Furnes et al., 2012), which adds credence to the hypothesis
655 that a subducting slab may have enriched the lithospheric mantle in Mo (Pettke et al., 2010).
656 However, this hypothesis remains contentious because many authors argue that subduction zones
657 mainly arose after 3.2 Ga (e.g., Condie and Kröner, 2008; Tang et al., 2016, and references
658 therein).

659 In the Barberton samples, Mo correlates with Ni (Fig. 7a) and Cr (Fig. 7b). Additionally, the
660 overall Mo enrichment of the NLG pluton relative to LREE resembles that of MORB and
661 Hawaiian lavas (Fig. 4), suggesting a mafic, *i.e.*, mantle, origin for the Mo. Lithospheric mantle-
662 derived Mo is a something of a paradox because the lithospheric mantle is refractory and should
663 be depleted in incompatible Mo. This paradox could be resolved if the lithospheric mantle were
664 metasomatized with fluids derived from a subducting slab, and then partially melted during a
665 subsequent rifting event (Pettke et al., 2010). Alternatively, it is possible that the Mo enrichments

666 may be derived from partial melting of Mo-rich cumulates (e.g., Fe-Ti oxides and rutile bearing
667 rocks such as amphibolites and eclogites) during continental rifting. In this scenario, lower
668 crustal rocks may contain the missing Mo recorded in granitic suites and explain the origin of the
669 Mo enrichment in various rift-related magmatic suites. This hypothesis implies that sequestration
670 of Mo in Fe-Ti oxides in lower crustal cumulates must be significant, and further analyses of Mo
671 abundances in such rocks are needed to evaluate this idea.

672 **Conclusions**

- 673 • In 'common' UCC granitic rocks, Mo is hosted primarily in weathering-resistant, titaniferous
674 phases such as titanite, ilmenite, and magnetite, while in basaltic to andesitic volcanic rocks,
675 Mo is predominately hosted in ilmenite, magnetite, and interstitial glass. Molybdenum mass
676 balance based on in situ analyses of Mo in silicates and oxides cannot be completed in a few
677 granitic samples, suggesting nuggets of MoS₂ may be a significant Mo host in some felsic
678 plutonic rocks.
- 679 • Silicates (e.g., quartz, biotite, and amphibole) generally contain less than 0.2 ~~µg/gppm~~ Mo,
680 but may be volumetrically significant hosts, contributing up to 25% of the whole-rock Mo in
681 one granitic rock analyzed here.
- 682 • Common accessory phase sulfides (e.g., pyrite, chalcopyrite, immiscible sulfide blebs) are
683 not significant hosts of Mo in granitic or basaltic rocks.
- 684 • Nearly all analyzed granitic rocks are depleted in Mo (by 20 – 90%, mean = 60%), relative to
685 Ce and Pr. This may reflect MoS₂ precipitation from fugitive magmatic vapor phases or loss
686 of Mo to fractionating Ti- and Nb-bearing phases during slab melting or magmatic
687 differentiation. Some plutonic suites show correlations between Mo and Nb, suggesting loss
688 of Mo due to fractionation of Fe-Ti oxides or other titaniferous phases. Other plutonic suites

Comment [RLR1]: You mention titanite in the response to reviews.

689 show correlations between Mo and fluid-soluble elements (e.g., Cs, Pb, As, etc), potentially
690 pointing to Mo loss in an aqueous magmatic vapor phase.

- 691 • If all Mo lost from granitic rocks is attributed to aqueous fluid exsolution and subsequent
692 MoS₂ precipitation, then, on average, 60% of the Mo budget in a pluton would have to be
693 concentrated in distal, epithermal veins that crystallized MoS₂. This is most likely an
694 overestimate as it represents the endmember scenario where all Mo is lost through vapor-
695 phase fractionation.
- 696 • The ~3.2 Ga rift-related Nelshoogte pluton from the Barberton Greenstone Belt is the only
697 group of samples studied here that do not show a systematic Mo depletion. This is similar to
698 observations of Mo-enrichments in modern rift-related magmas. These data can be used to
699 rule out the hypothesis that Mo enrichments in rift-related magmas are derived from melting
700 of Mo-rich sediments like black shales, because Mo was not enriched in black shales prior to
701 the GOE at ~2.4 Ga. If subduction was occurring at this time, subduction-related
702 metasomatism of the lithospheric mantle could be the source of the enrichment in Mo in
703 these rift-related magmas (Pettke et al., 2010). Alternatively, mantle melts generated during
704 rifting may have assimilated Mo-rich residues in the lower crust or upper mantle to create
705 these Mo enrichments in rift-related magmas. This would imply that significant Mo is
706 removed from evolving magmas in Fe-Ti oxides. Further analyses of Mo in differentiated
707 suites and lower crustal cumulates are needed to test this hypothesis.
- 708 • The processes of Mo-loss through fluid/vapor-phase partitioning or fractionation of
709 titaniferous phases are likely not mutually exclusive. Here we present arguments for the two
710 end-member scenarios but emphasize that further research is needed to determine the
711 proportion of Mo-loss by these two processes.

Comment [RLR2]: I think you need to name it here so that people understand that it is not all of the Barberton samples that don't show Mo depletion.

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963

964

965 **Figure 1.** Photomicrographs of sulfides targeted for laser ablation analysis. A) Immiscible
966 sulfide bleb from the Kilauea Iki lava lake (KI67-3-76.2) showing needle-like exsolution
967 textures. A second minute ($\leq 1 \mu\text{m}$ diameter) sulfide is visible on the right. B) Pyrite from the
968 Archean Superior province tonalite (WXP99-119). C) Small chalcopyrite inclusion (yellow)
969 hosted in magnetite having ilmenite exsolution from a Mesozoic granite (10RMG005). D) Pyrite
970 rimmed by magnetite from the Paleozoic Ellicott City Granodiorite (AG1401).

971

972 **Figure 2.** Box and whisker plots of Mo abundances in all the minerals analyzed. Minerals are
973 arranged by their median [Mo], with the boxes representing 1st and 3rd quartiles and whiskers
974 representing min and max values measured. Upper plot: Granitic minerals from the Zimbabwe
975 craton, Superior Province, and Phanerozoic granitic rocks. Plagioclase, epidote, and chlorite
976 analyses were often below the detection limits. Lower plot: Minerals in basaltic to intermediate
977 lavas from Kilauea Iki (red; data from Greaney et al., 2017) and MORB (blue; glass data from
978 Jenner and O'Neill, 2012, sulfide data from Patten et al., 2013).

979

980 **Figure 3.** Pie charts depicting the total Mo distribution in four samples selected to show
981 variation in major host minerals. Mass balance is achieved in three of the samples depicted
982 (a,b,c), but 82% of the whole-rock [Mo] is missing from sample d. Sample numbers: A) WXP99-
983 123 B) AG1401 C) KI67-3-76.2 D) 10RMG005.

984

985 **Figure 4.** UCC normalized spider plots showing Mo behavior relative to LREE in granitic suites
986 (and their associated mafic enclaves/gabbros in the Superior and Baffin Island samples), and
987 modern basalts. The differentiation suites from Zimbabwe, Baffin Island, and Superior Province

988 are defined with a gradient color scale (note the SiO₂ range varies for each suite with black and
989 purple representing mafic or intermediate samples). Dashed lines indicate that Mo was below the
990 detection limit in that sample, so the detection limit is used as the [Mo] value (see Table 1). All
991 data are normalized to the UCC (Rudnick and Gao, 2014). Baffin Island data, except for Mo
992 abundances, come from Whalen et al. (2012). The Kilauea Iki field represents twenty samples
993 (Greaney et al., 2017) and the MORB field represents ~600 glass samples from Jenner and
994 O'Neill (2012), with the mean values for both datasets shown with a line.

995

996 **Figure 5.** Correlations between Mo/Ce and Nb/La in Archean and Proterozoic pluton suites.

997 Samples are color coded based on SiO₂ content with red being the most felsic and purple/black
998 being the least. The SiO₂ range varies between suites (see Table 1 and supplementary figures).

999 The Zimbabwe data include only the Mashaba tonalite suite. Error bars represent 2σ external
1000 reproducibility, as determined by AGV measurements.

1001

1002 **Figure 6.** UCC normalized spider plots for individual pluton suites in the Barberton Greenstone

1003 Belt representing different stages of accretion and post-orogenic collapse. Dashed lines indicate

1004 Mo was below the DL in the sample, so the DL is used instead of Mo concentration. Black =

1005 Steynsdorp; Green = Eerstehoek, Theespruit, Doornhoek, Stolzburg; Blue = Badplaas; Red =

1006 Nelshoogte.

1007

1008 **Figure 7.** Correlations between (A) Mo and Ni and (B) Mo and Cr in the Barberton TTGs. Color

1009 scheme is the same as in figure 6; dashed symbols represent samples that contain less Mo than

1010 the detection limit (0.16 $\mu\text{g/gppm}$). Error bars represent 2σ.

1011

1012 **Table 1.** Samples analyzed for whole-rock (WR) [Mo] and in-situ [Mo]. SA = standard addition
1013 ICP-MS; LA = laser ablation ICP-MS; MB = mass balance attained? (yes or no). The SiO₂
1014 (measured by the listed reference) and Mo values given are for the whole rock with 2σ
1015 representing internal error. Three samples were replicated by isotope dilution and those values
1016 are designated as “rep”. Complete whole rock major and trace element data can be found in the
1017 online supplement.

1018

1019 **Table 2.** Secondary standards analyzed by laser ablation and standard addition. Concentrations
1020 are in μg/gppm. LA = Laser ablation-ICP-MS and SA = Standard addition whole rock-ICP-MS.
1021 BHVO-1 and AGV-2 were measured during the same analytical session as data reported in
1022 Greaney et al. (2017). Complete analytical methods can be found in the supplementary
1023 information.

1024

1025 **Table 3.** Mean Mo concentrations in all minerals analyzed (including granitic rocks and basalts).
1026 2σ represents two standard deviations of the mean of repeated analyses. Analyses of sulfides,
1027 quartz, amphibole, K-feldspar, zircon, plagioclase, and epidote were occasionally below the
1028 detection limits (~0.01 μg/gppm), so the detection limit of 0.01 μg/gppm was included in place
1029 of those analyses when calculating the mean concentration. Therefore, these data may be skewed
1030 to slightly higher values than actually present in the mineral.

1031

Table 1

Sample	Unit/ Pluton	Age, Ga	Rock type	Analysis	MB	SiO ₂	Mo (µg/g)
Barberton							
NLG1	Nelshoogte	3.24-3.23	TTG	SA		70.1	0.34
NLG14	Nelshoogte	3.24-3.23	TTG	SA		NA	0.38
NLG15	Nelshoogte	3.24-3.23	TTG	SA		63.1	0.48
NLG25A	Nelshoogte	3.24-3.23	TTG	SA		71.1	0.32
BDP5A	Badplaas	3.29-3.24	TTG	SA		70.5	<0.16
BDP5C	Badplaas	3.29-3.24	tonalite dyke	SA		72.8	0.17
BDP8A	Badplaas	3.29-3.24	TTG	SA		74	0.18
EHK1	Eerstehoek	3.46-3.42	TTG	SA		72.4	<0.16
TH4A	Theespruit	3.46-3.42	TTG	SA		70.3	0.20
DNK1	Doornhoek	3.46-3.42	TTG	SA		74	0.23
STZ1	Stolzberg	3.46-3.42	TTG	SA		70.7	0.48
STZ17	Stolzberg	3.46-3.42	TTG	SA		71.6	0.34
STY1	Steynsdorp	3.55-3.49	TTG	SA		65.7	0.16
STY1 rep							0.14
STY3A	Steynsdorp	3.55-3.49	TTG	SA		72.9	0.16
STY4B	Steynsdorp	3.55-3.49	TTG	SA		75.1	<0.16
Zimbabwe							
Zb89-53	Chibi	2.7-2.6	granite	SA, LA	no	72	0.84
Zb89-57	Chibi	2.7-2.6	granite	SA		74.8	0.26
ZB89-10	Mashaba I	2.9	tonalite	SA, LA	no	71	0.25
ZB89-10 rep							0.13
ZB89-11	Mashaba I	2.9	tonalite	SA		67.3	0.07
Zb89-12	Mashaba I	2.9	tonalite	SA		69.4	0.14
Zb89-13	Mashaba I	2.9	tonalite	SA, LA	yes	68.5	0.20
Zb89-15	Mashaba I	2.9	tonalite	SA, LA	yes	70.5	0.13
Zb89-46	Mashaba I	2.9	tonalite	SA		70.1	0.07
Rh75-Mt7	Mashaba I	2.9	tonalite	SA		71.2	0.05
Superior							
WXP99-119	N. Caribou	2.999	tonalite	SA	no	63.7	0.16
WXP99-123	N. Caribou	2.999	tonalite	SA, LA	yes	62.6	0.14
WXP99-138	N. Caribou	2.999	quartz diorite	SA	no	61.7	0.21
WXP99-176	N. Caribou	3.006	trondhjemite	SA, LA		72.1	0.32
WXP99-129	N. Caribou	2.999	tonalite	SA		62.5	nd
WXP 99-139	N. Caribou	NA	quartz diorite	SA		63.8	<0.10
WXP 99-143	N. Caribou	NA	quartz diorite	SA		60.7	<0.10
WXP 99-143 rep							0.11
WXP 99-145	N. Caribou	2.992	gabbro enclave	SA		49.3	0.90
PBA99-2064c	N. Caribou	NA	gabbro enclave	SA		46.1	<0.10
PBA99-2072c	N. Caribou	NA	amph-lite encl.	SA		50.1	0.13
PBA99-2072e	N. Caribou	NA	pyx-ite encl.	SA		45.2	0.17
PBA97-23	C. Wabigoon	2.72-2.71	granite	SA, LA	yes	71.3	0.32
PBA97-319	C. Wabigoon	2.72-2.71	granodiorite	SA		69.6	0.17
Baffin Island							

Table 2

secondary standard	analysis	Mo (reported)	Mo 95 measured	2s	Mo 97 measured	2s	Mo 98 measured	2s	n
BHVO-2g	LA	3.8	4.09	0.86	4.07	1.15	4.03	1.16	89
NIST 612	LA	37.4	43.6	16.2	40.4	14.0	44.1	7.89	8
JB sulfide	LA	2.55	2.44	0.30	2.45	0.69	2.44	0.20	8
BHVO-1	SA	1.1*	1.17	0.34	1.19	0.33	1.17	0.34	8
AGV-2	SA	1.93*	1.94	0.13	1.93	0.1	1.92	0.07	5

* values from Gaschnig et al., 2015

Table 3

	Titanite	Niobite	Magnetite	OIB Glass	Ilmenite	Sulfides	Rutile	Garnet
Mo ($\mu\text{g/g}$)	15.9	9.83	5.83	4.83	4.09	1.44	0.95	0.33
2σ	27.2	n/a	17.5	5.58	11.2	4.09	0.86	0.09
n	59	1	36	101	53	78	10	12
	Olivine	Muscovite	Quartz	Hornblende	K-feldspar	Augite	Zircon	Plagioclase
Mo ($\mu\text{g/g}$)	0.10	0.08	0.05	0.04	0.03	0.02	0.02	≤ 0.01
2σ	0.15	0.13	0.06	0.10	0.08	0.02	0.03	0.03
n	5	9	25	36	24	5	21	37

Figure 1
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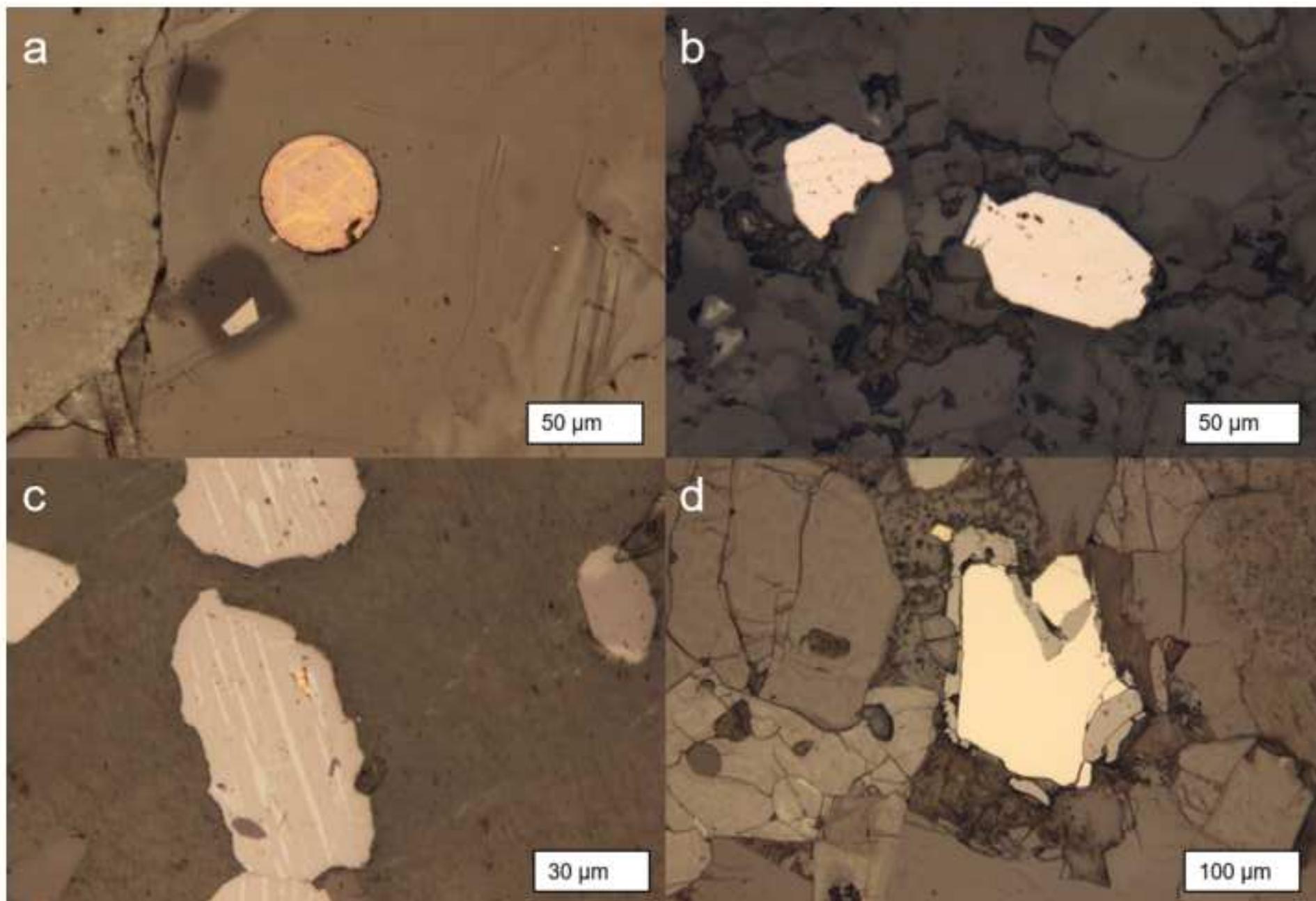


Figure 2
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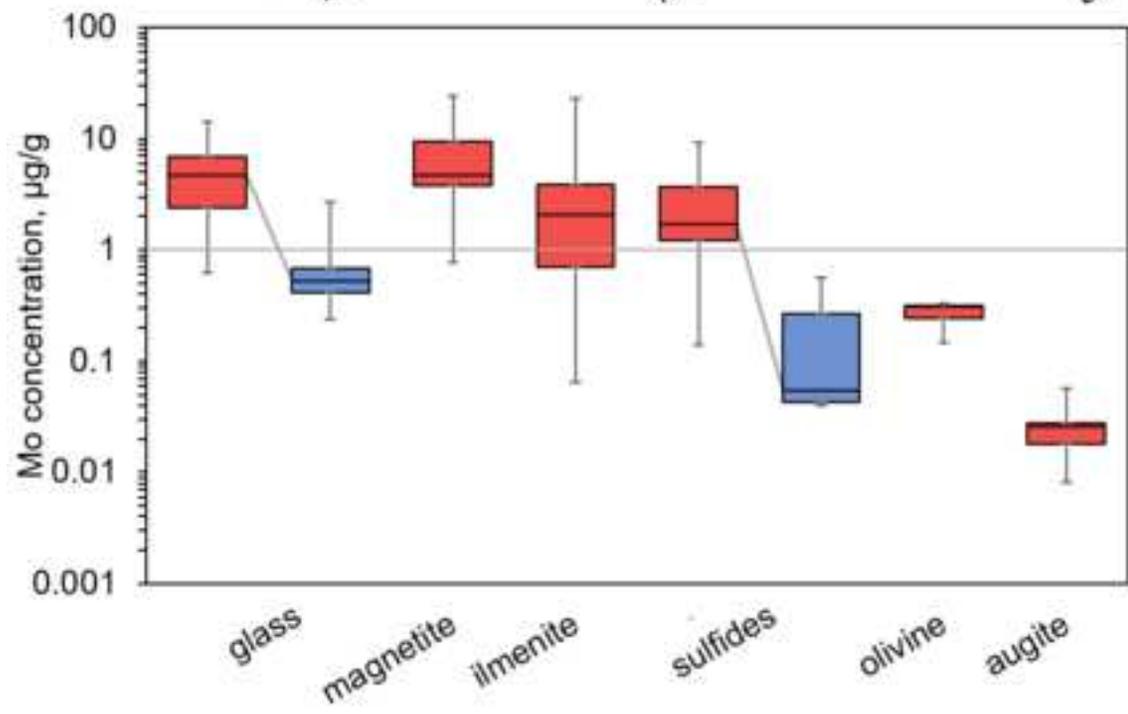
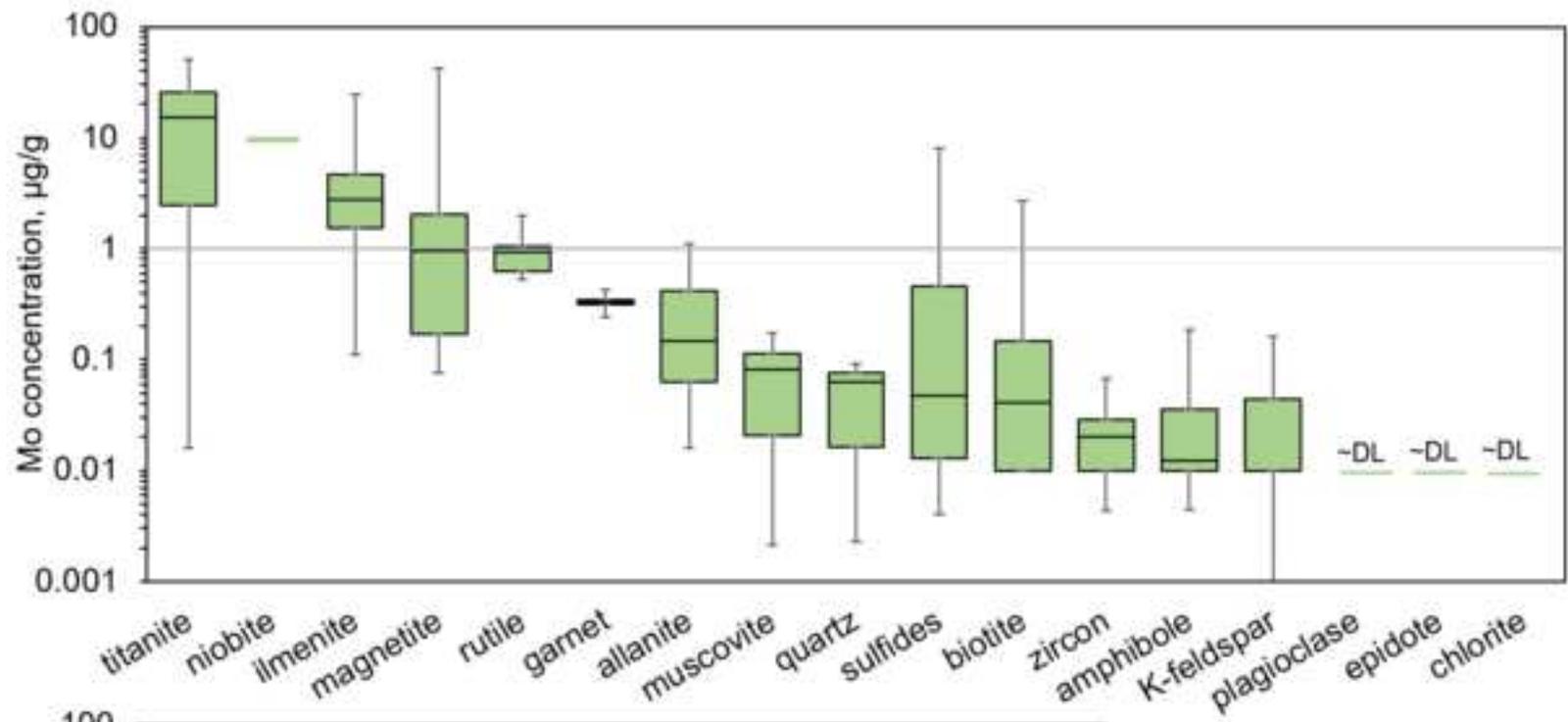
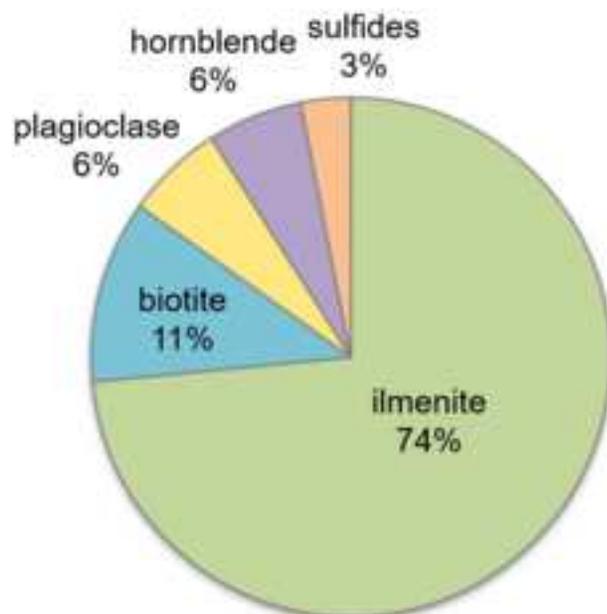
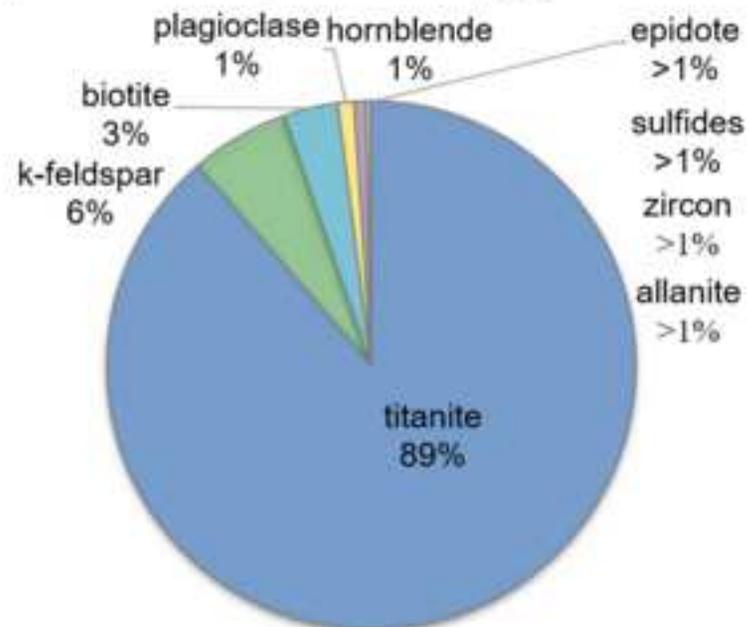


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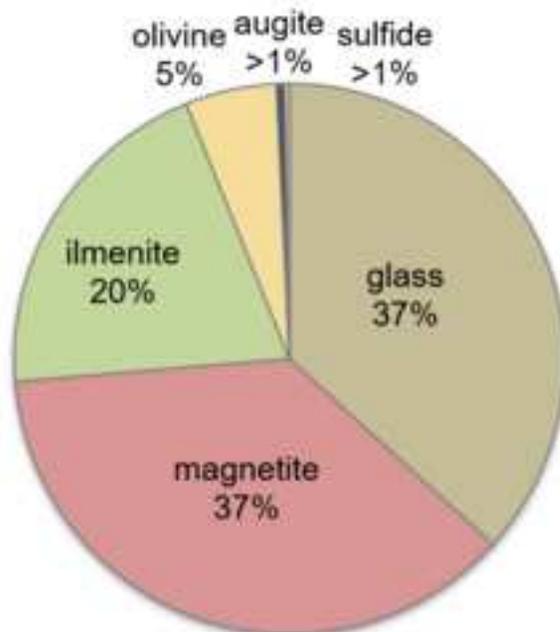
a) Archean tonalite, WR = 0.14 $\mu\text{g/g}$



b) Granodiorite, WR = 0.17 $\mu\text{g/g}$



c) Evolved KI basalt, WR = 2.0 $\mu\text{g/g}$



d) Tonalite, WR = 0.19 $\mu\text{g/g}$

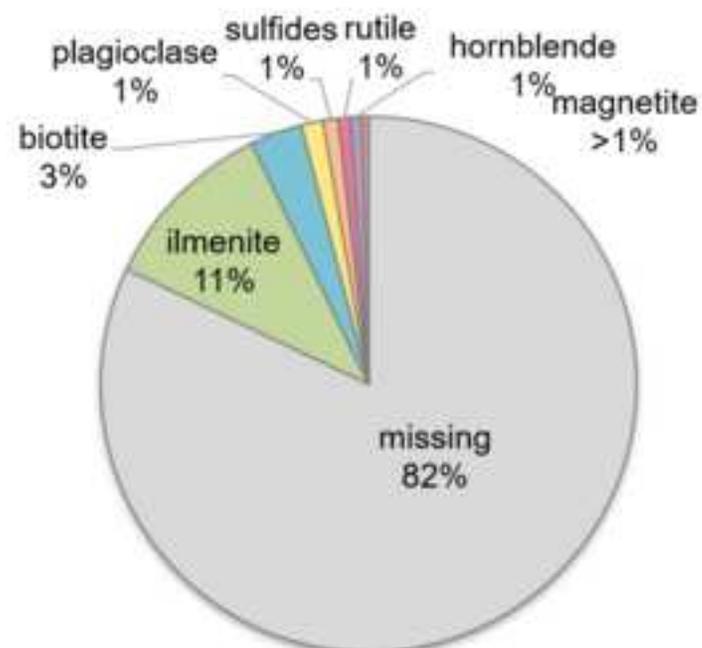


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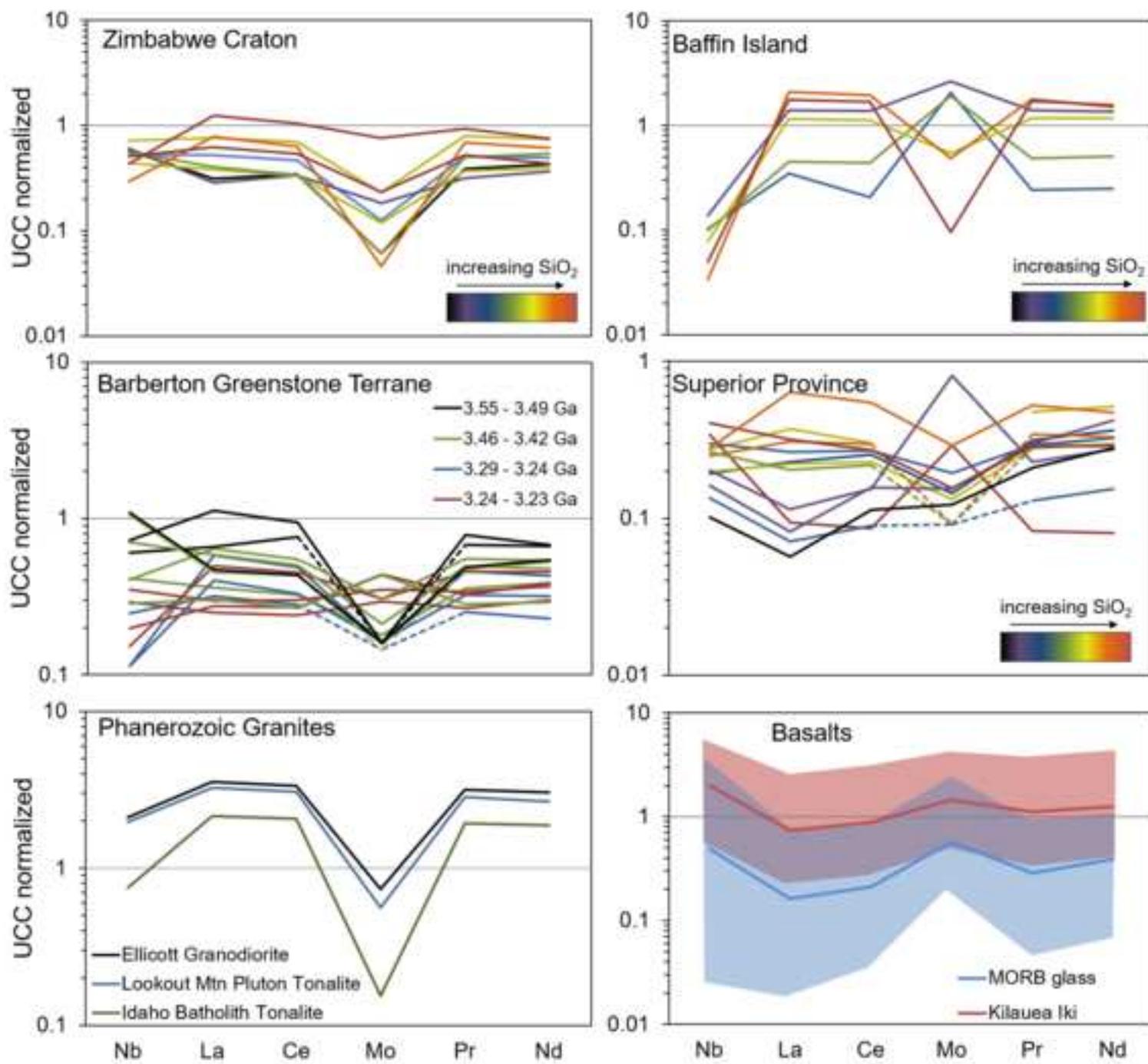


Figure 5

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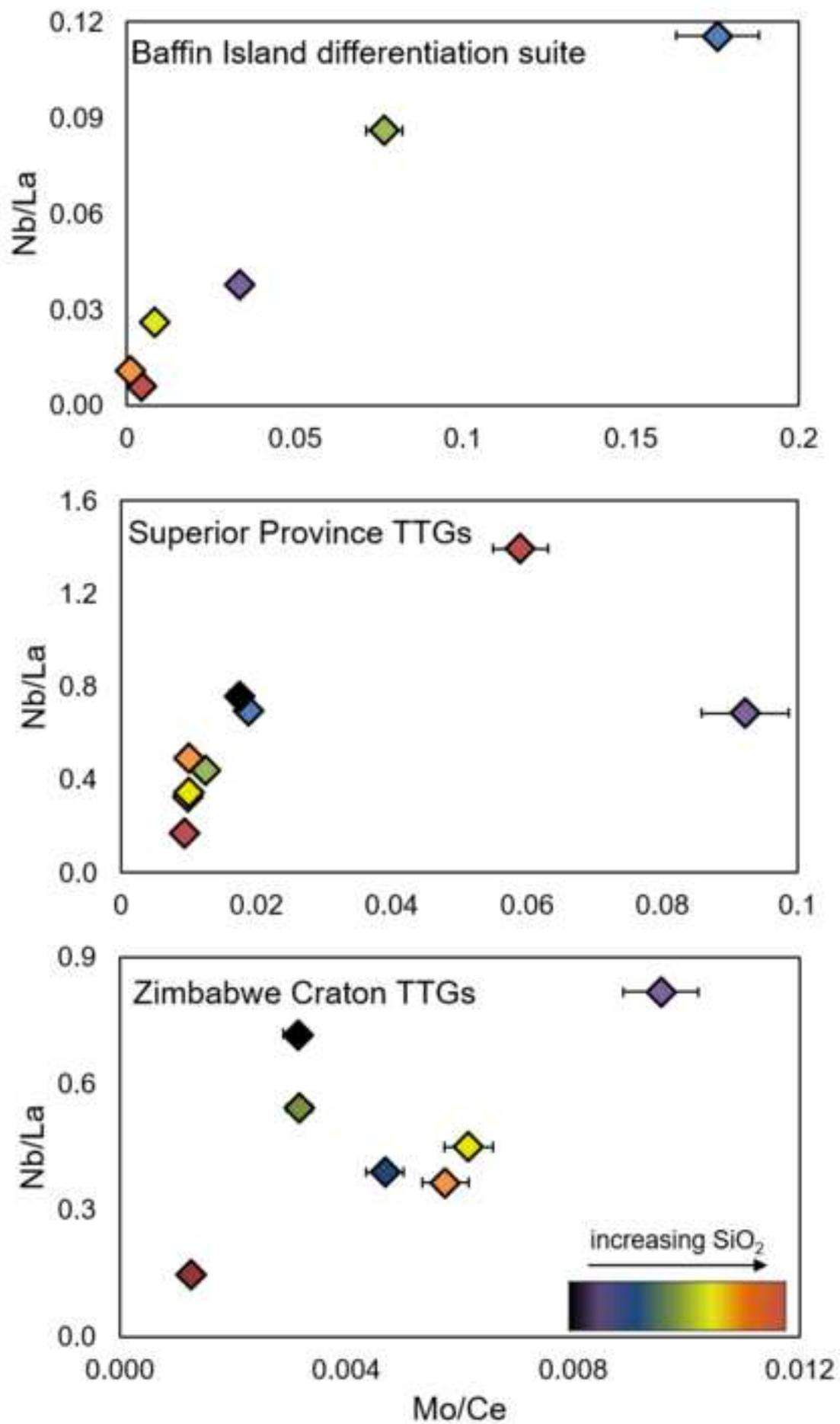


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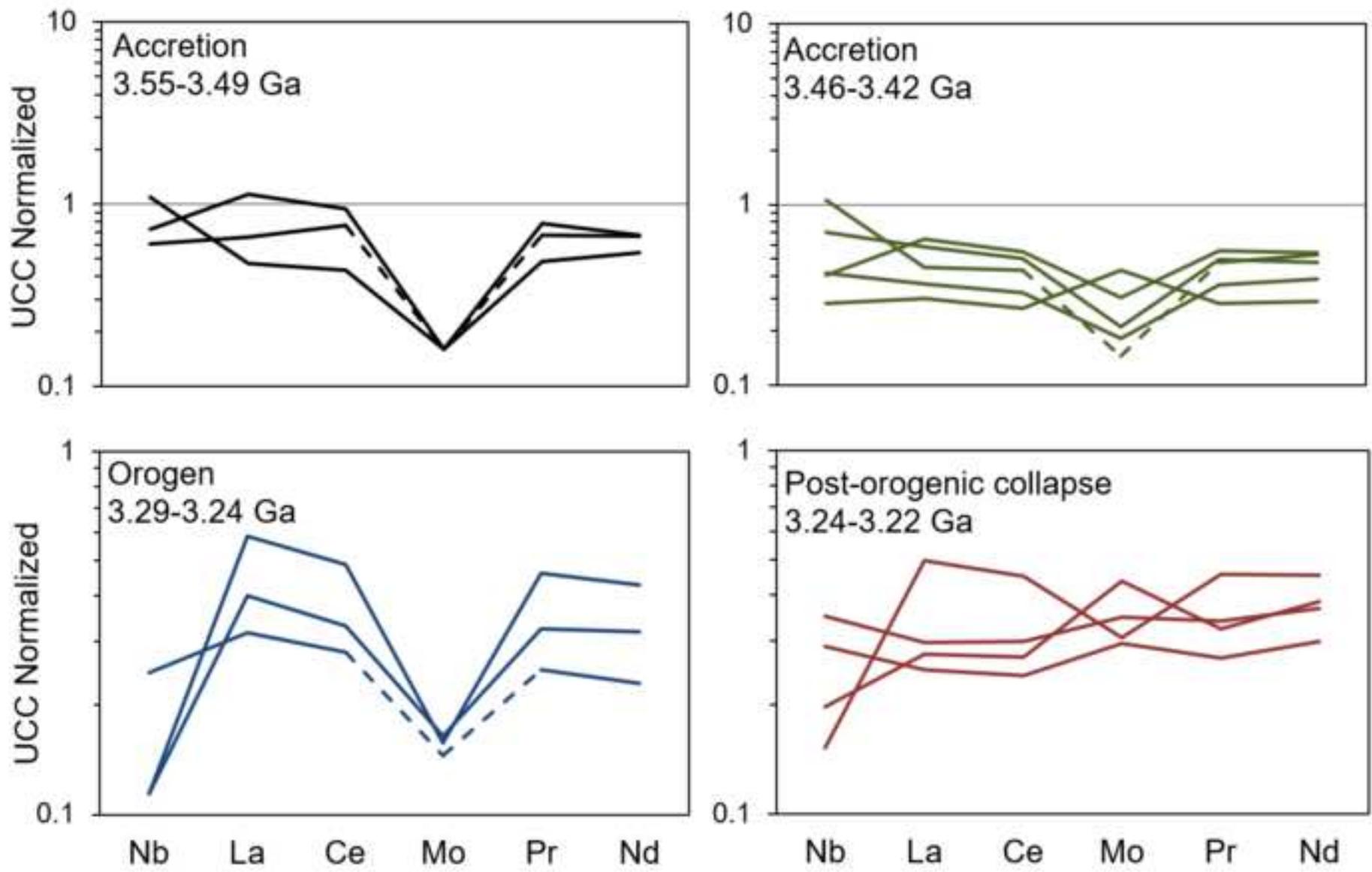
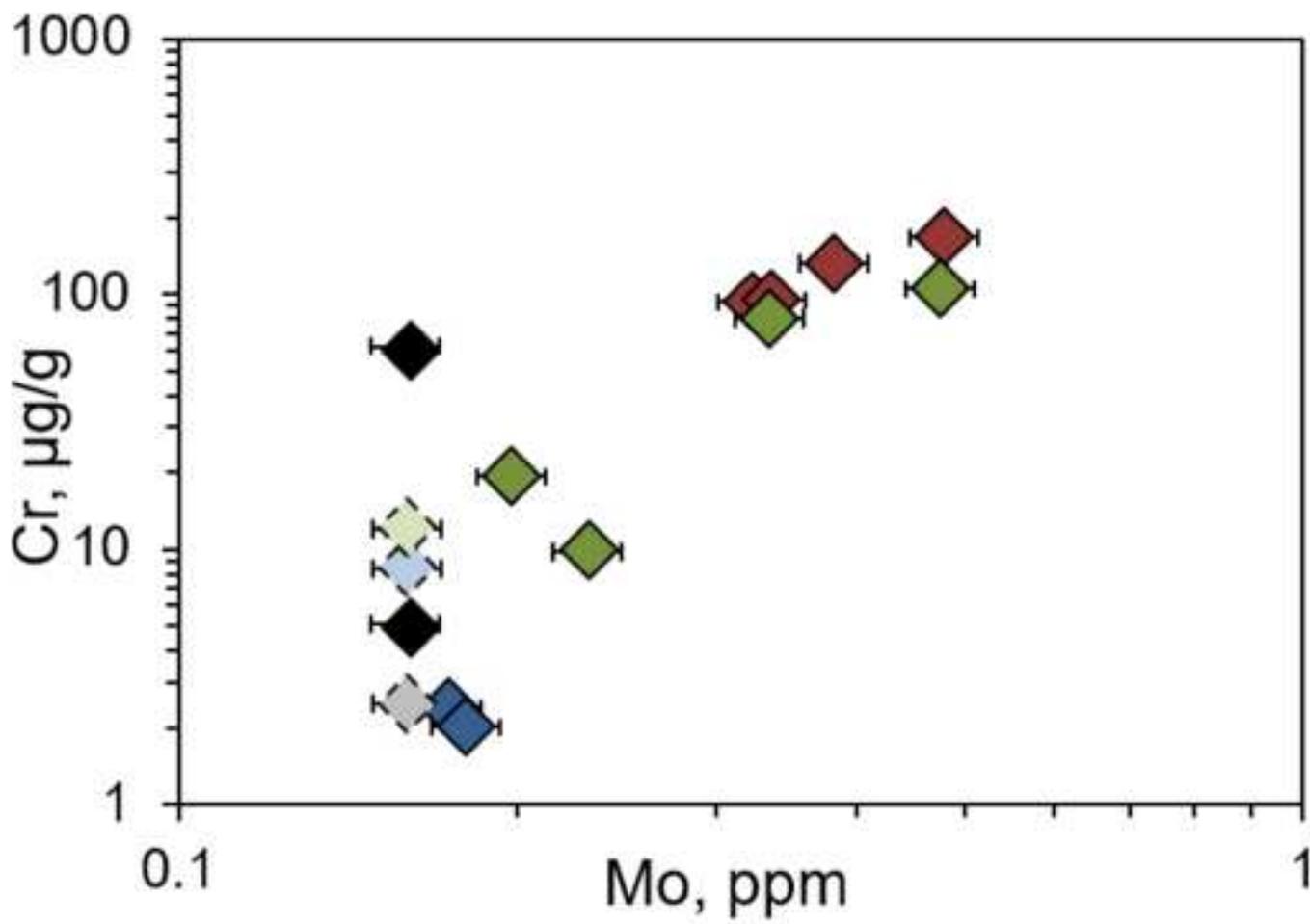
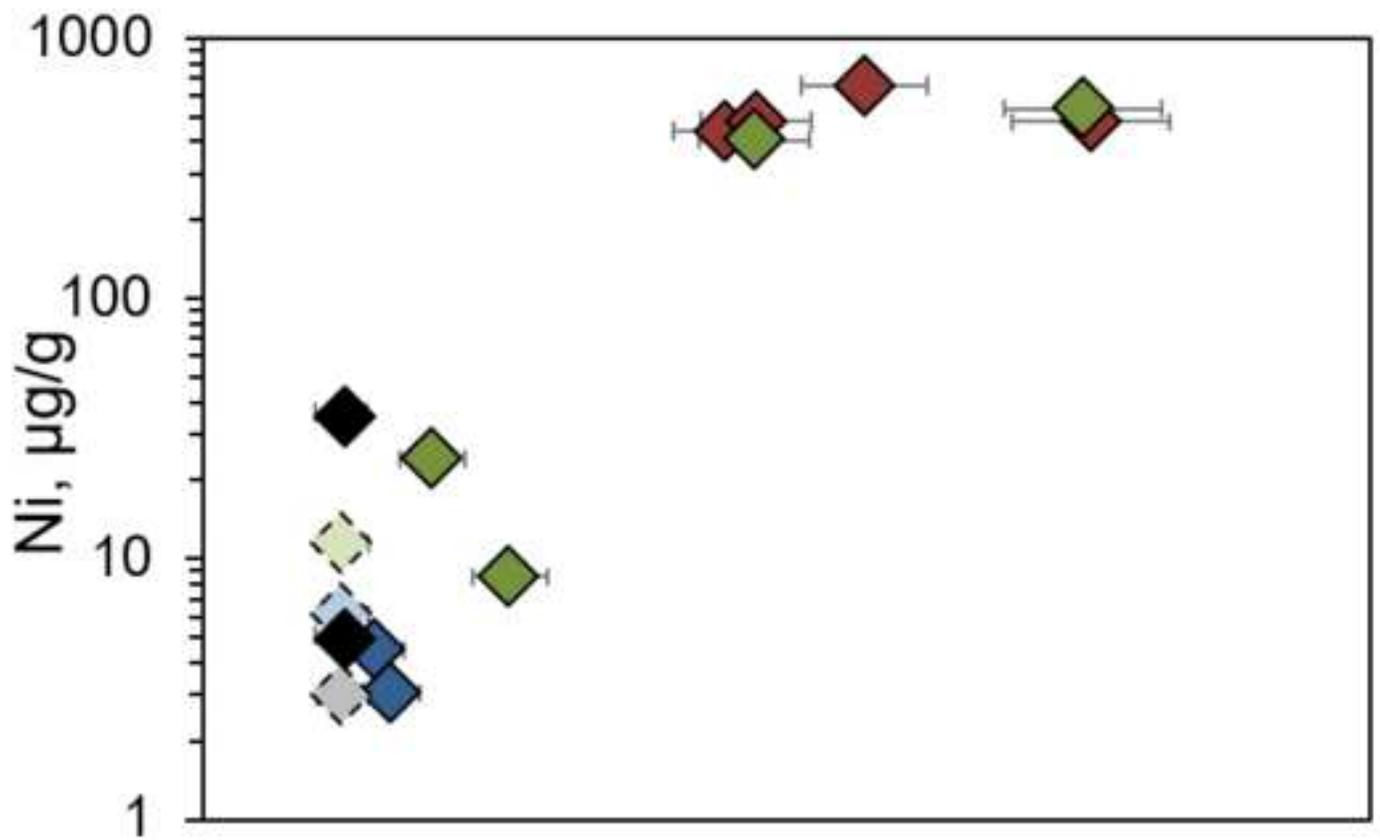


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Supplementary Table

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Appendix

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