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Jean-Pierre Lorand, R.H. Hewins, M. Humayun, L. Remusat, B. Zanda, et al.. Chalcophile-siderophile element systematics of hydrothermal pyrite from martian regolith breccia NWA 7533. *Geochimica et Cosmochimica Acta*, 2018, 241, pp.134-149. 10.1016/j.gca.2018.08.041 . hal-02182381

HAL Id: hal-02182381

<https://hal.science/hal-02182381>

Submitted on 12 Jul 2019

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Chalcophile-siderophile element systematics of hydrothermal pyrite from martian regolith breccia NWA 7533

Jean-Pierre Lorand¹, Hewins R.H.^{2,3}, Humayun M.⁴, Remusat L.², Zanda B.², La C.¹, Pont S.²

1 Laboratoire de Planétologie et Géodynamique à Nantes, CNRS UMR 6112, Université de Nantes, 2 Rue de la Houssinière, BP 92208, 44322 Nantes Cédex 3, France.

2 Institut de Minéralogie, de Physique des Matériaux, et de Cosmochimie (IMPMC) - Sorbonne Université- Muséum National d'Histoire Naturelle, UPMC Université Paris 06, UMR CNRS 7590, IRD UMR 206, 61 rue Buffon, 75005 Paris, France.

3 Department of Earth & Planetary Sciences, Rutgers University, Piscataway, NJ 08854, USA.

4 Department of Earth, Ocean & Atmospheric Science and National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, USA.

Corresponding author Jean-Pierre Lorand *Email address:* jean-pierre.lorand@univ-nantes.fr.
Phone number 33 2 51 12 54 63 ; *Fax number:* 33 2 51 12 52 68.

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56 Abstract: Unlike other martian meteorites studied so far, Martian regolith breccia NWA 7533 and
57 paired meteorites that have sampled 4.4 Ga-old impact lithologies show only sulfides of
58 hydrothermal origin (mostly pyrite (<1 vol.%) and scarce pyrrhotite). NWA 7533 pyrite has been
59 analyzed for 25 chalcophile-siderophile trace elements with laser ablation-inductively coupled
60 plasma mass spectrometer (LA-ICPMS). Micronuggets of highly siderophile elements-HSE (Os, Ir,
61 Pt, Ru, Rh) along with occasional detection of Mo and Re were observed in half of the 52 analyzed
62 crystals as random concentration spikes in time-resolved LA-ICPMS data. These nuggets are
63 interpreted as variably altered remnants from repeated meteorite bombardment of the early martian
64 crust, as are chondritic Ni/Co ratios of pyrite (10-20). Pyrite displays superchondritic S/Se (54,000
65 to 3,300) and Te/Se (0.3 - >1). The reasonably good positive correlation ($R^2=0.72$) between Se and
66 Ni reflects a temperature control on the solubility of both elements. Apart from the chalcogens S, Se
67 and Te, pyrite appears to be a minor contributor (<20%) to the whole-rock budget for both HSE
68 (including Ni and Co) and chalcophile metals Ag, As, Au, Cu, Hg, Pb, Sb, Tl and Zn. This deficit
69 can result from i) high (>400°C) temperature crystallization for NWA 7533 pyrite, as deduced from
70 its Se and Ni contents, ii) magmatic sulfide-depletion of brecciated early martian crust, iii)
71 precipitation from near neutral H₂S-HS-H₂O-rich hydrothermal fluids that did not provide halogen
72 ligands for extensive transport of chalcophile-siderophile metals. It is suggested that the 1.4 Ga
73 lithification event that precipitated hydrothermal pyrite left the chalcophile-siderophile element
74 budget of the early martian crust nearly unmodified, except for S, Se and Te.

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1. INTRODUCTION

78 Chalcophile and siderophile metals comprise nearly 30 different elements that in theory
79 prefer sulfide or iron metal structures, respectively. Most elements that are siderophile are usually
80 also somewhat chalcophile and vice versa so that they are conveniently grouped as chalcophile-
81 siderophile elements. (e.g. Arculus and Delano, 1981). Because they are concentrated in metallic
82 and sulfide minerals that are highly sensitive to differentiation processes, these elements provide
83 insight into a wide range of planetary-scale properties such as composition of planetary building
84 blocks, the physical conditions of core-mantle segregation, (Day et al., 2016, and references
85 therein), impactor signatures in impact craters (e.g. Dressler and Reimold, 2001; Koeberl et al.,
86 2012, and references therein) as well as exogenous components in brecciated meteorites (e.g.
87 Goderis et al., 2012). However, primordial patterns can be modified by secondary processes (e.g.,
88 hydrothermal alteration, metamorphic overprint) because chalcophile-siderophile elements show
89 highly variable mobility in hydrothermal fluids (Barnes, 1979, 2015 and references therein;
90 Kaasalainen et al., 2015).

91 Siderophile element contents (Ir, Ni) were used to identify Martian regolith breccia NWA
92 7533 and paired samples (e.g. NWA 7034; NWA 7475) as impact breccia rather than volcanic
93 breccia (Humayun et al., 2013). Their siderophile element contents require the equivalent of 3 wt%
94 of CI chondrite impactors admixed into Pre-Noachian lithologies (4.4 Ga) (Wittmann et al., 2015;
95 Goderis et al., 2016). Subsequently near-neutral, H₂S-HS-rich fluids precipitated accessory pyrite
96 (<1 vol.%) and scarce pyrrhotite at minimum log fO₂ > FMQ (fayalite-magnetite-quartz) + 2 log
97 units and maximum T of 500°C (Lorand et al., 2015). Hence, these meteorites provide an
98 opportunity for examining how the chalcophile-siderophile element budget of the early martian
99 crust was processed by hydrothermal fluids.

100 Pyrite is by far the most abundant hydrothermal sulfide now reported from the three most
101 studied stones of the martian impact breccia (NWA 7034, Muttik et al., 2014; NWA 7475, Wittmann
102 et al., 2015; and NWA 7533, Lorand et al., 2015). Any inference on impactor debris and
103 compositional features of the hydrothermal fluids must be constrained at first by estimating the part
104 played by pyrite in the bulk-rock chalcophile-siderophile element budget. A scanning electron
105 microscope (SEM) study of several hundreds of NWA 7533 pyrite crystals identified two
106 micronuggets of highly siderophile elements (HSE, Os-Ir) that could be impactor debris (Lorand et
107 al., 2015). About one-third of the 350 EDX (energy dispersive X-ray emission) and electron
108 microprobe analyses (EMPA) analyses performed on pyrite detected Ni (up to 4.5 wt.%) and some
109 Co (up to 1800 ppm) with a few analyses displaying a loosely constant Ni/Co around 10,
110 reminiscent of meteoritic metal compositions (Lorand et al., 2015). Copper, Zn and As were found
111 by these authors to occur at concentration levels below detection limits of trace element analyses by
112 EMPA (<77, <91 ppm and <117 ppm, respectively) and Se (>64 ppm) was detected only in the most
113 Ni-rich grains in the same study.

114 The present paper reports a more comprehensive data set for 25 chalcophile-siderophile
115 trace elements analyzed with LA-ICPMS in NWA 7533 pyrite. LA-ICPMS analyses provide much
116 better reproducibility for trace elements (Cu, Zn, As, Se) and sensitivity compared to EMPA. To
117 date, LA-ICPMS analyses of martian sulfides were reported only for magmatic sulfides from young
118 (< 1 Ga) basaltic rocks (shergottites) by Baumgartner et al (2017). Our results for NWA 7533 pyrite
119 is therefore the only trace element concentration data that are available for martian sulfides of
120 indisputable hydrothermal origin. Although pyrite is not uncommon in some martian meteorites
121 (Lorand et al., 2018 and references therein), it was always reported as grains occurring as complex
122 intergrowth with pyrrhotite too small-sized to be suitable for LA-ICPMS analyses.

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2. MAIN PETROGRAPHIC FEATURES OF NWA 7533

2.1. Lithology

127 The NWA 7533 regolith breccia has been studied in detail by Hewins et al (2013, 2014a),
128 Humayun et al., (2013, 2016), Nemchin et al (2014), Beck et al (2015), Belluci et al (2015) and
129 Leroux et al (2016); a comprehensive review was given by Hewins et al. (2017). This meteorite
130 consists of a fine-grained inter-clast matrix (acronym ICM) containing lithic clasts of microbasalt,
131 norite, monzonite and single minerals derived from these rocks and probably orthopyroxenite, as
132 well as clast-laden impact melt rocks (CLIMR) and impact melt spherules.

133 Noritic clasts consist of ferroan pyroxene ($En_{<72}$), orthopyroxene or inverted pigeonite,
134 plagioclase (An_{50-30}) and Cr-rich magnetite. Monzonitic clasts show alkali feldspar, often perthitic,
135 associated with plagioclase ($An_{<30}$), ferroan pyroxene, chlorapatite and magnetite+ilmenite+
136 accessory rutile. Zircon and baddeleyite are found in these highly fractionated rock clasts, and also
137 as individual mineral clasts. Zircon in monzonitic clasts gave a Pre-Noachian, U-Pb crystallization
138 age of $4,423 \pm 26$ Myr (1 sigma level; Humayun et al., 2013). Crystal clasts are fragments of
139 disaggregated lithic clasts. The most magnesian orthopyroxene (En_{80-73}) is never attached to
140 plagioclase, though associated with chrome spinel and rarely augite. It most probably derives from
141 orthopyroxenites, perhaps pristine crustal rocks of the early Martian crust as suggested by its very
142 low (<50 ppm) Ni concentrations (Hewins et al., 2014a). By contrast, noritic and monzonitic clasts
143 contain high levels of siderophile elements (up to 1,000 ppm Ni, $1 < Ir < 10$ ppb) that indicate
144 impactor-derived contamination (Humayun et al., 2013). The pervasive siderophile enrichment even
145 in the melt rocks suggests a thick sequence of impact-generated rocks including mature regolith.
146 Pyroxenes are either deep-seated clasts containing exsolution, or zoned pyroxenes of near surface
147 origin.

148 Clast-laden melt rocks (CLMR) are dominated by plagioclase laths and subophitic pyroxene.
149 Fine-grained basalt clasts (Hewins et al., 2013) with subophitic to granoblastic textures, grain size
150 $\sim 20-100 \mu m$, are composed of orthopyroxene (En_{73-63}) or pigeonite (En_{63-49}) augite (En_{46-29}),
151 plagioclase (An_{66-30}) and Fe-rich spinel. Their bulk compositions are close to those of the clast-
152 laden ~~impact~~ melt rocks, including even higher contents of Ir (up to 100 ppb) (Humayun et al.,
153 2013). They are interpreted as impact melt that crystallized less rapidly than CLMR, which were
154 quenched more rapidly due to incorporation of abundant clasts. Regarding lithophile trace element
155 geochemistry, the spherules, the groundmass of the melt rock and the microbasalts resemble melted
156 wind blown dust and regolith debris (Humayun et al., 2013). The chemical composition of the fine-
157 grained material in both the clasts and in the interclast matrix is very similar and was modeled as
158 derived from crystallization products from a low-degree partial melt (<5%) of a chondritic garnet
159 peridotite source (Humayun et al., 2013). The dense nanocrystalline matrix looks like annealed
160 wind-blown dust with a granoblastic texture (Hewins et al., 2013; Muttik et al., 2014; Leroux et al.,
161 2016). It consists of anhedral micrometer-sized plagioclase with sub-micrometer sized pyroxene

162 surrounding and embedded in it, plus fine-grained Fe-(Ti) oxides - magnetite, often symplectitic or
163 lacy, and maghemite. The annealing and lithification process is related to a probable major
164 reheating at 1.35–1.4 Ga which was recorded by several isotopic systems (see more details in
165 McCubbin et al. (2016) and Hewins et al., 2017; Cassata et al., 2018). Some zircon grains show
166 discordant ages corresponding to annealing at ~1.7–1.4 Ga (Humayun et al. 2013). The alkali-
167 feldspars in leucocratic clasts record a very short-lived resetting event or mixing between feldspars
168 and the whole rock at 1.4 Ga, and Pb-Pb age resetting at 1.36-1.45 Ga was documented in
169 phosphates from all matrix domains of NWA 7034 and NWA 7533 (Bellucci et al., 2015).
170 Disturbance giving ages at around 1.4-1.5 Ga was recently identified in the Re-Os of bulk sample
171 fractions of NWA 7034 (Goderis et al., 2016).

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173 2.2. Pyrite

174 Pyrite (<1.0 vol.%) occurs as cubes, truncated cubes and octahedra (average grain size 30-40
175 μm) in each lithology of the meteorite, from the Pre-Noachian lithic clasts to late veins postdating
176 the 1.4 Ga-old annealing and lithification event of the fine-grained matrix (Lorand et al., 2015).
177 Cubic crystals were observed mostly inside open cracks, low-Ca pyroxene clots and ICM. These
178 crystals are inferred to have crystallized after the final assembly of the breccia at $T < 400\text{-}500^\circ\text{C}$
179 from its maximum Ni content (up to 4.5 wt.%; EMPA and SEM EDS/EDX data). The few highly
180 resorbed pyrrhotite relicts coexisting with the pyrite indicate near neutral H_2S -HS-rich
181 hydrothermal fluids ($6 < \text{pH} < 10$), at minimum $\log f\text{O}_2$ of $> \text{FMQ} + 2 \log$ units (Lorand et al., 2015;
182 Wittmann et al., 2015). Several pyrite-producing sulfidation reactions took place, involving either
183 magnetite/maghemite, the low-Ca pyroxene, or direct precipitation of dissolved divalent iron. Many
184 pyrite grains have trapped the fine dust of iron oxides (micron-sized Fe-(Ti) oxides identified as
185 magnetite-maghemite; Agee et al., 2013) that are so abundant in NWA 7533 (Hewins et al. 2017).

186 All pyrite grains show fracture networks which result from the weak shock event that
187 liberated the meteorite from the Martian subsurface crust. These fractures acted as preferential
188 pathways for partial replacement of pyrite by iron oxyhydroxides of terrestrial origin, as suggested
189 by their D/H values and their distribution defining an alteration gradient through
190 the meteorite (Lorand et al., 2015). The net effect of this alteration was to remove most of the S
191 originally present as pyrite. The sharp difference between the bulk-rock S analysis (820 ppm;
192 Humayun et al., 2013) and the theoretical S content that can be deduced from pyrite modal
193 abundances (up to 5,400 ppm) indicates that terrestrial alteration may have leached up to 80% of the
194 initial S budget. Meteorites that experienced such hot desert alteration generally display similar S
195 losses (e.g., Dreibus et al. 1995).

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3. ANALYTICAL METHODS.

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Three polished sections were studied (NWA 7533-5 and NWA 7533-7 at Université de Nantes and NWA 7533-3 at Florida State University). NWA 7533-5 contains the least altered pyrites (15 of the 23 crystals analyzed are less than 50% altered; see Fig. 1 in Lorand et al., 2015). Their major (Fe, Ni, S) and minor element (Co, Zn, Cu, As, Se) compositions (Camparis SXFive Cameca EMP) were documented in Lorand et al (2015). NWA 7533-7 is a new thick section made for the purpose of this study. Its pyrite modal abundance (1 vol.%; determined by point counting on 9000 points at 50 micron steps) fits well the range published for the other sections. NWA 7533-7 pyrites were studied with a Tescan VEGA II LSU Scanning Electron Microscope (SEM) operating in conventional (high-vacuum) mode, and equipped with an SD3 (Bruker) EDS detector (Muséum National d'Histoire Naturelle Paris, France, MNHN). Major element concentrations (Fe, Ni, Co, S) were determined at 15 kV accelerating voltage with a PhiRoZ EDS standardless procedure. Lorand et al. (2015) provided comparison between SEM-EDX and EMP analyses of NWA 7533 pyrites, demonstrating that such a procedure can produce reliable data for major element compositions of pyrite.

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Chalcophile-siderophile trace element concentrations were obtained in-situ using an LA-ICP-MS at the «Laboratoire de Planétologie et Géodynamique à Nantes». The samples were ablated and elements collected using a Photon Machine Analyte G2 equipped with an excimer laser (193 nm laser wavelength) and a dual volume sample cell that keeps the sample volume small and constant. Most analyses were performed with a repetition rate of 10 Hz in spot mode using a laser output energy of 90 mJ with a 50% attenuator and 20x demagnification, resulting in low fluences on the sample ($<4 \text{ J/m}^2$), to minimize pyrite melting and attendant trace-element fractionation (e.g. Wohlgemuth-Ueberwasser et al., 2007). The ablated sample material was transported in a mixture of H-He-Ar through a cross-flow nebulizer to a Varian 880 quadrupole ICP-MS. Given the small fine grain size and scarcity of sulfide grains suitable in size for LA-ICP-MS analysis, spot sizes for standards and samples were set to 25 μm for small grains, and one to three spots per grain were analyzed, depending on grain size. Only the largest crystals ($>30 \text{ microns}$; preserving unaltered core zones) were suitable for laser ablation analyses of pure pyrite. Smaller spot sizes (down to 10 μm) were used on particularly fine-grained pyrite isolated within Fe oxyhydroxides or Fe (Ti) oxides. These mixed (pyrite + Fe (Ti) oxide or pyrite + Fe oxyhydroxides) grains analyzed are hereafter referred to as mixes. A total of 84 spot analyses were conducted on 52 pyrite grains (Table S1).

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The following isotopes were collected ^{29}Si , ^{34}S , ^{51}V , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{61}Ni , ^{63}Cu , ^{65}Cu , ^{66}Zn , ^{75}As , ^{77}Se , ^{95}Mo , ^{99}Ru , ^{102}Ru , ^{103}Rh , ^{105}Pd , ^{106}Pd , ^{107}Ag , ^{108}Pd , ^{118}Sn , ^{120}Sn , ^{121}Sb , ^{125}Te , ^{126}Te , ^{189}Os , ^{190}Os , ^{191}Ir , ^{193}Ir , ^{194}Pt , ^{195}Pt , ^{197}Au , ^{202}Hg , ^{205}Tl , ^{207}Pb , ^{208}Pb and ^{209}Bi). Possible contamination from matrix silicates or Fe oxides or

232 oxyhydroxides were detected by monitoring signals for Si and Fe. Isotopes of each element to be
233 analyzed, length of analysis (for spots) and dwell time were set to minimize potential interferences
234 and maximize counting statistics – with overall mass sweep time kept to ~1 s. Major elements (S,
235 Fe) were counted in the low-count rate mode to avoid saturation of detectors. Synthetic sulfides
236 (i.e., NiS₂ and CuFeS₂) devoid of PGE (< ppb concentration levels) were analyzed for evaluating
237 mass interference corrections between Ni- as well as Cu-argides (⁶²Ni⁴⁰Ar, ⁶³Cu⁴⁰Ar and
238 ⁶⁵Cu⁴⁰Ar) and the isotopes ¹⁰²Ru, ¹⁰³Rh and ¹⁰⁵Pd used for the element quantifications. No
239 significant interference was observed. There is no correlation between Rh and Cu concentrations
240 that are very low (< 104 ppm) in NWA 7533 pyrite (Table S1). The interference of ⁵⁹Co⁴⁰Ar on
241 ⁹⁹Ru was also negligible.

242 Data were acquired in four 8-hours separate analytical sessions over an interval of one year.
243 In each analysis, the gas blank (laser off) was collected for 30/40 s prior and after laser ablation.
244 Each ablation run was analyzed in detail in time-integrated count diagrams to retrieve any metal-
245 rich microparticles not residing inside the pyrite. In practice, due to the small area of unaltered
246 pyrite available, a few tens of seconds were available for extracting elemental concentrations of
247 pyrite before contamination from Fe oxides/hydroxides or surrounding silicates increased Si, Ga, Fe
248 and V concentrations. Data reduction was done using Glitter™ software (Griffin et al., 2008).
249 External calibration was performed with synthetic standards MASS-1 (pressed Zn sulfide powder;
250 Wilson et al., 2002), NIST-610 and an in-house synthetic PGE-doped NiS (SARM-7 10) which is a
251 7.5 g fused nickel sulfide doped with 15 g of South African rock standard SARM-7 (Lorand et al.,
252 2010). Both standards were compared with published values to confirm homogeneity of standards
253 with respect to elements of interest and proved to be well within error. Each standard was analyzed
254 twice every ten analyses to bracket sample measurements at the beginning and at the end of a single
255 ablation run to reduce the effects of possible standard heterogeneity. Analyses of pyrite were
256 quantified with S as internal standard, using S concentration measured by EMPA (Lorand et al.,
257 2015). Analyses of mixes starting in pyrite and ending in Fe oxyhydroxides were quantified with S
258 and Fe as internal standard assuming that EMPA data of pure phases apply (Lorand et al., 2015;
259 Hewins et al., 2017) and linear mixing between pyrite and Fe-oxyhydroxides, the pyrite/Fe
260 oxyhydroxide ratio being calculated from Fe/S count rates in time-integrated count diagrams. Of
261 course, these metal concentration data are to be considered as semi-quantitative although they
262 should not alter correlations in binary plots between metals. The detection limits in each
263 quantification were calculated for each analysis from the gas blank and the sensitivity of the
264 reference materials following the equations in Longerich et al. (1996).

265 The full results of LA-ICP-MS analyses including standard deviation and limit of detection
266 for each analysis are listed in Table S1; correlation coefficients for element pairs are given in Table

267 S2. The accuracy of analyses of external standards measured as unknowns (SARM-7 10 and
268 MASS-1) was good for Os, Ir, Pt, Pd and Au (<10% relative difference to certified/theoretical
269 values) (supplementary Tables S3 and S4). Analytical reproducibility was monitored by the repeated
270 analysis of the sulfide standard MASS-1 yielding 5% relative standard deviation (RSD) for all
271 elements (supplementary Table S4). In addition to pyrite, four crystals totally replaced by Fe
272 oxyhydroxides and one grain of Fe-Ti oxide were analyzed with MASS-1 and NIST 610 as external
273 standard and Fe as internal standards (EMPA data: Lorand et al 2015; Hewins et al., 2017).

274 In addition to spot analyses of pyrite, chalcophile-siderophile trace elements were also
275 analyzed on the matrix of NWA 7533-3 using an Electro Scientific Industries New Wave™
276 UP193FX excimer laser ablation system coupled to a Thermo Element XR™ magnetic sector ICP-
277 MS at Florida State University (Humayun et al., 2013). Pyrite (or mixed pyrite-matrix) composition
278 was investigated by running a 2,000 µm line scan along the length of a CLMR clast (Clast XIV)
279 with a 20 µm spot size, at 5 µm/s, with 50 Hz repetition rate and examining the data in time-
280 resolved mode. The mass spectrum was swept repeatedly for the intensities of 60 elements (Yang et
281 al., 2015). Detection limits were estimated conservatively using the 3-sigma variation of 12 blanks
282 taken before and after the analysis, and standardization followed Yang et al. (2015).

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4. RESULTS

285

286 Results for the transect through the CLMR clast (XIV) are shown in Fig. 1. The line scan
287 intersected 2 larger pyrite grains and about 5 smaller ones. The abundances of Se and Te roughly
288 correlate in the pyrites (as do Pb, Co and Ni). However, the correlation with S is weak because each
289 ablated pyrite experienced a different degree of terrestrial oxidation and S loss (Lorand et al., 2015),
290 in addition to being variably enriched in Se and Te (see below). Distance-integrated count diagrams
291 produced transient concentration spikes for several HSE. Such transient spikes are usually
292 interpreted as reflecting occurrence of HSE-rich micronuggets in the ablated area (Lorand et al.,
293 2008; 2010; Lorand and Luguet, 2016; O'Driscoll et al., 2016). These are Ru-, Pt- or Os-rich
294 micronuggets, not necessarily located inside the pyrite, as shown by the decoupling between S, Se
295 or Te peaks and HSE spikes: the largest micronugget (a Ru+Ir grain with subchondritic levels of Rh,
296 Os and Pt) was probably pasted (i.e. not fully enclosed) on a pyrite crystal because the
297 corresponding HSE concentration peaks are clearly offset from the S peak in Fig. 1.

298 Spot analyses of pyrite and mixes produced a wide range of trace element concentrations for
299 chalcophile-siderophile elements, from sub-ppm levels to hundreds of ppm, except Ni and Co, that
300 reach major and minor element concentrations respectively, as expected from previous EMP and
301 SEM-EDX analyses. For convenience, the results will be discussed by sorting the analyzed

302 elements from the highly siderophile, most refractory elements (HSE) to the most volatile
303 chalcophiles.

304

305 **4.1 Highly siderophile elements.**

306 As observed in the transect through clast XIV, time-integrated count diagrams of pyrite
307 analyses produced transient concentration spikes for each of the six platinum-group element (PGE
308 = Os, Ir, Ru, Rh, Pt and Pd) in about half of the analysed pyrite (Fig. 2). Previous SEM detections in
309 NWA 7533 pyrite supports this widespread occurrence of HSE micronuggets (Lorand et al., 2015).
310 Up to 3 micronuggets were detected in a single analysis, displaying various combinations between
311 Os, Ir, Ru, Pt and Rh (Fig. 2). Rhenium was detected in one nugget that combines Os-Ir-Re-Mo-Pt-
312 Rh (Fig. 2). The size of each nugget (estimated with Longerich et al. (1996) formulas relating the
313 average volume ablated by time unit to the analytical conditions) is estimated to range between one
314 micrometer or less, to 4-5 μm for the largest one (assuming spherical micronuggets). Palladium is
315 not associated with refractory PGEs, being found to occur alone or occasionally with Au peaks (four
316 micronuggets). However, such Pd spikes could be analytical artifact because they show very low (<
317 10) peak/background ratio.

318 Calculated HSE concentrations range between 0.01 and 0.6 ppm, apart from Ru that shows
319 on average higher mean values (up to 4 ppm; Table S1). Although half of their concentrations were
320 below detection limits, Os, Ir and Pt produce positive correlations in binary plots ($R^2 = 0.62$ for Os
321 vs. Ir, 0.70 for Pt vs. Ir and 0.56 for Pt vs. Os respectively; Table S2) (Fig. 3A), if pure pyrite
322 analyses are taken into account. Platinum/iridium and Pt/Os ratios are close to chondritic, without a
323 clear match to any specific chondrite class. All of the analyzed pyrites are Mo-enriched relative to
324 chondritic ratios although some analyses define a positive correlation between Mo and Pt ($R^2 =$
325 0.74; Table S2) (Fig. 3B). The Re vs Os plot (not shown) shows virtually no correlation and a wide
326 range of Re/Os ratios (from Re/Os = 0 to Re/Os > 10). Rhenium correlates neither with Mo nor with
327 any other element in the pyrites, except Pt ($R^2 = 0.51$, pyrite analyses only). It is worth noting that
328 these correlations are strongly biased by a few HSE-rich outliers likely corresponding to HSE-rich
329 micronuggets integrated in the quantification (e.g. 7533-5-20; 7533-7-9).

330 As suggested by the decoupling between Pd-dominated and Pt-dominated HSE
331 micronuggets, there is virtually no correlation between Pd and Pt ($R^2 = 0.13$), nor between Pd and
332 Ru or Rh. Likewise, the correlation between Ru and Ir is poor ($R^2 = 0.26$) (Table S2).

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334 **4.2 Moderately siderophiles Ni, Co, Ag, Au, Cu**

335 LA-ICP-MS data strongly support previous EMPA and SEM-EDX analyses of Lorand et al.
336 (2015) in showing that NWA 7533 pyrite are Ni- and Co-enriched ($156 < \text{Ni} < 23,417$ ppm Ni;

337 57.8<Co<568 ppm). A few EMP analyses defined a loosely constant Ni/Co around 10, reminiscent
338 of meteoritic metal compositions: the new LA-ICP-MS analyses produce a more robust correlation
339 between Ni and Co ($R^2 = 0.72$; Table S2); their Ni/Co ratios (10 to 20) are close to those of
340 chondritic nickel-iron alloys (Fig. 4). This correlation is not significantly degraded if mixes (pyrite
341 + Fe oxyhydroxides) are taken into account. Few analyses show Ni/Co >20, reflecting Ni-
342 enrichment. As shown in Lorand et al (2015), the high-Ni pyrite occurs as irregularly shaped,
343 discontinuous areas that are randomly distributed inside a single pyrite crystal. Such areas may not
344 be adequately sampled by the laser beam during LA-ICPMS analyses.

345 Gold does not show any specific correlation with Ag and Cu, or with the other elements
346 analyzed in NWA 7533 pyrite, apart perhaps with Pd ($R^2 = 0.56$), in agreement with the few Au-Pd
347 micronuggets detected in time-integrated LA-ICPMS diagrams. Silver concentrations (0.01-1 ppm)
348 are similar to Au concentrations (0.01-0.7 ppm); however Ag/Au ratios (0.4-25) are higher than
349 chondritic (0.5-1.25; Wasson and Kallemeyn, 1988; Tagle and Berlin, 2008; Fisher-Gödde et al.
350 2010).

351 LA-ICPMS Cu data (12.7-104 ppm) are consistent with previous EMP analyses that did not
352 detect Cu (<91 ppm). Copper does not correlate with Ni, Co, or Zn (Table S2). Copper is severely
353 depleted with respect to Ag ($0.0015 < \text{Ag/Cu} < 0.05$) when compared with chondrite compositions
354 ($0.0015 < \text{Ag/Cu} < 0.0007$; Wasson and Kallemeyn, 1988; Tagle and Berlin, 2008; Fisher-Gödde et al.
355 2010).

356

357 **4.3 Volatile chalcogen and semi-metals Se, Te, As, Sb, Bi**

358

359 Selenium concentrations range between 8.8 and 149 ppm, and those of Te between 4.4 and
360 104 ppm, respectively, excluding a few Te-rich outliers (up to 262 ppm, Table S1). As suggested by
361 EMP analyses on 7533-5 pyrites (Lorand et al., 2015), Se and Ni correlate positively ($R^2 = 0.71$) as
362 do Co and Se ($R^2 = 0.60$), regardless of whether the grains analyzed were pure pyrite or mixes.
363 However, the curve in Fig. 5 extends down to much lower Se concentrations compared to EMPA
364 because LA- ICPMS analyses have much better limits of detection (down to 10 ppm vs. 64 ppm).
365 Taken as a whole, Se/Ni ratios are superchondritic (>0.06 vs 0.01) as are S/Se ratios (3,300-54,000
366 vs. 2,560+/-200; Dreibus et al., 1995; Palme and O'Neill, 2014).

367 Tellurium also positively correlates with Se while being strongly enriched with respect to
368 chondritic Se/Te ratios. However, the correlation in Fig. 5B is much weaker ($R^2 = 0.16$; Table S2)
369 because several Te-enriched outliers corresponding to both analyses of pyrite and mixes have
370 extreme Te/Se ratios (4 to 10). Three outliers (all corresponding to mix analyses) also stand out by
371 coupled concentration ranges (e.g. 7533.5-24; 7533.7-20; Fig. 6; Table S1). Such Te-Bi-Pb-rich

372 areas may correspond to telluride microinclusions although corresponding concentration spikes are
373 lacking in the time-resolved LA-ICP-MS spectra of these grains.

374 Arsenic concentrations (2.5-32.3 ppm) are well below the limit of detection (117 ppm) of
375 previous EMP analyses reported by Lorand et al. (2015). Antimony is even more depleted (0.02-
376 0.30 ppm) as is Bi (0.11-1.8 ppm). Correlations between Se and As or Sb vs. As are lacking (Table
377 S2). Some mixes that incorporated major amounts of Fe oxyhydroxides (7533-7-36 to 7533-7-40)
378 are enriched in As and Sb by a factor 2 to 5 compared to pyrite (5.7-30 ppm; Table S1).

379

380 **4.4 Volatile chalcophiles Pb, Hg, In, Tl**

381 Lead (2-70.0 ppm) positively correlates with Te ($R^2 = 0.66$) and Bi ($R^2 = 0.62$; Fig. 6).
382 These correlations are significantly poorer if the mixes are taken into account owing to their larger
383 range of Bi and Pb concentrations. No noticeable covariation trend between Tl (0.02-0.65 ppm), Hg
384 (0.003-0.6 ppm) and In (0.008-0.13 ppm) or between one of these elements and the other elements
385 analyzed here can be detected (Table 2).

386

387 **4.5 Moderately chalcophiles Sn, Zn, Ga, V**

388 These four elements that also have lithophile properties (e.g. Palme and O'Neill, 2004)
389 produce a series of rather good positive correlations between Ga and V ($R^2 = 0.8$), Sn and V ($R^2 =$
390 0.63), Ga and Sn ($R^2 = 0.59$) and Ga and Zn ($R^2 = 0.58$; Table S2). The V- and Ga-rich end-member
391 in the V vs. Ga plot of Fig. 7A is the only Fe-Ti oxide so far analyzed (40 ppm Ga, 460-500 ppm Zn
392 and 300 ppm V). Thus, the trend in Fig. 7A is probably a mixing trend between pyrite and iron-
393 titanium oxides resulting from beam overlap. The regression line in Fig. 7A intercepts the x- and -y
394 axes at very low V (<50 ppm) and Ga contents (<2 ppm) that may represent the actual amount
395 inside pyrite. Zinc also positively correlates with V; however most of the pyrite analyses show
396 variable Zn contents (10-140 ppm) for a narrow V concentration range (Fig. 7B).

397

398

399

5. DISCUSSION

400 **5.1 Mass balance calculation of the contribution of pyrite.**

401 Because no data base is available for martian pyrite, any comparison must be made with
402 terrestrial samples. Compared to terrestrial pyrites of hydrothermal origin, NWA 7533 pyrites are
403 enriched in Ni and Co, and on average depleted in all of the chalcophile-siderophiles including
404 gold, silver, copper and semi-metals except selenium and tellurium as well as all fluid-mobile
405 volatile elements (Hg, Tl, In; Fig. 8). This conclusion also pertains to HSE, especially Ru, Ir and Os
406 that are the most soluble HSE in pyrite (up to 470 ppm Ru and 390 ppm Ir; e.g. Dare et al., 2011;
407 Lorand et al., 2011; Pina et al., 2015; not shown in Fig. 8).

408 Pyrite is by far the most abundant hydrothermal sulfide and no other major S-bearing
409 mineral has been identified in the NWA 7533/7034/7455 paired meteorites. Before discussing the
410 origin of its chalcophile-siderophile element budget, it is interesting to estimate the contribution of
411 pyrite to the whole-rock budget first. Details of the mass balance calculation, which combines the
412 bulk analyses of NWA 7533 lithological units, the pyrite modal abundances and the in-situ analyses
413 of unaltered pyrite grains only, are given in supplementary Table S5. Fig. 9 shows that pyrite is a
414 minor contributor for all elements but the chalcogens Se and Te (50-70%) in addition to S. The
415 contribution of some elements (Mo, Ru, Ni, Au, As and Ag) may be underestimated, owing to their
416 large concentration range. It is worth noting that all of these elements are known to enter the pyrite
417 crystal lattice, Se (and Te) by replacing S^{2-} in the anionic sublattice of pyrite, divalent Co and Ni
418 (like Os^{2+} and Ru^{2+} that have ionic radii quite similar to those of Fe^{2+}) replacing Fe by
419 stoichiometric substitution (e.g. Vaughan and Craig, 1997; Abraitis et al., 2004; Lorand and Alard,
420 2011; Pina et al., 2013). Gold has been found to enter pyrite by coupled substitution with As (Reich
421 et al., 2005; Deditius et al., 2014). Pyrite accounts for <10% of the bulk-rock budget of all other
422 analyzed elements, especially the weakly chalcophiles (Zn, Sn, V, Ga) and the volatile chalcophiles
423 (Hg, In, Cd, Tl).

424 Of course, the whole-rock budget of HSE is assumed to be balanced by HSE-rich
425 micronuggets that occur outside pyrite (e.g. Fig. 1). Major hosts for Ni and Co are mafic silicates
426 (low-Ca and high-Ca pyroxenes which represent more than 43 % by volume of the impact breccia
427 (Agee et al., 2013), chromite, Fe-(Ti) oxides, (up to 0.3-0.4 wt% NiO in Ti- and Cr- magnetite;
428 Hewins et al., 2014a; 2017) (see also Table S1). Regarding Cu, Zn, Pb, no discrete (sulfide?)
429 minerals were discovered, despite careful SEM investigations on eight polished thin sections. Lead
430 has been suggested to be partitioned between apatite, feldspar, zircon and other minor minerals
431 (Humayun et al., 2013; Belluci et al., 2015). The most significant contributors for Pb, Zn, V, Ga, In,
432 and Sn are Fe-Ti oxides in addition to chromite (Zn, V), low-Ca and high-Ca pyroxenes and apatite
433 (V). Our LA-ICP-MS analysis (Table S1) coupled with the modal proportions of Fe-Ti oxides
434 reported by Agee et al. (2013) for NWA 7034 (9.7 \pm 2.6 wt.%) indicate that Fe-Ti oxides can
435 balance half of the whole-rock budget of NWA 7533 for V, Zn, and Ga. Magnetite can also
436 accommodate Ru, Rh and Ir in its 'divalent' octahedral sites (Capobianco and Drake, 1994; Pagé et
437 al., 2012; Brennan et al., 2016). The only analysis of Fe-Ti oxide available is Rh-enriched compared
438 to pure pyrite (>0.1 ppm) as are several analyses of mixes that may have incorporated Fe-Ti oxides
439 (Table S1).

440 The four Fe-oxyhydroxide crystals analyzed are strongly depleted in S compared to pure
441 pyrite (3,900-5,000 vs. 54,000 ppm; Table S1); their S/Se ratios (137-1,193) are one order of
442 magnitude lower than those of unaltered pyrite (3,350-54,000) thus supporting the huge S loss that

443 occurred during terrestrial weathering. By contrast, the four analyzed crystals do not show
444 indisputable evidence of enrichment/depletion trends in their chalcophile/siderophile element
445 systematics compared to pyrite, even for highly volatile elements such as Tl and Hg. Only the fluid-
446 mobile elements Pb, Sb, Bi and As show evidence of scattered distribution toward depletion (Pb) or
447 enrichment (As) (Table S1).

448

449 **5.2 Early impactor(s)-derived HSE material inside pyrite.**

450 There is a consensus for considering the siderophile element budget (HSE, Ni, Co) of
451 martian regolith impact breccias NWA 7034 and paired samples as impactor materials from the
452 early bombardment of the ancient martian crust, accumulated more than 4.3 Ga ago (Humayun et
453 al., 2013; Wittmann et al., 2015; Goderis et al., 2016). Goderis et al (2016) found weighted mean
454 whole-rock HSE contents for NWA 7034 corresponding to 3 wt. % of chondritic impactor material
455 (isotope dilution-ID-ICP-MS analyses). In line with Lorand et al. (2015), one may therefore assume
456 that the HSE-rich micronugget inclusions in NWA 7533 pyrite are impactor materials that were
457 trapped by pyrite. These HSE micronuggets actually occur indiscriminately in pyrite, altered pyrite,
458 and outside the pyrite, which supports the idea of random trapping by pyrite. This occurred ca 3
459 B.Y. after the early bombardment if we accept that pyrite is one of the latest minerals in the Martian
460 chronology of NWA 7533, crystallized during the 1.4 Ga lithification and annealing events
461 (McCubbin et al., 2016; Hewins et al., 2017). However there is no evidence that such micronuggets
462 served as nucleation sites for pyrite because they were not identified in all of the pyrite crystals
463 analyzed by LA-ICP-MS.

464 Compared to partial SEM analyses reported by Lorand et al (2015), LA-ICP-MS analyses
465 indicate a much wider compositional range combining mainly refractory PGE (Os, Ir, Ru, Rh, Pt)
466 with Mo and Re. Such alloy compositions are known only in refractory metal nuggets (RMN) from
467 carbonaceous chondrites and unknown as magmatic and hydrothermal platinum-group minerals
468 (Cabri, 1981; O'Driscoll and Gonzales-Jimenez, 2016 and references therein). RMN are interpreted
469 as early condensates of Calcium Aluminium inclusions (Palme and Wlotzka, 1976; Harries et al.,
470 2012; Hewins et al. 2014b). However, the micronuggets identified in NWA 7533 pyrites are highly
471 fractionated and not exactly rich in all of the refractory siderophiles (especially Mo and Re) seen in
472 carbonaceous chondrites studied so far. Moreover, HSE nuggets are not found in some CAIs (e.g. in
473 Efremovka or Leoville) where HSEs are dissolved in Fe-Ni alloy (e.g., Campbell et al., 2003). The
474 more likely scenario, given that most of the original mineralogy of the breccia, including impactor
475 components, has been erased by pre-Noachian alteration, is that the micronuggets probably formed
476 or were modified by weathering and impact melting prior to the assembly of the breccia. The large
477 range of micronugget compositions detected by LA-ICP-MS accounts for significant deviations

478 from chondritic patterns measured for many whole-rock subsamples of NWA 7034 that cannot be
479 accounted for by the respective analytical uncertainties (Goderis et al., 2016). Goderis et al. (2016)
480 pointed out that such deviations definitely preclude reliable identification of projectile components
481 from whole-rock analyses, inasmuch as multiple impactor components were probably admixed
482 during regolith formation (Humayun et al., 2013). The same is also true for pyrite-hosted HSE
483 micronuggets.

484 In addition to early Noachian alteration in the martian regolith, HSE micronuggets were also
485 variably reprocessed within pyrite. The high (up to 2-4 ppm) Ru contents of some pyrite that are
486 independent of concentration spikes in time-resolved diagrams can be explained by such
487 reequilibration with Ru-bearing HSE micronuggets. Time to reequilibrate pyrite at 400°C is quite
488 short (about 100 years; Barton, 1970). By contrast, Os shows stronger preference for Pt-Ir-(Os)
489 alloys (Cabri et al., 1996; Lorand et al., 2010; O'Driscoll and Gonzales-Jimenez, 2016 and
490 references therein). It requires higher fugacity of S compared to Ru to occur as sulfides and the
491 uptake of Os in pyrite only occurs when grain growth occurs because the diffusion of Os in pyrite is
492 limited to near the surface (Brenan and Rose, 2000). One may surmise that such decoupled
493 behaviour between Ru and Os is responsible for the poor correlation coefficient of the Ru vs. Os
494 plot (e.g. Table S2).

495 In contrast to HSE, Ni and Co produce smooth signals in time-integrated LA-ICPMS
496 diagrams which rule out occurrences of Fe-Ni alloy micronuggets at the submicron scale. This
497 observation provides further support to the Lorand et al (2015) suggestion that meteoritic Fe-Ni
498 metal was likely oxidized into Fe-(Ti) oxides well before pyrite formation, which then served as the
499 Fe-Ni-Co reservoir for pyrite crystallization. The wide range of Ni-Co concentrations revealed by
500 LA-ICPMS analyses is therefore consistent with occasional contamination of growing pyrite
501 crystals by such oxides, followed by diffusion of Ni and Co inside the pyrite.

502

503 **5.3 Input of hydrothermal fluids to NWA 7533 pyrite.**

504 At first sight, siderophile-chalcophile metal contents occur in NWA 7533 pyrite as trace
505 concentration levels far from the saturation threshold suggested by terrestrial hydrothermal pyrites
506 in Fig. 9. Apart from the most siderophile elements (PGE, Re, Au) that were likely recycled from
507 early impactor materials predating pyrite, all the other chalcophile-siderophile elements are
508 assumed to be now in solid solution inside pyrite. They were most probably delivered by the fluid
509 pulse(s) that precipitated pyrite during the 1.4 Ga-old hydrothermal event. As said before, pyrite
510 controls the bulk-rock budget of only three elements: the chalcogens (Se, Te; Fig. 9), along with S
511 (not shown). It is worth recalling that martian impact breccias are conspicuously poor in magmatic
512 sulfides, i.e. po-pn (Cu) sulfides assemblages crystallized from sulfide melts as documented for

513 example in SNC meteorites (e.g. Baumgarnter et al., 2017; Lorand et al., 2018). Lorand et al. (2015)
514 detected only two tiny (<10 µm across) sulfide blebs of Ni-rich pyrrhotite + pentlandite enclosed in
515 plagioclase clasts in the 8 polished thin sections studied. The reason for this depletion is probably
516 twofold (1) The heavy bombardment by chondritic meteorite material may have degassed S, a
517 volatile element. Nickel was demonstrated to behave as a lithophile element in the crystallization
518 sequence of impact-melt derived monzonitic clasts, which means that the impact melt was S-
519 undersaturated (Hewins et al., 2014a). (2) The brecciated crust underwent early Noachian
520 weathering and oxidation producing abundant Fe³⁺-rich oxides (magnetite/maghemite; Nemchin et
521 al., 2014; Humayun et al., 2014). These conditions would have also oxidized any relict of magmatic
522 Fe-Ni-Cu sulfides not enclosed within silicates into sulfates. Regardless of which (not mutually
523 exclusive) interpretation holds true, it is pyrite, the only major S mineral found in NWA 7533
524 (Hewins et al., 2017) that rejuvenated the S budget of martian regolith breccias.

525 The same is also true for Se and Te that are strongly tied to S chemistry. All three elements
526 are transported as H₂S, H₂Se and H₂Te in reduced hydrothermal fluids (Grundler et al., 2013).
527 Although within the accepted range for hydrothermal sulfides (Huston et al. 1995; Luguët et al.
528 2004; Lorand and Luguët, 2016 and references therein), S/Se ratios vary within a factor of 15
529 (3,375–54,000), mainly because of the highly variable Se concentrations in NWA 7533 pyrite (8.8-
530 149 ppm). Sulfur and selenium can be fractionated from each other by hydrothermal fluids within a
531 narrow window of redox conditions above FMQ because sulfur dioxide coexists with elemental Se
532 (Huston et al., 1995; Lorand et al., 2003 and reference therein). Temperature also plays a major role
533 in the incorporation of Se and Te in the anionic sublattice of the pyrite structure (Maslennikov et al.,
534 2009; Wohlgemuth-Ueberwasser et al., 2015; Keith et al., 2016). Studies of fossil and active
535 hydrothermal systems revealed that Se-rich pyrites are high temperature pyrite precipitates (Auclair
536 et al., 1987; Maslennikov et al., 2009; Genna and Gaboury, 2015). Selenides form at higher T than
537 corresponding sulfides and high-T sulfides show higher Se contents (Keith et al., 2016). Since Ni
538 concentrations in pyrite also show the same positive temperature-dependence (e.g. Abraitis et al.,
539 2004), the Se vs Ni positive correlation of Fig. 5 is assumed to result from crystallization of NWA
540 7533 pyrite over a wide temperature range (from 500°C to unknown value; Lorand et al., 2015).

541 In addition to superchondritic S/Se ratios, NWA 7533 pyrites display superchondritic Te/Se
542 that is not expected because tellurium is less chalcophile than Se and preferential uptake of Te by
543 the pyrite lattice is counterintuitive. As a semi-metal, Te shows more metallic behavior (e.g. Brennan
544 et al., 2016 and references therein). It is commonly found as metal tellurides and as native tellurium
545 (e.g., Te(0)) in magmatic and hydrothermal ore deposits (e.g. Cook et al., 2007; Voudouris et al,
546 2011); tellurides are stable over a wider fO₂ range (below the magnetite–hematite buffer) compared
547 to sulfides and selenides and the stability of native tellurium overlaps the magnetite–hematite buffer

548 (e.g., Grundler et al., 2013; Schirmer et al., 2014). Thus, during martian oxidation, one would
549 expect preferential uptake of Te in the oxidized source and less availability of this element for S-
550 rich fluids. The fact that NWA 7533 pyrite exhibits superchondritic Te/Se may result from
551 precipitation of Bi-Pb-Te tellurides or intermetallic compounds at the interface between pyrite and
552 hydrothermal fluid. This interpretation is supported by rather good positive correlations in the Te vs.
553 Bi and Te vs. Pb plots of Fig. 6 for unaltered pyrite as well as Pb-, Te- and Bi-enriched outliers.

554 We may also speculate that the hydrothermal fluids tapped a pre-enriched Te source
555 resulting from accumulation of chondritic impactor-derived Fe-Ni metals. While the purely
556 chalcophile element Se is exclusively hosted in sulfides (e. g. Dreibus et al. 1995; Lorand and
557 Luguet, 2016; Baumgartner et al., 2017), the partly siderophile element Te can also be incorporated
558 in the metal phases in chondritic meteorites (Funk et al., 2015). In CK and R chondrites and
559 refractory inclusions in CV chondrites, Te additionally forms noble metal-rich tellurides such as
560 chengbolite (PtTe_2) and moncheite (PtTe_2). Accreted Fe-Ni metal degraded by oxidizing fluids may
561 be an extraneous supply of Te that was then recycled as reduced tellurides by hydrothermal fluids.
562 Of course, this interpretation is consistent with the theory of telluride precipitation discussed above.

563 The typically euhedral crystals (cubooctahedra, with no framboids, no colloform growths) of
564 NWA 7533 pyrite suggest that its depositional process was near equilibrium, under a low degree of
565 supersaturation in the fluids (Murowchick and Barnes, 1986; Keith et al, 2016). Rapid precipitation
566 in high-gradient zones generates strong zoning that are lacking in NWA 7533 pyrite crystals
567 (Vaughan and Craig, 1997; Patten et al., 2016; Duran et al., 2015). The chalcophile element
568 depletion of NWA 7533 pyrite cannot therefore be explained by disequilibrium partitioning
569 processes. We may also speculate that the current compositions of pyrite potentially equilibrated
570 with different hydrothermal fluid(s) but this alternative remains difficult to address without
571 systematic age determinations on pyrite that are presently lacking. Our discussion will be focused
572 on three points i) physical conditions (temperature) of partitioning between hydrothermal fluid(s)
573 and pyrite, ii) nature and composition (redox) of hydrothermal fluids, iii) the availability of these
574 elements in the pre-Noachian crust sampled by martian impact breccias.

575 Clearly, one central reason for the chalcophile metal-depleted composition of NWA 7533
576 pyrite may be the lack of precursor magmatic sulfides in the heavily impacted Noachian crust
577 sampled by NWA 7533. On Earth, metal-rich hydrothermal ore deposits generally have ore sources
578 located in magmatic rocks that host base metal sulfides (Cu-Fe-Ni sulfides). Leaching of magmatic
579 sulfides under high-temperature greenschist facies conditions is considered to be an important
580 source of metals (Au, Cu, Pb, Ag, Ni, Au, As, Sb, Te) while silicate alteration can release Zn, As,
581 Mo, Sb from Fe-Ti oxides (Kaasalinen et al 2015; Hannington et al, 1990; Patten et al, 2016 and
582 references therein).

583 The compositional and textural features of pyrite are closely related to the temperature and
584 chemical characteristics of its host environment (Abraitis et al., 2004). Changing temperature
585 affects the solubility of many minerals in hydrothermal fluids (Seyfried and Ding, 1995, Wilkin and
586 Barnes 1997; Findlay et al 2015). Selenium, Bi, Sn, Mo, Te, and Co, are low solubility elements
587 that precipitate at high T (>350°C) in terrestrial active hydrothermal vents (Maslennikov et al.,
588 2009). By contrast, chalcophile metals (Au, Ag, As, Sb, Pb, Zn, Cd, Hg, Tl, Ga) are associated with
589 lower T pyrite (<350°C; e.g. Hannington et al, 1991). Thallium, a high solubility element in
590 hydrothermal fluids, is concentrated (up to 10,000 ppm) in low-T (100-250°C) pyrite and marcasite
591 deposition within the outer walls of hydrothermal chimneys (Smith and Carson, 1977; Sobbot et al.,
592 1987). The chalcophile element systematics of NWA 7533 pyrite is therefore perfectly consistent
593 with the high crystallization temperature deduced from Ni and Se contents.

594 It is well known that speciation of such metals in hydrothermal fluids strongly depends on
595 fluid composition, especially on ligands and pH. Solubility values can be estimated for several
596 elements (Cu, Pb, Zn, Au). Sulfur and chlorine are the two most important ligands accounting for
597 metal transport in hydrothermal fluids (Helgeson, 1970; Barnes, 1979; 2015; Kaasalinen et al.,
598 2015). According to Fig. 10A, the assemblage pyrite-magnetite-hematite for FMQ + 2 log units
599 corresponds to near neutral fluids (pH = 6-7) in equilibrium with pyrite-magnetite-hematite at
600 350°C. Such fluids are expected to contain a moderate amount of H₂S with all metals including Cu,
601 Pb and Zn delivered as hydrosulfides. Numerical modelling by Zhong et al (2015) suggests that
602 low-salinity hydrous fluids (<3wt.% NaCl) in equilibrium with magnetite-pyrite-hematite at 400°C
603 can dissolve 1 to 100 ppm Cu, Pb and Zn, whereas the experiments of Gibert et al. (1998) indicate
604 0.1 ppm Au as Au(HS)²⁻ (Fig. 10B). These concentration ranges measured in synthetic fluids are
605 very similar to those measured in NWA 7533 pyrites. Unless unrealistically low pyrite-fluid
606 partition coefficients close to 1 are assumed, we may conclude that fluids that precipitated NWA
607 7533 pyrite did not reach saturation for these four elements.

608 As high-valence, small ions, Zn and Pb can be more readily complexed with Cl⁻ over a wide
609 range of T and acidic conditions (Zhong et al, 2015). Chlorine-bearing fluids may have been present
610 at some stage of the 1.4 Ga-old sequence of hydrothermal alteration in NWA 7533: apatite is a
611 major Cl-rich mineral (up to 7.2 wt.%) in NWA 7533 (Hewins et al., 2017). Belluci et al (2017)
612 documented a core-rim increase of Cl/F ratios coupled with some fractionation in Cl isotopic
613 compositions in matrix apatite, compared to original magmatic δ³⁷Cl signatures. One may surmise
614 that apatite continued to re-equilibrate with fluids down to temperatures of 500°C and buffered the
615 fluid composition to near zero Cl contents, thus reducing metal-chloride complexing. Except for a
616 few smectites of uncertain origin (Muttik et al., 2014), NWA 7533 silicate assemblages are
617 remarkably immune to acid leaching that typically generates microcrystalline silica, kaolinite,

618 pyrite, barite and sericite (see Einaudi et al., 2003; Scher et al., 2013). Potassium-rich feldspar does
619 not show evidence of alteration to kaolinite, not even incipient sericitization, which is expected for
620 highly saline acidic fluids at pH <6 (Fig. 10).

621

622

6. Conclusions

623 Pyrite accounts for more than 50-70 (+/- 20) % of the bulk rock budget for Se and Te (and
624 probably for S too before terrestrial weathering). It displays superchondritic S/Se consistent with its
625 hydrothermal origin.

626 Apart from the chalcogens S, Se and Te, pyrite appears to be a minor contributor (<20%) of
627 the whole-rock budget for both siderophile HSE (including Ni, Co and HSE) and chalcophile metals
628 Ag, As, Au, Cu, Hg, Pb, Sb, Tl and Zn. The missing fraction of HSE occur as nanometer-sized
629 particles (e.g. Ir-Os alloys), identified along with occasional detection of Mo and Re in half of the
630 52 analyzed crystals as well as outside pyrite, inside impact lithologies. These micronuggets are
631 interpreted as variably altered remnants from repeated meteorite bombardment of the early martian
632 crust. Nickel and cobalt are also impactor-derived, although now residing in solid solution in pyrite.
633 Both elements, like chalcophile metals (e.g. As, Pb), are also present as trace elements dispersed in
634 major minerals like pyroxene, Fe-Ti oxides or apatite (Humayun et al., 2013; Hewins et al., 2014c)

635 The chalcophile metal deficit can result from i) a high (>400°C) temperature crystallization
636 for NWA 7533 pyrite, as deduced from its Se and Ni contents, ii) magmatic sulfide depletion of
637 brecciated early martian crust, iii) precipitation from near neutral H₂S-HS-H₂O-rich hydrothermal
638 fluids that did not provide halogen ligands for extensive transport of chalcophile-siderophile metals.

639 It is suggested that the 1.4 Ga lithification event that precipitated hydrothermal pyrite left the
640 chalcophile-siderophile element budget of the early martian crust nearly unmodified, except for S,
641 Se and Te.

642

643 Acknowledgments—We are indebted to L. Labenne for the sample. We are grateful for funding
644 from CNES-INSU grant 2014-PNP (J.-P. L.). The LA-ICP-MS facility at the LPG Nantes was
645 established by funds from the Region Pays de la Loire. Support by the NASA Solar System
646 Workings program (NNX16AP98G) for research at FSU is acknowledged. The revised version was
647 greatly improved thanks to comments from three reviewers and editorial suggestions of Rich
648 Walker.

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Figure captions:

966 Figure 1. Concentration profile of selected chalcophile-siderophile elements along the laser traverse
967 through a lithic clast (Clast XIV). The HSE spikes are interpreted as submicrometer-sized nuggets
968 that are evenly distributed in impact lithologies of NWA 7533. Some micronuggets are clearly offset
969 from the concentrations peaks of S, Fe, Ni, Pb and Te corresponding to pyrite (Py).

970

971 Figure 2. Time-resolved LA-ICPMS spectra collected during four analyses of pyrites (count per
972 second (cp/s) vs. time (s)). The spikes of PGE, Re and Mo concentrations are interpreted to be
973 submicrometer-sized highly siderophile element (HSE)-rich nuggets intercepted by the laser beam.
974 Log scale (left) for S; linear scale (right) for HSE micronuggets. Note that the four micronuggets
975 show peak/background ratios > 30 ($30 -1,000$) that rule out any analytical artifact in their
976 identification.

977

978 Figure 3. Ir vs. Pt and Pt vs. Mo diagrams for NWA 7533 pyrite. Insert: Ir and Pt-rich outliers. Note
979 the broad positive correlation between Pt and Ir and the Mo enriched population in NWA 7533
980 pyrites. Carbonaceous chondrites (CI, CM, CK, CO); Ordinary chondrites (H); Enstatite chondrites
981 (EH). Chondritic ratios after Wasson and Kallemeyn (1988); Tagle and Berlin (2008) and Palme and
982 O'Neill (2014). Mix = pyrite +/- Fe oxyhydroxides. For error bars see Table S1.

983

984 Figure 4. Co vs. Ni diagram for NWA 7533 pyrite. EMPA: electron microprobe analyses. Other
985 captions as in Fig. 3.

986

987 Figure 5. Se vs. Ni and Se vs. Te plots for NWA 7533 pyrite. CI-chondritic ratio after Wang and
988 Becker (2013) and Palme and O'Neill (2014). Short dashed lines in Fig. 5B were arbitrarily drawn
989 to delineate covariation trends between Se and Te. Note the overall Te enrichment with respect to
990 chondritic Se/Te. CI chondrites after Wang and Becker (2013) and Palme and O'Neil (2014).

991

992 Figure 6. Plots of Pb and Bi vs. Te. Inserts: Pb-Bi-Te-rich outliers. Short dashed lines were
993 arbitrarily drawn to delineate covariation trends between Pb and Te and Bi and Te. Note the Pb and
994 Bi enrichments of mix analyses. Other captions as in Fig. 3.

995

996 Figure 7. Plots of Ga and Zn vs Sn. Note the positive correlation in Fig. 7A; the outliers in Fig. 7B
997 correspond to mix analyses that incorporated significant amount of Fe-oxyhydroxides. Circle: Fe-
998 (Ti) oxide. CI = CI-chondrites (Palme and O'Neill, 2004).

999

1000 Figure 8. Concentration ranges of major and trace chalcophile-siderophile element concentrations in
1001 NWA 7533 pyrite (in bold) compared with terrestrial hydrothermal pyrite (thin grey lines).
1002 Terrestrial pyrite compositions after Abruatis et al. (2004), Large et al. (2007), Scher et al. (2013),
1003 Deditius et al. (2014), Li et al. (2014), Duran et al. (2015) and Patten et al. (2016). Note the
1004 logarithmic concentration scale.

1005

1006 Figure 9. Mass balance estimates of the contribution of pyrite to the whole-rock budget of NWA
1007 7533 (whole-rock data after Humayun et al., 2013). Details of calculations in supplementary Table
1008 S5.

1009

1010 Figure 10: Log fO_2 vs. pH (A) and Log fO_2 vs. Log fS_2 (B) diagrams for the Fe-S-O system at T =
1011 350°C displaying the concentrations of the different Au species dissolved in the putative
1012 hydrothermal fluids involved in the 1.4 Ga hydrothermal events (after Gibert et al., 1998). Black
1013 arrows delineate the range of redox conditions inferred for NWA 7533 (Lorand et al., 2015). Hm:
1014 hematite; Py: pyrite; Mt: magnetite; Po: pyrrhotite. The curves corresponding to kaolinite-illite (1)
1015 and K-feldspar (2) stability after Scher et al. (2013). Oxygen fugacity relative to the FMQ buffer
1016 after Lorand et al. (2015).

Figure

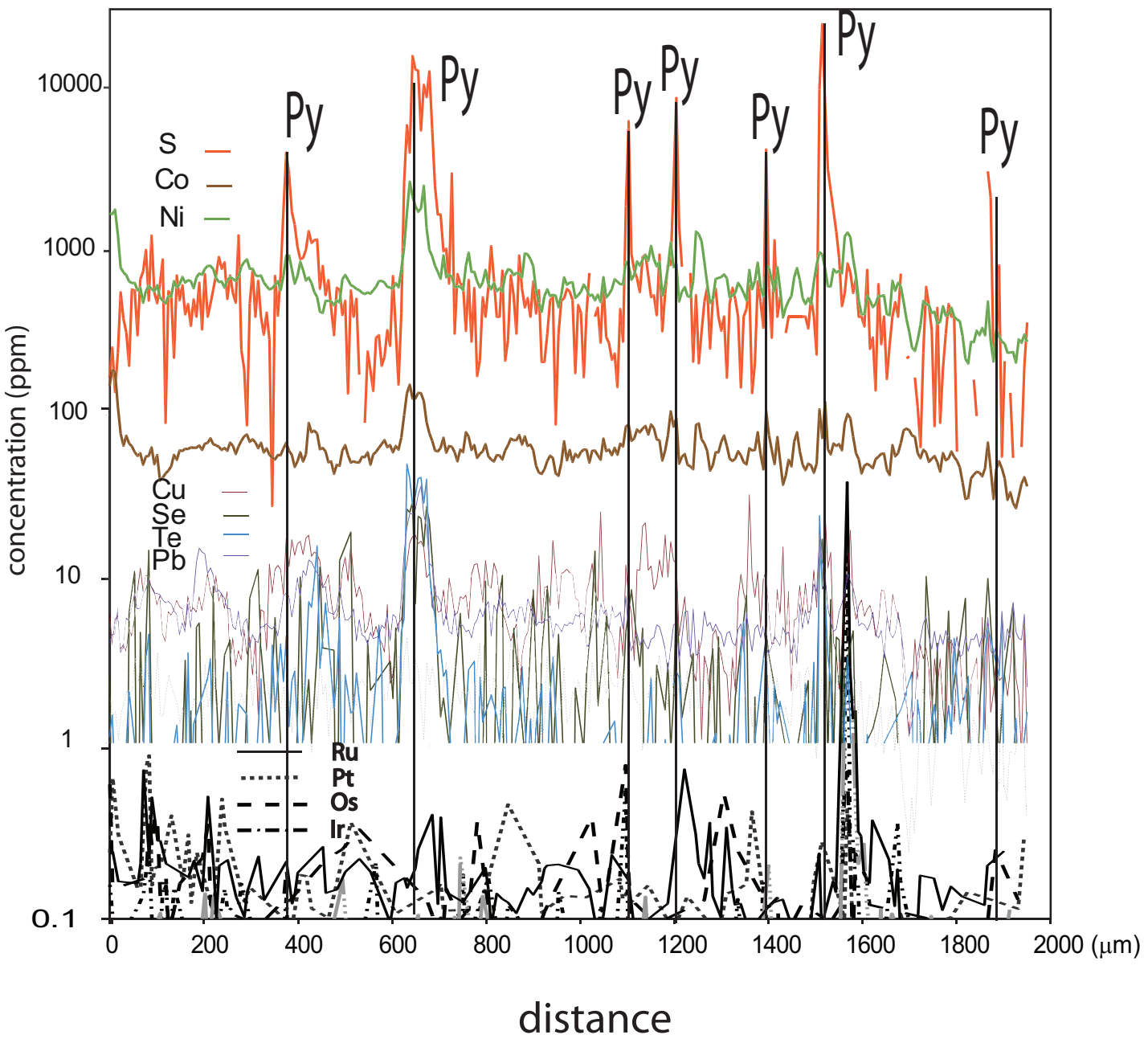


Fig. 1

Figure

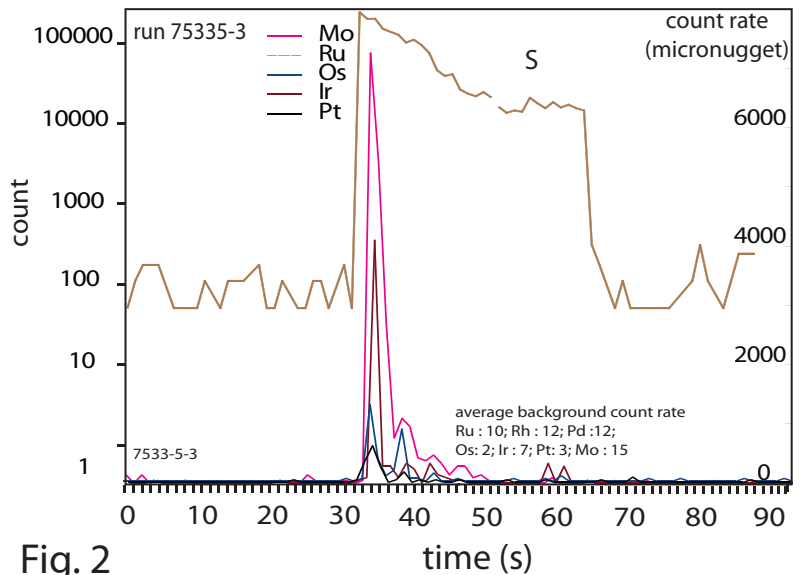
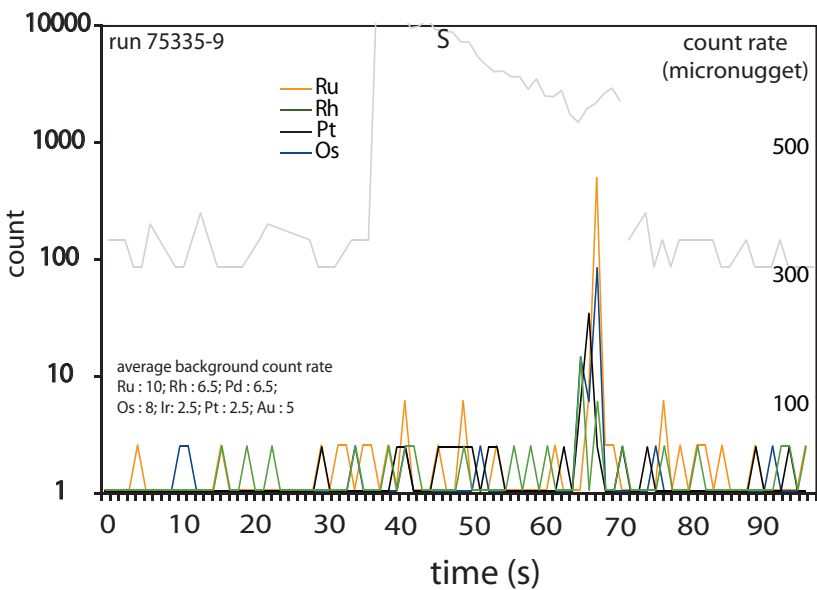
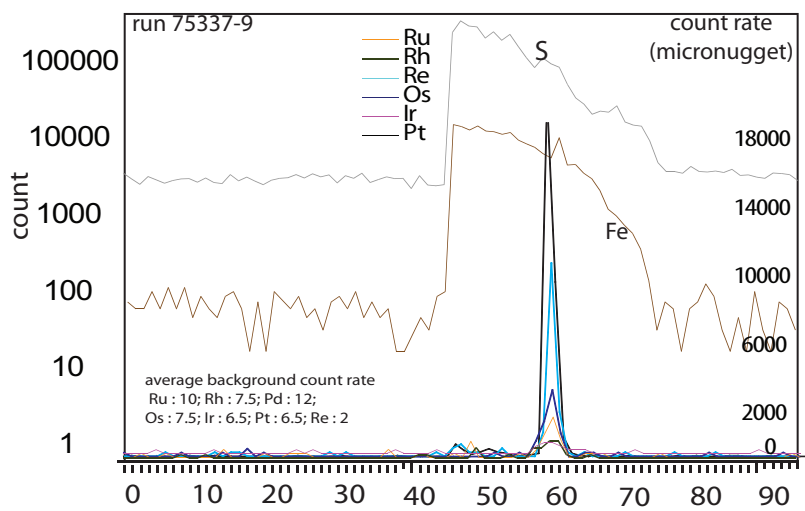
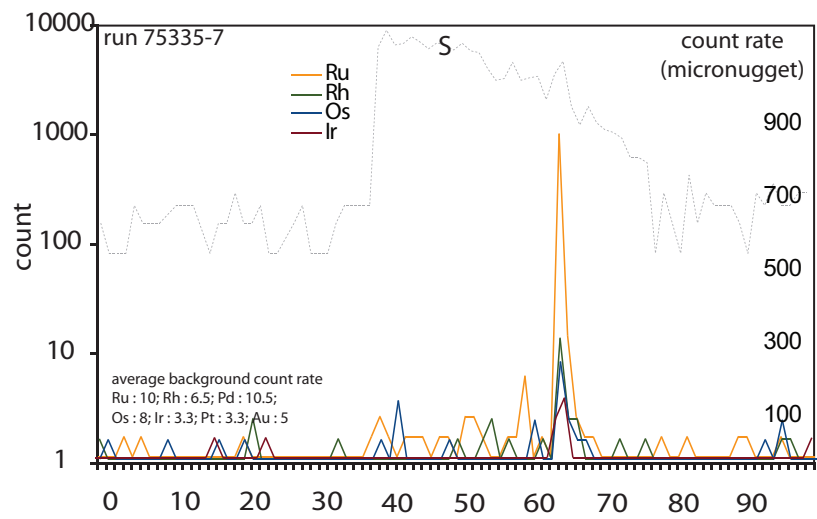


Fig. 2

time (s)

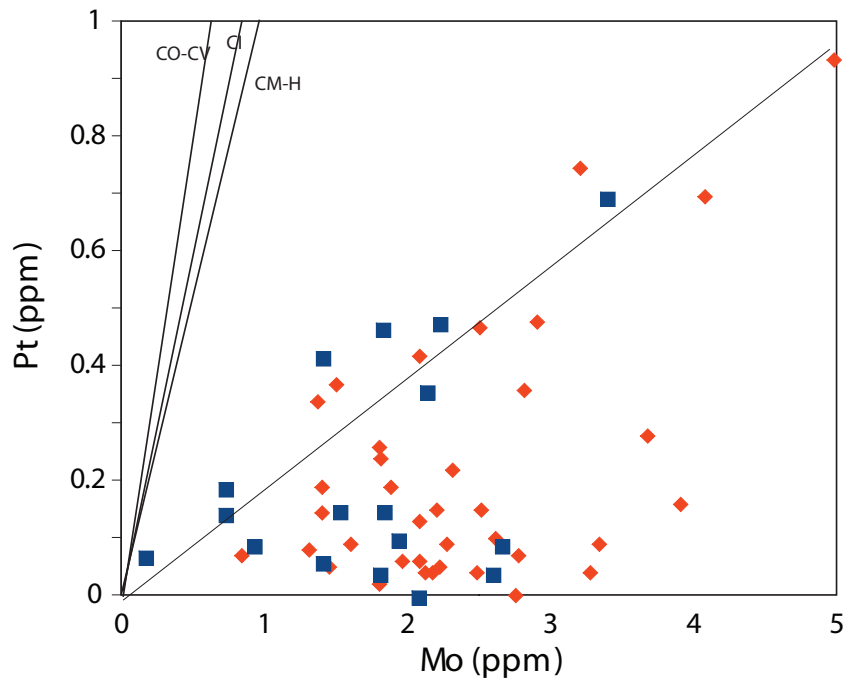
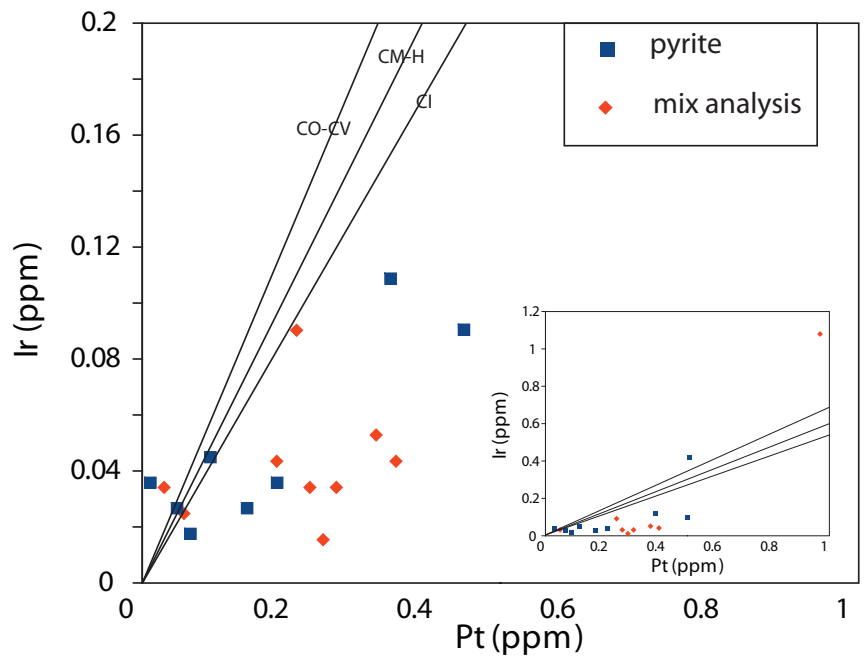


Fig. 3

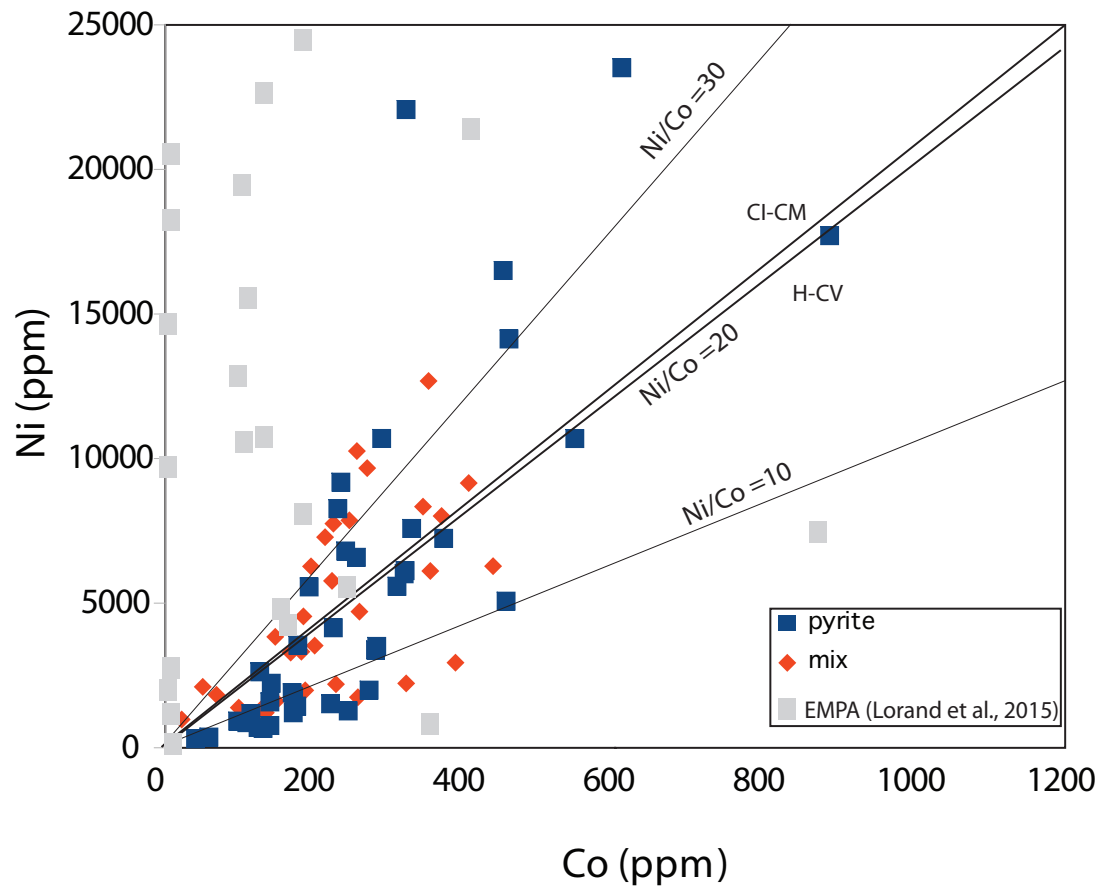
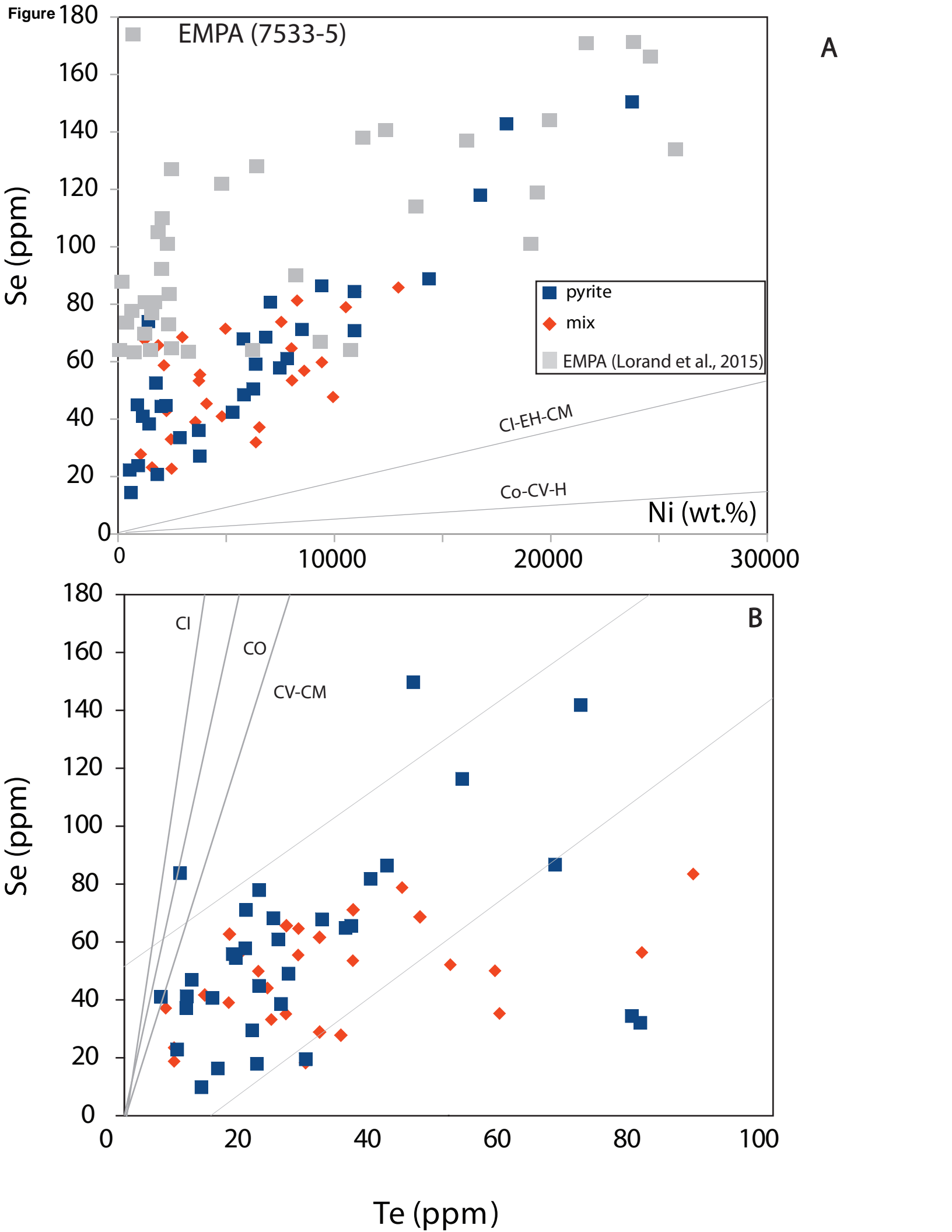


Fig. 4



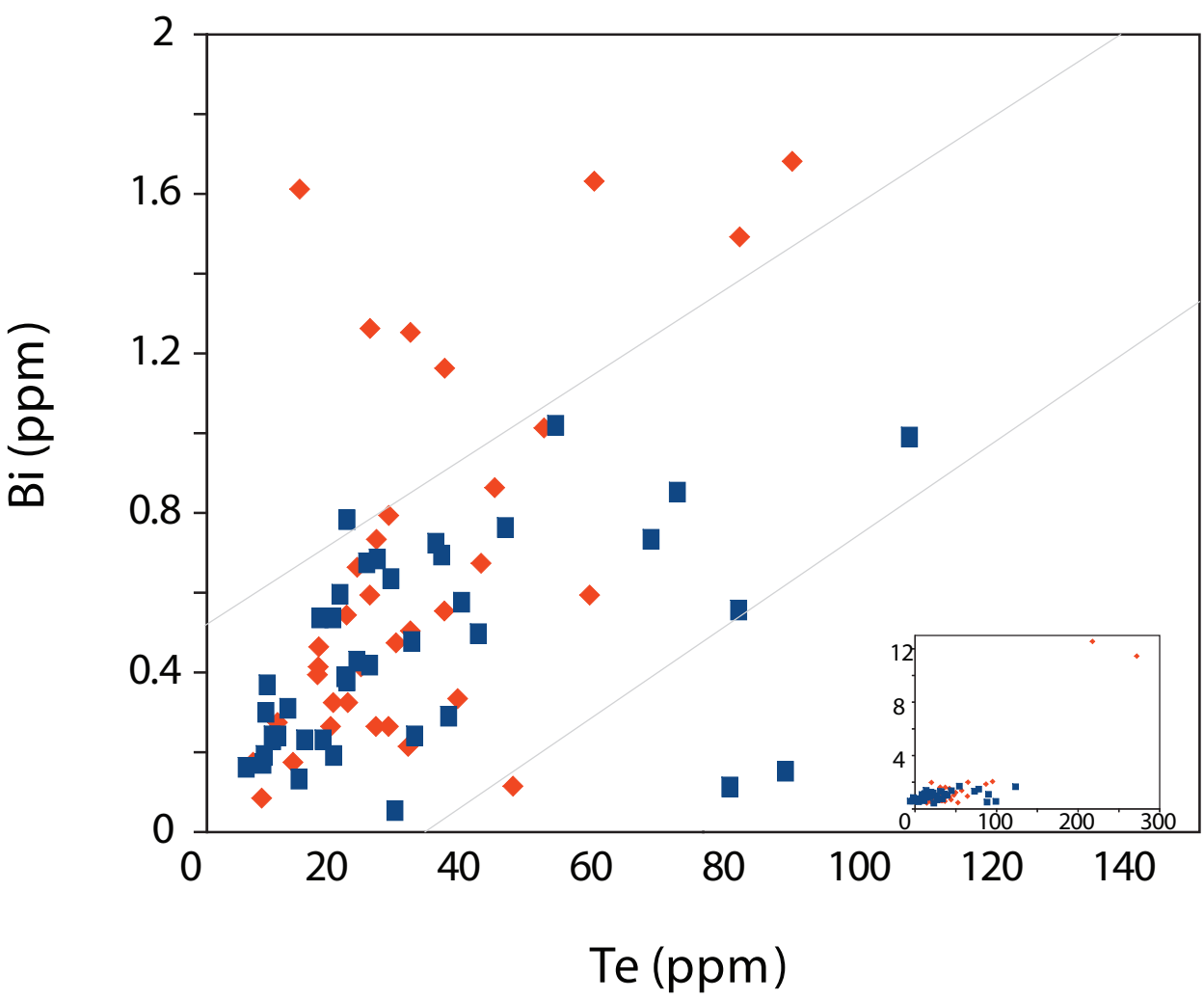
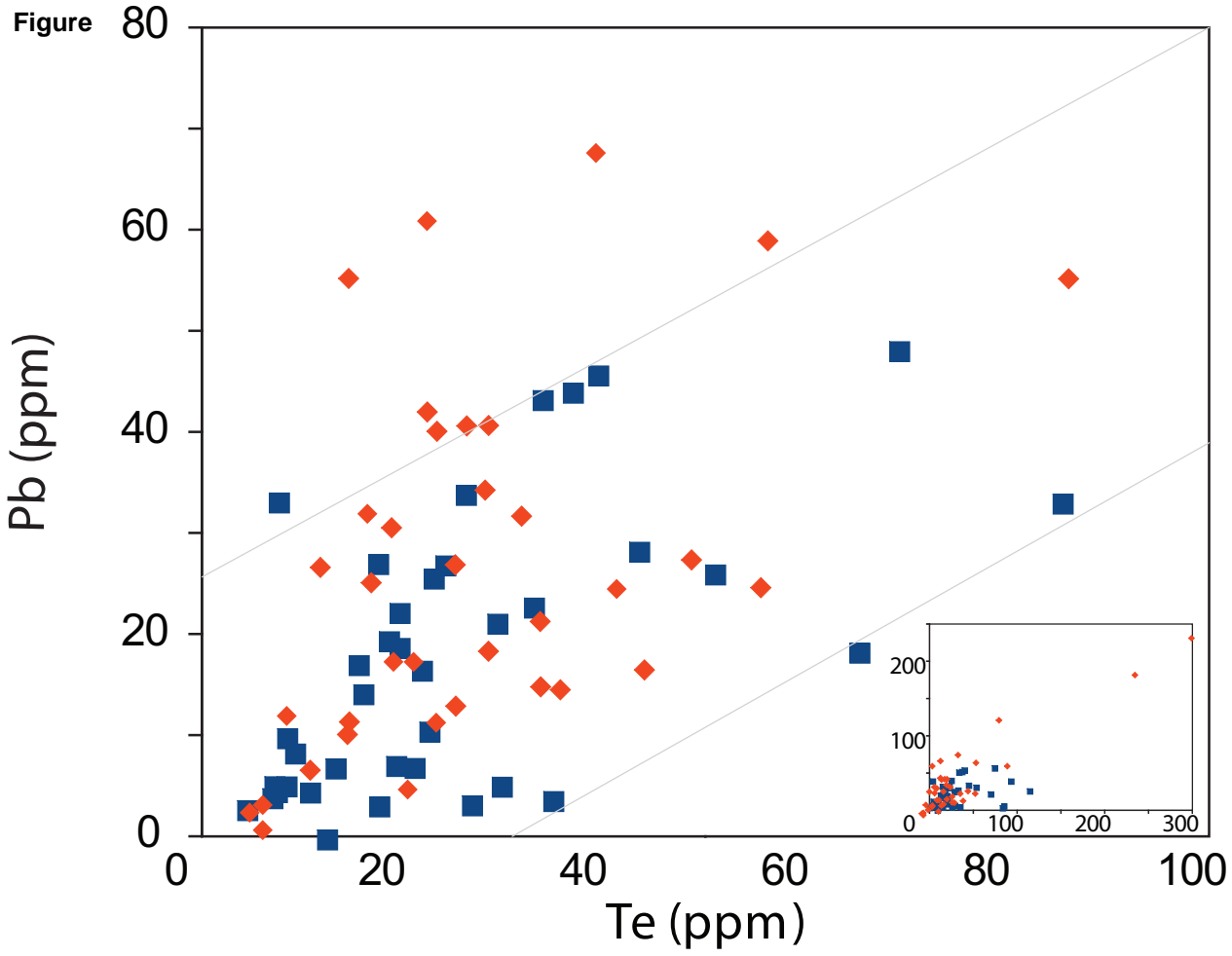


Fig. 6

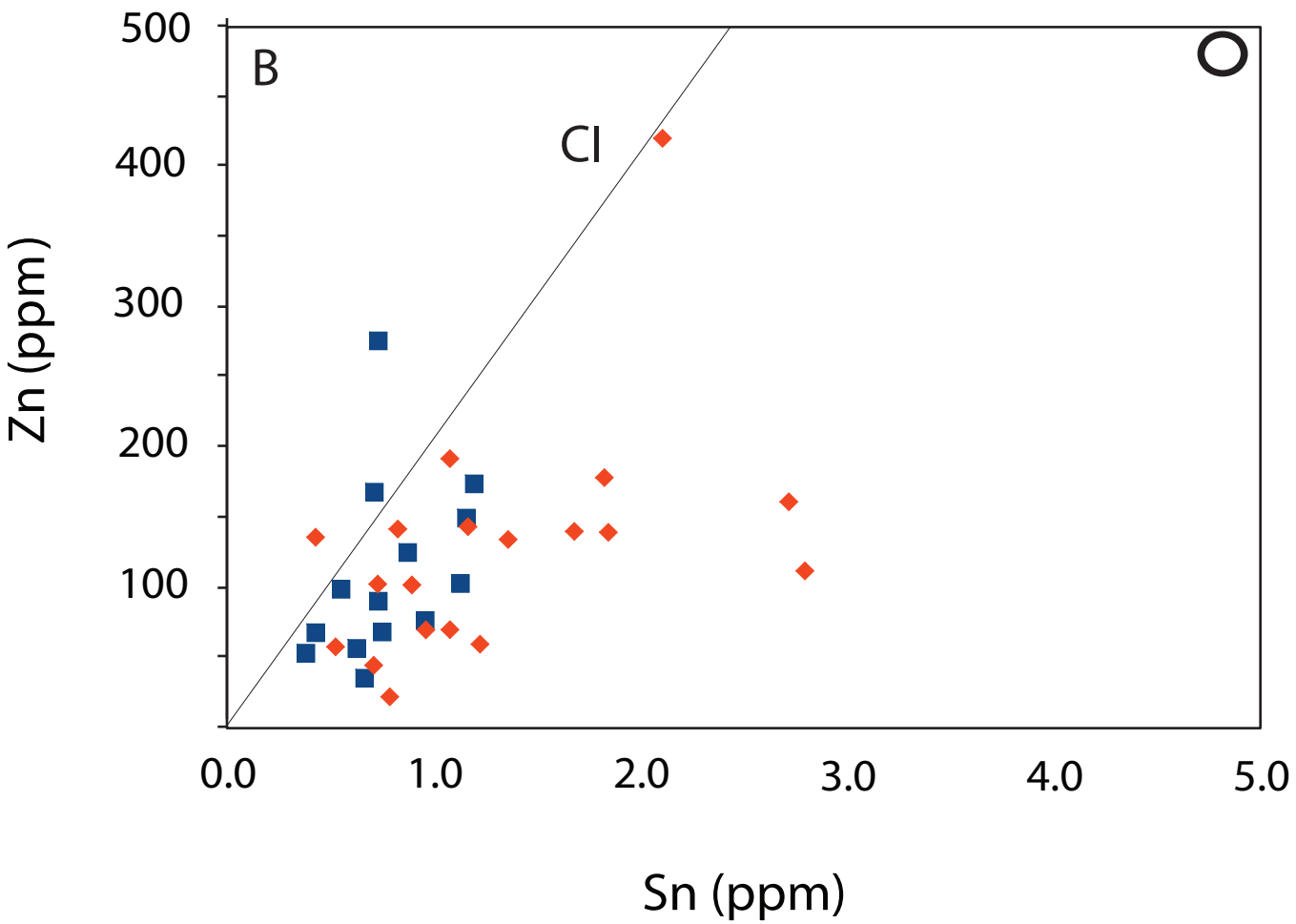
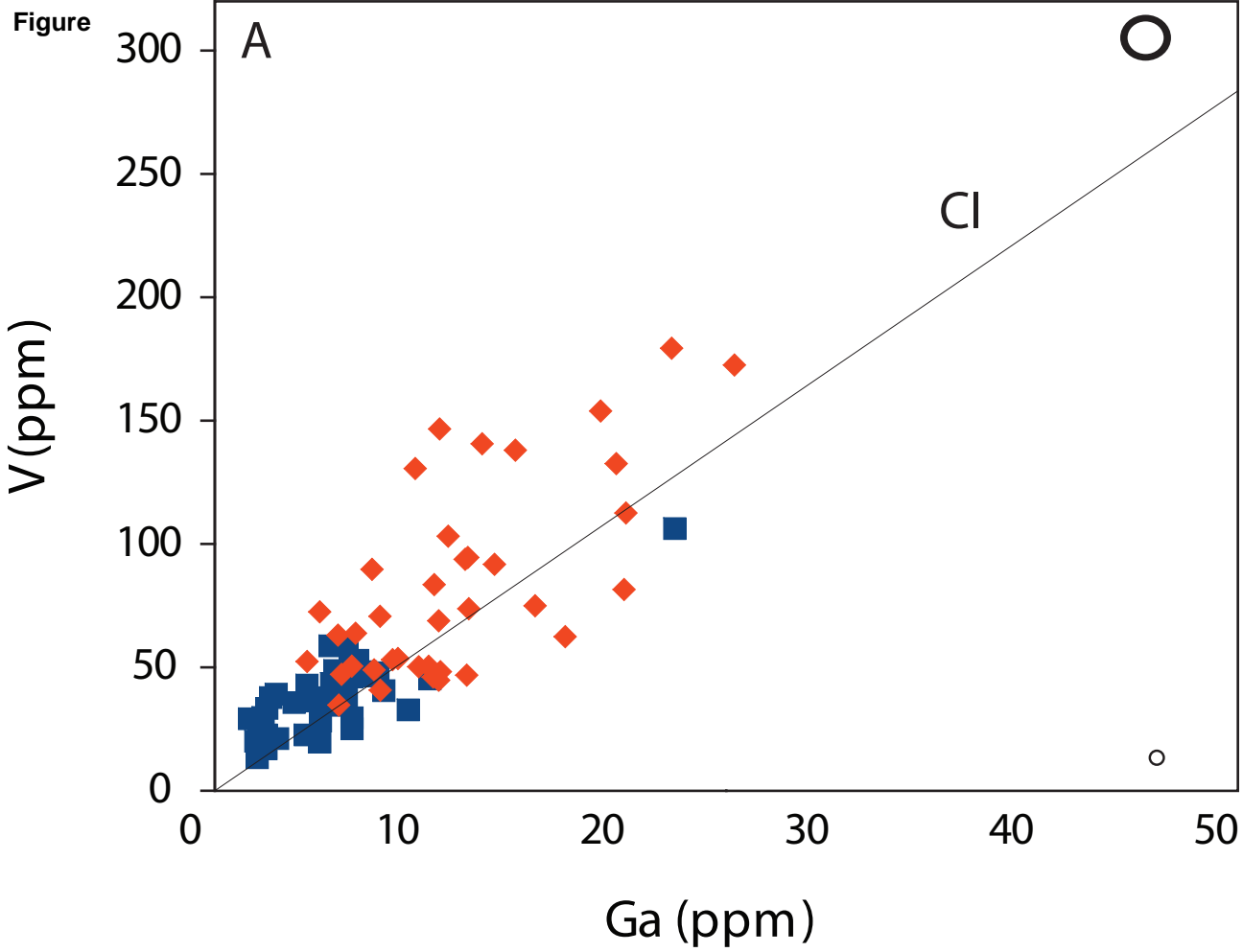
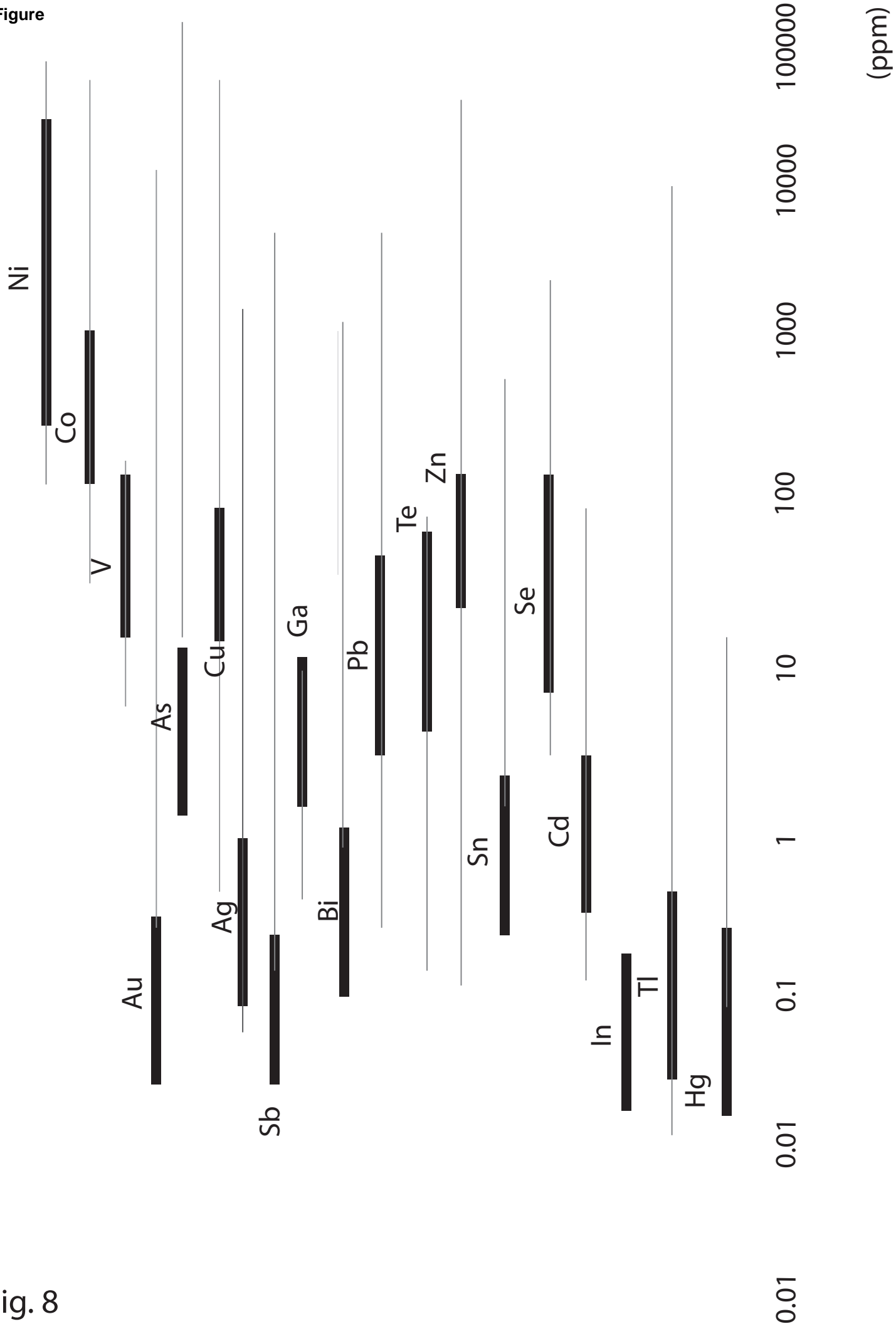


Fig. 7



Figure

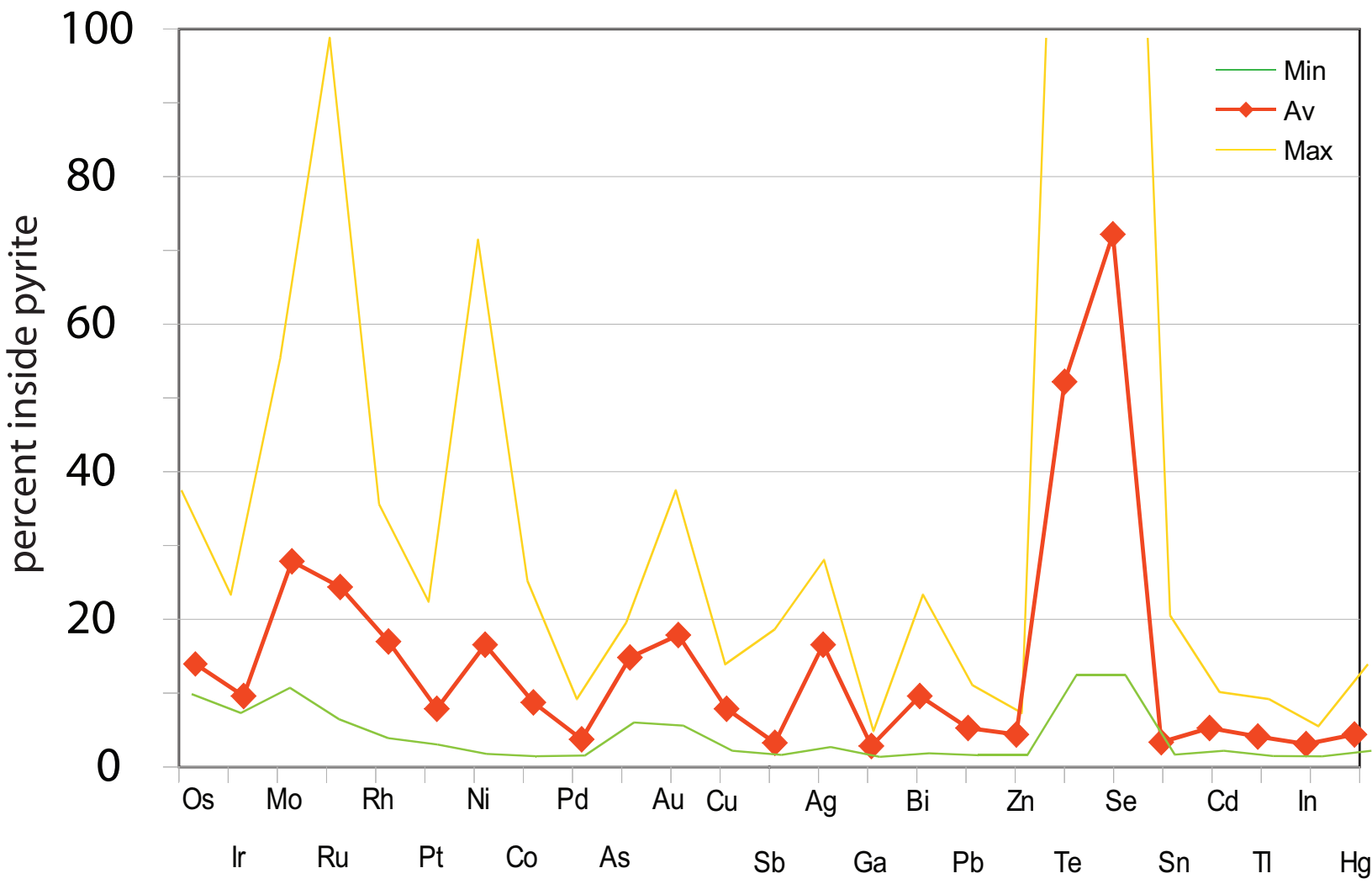


Fig. 9

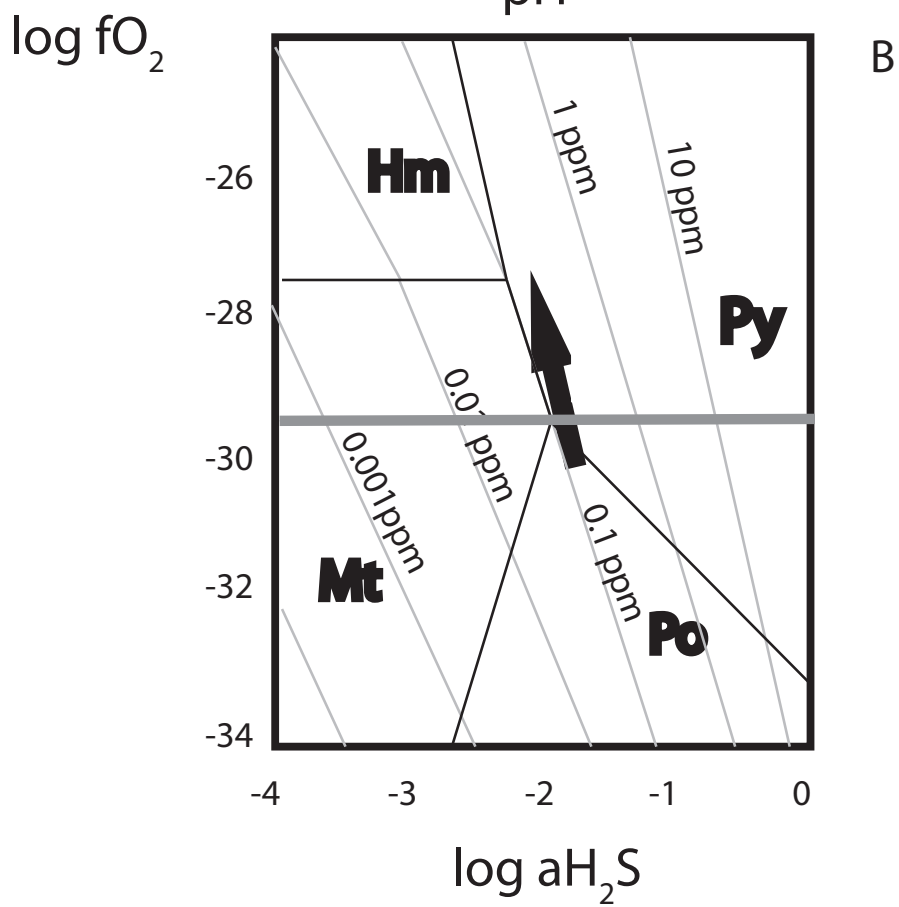
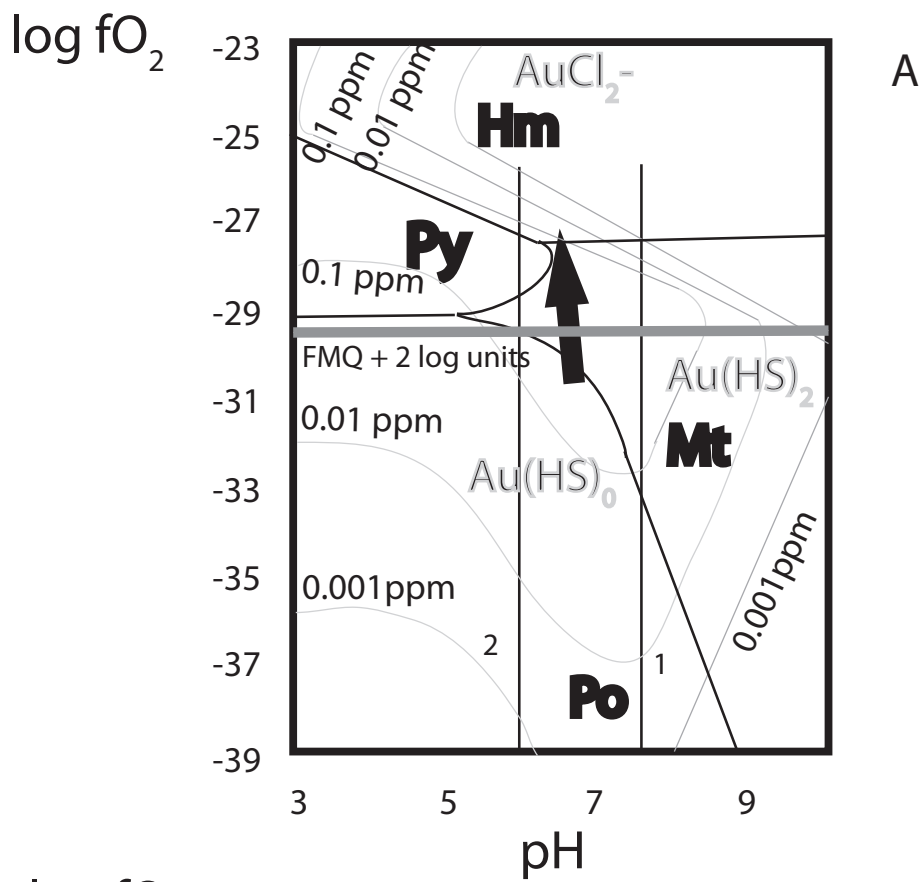


Fig. 10