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# Syneruptive incorporation of martian surface sulphur in the nakhlite lava flows revealed by S and Os isotopes and highly siderophile elements: implication for mantle sources in Mars

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1 **Syneruptive incorporation of martian surface sulphur in the nakhlite lava flows revealed**  
2 **by S and Os isotopes and highly siderophile elements: implication for mantle sources in**  
3 **Mars**

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28 *Abstract*

29 Martian lava flows likely acquired S-rich material from the regolith during their emplacement on the  
30 planet's surface. We investigated five of the twenty known nakhlites (Nakhla, Lafayette, Miller Range  
31 (MIL) 090032, Yamato 000593, and Yamato 000749) to determine whether these lavas show  
32 evidence of regolith assimilation, and to constrain the potential implications that this process has on  
33 chemical tracing of martian mantle source(s). To establish the proportionate influence of  
34 atmospheric, hydrothermal, and volcanic processes on nakhlite isotopic systematics we obtained *in*  
35 *situ* sulphur isotope data ( $\Delta^{33}\text{S}$  and  $\delta^{34}\text{S}$ ) for sulphide grains (pyrrhotite and pyrite) in all five nakhlite  
36 samples. For Nakhla, Lafayette, and MIL 090032, these data are integrated with highly siderophile  
37 element (HSE) abundances and Os-isotope compositions, as well as textural information constrained  
38 prior to isotopic analysis. This work thereby provides the first Re-Os isotope systematics for two  
39 different nakhlites, and also the first Re-Os isotope data for martian sample for which detailed  
40 petrographic information was constrained prior to digestion.

41 We report the largest variation in  $\delta^{34}\text{S}$  yet found in martian meteorites (-13.20 ‰ to +15.16 ‰). The  
42 relatively positive  $\Delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  values of MIL 090032 ( $\delta^{34}\text{S} = +10.54 \pm 0.09$  ‰;  $\Delta^{33}\text{S} = -0.67 \pm 0.10$  ‰)  
43 indicate this meteorite assimilated sulphur affected by UV-photochemistry. In contrast, the strongly  
44 negative values of Lafayette ( $\delta^{34}\text{S} = -10.76 \pm 0.14$  ‰;  $\Delta^{33}\text{S} = -0.09 \pm 0.12$  ‰) are indicative of  
45 hydrothermal processes on Mars. Nakhla, Yamato 000593, and Yamato 000749 sulphides have a  
46 narrower range of sulphur isotope compositions ( $\Delta^{33}\text{S}$  and  $\delta^{34}\text{S} \sim 0$ ) that is consistent with no  
47 assimilation of martian surface materials during lava flow emplacement. Consequently we used this  
48 second group of  $\Delta^{33}\text{S}$  values to approximate the  $\Delta^{33}\text{S}$  of the nakhlite source, yielding a  $\Delta^{33}\text{S}$  value of -  
49 0.1 ‰.

50 Nakhlite HSE patterns result from a sulphide-saturated melt where Ru-Os-Ir alloys/sulphide were  
51 likely crystallized during earlier phases of magmatic processing in Mars to result in the fractionated  
52 HSE patterns of the nakhlites. Our data, alongside a synthesis of previously published data, suggest  
53 assimilation of an enriched component to the primary nakhlite melt, potentially a late-stage  
54 crystallization cumulate from the martian magma ocean stage. In the context of this model, and  
55 within large uncertainties, our data hint at perturbation and potential decoupling of nakhlite Re-Os  
56 isotope systematics from other isotopic systems as a result of small degrees of assimilation of a  
57 regolith component with highly radiogenic  $^{187}\text{Os}/^{188}\text{Os}$ .

58

59

## 60 1 – Introduction

61 Magmas represent windows to comprehend the interior evolution and geochemical diversity of  
62 terrestrial planets. Magmatic activity and degassing are key processes for transferring sulphur, along  
63 with other elements, from the interior to the surface during the evolution of a planetary body. In the  
64 case of Mars, low water activity, low temperatures, and the lack of plate tectonics has favoured the  
65 preservation of a sulphur-rich regolith during the last ~2 billion years (King and McLennan, 2010). In  
66 fact, the martian regolith contains concentrations of SO<sub>2</sub> up to 8 wt.% (Clark et al., 1976; Foley et al.,  
67 2003).

68 The terrestrial and martian mantles have been reported to contain similar and chondrite-relative  
69 highly siderophile elements (HSE; Os, Ir, Ru, Rh, Pt, Pd, Au, and Re) abundances (Birck & Allegre,  
70 1994; Warren & Kallemeyn, 1996; Brandon et al., 2000, 2012; Dale et al., 2012; Tait and Day, 2018),  
71 which has important implications for accretion theory and astrophysical modelling of Solar System  
72 evolution (e.g., Bottke et al., 2010). However, sulphur abundance estimates for the martian mantle  
73 range between 400 and 2200 ppm (Wang and Becker, 2017 and references therein) - much higher  
74 than the Earth's mantle (around 250 ppm; McDonough and Sun, 1995). The aim of this study was to  
75 use rhenium-osmium (Re-Os) isotope systematics and HSE abundances, alongside S-isotope  
76 systematics, to test whether the nakhlite group of martian meteorites preserve robust isotopic  
77 information from the martian interior (Morgan, 1986; Shirey & Walker, 1998; Righter et al., 2000;  
78 McSween & Huss, 2010; Walker, 2016).

79 Martian meteorites are the only available rocks from the surface of Mars. These meteorites can be  
80 divided into shergottites (basalts), nakhlites (clinopyroxene-rich rocks), and chassignites (olivine  
81 cumulates), with a few other exceptional meteorites. Berkley et al. (1980), Treiman (1986, 2005),  
82 and Bridges & Grady (2000) argued that nakhlite petrographic features are consistent with this suite  
83 of meteorites sampling a single cumulate pile. However, recent <sup>40</sup>Ar-<sup>39</sup>Ar geochronology suggests  
84 that their crystallization ages differ by ~93 Ma, consistent with the nakhlites being derived from a  
85 series of lava flows or sills that were emplaced between ~1416 and 1322 Ma, probably from the  
86 same source (Cohen et al., 2017; Udry and Day, 2018). In this manuscript, we refer to the nakhlites  
87 as a series of lava flows.

88 Franz et al. (2014) used a combination of bulk rock sulphur analyses ( $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$ ,  $\Delta^{36}\text{S}$ ) and *in situ*  
89 pyrrhotite mineral analyses ( $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$ ) to determine sulphur isotope anomalies in martian  
90 meteorites. These authors determined the  $\Delta^{33}\text{S}$  of the shergottite mantle source to be 0.009 ‰,  
91 based on the mean value of 28 meteorites. This value closely corresponds to the value measured for  
92 the shergottite Yamato (Y)-980459, which reportedly retains the most reliable signatures of the

93 martian mantle (e.g., Usui et al., 2012). However, Franz et al. (2014) were unable to calculate a  
94 robust value for the nakhlite mantle source region, as *in situ* secondary ion mass spectrometry  
95 (SIMS) analyses of sulphide grains were acquired from only two of the nakhlites (Nakhla and Miller  
96 Range (MIL) 03346) and their  $\Delta^{33}\text{S}$  values varied widely ( $0.06 \pm 0.21 \text{ ‰}$  and  $-0.72 \pm 0.13 \text{ ‰}$ ,  
97 respectively). This variation was reported to have been caused by sulphate assimilation during melt  
98 eruption, affecting subsequent pyrrhotite crystallization. Franz et al. (2014) argued that sulphides  
99 and sulphates in the martian meteorites can thus be affected by assimilation of sulphur derived from  
100 atmospheric UV photochemical reactions, which was deposited at the surface as oxidized sulphur  
101 and incorporated in the martian regolith. This data is in agreement with other previously published  
102 sulphur isotope data for the nakhlites, including evidence for mass independent fractionation (MIF),  
103 which suggests assimilation of sulphur occurred at some point during nakhlite formation (e.g.,  
104 Farquhar et al., 2000, 2007; Greenwood et al., 2000a,b; Dottin III et al., 2018).

105 These sulphur isotope systematics can be used to discern if the HSE abundances in nakhlite magmas  
106 are affected by crustal assimilation, or if they represent Mars mantle reservoirs. The HSE systematics  
107 of martian meteorites have been used to infer chondritic relative abundances of these elements in  
108 the martian mantle, and to thereby trace late-accretion of broadly chondritic materials to Mars after  
109 the last major magma ocean phase at  $\sim 4.5 \text{ Ga}$  (e.g., Brandon et al., 2000, 2012; Riches et al., 2011;  
110 Tait and Day, 2018). Crucially, the HSEs exhibit chalcophile element behaviour when metal is absent  
111 from the mineralogical assemblage, preferring to partition into sulphides (Day et al., 2016, and  
112 references therein), which is important in terms of HSE partitioning.

113 Rhenium-Os isotope data are available for many shergottites and one chassignite, but with respect  
114 to the nakhlite meteorites there are only two analyses of Nakhla (Brandon et al., 2000; Dale et al.,  
115 2012). This lack of published data is, in part, due to the low abundance of HSE (0.1-2 ppb or less) in  
116 the nakhlites (Treiman et al., 1986; Jones et al., 2003). In addition, a large age correction needs to be  
117 applied (1.3 Ga since nakhlite crystallization), and the effects of crustal assimilation within Nakhla  
118 are not clear (McCubbin et al., 2003; Franz et al., 2014; Udry and Day, 2018). Therefore, Nakhla may  
119 not be a reliable indicator of the nakhlite's true Os-isotopic mantle source composition. To address  
120 these challenges, we have expanded the nakhlite Re-Os isotope and HSE dataset to include Lafayette  
121 and one of the paired Miller Range nakhlites (MIL 090032). These two meteorites are potentially  
122 highly informative as they plot at the two extremes of S-isotope composition for the nakhlites  
123 (Farquhar et al., 2000; Greenwood et al., 2000; Franz et al., 2014). We also analysed a fraction of  
124 Nakhla. This nakhlite is known to have S-isotope composition of aggregated sulphides intermediate  
125 to the Miller Range and Lafayette meteorites. Sulphur isotope ( $\Delta^{33}\text{S}$  and  $\delta^{34}\text{S}$ ) data were acquired  
126 from sulphide grains in Nakhla, Lafayette, MIL 090032, Y-000749, and Y-000593 to determine the

127 amount of crustal assimilation that has occurred in each meteorite during eruption, and to define  
128 the possible  $\Delta^{33}\text{S}$  range for the nakhlite mantle source.

129

## 130 **2 – Methodology**

### 131 ***2.1 – Sample preparation and chemical mapping***

132 Chips were used for Re-Os isotope and HSE analysis, while thin sections were used for S-isotope  
133 analyses. The chips (~0.5 g) were from Nakhla (BM.1913,25), Lafayette (BM.1979,755), and MIL  
134 090032 (100); thin sections were from Nakhla (BM.1913,26#2), Lafayette (BM.1979,755), MIL  
135 090032 (28), Y-000593 (37), and Y-000749 (59). Samples were obtained from the Natural History  
136 Museum of London (Nakhla, Lafayette), NASA Johnson Space Center (MIL 090032), and JAXA (Y-  
137 000593, Y-000749). All samples were from the interior portions of the meteorite, lacking any fusion  
138 crust.

139 We used a novel methodology in which petrographic information was constrained, for the first time,  
140 prior to destruction of that same sample volume via acid digestion. This approach provides  
141 mineralogical context to inform our interpretations of HSE-abundance and Re-Os isotopic data. To  
142 achieve this, we polished the sample chips of Nakhla (0.4 g) and Lafayette (0.6 g) using disks of SiC  
143 and 0.3  $\mu\text{m}$  of  $\text{Al}_2\text{O}_3$ , then rinsed with MQ  $\text{H}_2\text{O}$ . The procedure was undertaken to remove any  
144 potential contamination to the chips' surface from earlier cutting and processing by the meteorite  
145 curators. As the final step of this treatment involved repeated rinsing in MQ  $\text{H}_2\text{O}$  and visual  
146 inspection, we believe that any potential contamination of the sample by  $\text{Al}_2\text{O}_3$  residue was  
147 removed. However, it remains possible that microscopic traces of  $\text{Al}_2\text{O}_3$  could introduce Re, very  
148 small amounts of radiogenic Os, and potentially perturb the HSE and Os-isotopic systematics, in  
149 which case we would anticipate variable chondrite-relative HSE patterns for the analysed nakhlites.  
150 The MIL 090032 chip (0.5 g) had a flat surface and did not require polishing. These chips were not  
151 subject to carbon coating during the acquisition of high spatial resolution images and compositional  
152 mapping. Corresponding thin sections for each of the nakhlites used in this work were carbon coated  
153 to a thickness of 20-25 nm for compositional mapping by secondary electron microscopy prior to ion  
154 microprobe work.

155 A Zeiss field-emission Scanning Electron Microscope (SEM), housed in the Imaging Spectroscopy and  
156 Analysis Centre of the University of Glasgow, was used to characterise thin-sections and the flat side  
157 of the prepared chips. Operating conditions were: 8.5 mm working distance, 2.15 nA beam current,  
158 and 20 kV accelerating voltage. Acquired X-ray spectra were calibrated using mineral standards.

159 Backscattered electron (BSE) images and energy dispersive spectroscopy (EDS) X-ray element maps  
160 (for Si, Mg, Fe, Ca) were obtained for the chips lacking carbon coating with the SEM operated in low  
161 vacuum. Backscattered electron images and EDS X-ray spectra were generated for carbon coated  
162 thin sections of Nakhla, Lafayette, MIL 090032, Y-000749, and Y-000593 with the SEM operated at  
163 high vacuum. Of particular interest were the sulphides (pyrrhotite/pyrite). Every recognized sulphide  
164 on the exposed surface was imaged and quantitatively chemically analysed to determine its  
165 mineralogy (see **Supplementary Materials** for further details).

166

## 167 **2.2 – Sulphur isotope systematics**

168 To obtain the desired spatial resolution during *in situ* analysis of pyrrhotite and pyrite for  $\delta^{34}\text{S}$ ,  $\delta^{33}\text{S}$ ,  
169 and  $\Delta^{33}\text{S}$ , five polished thin-sections (one each of Nakhla, Lafayette, MIL 090032, Y-000749, and Y-  
170 000593) were analysed via SIMS. Samples were cleaned with ethanol and coated with gold to a  
171 thickness of  $\sim 20\ \mu\text{m}$ , to permit conductivity, before loading into the sample chamber of the ion  
172 probe.

173 Sulphur isotope compositions were measured on the CAMECA IMS 1280 ion microprobe (SIMS) at  
174 the Centre de Recherches Pétrographiques et Géo-chimiques (CRPG) in Nancy (France) by  
175 simultaneous measurements of  $^{32}\text{S}^-$ ,  $^{33}\text{S}^-$ , and  $^{34}\text{S}^-$  in multicollection mode with three off-axis Faraday  
176 cups (FCs) in slit 2 mode that allows for a mass resolution  $M/\Delta M = 5000$ . The FCs were  
177 intercalibrated before the analytical session to determine their relative yields. Samples were  
178 sputtered with a  $\text{Cs}^+$  primary beam of 3-nA intensity, accelerated at 13 kV and focused on a spot of  
179  $\sim 15\ \mu\text{m}$  diameter. Pyrite, pyrrhotite and galena standards were used to determine the instrumental  
180 mass fractionation (IMF) and the reference mass instrumental law (allowing  $\Delta^{33}\text{S}$  to be calculated).  
181 Typical  $^{32}\text{S}$  count rates were between  $\sim 1.2 \times 10^9$  and  $1.5 \times 10^9$  cps, depending on the sulphide  
182 standard analysed. A typical analysis consisted of 2 min of pre-sputtering with a  $20\ \mu\text{m}$  raster,  
183 followed by data acquisition for 40 cycles of 5 s each. Faraday cup backgrounds were measured  
184 during the pre-sputtering before each analysis and then used for correcting the data. Automatic  
185 mass and transfer deflector centerings were implemented in the analysis routine to ensure  
186 reproducible analytical conditions during the session. Each measurement takes around 7 minutes  
187 per spot. Typical  $\pm 2\sigma$  standard errors achieved under these conditions were  $\sim 0.1\text{-}0.3\ \text{‰}$  for  $\delta^{34}\text{S}$ ,  
188  $\sim 0.1\text{-}0.2\ \text{‰}$  for  $\delta^{33}\text{S}$ , and  $\sim 0.1\text{-}0.25\ \text{‰}$  for  $\Delta^{33}\text{S}$ .

189

## 190 **2.3 – Analytical procedure for Os-isotope systematics and HSE**

191 Nakhla, Lafayette, and MIL 090032 were analysed for HSE abundances and Re-Os isotope  
192 compositions. Textural characterisation of each sample fragment was retained prior to destruction  
193 of the same material fraction. All samples were weighed before and after crushing so that any loss of  
194 sample during this process could be quantified. The HSE chemical separation for Nakhla and  
195 Lafayette was conducted in ultra-clean laboratories at the Durham Geochemistry Centre (class 100),  
196 Durham University (see **Supplementary Materials** for further details). We used a mixed  $^{190}\text{Os}$ – $^{191}\text{Ir}$ –  
197  $^{99}\text{Ru}$ – $^{194}\text{Pt}$ – $^{106}\text{Pd}$ – $^{185}\text{Re}$  basalt spike for Nakhla and Lafayette. This spike was selected because we  
198 anticipated fractionated HSE in the nakhrites relative to chondrite or peridotite-like HSE abundances;  
199 the basalt spike has high Re/Os thereby ensuring accurate spiking. The Total Procedural Blank (TPB)  
200 and sample digestions were processed in a high pressure asher and run at 270° C for 18 hours to  
201 liberate the HSE from sample powders and to achieve sample-spike equilibration. Following this  
202 digestion step, extraction of Os from the solution was performed using a chloroform solvent  
203 extraction approach (after Cohen and Waters, 1996). Osmium was then back-extracted into HBr, and  
204 was purified via microdistillation (Birck et al., 1997) prior to filament loading. All the other analysed  
205 HSE were separated and purified using anion exchange and LN-spec chromatography (cf., Pearson  
206 and Woodland, 2000; Puchtel et al., 2008; Chu et al., 2015; **Supplementary Materials**).

207 MIL 090032 was analysed in the laboratories at the Freie Universität Berlin following similar  
208 laboratory processing protocols to those of Durham University. The polished surface of the sample  
209 chip was cleaned with some ethanol but not further abraded because the surface appeared porous  
210 and the chip fragile. Afterwards the chip was powdered in an agate mill. Sample digestion and  
211 chemical separation was conducted following the protocol of Fischer-Gödde et al. (2010, 2011). To  
212 remove Zr an additional clean-up step was applied for Pd following the protocol of Chu et al. (2015).  
213 Acquisition of  $^{187}\text{Os}/^{188}\text{Os}$  for this one sample fragment was unsuccessful.

214 The HSE were measured using an Element XR instrument (Berlin) and Element 2 (Durham). The  
215 sample was introduced via a conventional Scott-type glass spray chamber. An Aridus I membrane  
216 desolvation system was used for HSE at Berlin. Highly siderophile element signals were detected in  
217 low resolution mode with a secondary electron multiplier. Rubidium, Sr, Y, Zr, Mo, Cd, Tm, Yb, Lu, Hf,  
218 Ta, Os, and Hg were analyzed to monitor isobaric interferences and potentially interfering oxide  
219 species. Oxide formation rates were <4.5 % and <0.8 % for the Scott-type spray chamber at Berlin  
220 and Durham, respectively, and <0.15 % using the Aridus at Berlin. The internal precision of measured  
221 isotope ratios ranges from 0.2 to 0.8 % ( $2\sigma$ ). Background-corrected element ratios were corrected  
222 for mass discrimination using IUPAC values by comparison with ratios in a HSE standard solution  
223 measured in the same sequence. Isotopic ratios of  $^{99}\text{Ru}/^{101}\text{Ru}$ ,  $^{105}\text{Pd}/^{108}\text{Pd}$ ,  $^{185}\text{Re}/^{187}\text{Re}$ ,  $^{191}\text{Ir}/^{193}\text{Ir}$  and  
224  $^{194}\text{Pt}/^{195}\text{Pt}$  were used for isotope dilution calculations. Isotope ratios  $^{105}\text{Pd}/^{106}\text{Pd}$  and  $^{194}\text{Pt}/^{196}\text{Pt}$  were



225 used to monitor possible interferences. Concentrations of monoisotopic Rh and Au were determined  
226 via a combined internal/external standardization technique for the  $^{197}\text{Au}/^{191}\text{Ir}$  and  $^{103}\text{Rh}/^{101}\text{Ru}$  ratios  
227 (Fischer-Gödde et al., 2010). Consistency and possible interferences were checked by comparison to  
228 results from  $^{197}\text{Au}/^{195}\text{Pt}$  and  $^{103}\text{Rh}/^{191}\text{Ir}$  ratios. Four blanks were determined. Blank contributions are:  
229 8.4 % Re; 24 % Ir; 3.8 % Ru; 1.1 % Pt; 2.9 % Rh; 17.5 % Pd; 24 % Au at Berlin; while blank  
230 contributions at Durham are Re, 0.42-0.49 %; Os, 0.70-4.20 %,  $^{187}\text{Os}/^{188}\text{Os} = 0.132$ ; Ir, 0.10-0.26 %;  
231 Ru, 0.04 %; Pt, 0.25-0.4 %; Pd, 0.87-1.0 %. The elemental abundances of the samples were corrected  
232 using the blank values reported in the **Supplementary Materials**.

233

### 234 **3 – Results**

#### 235 **3.1 – Textural characterization of the chips**

236 The Nakhla chip (Fig. 1a) was characterized by a high proportion of mostly euhedral augite (~80%; 1-  
237 1.5 mm), and a lesser volume of euhedral to subhedral olivine (~8%; 0.3-1 mm in maximum  
238 dimension) – extensive areas of the chip had no olivine crystals. Plagioclase made up ~5 vol.% of the  
239 sample, while mesostasis represented ~7 vol.%. Texturally, a low degree (< 10%) of fracturing was  
240 observed among the minerals. A single 0.3 mm long sulphate grain was present in a Si-rich area of  
241 the chip (Fig. 1a). Other smaller (< 0.1 mm) sulphates and sulphides were present throughout the  
242 chip.

243 The Lafayette chip (Fig. 1b) was characterized by a higher proportion of euhedral to subhedral  
244 olivine (~15%; 200-800  $\mu\text{m}$  crystal size) and a lower volumetric percentage of pyroxene (~75%; 500-  
245 1800  $\mu\text{m}$  in maximum dimension) relative to the Nakhla chip; mesostasis was ~10 vol.%. Pyroxene  
246 was mostly subhedral and in some cases contained olivine inclusions of <50  $\mu\text{m}$ . The chip was  
247 characterized by a low degree (< 10%) of mineral fracturing and several small (< 0.1 mm) sulphates  
248 and sulphides.

249 The MIL 090032 chip (Fig. 1c) was characterized by a high proportion of mostly euhedral pyroxene  
250 (~80%; 1000-1300  $\mu\text{m}$  crystal sizes), with a minor amount of olivine (~10%; generally 500-700  $\mu\text{m}$  in  
251 maximum dimension) and a magnetite/olivine-rich mesostasis (~10%) that contains numerous  
252 microcrystals (<5  $\mu\text{m}$ ) of olivine. The chip shows a low degree (< 15%) of fracturing. In some areas,  
253 both olivine and pyroxene contained glassy inclusions of 30  $\mu\text{m}$  in maximum dimension. Olivine was  
254 distributed heterogeneously and it occurred only in one area.

255 Our observations of these nakhlite chips are in agreement with previous petrographic observations  
256 of thin sections and chips of Nakhla (Treiman, 1990; Lentz et al., 1999; Corrigan et al., 2015; Udry

257 and Day, 2018), Lafayette (Bunch and Reid, 1975; Boctor et al., 1976; Treiman et al., 1993; Corrigan  
258 et al., 2015; Udry and Day, 2018), and MIL 090032 (Day et al., 2005, 2006; Stopar et al., 2005; Udry  
259 et al., 2012; Corrigan et al., 2015; Udry and Day, 2018). However, the Nakhla chip studied here  
260 differs from previous observations in hosting a large sulphate grain, supporting heterogeneously  
261 distributed HSE-carrying trace phases in nakhlites.

262

### 263 **3.2 – Sulphur isotopes**

264 Pyrrhotite and pyrite grains were identified adjacent to mesostasis (glass) in each thin section, and  
265 also occur as inclusions within augite (Fig. 2). These sulphides differ in size between meteorites:  
266 Nakhla 20-40  $\mu\text{m}$ ; Lafayette 20-60  $\mu\text{m}$ ; MIL 090032 10-60  $\mu\text{m}$ ; Y-000593 50-250  $\mu\text{m}$ ; and Y-000749  
267 15-40  $\mu\text{m}$ . The sulphide grains are relatively pure, containing few inclusions, or exsolved  
268 blebs/lamellae, of other phases. Sulphides in the five nakhlites analysed here show significant  
269 variation in sulphur isotopic composition, with  $\Delta^{33}\text{S}$  from -0.76 to 0.04 ‰ and  $\delta^{34}\text{S}$  from -13.2 to 15.1  
270 ‰ (Table 1). Sulphur isotopes analysed from five pyrrhotite grains in Nakhla give a range of  $\Delta^{33}\text{S}$   
271 from -0.12 to 0.02 ‰, with an average of  $-0.05 \pm 0.08$  ‰ and an average  $\delta^{34}\text{S}$  of  $-1.59 \pm 0.10$  ‰.  
272 These values are in agreement with  $\Delta^{33}\text{S} = -0.09$  ‰ analysed via acid extraction and with  $\delta^{34}\text{S}$  of -1.6  
273 ‰ analysed via chrome reducible sulphur extraction in sulphides from Nakhla by Farquhar et al.  
274 (2007). However, our data show a slightly more negative result relative to the data of Franz et al.  
275 (2014) (mean  $\Delta^{33}\text{S} = 0.08$  ‰ with some grains as low as -0.33 ‰, and mean  $\delta^{34}\text{S} = -0.51$  ‰. The SIMS  
276 measurements of Greenwood et al. (2000b) for pyrrhotite grains in Nakhla agree well with our  
277 values, having a range in  $\Delta^{33}\text{S} = -0.4 \pm 0.5$  to  $-0.07 \pm 0.5$  ‰ and a  $\delta^{34}\text{S} = -4.5 \pm 0.4$  to  $1.4 \pm 0.4$  ‰.

278 Similar to Nakhla, two pyrrhotite grains in Y-000749 gave an average  $\Delta^{33}\text{S} = -0.10 \pm 0.15$  ‰ and  $\delta^{34}\text{S}$   
279  $= -1.1 \pm 0.11$ , while only one pyrrhotite was analysed for Y-000593 ( $\Delta^{33}\text{S} = -0.18 \pm 0.07$  ‰;  $\delta^{34}\text{S} =$   
280  $-1.3 \pm 0.08$ ). Lafayette pyrite analysis (five grains) yielded a range of values in  $\Delta^{33}\text{S} = -0.26$  to 0.04 ‰  
281 and a  $\delta^{34}\text{S} = -13.2$  to -8.53 ‰, with an average  $\Delta^{33}\text{S} = -0.09 \pm 0.12$  ‰, which approaches the  $\Delta^{33}\text{S} =$   
282 0.07 ‰ in Lafayette pyrite analysed by Farquhar et al. (2000). Sulphur isotope data obtained for five  
283 grains of MIL 090032 show a  $\Delta^{33}\text{S} = -0.76$  to -0.62 ‰ and a  $\delta^{34}\text{S} = 7.60$  to 15.1 ‰, with an average  
284  $\Delta^{33}\text{S} = -0.67 \pm 0.10$  ‰ and  $\delta^{34}\text{S} = 10.5$  ‰. Previous measurements via chemical extractions from the  
285 four paired Miller Range nakhlites gave a range of  $\Delta^{33}\text{S}$  from -0.43 to -0.53 ‰, in particular an earlier  
286 study of the MIL 090136 material gave values that are in the range of our own analysis, with an  
287 average  $\Delta^{33}\text{S} = -0.4$  ‰ and  $\delta^{34}\text{S} = 7.66$  ‰ (Franz et al., 2014; Dottin III et al., 2018).

288

### 289 **3.3 – Rhenium-Os isotope systematics and HSE**

290 Lafayette and Nakhla have broadly similar CI-normalized HSE patterns (Fig. 3a), with a general  
291 depletion of Os, Ir, and Ru relative to Pd and Re (Table 2). However, osmium normalised to CI-  
292 chondrite/10,000 ( $Os_N$ ) is slightly more abundant (1.69) in Lafayette than in Nakhla (0.25). Osmium,  
293 Ir, Ru, and Pt are in agreement with earlier HSE-abundance studies of Nakhla (as reviewed by Jones  
294 et al., 2003), with the exception of Pd and Re that show higher abundances in our new data (2.24  
295 and 0.117 ppb, respectively). In general, Os, Ir, Ru, and Pt in Nakhla fall in the range between  
296 previous HSE analyses of Nakhla by Dale et al. (2012) and Jones et al. (2003). Platinum, Pd, and Re of  
297 Nakhla and Lafayette show similarities with measured Pt and Pd in Chassigny (Jones et al., 2003).  
298 Nakhla has the highest  $(Re/Ir)_N = 148$  and  $(Pt/Ir)_N = 96$  among the studied set of samples, while  
299 Lafayette has the highest value in  $(Os/Ir)_N = 3.44$  for these nakhlites (Fig. 5). The MIL 090032 CI-  
300 normalised HSE pattern is slightly different from the patterns of Nakhla and Lafayette, with higher  
301 absolute Os, Ir, and Ru, and Pt (4.54 ppb) having the highest CI-chondrite normalised value.

302 Nakhla and Lafayette display different Re and Os abundances and Re-Os isotope systematics (Table  
303 2; Fig. 3b). Lafayette has a  $^{187}Re/^{188}Os$  and  $^{187}Os/^{188}Os$  of  $6 \pm 6$  and  $0.1849 \pm 0.0003$  (uncertainties are  
304 expressed as  $2\sigma$  internal precision), respectively. Nakhla is characterized by the highest  $^{187}Re/^{188}Os$   
305 value of  $49 \pm 49$  and an  $^{187}Os/^{188}Os$  of  $0.4542 \pm 0.0018$ . Despite large uncertainties on  $^{187}Re/^{188}Os$  and  
306 crystallisation ages  $>1$  Gyr, we tried to calculate the initial  $^{187}Os/^{188}Os$  composition of the sample  
307 with its percent deviation from the chondritic reference (Shirey & Walker, 1998) using the  $\gamma Os_i$   
308 notation. The assumed crystallization ages of the most recent  $^{39}Ar$ - $^{40}Ar$  dating (Cohen et al., 2017)  
309 were used for our calculations. The calculated  $\gamma Os_i$  is strongly negative. Data on initial  $^{187}Os/^{188}Os$   
310 and  $\gamma Os_i$  are reported in Table 2.

311

## 312 **4 – Discussion**

### 313 **4.1 – Potential for terrestrial alteration and weathering**

314 Some of the nakhlites analysed here could have been affected by alteration during their residence  
315 on Earth. In samples recovered from hot deserts the formation of terrestrial clay and carbonate (e.g.,  
316 Crozaz et al., 2003) can modify lithophile isotope systematics (e.g., Symes et al., 2008) and  
317 potentially perturb the Re-Os isotope system. Nakhla was seen to fall, and was recovered shortly  
318 thereafter. The provenance of Lafayette is less clear, but its fresh fusion crust suggests it was  
319 collected soon after it fell (e.g., Graham et al., 1985). However, even weathering events lasting a few  
320 hours have been shown to cause Re and minor Os redistribution in chondrites from fresh falls

321 (Walker et al., 2018). Terrestrial clays or carbonates are not found within either of these nakhlites,  
322 hence the Re-Os isotope system and their sulphides (as supported by our petrographic observations)  
323 should not be significantly affected by terrestrial alteration. In addition, initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of  
324 Nakhla and Lafayette (0.70254 and 0.70260, respectively) also show little variation (Gale et al., 1975;  
325 Shih et al., 1998), suggesting minor or no modification of Sr isotope due to clay and carbonate  
326 mineralization.

327 In contrast, the Miller Range and Yamato nakhlites are Antarctic finds, hence have had greater  
328 exposure to the terrestrial environment. The light rare earth element, cerium (Ce) can act as an  
329 alteration tracer via the conversion of  $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$  due to oxidation, with pigeonite being the most  
330 susceptible mineral (Croaz et al., 2003). Cerium anomalies can be found in silicates of the Antarctic  
331 Yamato nakhlites (Croaz et al., 2003), and terrestrially derived jarosite sulphate has been reported  
332 towards the exterior of Yamato 000749 (Changela and Bridges, 2011). However, Pb isotope  
333 systematics within these nakhlites reflect minimal terrestrial contamination (Yamashita et al., 2002),  
334 and the Rb-Sr and Sm-Nd isotope systematics provide little evidence for terrestrial weathering.  
335 Olivine and sulphide within the Miller Range nakhlites has suffered aqueous corrosion during  
336 residence in Antarctica (Dyar et al., 2005; Hallis and Taylor, 2011; Hallis, 2013; Velbel, 2016). Long  
337 exposure to water/snow may have resulted in an addition of anthropogenic radiogenic osmium  
338 (Chen et al., 2009). However, terrestrial alteration in the Miller Range nakhlites was considered in  
339 previous studies to have no significant impact on the  $\Delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  of its unweathered sulphides,  
340 which thereby robustly trace processes on Mars (Dottin III et al., 2018). Hafnium-W isotope values  
341 for Nakhla, Lafayette, and MIL 03346 are 0.7-2.25 (Lodders, 1998; Barrat et al., 2006), with a  
342 calculated  $\epsilon^{182}\text{W}$  of  $3.13 \pm 0.30$  for Nakhla (Lee & Halliday, 1997) and of  $-2.95 \pm 0.08$  for MIL 03346  
343 (Wadhwa & Borg, 2006), thus demonstrating minor variation and minimal Hf-W isotope disturbance  
344 between these nakhlites.

345 The potential effects of terrestrial alteration on HSE abundances and Re-Os isotopic compositions  
346 are addressed in Section 4.3.1.

347

#### 348 ***4.2 – Origin of sulphur isotopic anomalies in sulphides of nakhlites***

349 The variation of  $\Delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  in the nakhlites, in reference to our dataset, could be due to  
350 differences in the chemistry of the atmosphere and surface or alteration by subsurface martian  
351 fluids (Farquhar et al., 2000; Franz et al., 2014). To have confidence in which of our nakhlite HSE and  
352 Re-Os isotope data are the most representative of the martian magma source(s) for nakhlite

353 meteorites, it is useful to know the extent to which each nakhlite might have been affected by  
354 regolith assimilation; where with 'regolith' we refer to heterogeneous, unconsolidated, and  
355 relatively superficial martian surface deposits.

356

#### 357 4.2.1 – Isotopic fractionation of $\Delta^{33}\text{S}$ in sulphides of nakhlites

358 Our analyses of Nakhla, Lafayette, MIL 090032, Y-000749, and Y-000593 sulphide grains gave mean  
359  $\Delta^{33}\text{S}$  values of  $-0.05 \pm 0.08 \text{ ‰}$ ,  $-0.09 \pm 0.12 \text{ ‰}$ ,  $-0.67 \pm 0.10 \text{ ‰}$ ,  $-0.10 \pm 0.15 \text{ ‰}$ , and  $-0.18 \pm 0.07 \text{ ‰}$ ,  
360 respectively (Fig. 4a). Assuming that some of these sulphide grains may be more isotopically  
361 fractionated than others, it is important to determine whether the sulphur isotopic signatures are  
362 representative of the sample as a whole, and if they are magmatic or non-magmatic in origin.

363 Appraisal of the petrographic characteristics of our studied samples prior to SIMS analyses showed  
364 that we sampled a representative set of pyrite and pyrrhotite grains in terms of textural associations,  
365 but that we observed a bias toward grains  $> 10 \mu\text{m}$  in size. Virtually, the magma involved in the  
366 generation of the nakhlites can be considered as affected by a degree of crustal assimilation  
367 coincident with eruption onto the martian surface (e.g., Franz et al., 2014). The challenge is to  
368 disentangle the degree to which the chemistries of the analysed nakhlites were affected by  
369 assimilation during the transit of magmas through Mars' crust and during eruptive processes.

370 Anomalous sulphur is constrained by its mass-independent fractionation (MIF) signature. Large  
371 variations in  $\delta^{34}\text{S}$  can modify the  $\Delta^{33}\text{S}$  of a sulphide by chemical mixing. However, it has been  
372 demonstrated that the values of  $\delta^{34}\text{S}$  in martian meteorites do not vary enough to be able to explain  
373 the observed variation in  $\Delta^{33}\text{S}$  (Farquhar et al., 2000; Farquhar et al., 2007; Franz et al., 2014).  
374 Detection of MIF or non-MIF signatures for sulphur could be constrained by the displacement of  
375 non-zero values of  $\Delta^{33}\text{S}$  for each meteorite analysed here, where a magmatic only  $\Delta^{33}\text{S}$  is  
376 characterized by near zero values (i.e.,  $\Delta^{33}\text{S} = 0$ ). Lafayette has zero ( $0.03 \pm 0.08\text{ ‰}$ ) to slightly  
377 negative ( $-0.26 \pm 0.08\text{ ‰}$ )  $\Delta^{33}\text{S}$  in its sulphide grains. This inter-grain variation in Lafayette is the  
378 largest heterogeneity in  $\Delta^{33}\text{S}$  of the meteorite dataset that we analysed, implying the presence of  
379 both non-MIF (i.e., magmatic) and MIF signatures (assimilation) in Lafayette sulphur. In the case of  
380 MIF signatures, these were likely induced by assimilation of regolith-derived sulphur (including  
381 regolith affected by brines) during emplacement of Lafayette lava flow on the martian surface.  
382 Though relevant for the present-day Mars, data from NASA's Curiosity rover shows a  $\delta^{34}\text{S}$  with a  
383 range far in excess of that observed among nakhlites ( $-47$  to  $28\text{ ‰}$ ; Franz et al., 2017), it is reasonable  
384 to conclude that these observations imply that the assimilation of even a small percentage of Mars'

385 regolith at the time of nakhlite formation could significantly shift the sulphur isotopic composition of  
386 these nakhlites (by several ‰).

387 For Nakhla we obtained a  $\Delta^{33}\text{S}$  equal to zero ( $-0.05 \pm 0.08\text{‰}$ ,  $n = 5$ ), suggesting a magmatic origin  
388 (non-MIF signature) for all sulphur in Nakhla. This value is in accordance with a previously reported  
389 mean  $\Delta^{33}\text{S}$  of  $0.06\text{‰}$  for Nakhla sulphides (Franz et al., 2014). However, Nakhla is internally variable  
390 and some of the studied sulphides show more negative  $\Delta^{33}\text{S}$ , with  $\Delta^{33}\text{S}$  as low as  $-0.33\text{‰}$  and  $-0.4\text{‰}$   
391 (Greenwood et al., 2000a,b; Franz et al., 2014). We report similar near zero values of  $\Delta^{33}\text{S}$  from the  
392 three sulphide grains in Y-000749 (average  $\Delta^{33}\text{S} = -0.10 \pm 0.15 \text{‰}$ ; with one sulphide having a  
393 magmatic  $\Delta^{33}\text{S} = 0.00 \pm 0.13 \text{‰}$ ) and from the sulphide grain in Y-000593 ( $\Delta^{33}\text{S} = -0.18 \pm 0.07 \text{‰}$ ).  
394 However, we were not able to analyse sulphide grains smaller than  $10 \mu\text{m}$  in these nakhlites and  $\Delta^{33}\text{S}$   
395 values may be somewhat internally variable. Based on the analysed sulphide grains, we suggest a  
396 non-primordial mantle sulphur signal but still a dominantly magmatic origin for the sulphur isotopic  
397 systematics of Nakhla, Y-000749, and Y-000593, without large extents of regolith assimilation during  
398 their magmatic emplacement. Miller Range 090032 represents the meteorite with the most marked  
399 MIF signatures in sulphide grains, with a negative mean  $\Delta^{33}\text{S}$  of  $-0.67 \pm 0.10\text{‰}$ , with wide variability  
400 between grains (Fig. 4). Large variability in  $\Delta^{33}\text{S}$  in sulphides of the Miller Range paired nakhlites is  
401 also in agreement with Franz et al. (2014) and Dottin III et al. (2018). These values suggest that  
402 sulphides in MIL 090032 are affected by MIF signatures, probably caused by secondary processes  
403 that occurred on Mars (Mikouchi et al., 2003), as suggested by Franz et al. (2014) for the paired  
404 stone MIL 03346. Secondary processing possibilities are explored below.

405

#### 406 4.2.2 – Isotopic fractionation of $\delta^{34}\text{S}$ in sulphides of nakhlites

407 The absence of crustal recycling on Mars may have been effective in leaving heterogeneous sulphur  
408 signatures on the surface. Sulphur isotope ratios can be fractionated by three main processes:  
409 hydrothermal (e.g., Ohmoto & Goldhaber, 1997), photochemical (e.g., Zmolek et al., 1999; Farquhar  
410 et al., 2001), and biological (e.g., Parnell et al., 2010). In addition to these processes, we discuss also  
411 possible magmatic processes that can fractionate  $\delta^{34}\text{S}$ . Large isotopic fractionations of  $\delta^{34}\text{S}$  have  
412 been investigated recently by the NASA's Curiosity rover from a 13 km long transect in Gale Crater  
413 (Franz et al., 2017). The measured  $\delta^{34}\text{S}$  ranged from  $-47 \pm 14 \text{‰}$  to  $28 \pm 7 \text{‰}$  (Fig. 4b); whether the  
414 negative values occurred in sulphides and the positive values occurred in sulphates or sulphites  
415 (mudstone and sandstone) is yet to be resolved. The reason Curiosity reported a greater range in  
416  $\delta^{34}\text{S}$  than that observed in martian meteorites is probably due to the accumulation of fine crustal  
417 materials in Gale crater following long periods of fluvial and/or aeolian transport.

418 Nakhlite sulphur isotopic signatures have been interpreted as reflecting both equilibrium  
419 fractionation in a warmed martian groundwater environment (low  $\delta^{34}\text{S}$ ) or atmospheric  
420 photochemical processes (high  $\delta^{34}\text{S}$ ) (Franz et al., 2017). In particular, the  $\delta^{34}\text{S}$  enrichment is  
421 reported to derive from atmospheric processing of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  via martian volcanic activity  
422 (processes capable of producing positive  $\delta^{34}\text{S}$  signatures) with subsequent incorporation of these  
423 products into the martian surface/subsurface (Franz et al., 2017, see Fig. 2). This was also deduced  
424 experimentally (Franz et al., 2013) and from oxidation of  $\text{SO}_2$  in volcanic ashes (Savarino, 2003).

425 Fractionation of  $\delta^{34}\text{S}$  differs for all the five nakhrites analysed here (Fig. 4b). However, it is important  
426 to notice that the  $\delta^{34}\text{S}$  variation could not be a full signature of the contaminant. It is possible that S  
427 loss processes can fractionate  $\delta^{34}\text{S}$ , and such processes would not be expected to significantly shift  
428 the  $\Delta^{33}\text{S}$ . Thus, the  $\delta^{34}\text{S}$  of the samples with the most anomalous  $\Delta^{33}\text{S}$  might reflect a different  
429 combination of processes, related to addition of sulphur, that would exert the first order control on  
430  $\Delta^{33}\text{S}$ , and then loss of sulphur that would exert a first order control on  $\delta^{34}\text{S}$  due to kinetic stable  
431 isotopic fractionation. Sulphides in Nakhla, Y-000749, and Y-000593 have the most convincing  
432 magmatic signatures, being characterized by a near zero mean  $\delta^{34}\text{S}$  (mean  $-1.59 \pm 0.10\text{‰}$ ,  $-1.18 \pm$   
433  $0.11\text{‰}$ , and  $-1.36 \pm 0.08\text{‰}$ , respectively), supported also from their magmatic  $\Delta^{33}\text{S}$  values described  
434 above. Conversely, MIL 090032 has an enriched  $\delta^{34}\text{S}$  (mean  $+10.54 \pm 0.09\text{‰}$ ), that is the largest  
435 intra-meteorite variation in sulphur isotopic fractionation and the largest positive  $\delta^{34}\text{S}$  value  
436 obtained in a martian material ( $+15.2 \pm 0.1\text{‰}$ ). These values suggest enrichment of  $\delta^{34}\text{S}$  due to  
437 martian atmospheric processes characterised by oxidation of  $\text{H}_2\text{SO}_4$  or photolysis of sulphur  
438 compounds (gases) introduced by volcanic eruptions and outgassing (Savarino, 2003; Franz et al.,  
439 2017). This finding is similar to reported measurements of  $\delta^{34}\text{S}$  fractionation close to the vents of  
440 terrestrial volcanoes ( $+7.7 \pm 0.8\text{‰}$ ; Mather et al., 2006).

441 Lafayette has the greatest  $\delta^{34}\text{S}$  depletion yet described for a martian meteorite (average of  $-10.7 \pm$   
442  $0.2\text{‰}$ ), with values of  $\delta^{34}\text{S}$  reaching  $-13.2 \pm 0.1\text{‰}$  – and lower than the Allan Hills (ALH) 84001,  $\delta^{34}\text{S}$   
443 values ( $\sim -9\text{‰}$ ) previously reported for pyrite grains (Greenwood et al., 2000a). These values are  
444 suggestive of late-stage equilibrium fractionation with martian groundwater, consistent with the  
445 Lafayette  $\Delta^{33}\text{S}$  results. Previous analysis of Lafayette reported values of  $\delta^{34}\text{S}$  of  $-3.2 \pm 2.1\text{‰}$   
446 (Greenwood et al., 2000b; Farquhar et al., 2000). The greater depletion in our  $\delta^{34}\text{S}$  values may reflect  
447 heterogeneous assimilation of sulphur from the martian regolith. Alternatively (or in addition),  
448 Lafayette sulphides have ‘spongy’ textures (Fig. 2c), which could be the product of alteration by  
449 shock melting with subsequent volatilisation effects (e.g., Gattacceca et al., 2013). Both Greenwood  
450 et al. (2000b) and Farquhar et al. (2000) proposed mixing of fluids with heavy ( $\delta^{34}\text{S} > 0$ ) and light

451 sulphur ( $\delta^{34}\text{S} < 0$ ) as a hydrothermal process that can produce negative  $\delta^{34}\text{S}$ . Some of the nakhlite  
452 lava flows may have been in contact with, or in close proximity, to a heavy sulphur source, while, in  
453 general, all may have been affected by mixing with fluids characterized by contrasting  $\delta^{34}\text{S}$  values.

454 At temperatures  $<1200^\circ\text{C}$  the magmatic degassing of  $\text{SO}_2$  can modify the sulphur isotope ratios of  
455 magmas (Sakai et al., 1982), depending on the  $f\text{O}_2$  (Carroll and Webster, 1994). Two cases are  
456 possible: 1) if  $f\text{O}_2 \gg$  quartz-fayalite-magnetite (QFM) buffer, sulphate is the dominant sulphur phase  
457 in the magma. The consequent equilibrium isotopic fractionation factor will be positive ( $\Delta\text{SO}_4^2-\text{SO}_2 >$   
458  $0$ ; Sakai et al., 1982), hence the residual melt is enriched in  $\delta^{34}\text{S}$  due to  $\text{SO}_2$  degassing, producing  
459 sulphides enriched in  $\delta^{34}\text{S}$ . 2) If  $f\text{O}_2 = \text{QFM}$  or  $f\text{O}_2 < \text{QFM}$  sulphide is the dominant sulphur phase in  
460 the magma, with consequent negative equilibrium isotopic fractionation factor ( $\Delta\text{S}_2-\text{SO}_2 < 0$ ; Sakai et  
461 al., 1982). In this way, the melt may become depleted in  $\delta^{34}\text{S}$ . This mechanism leads to crystallization  
462 of sulphides that are depleted in  $\delta^{34}\text{S}$ . Magmatic degassing could have been the cause of the positive  
463  $\delta^{34}\text{S}$  signature in MIL 090032, by shifting the  $\text{SO}_4$  in the silicate melt structure sulphates can be  
464 reduced to yield more positive  $\delta^{34}\text{S}$  values (see Labidi et al., 2015; Mandeville et al., 2009; Dottin III  
465 et al., 2018), that was subsequently reduced to form the sulphides.

466

#### 467 4.2.3 – Assimilation versus acquisition of Martian regolith during lava emplacement

468 The  $\Delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  values presented here (Fig. 4), along with the fact that nakhlite sulphides are  
469 associated with the mesostasis (hence are some of the last phases to crystallise) (Chevrier et al.,  
470 2011; Fig. 2), indicate assimilation of an S-rich martian regolith occurred within at least some of the  
471 nakhlite lava flows (Lafayette and MIL 090032). The range in  $\Delta^{33}\text{S}$  among the nakhlites may be  
472 broadly related to the total sulphur content of each lava flow, where nakhlites with larger  $\Delta^{33}\text{S}$   
473 anomalies were in proximity of a "sulphur source", contrary to nakhlites with smaller  $\Delta^{33}\text{S}$  anomalies  
474 (Dottin III et al., 2018). This sulphur source could be represented by the S-rich martian regolith (Foley  
475 et al., 2003). Sulphides also occur in several different sizes and modal abundances in all nakhlite  
476 meteorites. In the meteorite samples studied sulphide grain sizes range from  $10\ \mu\text{m}$  to  $250\ \mu\text{m}$  (Fig.  
477 2). The recently recovered nakhlite Caleta el Cobre 022 has unusually abundant and coarse grained  
478 pyrrhotite (up to  $200\ \mu\text{m}$ ) (Gattacceca et al., 2018). These inter-meteorite differences in sulphide  
479 grain sizes are therefore further evidence to support the suggestion that sulphur-rich material was  
480 acquired at different points of lava extrusion on the martian surface.

481 Nakhla and the two Yamato nakhlites contain dominantly magmatic sulphur isotope signatures (near  
482 zero  $\Delta^{33}\text{S}$  and  $\delta^{34}\text{S}$ ), indicating a lack of regolith incorporation. A  $^{17}\text{O}$  excess of sulphate in Nakhla



483 reportedly suggests it spent a significant period of time in contact with the Martian atmosphere  
484 (Farquhar et al., 2000). The simplest way of reconciling this atmospheric exposure with minimal  
485 regolith uptake is to place Nakhla at the top of a lava flow. Alternatively, it could have been present  
486 inside the carapace of a lava tube, where the main flow is in contact with the surface and easily  
487 acquires sulphide/sulphate material from the Martian regolith while the carapace of the lava tube is  
488 never in contact with the regolith but can be in contact with the atmosphere. This hypothesis could  
489 also explain the regolith uptake of MIL 090032, if it was part of the main lava tube. These two  
490 nakhlites have the same age (within uncertainty; Cohen et al., 2017), but they have different  $\delta^{34}\text{S}$   
491 (Nakhla =  $-1.59 \pm 0.10 \text{ ‰}$ , MIL 090032 =  $+10.54 \pm 0.09 \text{ ‰}$ ). This lava emplacement scenario is  
492 supported by the quench-textured mesostasis of MIL 090032 and the other paired MIL nakhlites,  
493 indicating surface exposure (Hallis and Taylor, 2011), possibly as a break-out event at the front or  
494 side of the lava flow (Hammer, 2009). Further, skeletal mineral phases, glass, and thin hedenbergite  
495 pyroxene rims in the MIL nakhlites has been taken as evidence of the fastest cooling rate among all  
496 the nakhlites ( $6 \text{ °C/h}$ ) (Hammer and Rutherford, 2005; Day et al., 2006). Alternatively, if the MIL  
497 nakhlites and Nakhla are not from the same lava flow, mineralogical evidence suggests that after  
498 quenching the MIL nakhlite lava flow may have been blanketed with another flow that slowed down  
499 the cooling rate (Domeneghetti et al., 2013) - this flow may have been that containing Nakhla.

500

#### 501 4.2.4 – $\Delta^{33}\text{S}$ of the nakhlite mantle source

502 Nakhla and the two Yamato meteorites have  $\delta^{34}\text{S}$  close to zero, and the smallest fractionation of  
503  $\Delta^{33}\text{S}$ . This signature is interpreted to have a magmatic origin, hence these meteorites represent the  
504 least isotopically disturbed of the nakhlites analysed here (from a sulphur isotope perspective), and  
505 by inference the most appropriate to constrain a possible  $\Delta^{33}\text{S}$  for the nakhlite mantle source region.  
506 The average  $\Delta^{33}\text{S}$  value obtained for Nakhla, Yamato 000749, and Yamato 000593 sulphide grains is -  
507  $0.1 \pm 0.09 \text{ ‰}$ . This is slightly more negative than the shergottite mantle source value ( $\Delta^{33}\text{S}$  of  $0.009$   
508  $\text{ ‰}$ ) calculated by Franz et al. (2014), possibly due to the fact that different mantle reservoirs were  
509 involved in the genesis of the shergottites and the nakhlites (e.g., Harper et al., 1995; Lee and  
510 Halliday, 1997; Wadhwa, 2001; Jones et al., 2003; Foley et al., 2005).

511 It is unlikely that a  $\Delta^{33}\text{S}$  of a mantle reservoir shifted by  $0.1 \text{ ‰}$  from an initial value of zero. Instead,  
512 we attribute this  $\Delta^{33}\text{S}$  value to contamination by mass-independent sulphur that would have  
513 originated in the martian atmosphere (Farquhar et al., 2000). It is conceivable that such atmospheric  
514 sulphur ( $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ), after its deposition as oxidized sulphur on the martian surface, could have  
515 affected the source of the nakhlite magmas by mobilization beneath the martian crust due to

516 geochemical cycling, therefore suggesting the presence of a shallow magma chamber for the  
517 generation of the nakhlites.

518

### 519 ***4.3 – Constraining the magmatic and chemical-physical processes in controlling Re-Os isotope*** 520 ***systematics and HSE***

521 Several different chemical-physical processes may have influenced the HSE-abundance Re-Os  
522 isotope systematics of the nakhlites. These processes can be distinguished essentially as: low-  
523 temperature disturbance(s), post-crystallization impact disturbance, and HSE partitioning under  
524 magmatic conditions. To discriminate which of these processes may have affected each of our  
525 samples, and to what degree, we discuss each sequentially and begin by appraising those processes  
526 that could modify the HSE and Re-Os isotope chemistry of a magmatic sample after its  
527 crystallisation.

#### 528 *4.3.1 – Low-temperature and post-crystallization impact disturbance*

529 Late-stage open-system effects on nakhlite HSE due to alteration on Mars' or Earth's surface have  
530 the potential to disturb nakhlite Re-Os isotope systematics and to mobilise and/or add HSE present  
531 in potentially susceptible phases. For example, the possibility of low-temperature alteration in  
532 deserts could result in the addition of Re (Peucker-Ehrenbrink and Jahn, 2001) (Fig. 3). However,  
533 there is limited variation of inter-element HSE ratios and we conclude that nakhlite HSE-abundance  
534 has not been significantly affected by low-temperature alteration on Earth or Mars after their  
535 magmatic crystallisation.

536 Impact disturbance as considered here refers to the process(es) through which materials of  
537 chondritic composition are transferred to martian magmatic materials due to impacts/shock events  
538 after their crystallisation. Such processes are capable of enriching the sample toward chondrite-  
539 relative HSE abundances following magmatic crystallisation (e.g. as was observed by Riches et al.  
540 2012). All studied nakhlites are characterised by highly fractionated HSE patterns relative to CI-  
541 chondrite (e.g., Pd/Os = 19.6 to 131.3), have relatively low total osmium abundances (< 0.08 ppb),  
542 and suprachondritic  $^{187}\text{Os}/^{188}\text{Os}$  (0.18 to  $0.45 \pm 0.0010$ ). These nakhlite HSE characteristics do not  
543 tend toward a potential chondritic contaminant and thereby preclude significant late-stage  
544 modification of the studied samples by chondritic materials on the martian surface or during their  
545 impact liberation.

546

547 *4.3.2 – Magmatic processes*

548 All three nakhlites analysed in this work display similar HSE patterns. It is unlikely that these  
549 similarities in HSE patterns are the product of alteration on Earth or Mars, instead these primarily  
550 reflect magmatic fractionation during formation of the nakhlite parent magma(s) and lava  
551 crystallisation. These nakhlite HSE characteristics indicate that the incorporation of small amounts of  
552 martian regolith (as testified by S-isotope systematics) resulted in a generally negligible modification  
553 to the nakhlite HSE inventory, suggesting a low HSE abundance of the martian regolith. Had  
554 significant contributions of regolith modified the overall HSE abundances of the studied nakhlites,  
555 we would anticipate variable HSE systematics among the nakhlites and a degree of correlation with  
556 sulphide S-isotope compositions. Such nakhlite HSE variability and a clear relationship to  
557 corresponding sulphide S-isotope systematics is lacking. However, Os-isotope compositions of  
558 nakhlites are variable and are decoupled from the overall nakhlite HSE-abundance systematics. The  
559 intra-sample variability in Re concentration and Os-isotopic composition testified by two Nakhla  
560 fractions (0.117 ppb, this work; 0.052, Brandon et al., 2000) supports perturbation of the Re-Os  
561 isotope systematics in these martian magmas, but with little consequent effect to the abundances of  
562 Os, Ru, Ir, Pt, Pd, ± Au. Such a process requires interaction with a martian regolith of variable Re  
563 content and low Os abundance, but with highly radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ( $> 0.7$  at total HSE abundances  
564 much less than 2 ppb and with 0.005 ppb Os in the ancient martian regolith) such that a small  
565 proportion of assimilated material has perturbed the Os-isotopic signature of the nakhlite lava flows.  
566 Fractionation of HSE during partial melting of the mantle and during possible late-sulphide  
567 saturation in evolved magmas will change HSE inventories in different ways (Jones et al., 2003; Sun  
568 et al., 2003; Fonseca et al., 2007; Mallmann & O'Neill, 2007). In the following sub-paragraphs we  
569 explore these possible processes.

570

571 *4.3.2.1 – Magmatic fractionation of HSE from the nakhlite and shergottite mantle source*

572 Regression approaches using MgO content have been used to infer Mars mantle composition and  
573 give similar abundances of Re, Os, Ir, and Ru for the mantle of Earth and Mars (e.g., Warren et al.,  
574 1999; Tait and Day, 2018). In addition, martian meteorites are characterised by Re abundances that  
575 are high, somewhat close to the terrestrial basalts, and define a broad anti-correlation of HSE  
576 abundances with the degree of magmatic evolution (e.g., Jones et al., 2003). Several prior studies  
577 have appraised martian magmatic process through the HSE abundances of martian meteorites (e.g.  
578 Warren et al., 1999; Jones et al., 2003; Riches et al., 2011; Brandon et al., 2012; Dale et al., 2012;  
579 Filiberto et al., 2012; Tait et al., 2015; Tait and Day, 2018). In general, what the HSE datasets of these

580 previous studies show are CI-normalised HSE patterns that vary from absolutely flat to increasingly  
581 fractionated (elevated Pd/Os) with decreasing total HSE abundance.

582 Nakhla, Lafayette, and MIL 090032 all show broadly similar HSE patterns (Fig. 3a). Though previous  
583 data showed that Nakhla and Chassigny are similar in their HSE patterns (Jones et al., 2003), here  
584 isotope dilution approaches show that Nakhla has more Pd and Re relative to Chassigny and that  
585 Lafayette and MIL 090032 are very similar to this pattern, rather than the HSE pattern of Chassigny.  
586 These substantial differences in the HSE fractionation evident among different classes of martian  
587 meteorite and thus their magmas, extended also to shergottite groups. Primitive shergottites  
588 (Mg/Mg+Fe > 0.7) have high Os/Pt, Ir/Pd and Ru/Pt (Brandon et al., 2012; Tait and Day, 2018). A  
589 broadly similar pattern was observed for the high MgO shergottites (Mg/Mg+Fe = 0.5-0.7), but with  
590 higher Re/Pt and Re/Pd than the primitive shergottites. Nakhrites analysed here diverge from the  
591 patterns of the primitive and high MgO shergottites in terms of relative abundances, but they  
592 approach the HSE patterns of the intermediate/low MgO shergottites having high Re/Ir, Pt/Ir, and  
593 Pd/Ru (Fig. 5). These differences could reflect different initial magmatic conditions between the  
594 nakhlite and shergottite parental melt(s), as for example, melting temperature,  $fO_2$ , and parental  
595 melt composition (including sulphur concentration and its relation to the point of sulphide  
596 saturation). We address the possible late-stage sulphide saturation as well as potential involvement  
597 of residual alloys during the production of magmas parental to nakhlite lavas below.

598

#### 599 *4.3.2.2 - HSE fractionation due to late-stage sulphide saturation and residual alloys formation*

600 Sulphides, silicate phases, and spinel can control the geochemical behaviour of the HSE during  
601 partial melting (Fonseca et al., 2007; Mallmann & O'Neill, 2007), with Os inclined to be partitioned  
602 into sulphide melts (Brenan, 2008). The solubility of Os and Ir has been constrained experimentally  
603 in sulphide melts, over a range of  $fO_2$  ( $-1.5 < QFM < +1.5$ ) and  $fS_2$  (Iron-Wüstite (IW)  $\sim -1$ ) at  $T =$   
604  $1300^\circ\text{C}$  (Fonseca et al., 2011). It is important to take into account that these experimental  
605 approaches can generally only replicate batch melting, and that a fractional melting scenario ( $\pm$   
606 aggregation of those fractional melts) may be applicable to both ancient and recent martian  
607 magmatic systems. Nevertheless, experimental approaches provide a useful framework through  
608 which we can infer key aspects of nakhlite petrogenesis. The outcome of these experiments has  
609 shown that Os and Ir have low solubilities in silicate melts and that high  $fO_2$  conditions can inhibit  
610 the solubility of Os and Ir in sulphide melts (Fonseca et al., 2011). Oxygen fugacity for nakhlites is  
611 higher than shergottites. For Nakhla,  $fO_2$  is equal to the quartz-fayalite-magnetite (QFM) oxygen  
612 buffer (at an equilibration temperature of  $810^\circ\text{C}$ ) while for Lafayette the  $fO_2$  is equal to QFM +0.1

613 (at an equilibration temperature of 780° C; Szymanski et al., 2010). For MIL 03346 (paired with MIL  
614 090032) the proportion of Fe<sup>3+</sup> in augite was found to be in agreement with high-temperature  
615 equilibration near the QFM buffer (Dyar et al., 2005). Conversely, estimated  $fO_2$  for the shergottites  
616 are low and varies from -1 to -4 QFM (e.g., Herd, 2003). These differences in  $fO_2$  would limit the  
617 solubility of Os and Ir in nakhlite sulphide melts, due to their higher  $fO_2$  than shergottites.

618 Residual alloys crystallised from parental melts and the formation of platinum group minerals  
619 throughout a magmatic column are able to control fractionation of Os, Ir, Ru, Rh, Pt, and Pd during  
620 magma genesis (Mungall and Brenan, 2014). In particular, Mungall and Brenan (2014) reported how,  
621 at low pressure, partial melting of Earth's mantle retains HSE in chondritic relative abundances (if  
622 correct as the starting proportions of these elements) until complete sulphide saturation, then  
623 evolving to very high Pt/Pd and low Pd/Ir - due to Pt and Ir alloy formation in the restite phase.  
624 Ruthenium, Os, and Ir are thought to be initially present in parts per million abundances in mantle  
625 sulphide melts, then, a decrease in  $fS_2$  during partial melting leads to the exolution of Ru-Os-Ir alloys  
626 from a refractory residue in the mantle (Fonseca et al., 2012). In particular, a sulphide melt appears  
627 to be required for Os-rich alloy formation since Os is likely the element that triggers the exolution of  
628 the Ru-Os-Ir alloys (Fonseca et al., 2012).

629 As described above, the higher  $fO_2$  in Nakhla, Lafayette, and MIL 090032 likely prevented the  
630 solubility of Os and Ir in possible late-stage sulphide melts, inducing formation of Pt- and Ir-alloys in  
631 the restite phase. Accordingly to Fonseca et al. (2011), the higher solubility of Os and Ir at high  $fO_2$   
632 would imply the existence of a melt saturated in sulphides (sulphide melt) for the generation of the  
633 nakhlite parent magmas. In contrast to nakhlite magmas, for which present data sets and constraints  
634 are relatively limited, it is well established that the parent magmas of the relatively well-studied  
635 shergottites were sulphide-undersaturated in their mantle sources (Wang and Becker, 2017). In  
636 particular, Pd/Pt in shergottites tend to reflect chondritic abundances, but this is not the case for Os-  
637 Ir-Ru, as indicated by suprachondritic Pd/Ir or Pt/Ir (Wang and Becker, 2017). The reason of this  
638 difference could be attributed to the formation of residual alloys of Os-Ir-Ru in the martian mantle  
639 (similar to the Earth's mantle; e.g., Fonseca et al., 2012 and references therein).

640

#### 641 ***4.4 – Implications for nakhlite mantle source and early Mars differentiation***

642 Mantle heterogeneities have been proposed for Mars based on the trace element and <sup>182</sup>Hf-<sup>182</sup>W,  
643 <sup>146</sup>Sm-<sup>142</sup>Nd, <sup>87</sup>Rb-<sup>87</sup>Sr, and <sup>187</sup>Re-<sup>187</sup>Os isotope systematics of magmatic products represented by  
644 martian meteorites (e.g., Harper et al., 1995; Lee and Halliday, 1997, 1995; Brandon et al., 2000,

645 2012; Wadhwa, 2001; Herd, 2003; Jones et al., 2003; Foley et al., 2005; Debaille et al., 2008, 2009;  
646 Herd et al., 2017; Lapen et al., 2017; Tait and Day, 2018; Day et al., 2018). In general, at least four  
647 mantle reservoirs have been previously argued to exist on Mars: two for the shergottites, one for the  
648 nakhlites/chassignites, and one for NWA 8159. These different mantle domains can be tapped by  
649 magmas and these magmas can mix producing different compositions as noticeable from the  
650 different groups of martian meteorites.

651 Magma mixing phenomena have been argued to be responsible of the generation of the depleted  
652 and enriched shergottites (Borg et al., 1997; Wadhwa, 2001; Herd, 2003; Borg and Draper, 2003;  
653 Shearer et al., 2008). However, the clear isotopic gaps that are present for their lithophile elements  
654 (Ferdous et al., 2017) are difficult to reconcile with magma mixing, since this process would not  
655 result in large isotopic gaps. This is especially noticeable for the nakhlites since they do not present  
656 clear signs of disequilibrium textures in their mineral assemblages. Instead, we propose a single  
657 magma composition for the generation of the nakhlites (as also suggested by their trace element  
658 compositions; Udry and Day, 2018), whether after the Nakhla eruption assimilation with an  
659 unknown enriched component affected the nakhlite source during 61 Myr, producing subsequently  
660 the Lafayette parent melt at  $1321 \pm 9$  Ma (ages accordingly to Cohen et al., 2017).

661 Assimilation of crustal materials with markedly elevated  $^{187}\text{Re}/^{188}\text{Os}$  could be a cause of the higher  
662  $^{187}\text{Re}/^{188}\text{Os}$  of Nakhla in respect to Lafayette. This enriched component possibly included ancient  
663 (primordial?) crustal materials, with consequent highly radiogenic Os isotopic compositions for  
664 which a very small fraction would significantly shift a magmatic Os isotopic signature but with  
665 potentially negligible effects on HSE abundances. On the other hand, this characteristic could also  
666 reflect phenomena of mantle metasomatism as recently argued for Mars magmatism (Day et al.,  
667 2018), or even inheritance from an interior reservoir that experienced variable earlier magmatic  
668 fractionation resulting in reservoirs with long-term high  $^{187}\text{Re}/^{188}\text{Os}$  and/or complementary low  
669  $^{187}\text{Re}/^{188}\text{Os}$ .

670 Mixing within mantle sources or enriched cumulates may have happened during early differentiation  
671 of Mars. By following this logic, the enriched crustal component of our hypothesis likely can be  
672 represented by a component generated during the last stages of a martian magma ocean (MMO).  
673 This possibility has been investigated for Nakhla and Lafayette by looking at their  $^{187}\text{Os}/^{188}\text{Os}$  versus  
674 Nd and Sr isotope distributions. The  $\gamma\text{Os}$  versus  $\epsilon^{143}\text{Nd}$  constrain a possible end-member for the  
675 nakhlite source mixing. The calculated  $\gamma\text{Os}$  and  $\epsilon^{143}\text{Nd}$  values of the primitive martian crust and the  
676 evolved Martian crust at 180 Ma from Brandon et al. (2000) and Norman (1999) were used (Fig. 6).  
677 The distribution of the nakhlites in respect to the primitive and evolved martian crust is inconsistent

678 with their magma sources being affected by assimilation of modern martian crust. The  $\gamma$ Os vs.  $\epsilon^{143}\text{Nd}$   
679 appear instead decoupled suggesting preferential/selective mixing of the nakhlite reservoir with an  
680 unknown enriched component that must have occurred early during Mars differentiation, possibly  
681 represented by assimilated ancient MMO cumulates. However, drawing conclusions from the initial  
682  $\gamma$ Os for Nakhla and Lafayette are currently thwarted by large uncertainties for these relatively  
683 ancient magmas with low Os abundances. Similarly, the correlation between  $\epsilon^{143}\text{Nd}$  and  $\gamma$ Os in  
684 shergottites suggested that the endmember sources were generated by mixing between residual  
685 melts and cumulates during the crystallization stages of a MMO (Debaille et al., 2008; Brandon et al.,  
686 2012).

687 Mixing within MMO cumulates and evolved liquids may explain our observed Re-Os isotope  
688 systematics as seen in Nakhla and Lafayette, as well as previously reported Rb and Sr isotope  
689 systematics. In fact, sulphides crystallisation from the last stage of MMO's melts could result in  
690 locally fractionated  $^{187}\text{Re}/^{188}\text{Os}$  within the martian mantle thereby presenting the possibility to trace  
691 different mantle reservoirs and to discern this from assimilation of primordial crust characterized by  
692 long-term elevated  $^{187}\text{Re}/^{188}\text{Os}$ . In addition, the first MMO cumulates that crystallize would be  
693 extremely depleted in REE, Rb and Sr, with the last more evolved liquids characterised by a  $\epsilon^{142}\text{Nd}$  of  
694 +0.64 (Debaille et al., 2009).

695 Magma ocean overturn could explain the early formation and isolation of these different local  
696 heterogeneities in the martian mantle (Debaille et al., 2009; Bouvier et al., 2018). This process likely  
697 happens as a result of instabilities due to the density stratification that occurs during the  
698 crystallisation of magma oceans on terrestrial planets (Elkins-Tanton et al., 2003).

699

## 700 **5 – Conclusions**

701 Sulphur isotopic compositions were determined for sulphides in five nakhlites to ascertain the  
702 degree to which they have been affected by assimilation of the martian regolith. Nakhla, Yamato  
703 000749, and Yamato 000593 are the meteorites that have most faithfully retained a magmatic  
704 signature, and which are therefore the most reliable for using osmium isotopes and HSEs to reveal  
705 the nature of nakhlite petrogenesis. For the first time, Re-Os isotope systematics and HSE  
706 abundances have been investigated for two different nakhlites, to constrain the degree to which  
707 they have been affected by crustal assimilation and the ability of martian meteorite HSE to testify to  
708 Mars' interior composition. The following results have been obtained:

709 (1) The Lafayette and MIL 090032 lava flows acquired S-rich martian regolith material that carry  
710 information about martian atmospheric and hydrological processes. Results show that UV-  
711 photochemistry and hydrothermal processes are the main cause of  $\Delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  fractionation. This  
712 result may have implications for the nature of the martian atmosphere and hydrothermal activity  
713 prior to nakhlite eruption.

714 (2) Nakhla, Yamato 000593, and Yamato 000749 retained a magmatic signature in their sulphides,  
715 and were unaffected by assimilation of martian regolith. Using these meteorites we estimate the  
716  $\Delta^{33}\text{S}$  of the nakhlite source to be -0.1 ‰.

717 (3) Nakhlite HSE patterns are in agreement with the presence of a sulphide melt involved in nakhlite  
718 petrogenesis. Ruthenium-Os-Ir alloys likely formed in this sulphide-saturated melt and controlled the  
719 abundances of Ru, Os, Ir in the final lava products.

720 (4) Our Re-Os isotope data for nakhlites hint at perturbation and potential decoupling of nakhlite  
721  $^{187}\text{Os}/^{188}\text{Os}$  isotope systematics from other isotopic systems as a result of small degrees of  
722 assimilation of an S-rich regolith with low total HSE contents but highly radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ( $> 0.7$   
723 at total HSE abundances much less than 2 ppb and with 0.005 ppb Os in the ancient martian  
724 regolith).

725 (5) Nakhlites formed from a primary magma that we consider to have been generated from a well-  
726 mixed martian mantle that subsequently (at some point after the Nakhla emplacement) assimilated  
727 an enriched component during ascent toward the surface, and where this enriched mantle material  
728 was potentially represented by a late-stage crystallization cumulate from a martian magma ocean.

729

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743

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1034 **Figure caption**

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1036 **Figure 1** – Backscatter electron (BSE) images, along with false-colour Fe-Mg-Si-S X-ray elemental  
1037 maps of the nakhlite chips used to retain information on the crystallographic features of our samples  
1038 prior to destructive analyses for HSE abundances and Os isotopic compositions. The colour-coded  
1039 elemental key is given at the bottom left of each X-ray image – olivine appears green to red,  
1040 sulphide/sulphate appears yellow, clinopyroxene appears cyan, and mesostasis appears dark blue.  
1041 (a) BSE image and X-ray map of Nakhla. In both images a 0.3 mm long sulphate is evident at the  
1042 bottom right corner, and salt is highlighted in purple in the BSE image; (b) BSE image and X-ray map  
1043 of Lafayette; (c) BSE image and X-ray map of MIL 090032. Ol, olivine; px, pyroxene; s, sulphate; me,  
1044 mesostasis.

1045

1046 **Figure 2** – Backscatter electron (BSE) images of sulphides in Nakhla, Lafayette, and MIL 090032  
1047 showing their petrographic relationships with the other minerals. Sulphides that have been selected  
1048 for sulphur isotopic analysis are rimmed in yellow. A) pyrrhotite (Po) grain in Nakhla; B, C) Pyrite (Py)  
1049 grains in Lafayette; D) pyrrhotite grain in MIL 090032. Po, pyrrhotite; Py, pyrite; Px, pyroxene  
1050 (augite); Mag, magnetite; me, mesostasis.

1051

1052 **Figure 3** – Highly siderophile element (HSE) abundances and Re-Os isotope systematics in nakhlites.  
1053 (a) CI chondrite normalized HSE data for Nakhla, Lafayette, and MIL 090032 are shown, along with  
1054 previously published data in grey (from Jones et al., 2003; Dale et al., 2012); (b)  $^{187}\text{Re}/^{188}\text{Os}$  vs.  
1055  $^{187}\text{Os}/^{188}\text{Os}$  data for Nakhla and Lafayette are shown, along with previous literature data (from  
1056 Brandon et al., 2000; Dale et al., 2012). The 1.3 Ga reference line is shown for comparison and  
1057 represents single-stage Re–Os isotope evolution from a chondritic  $^{187}\text{Os}/^{188}\text{Os}$  reservoir, assuming a  
1058 Solar System initial  $^{187}\text{Os}/^{188}\text{Os} = 0.9524$  (Smoliar et al., 1996). Uncertainty =  $2\sigma$ , vertical error bars  
1059 are less than symbol size.

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1061 **Figure 4** – Sulphur isotope ratios for the nakhlites, compared with previous data from Martian  
1062 meteorites and Mars rover missions data. (a)  $\delta^{34}\text{S}$  vs.  $\Delta^{33}\text{S}$  isotope ratios for the nakhlites analysed in  
1063 this work, compared with the same nakhlites analysed by previous authors. Labels serve to  
1064 emphasise which processes are inferred to have affected the sulphur isotopic composition of each

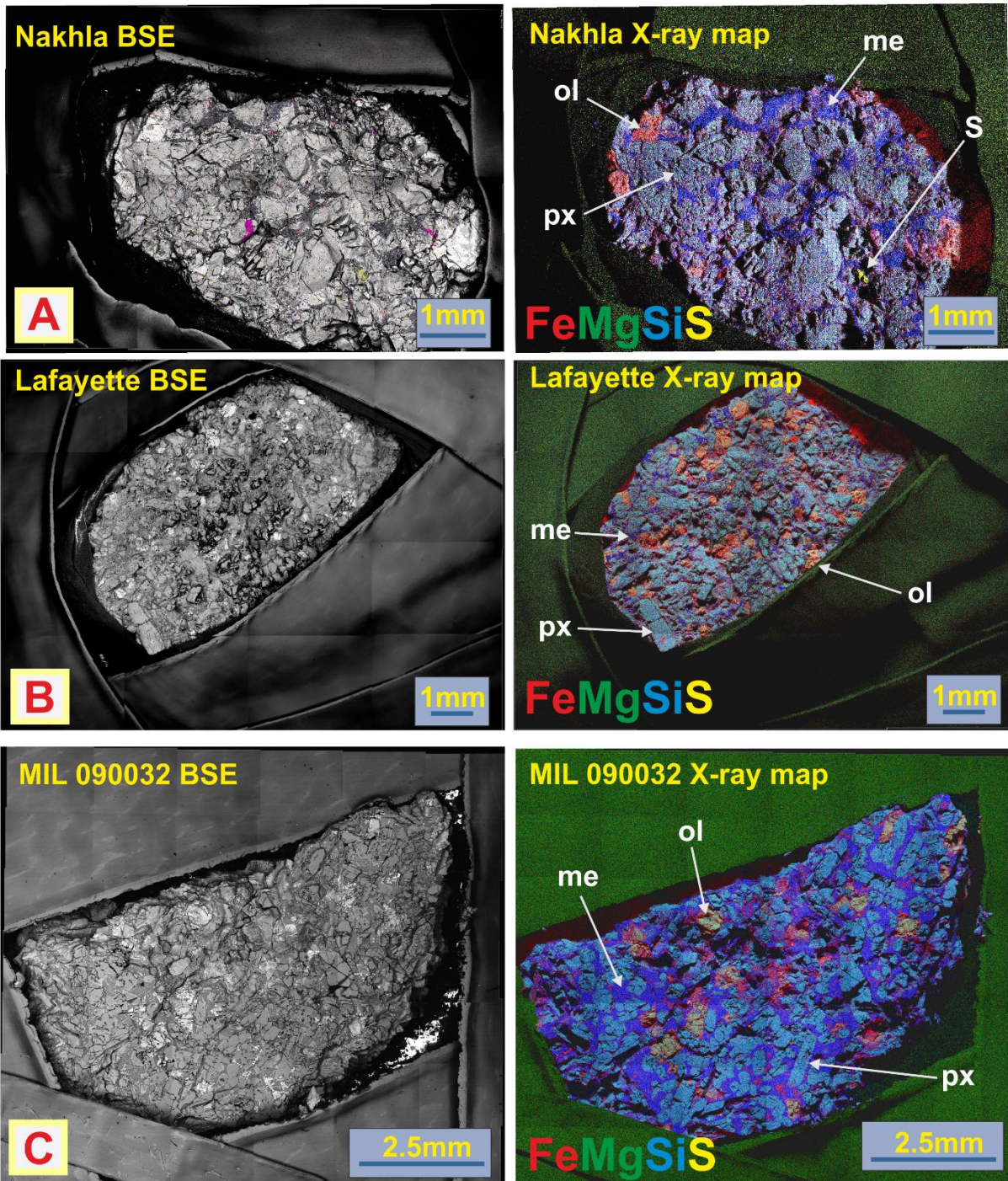
1065 data cluster.  $2\sigma$  uncertainties are shown, with X-axis uncertainties smaller than the symbols; (b)  
1066 Comparison of  $\delta^{34}\text{S}$  value between the present study (yellow symbols) and literature data from  
1067 martian meteorites (Farquhar et al., 2000; Greenwood et al., 2000a; Franz et al., 2014; Franz et al.,  
1068 2017) and the Curiosity rover (Franz et al., 2017). The  $\delta^{34}\text{S}$  value of the martian mantle (from Franz  
1069 et al., 2014) is shown by the dashed line. The red box identifies the nakhlites that have a  $\delta^{34}\text{S}$  very  
1070 close to the martian mantle  $\delta^{34}\text{S}$  value and so have been least affected by regolith assimilation  
1071 (Nakhla, Y-000749, and Y-000593). Some of the data used in the graphs are from previous studies  
1072 (Farquhar et al., 2000; Greenwood et al., 2000a; Franz et al., 2014; Franz et al., 2017).

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1074 **Figure 5** – Cl chondrite normalized HSE abundance comparison between nakhlites, primitive  
1075 shergottites ( $\text{Mg}/\text{Mg}+\text{Fe} = > 0.7$ ), high MgO shergottites ( $\text{Mg}/\text{Mg}+\text{Fe} = 0.5-0.7$ ), shergottites with  
1076 intermediate MgO ( $\text{Mg}/\text{Mg}+\text{Fe} = 0.4-0.5$ ), and low MgO shergottites ( $\text{Mg}/\text{Mg}+\text{Fe} < 0.4$ ). (a)  $(\text{Pt}/\text{Ir})_N$   
1077 vs.  $(\text{Pd}/\text{Ir})_N$ ; (b)  $(\text{Os}/\text{Ir})_N$  vs.  $(\text{Re}/\text{Ir})_N$ . The nakhlites plot closest to the low MgO shergottites in (a), and  
1078 within the scatter of these shergottites in (b). Highly siderophile element data for shergottites are  
1079 from Jones et al. (2003), Riches et al. (2011), Brandon et al. (2012), Dale et al. (2012), and Tait and  
1080 Day (2018).

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1082 **Figure 6** – Initial YO<sub>s</sub> vs.  $\epsilon^{143}\text{Nd}$  for nakhlites used to identify a possible end-member for the nakhlite  
1083 source mixing. The primitive martian crust and the evolved martian crust at 180 Ma are plotted with  
1084 values taken from Brandon et al. (2000) and Norman (1999). The plotted samples follow a direction  
1085 that diverge from the martian crust evolution (here represented by the dashed line), thus implying  
1086 that the mixing end-member is likely represented by a different enriched component (dashed box)  
1087 rather than the evolved martian crust. Alternatively, decoupling of the data could suggest that the  
1088 YO<sub>s</sub> is a sensitive tracer of strictly different process to that which  $\epsilon^{143}\text{Nd}$  provides evidence –  
1089 potentially recording involvement of early martian crust whereas  $\epsilon^{143}\text{Nd}$  may be more effective in  
1090 probing the nature of nakhlite mantle reservoirs. Error bars are less than symbol size. As the  
1091 calculated YO<sub>s</sub> in Lafayette and Nakhla is negative and below the Solar System initial of Smoliar et al.  
1092 (1996) disturbance of the Re-Os isotope system in these samples has taken place (linked to crustal  
1093 contamination). For these reasons, the strongly negative calculated YO<sub>s</sub> should be considered as an  
1094 extreme minimum at  $\sim 1.4$  Ga. Unperturbed samples, not impacted by crustal assimilation, would  
1095 likely have been derived from internal reservoirs characterized by higher YO<sub>s</sub> at that time (blue  
1096 arrow).



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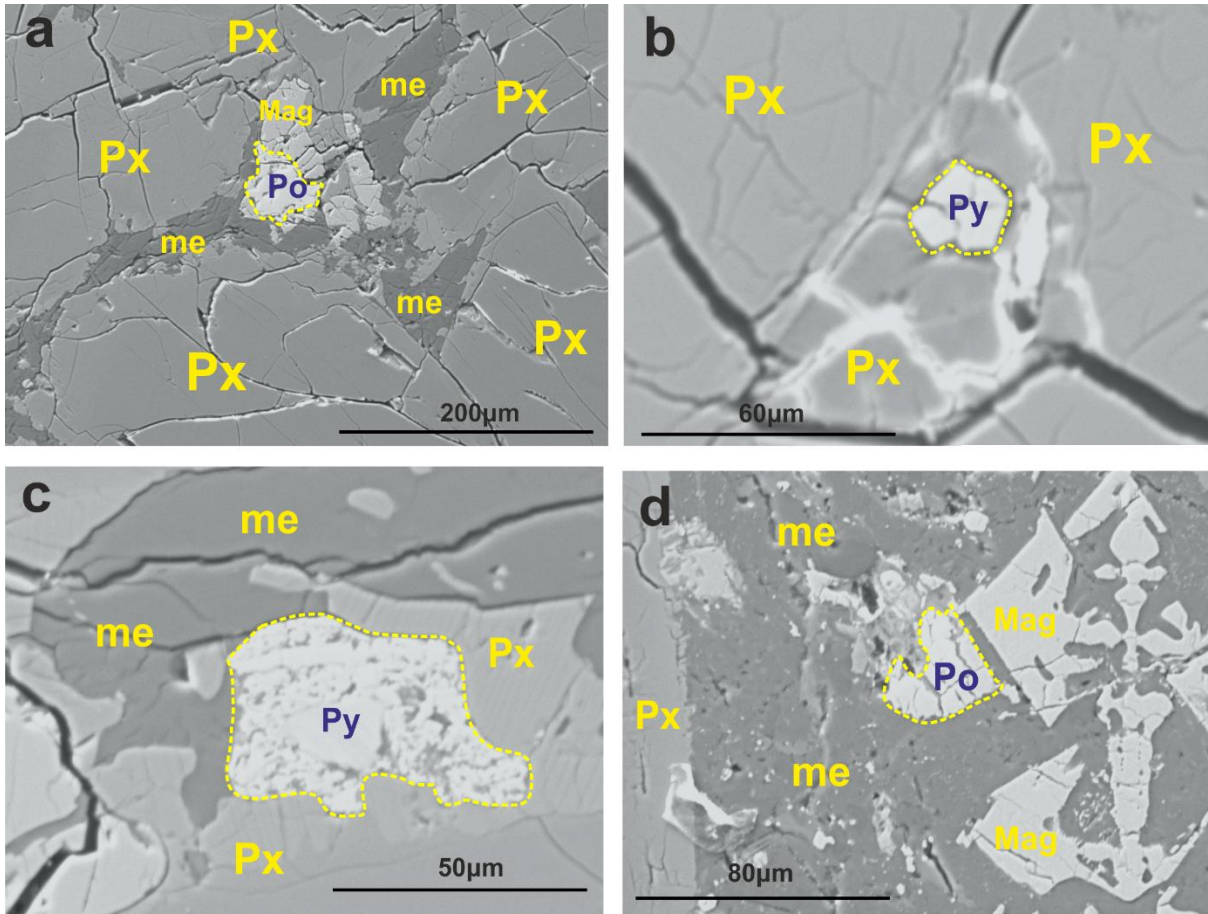
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Fig. 1

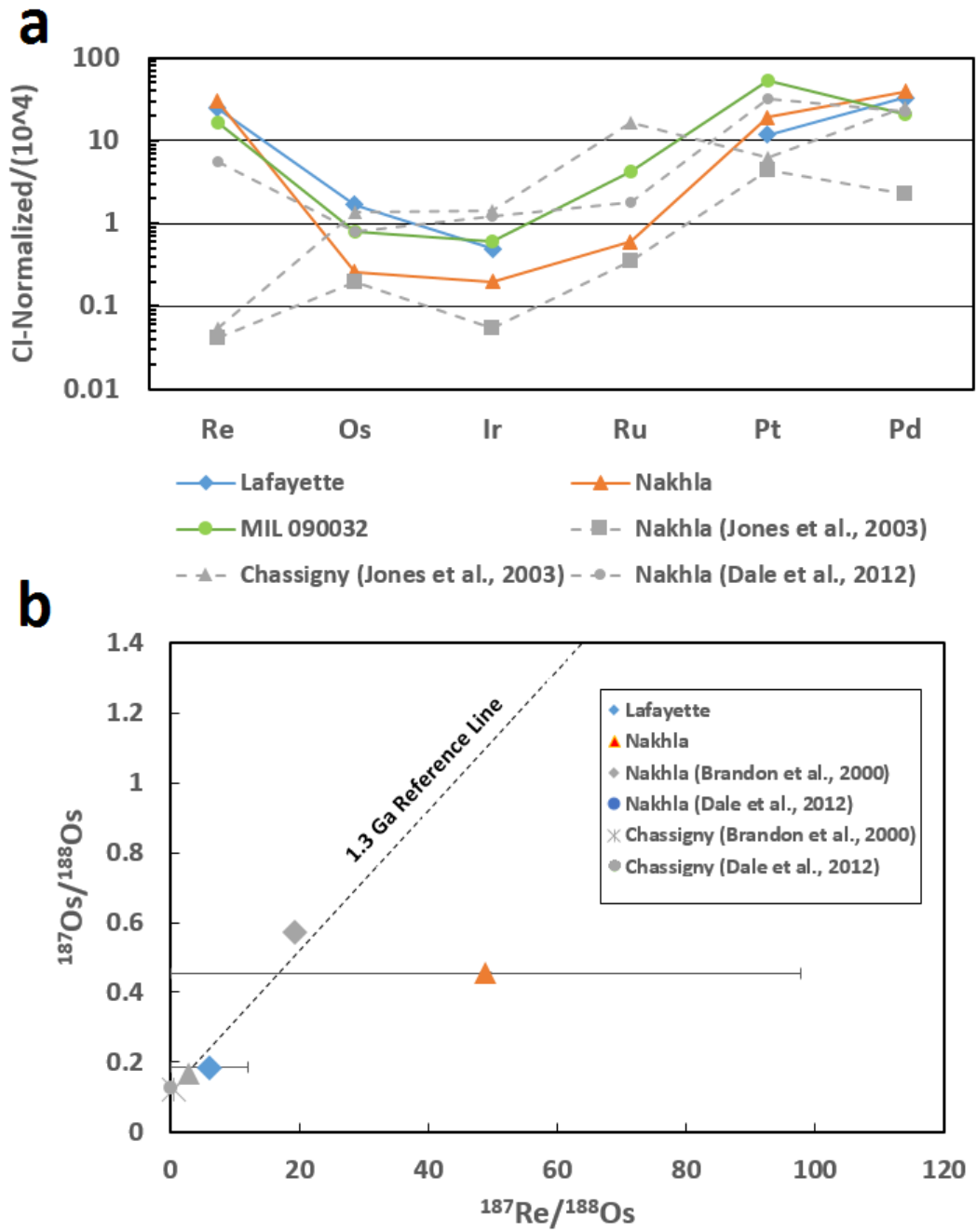


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Fig. 2



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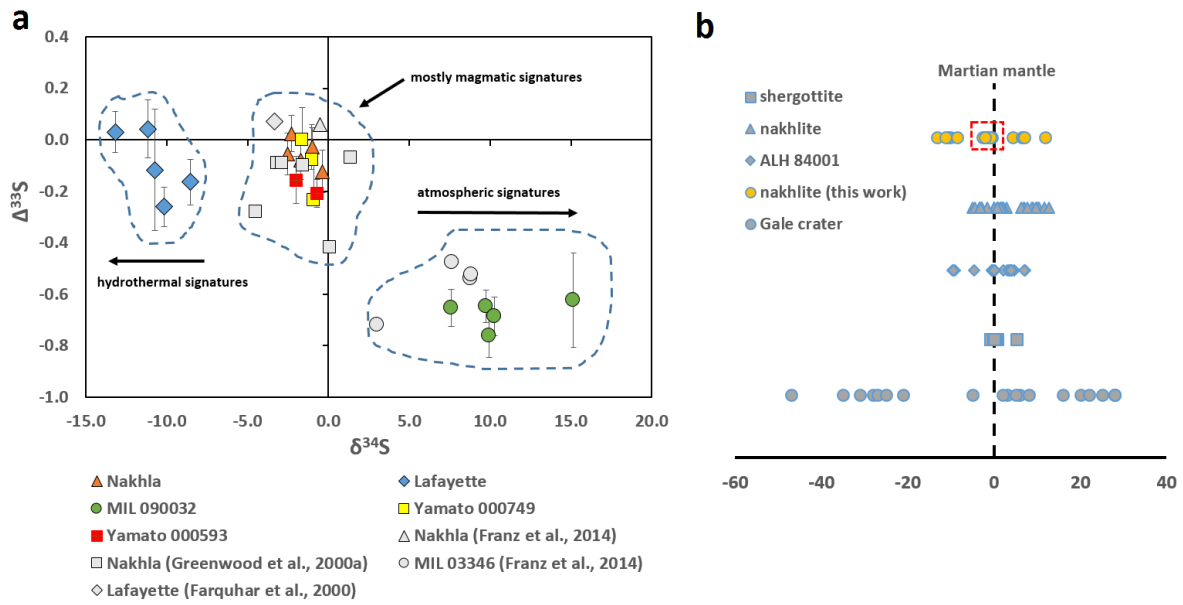
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Fig. 3

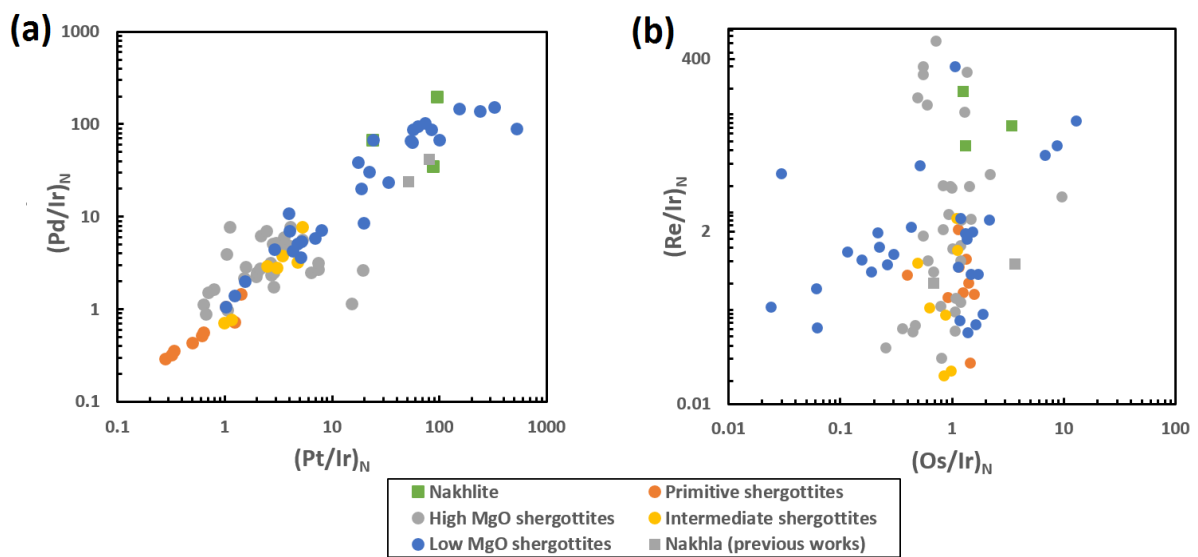


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Fig. 4



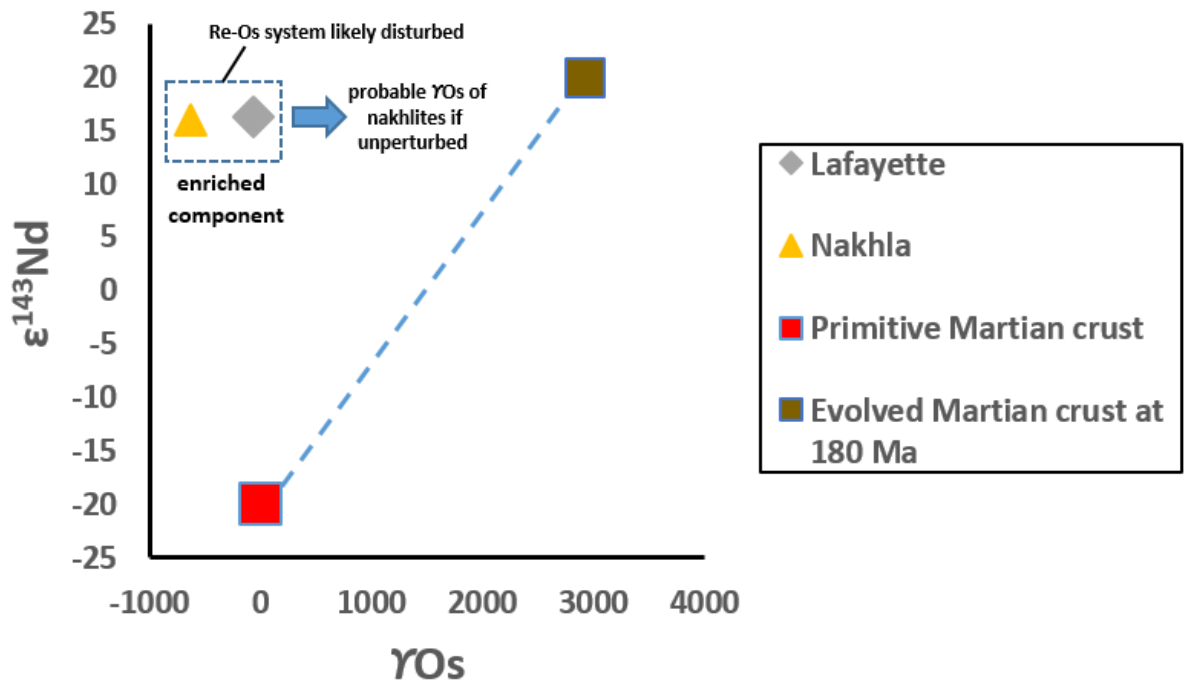
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Fig. 5





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Fig. 6

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**Table 1** – S-isotopic compositions for pyrrhotite and pyrite in Nakhla, Lafayette, MIL 090032, Y-000749, and Y-000593.

Sample	Phase	$\delta^{34}\text{S}$ (‰)	$\pm 2\sigma$	$\delta^{33}\text{S}$ (‰)	$\pm 2\sigma$	$\Delta^{33}\text{S}$ (‰)	$\pm 2\sigma$
Nakhla	pyrrhotite	-0.4	0.11	-0.33	0.08	-0.12	0.08
Nakhla	pyrrhotite	-2.2	0.10	-1.15	0.08	0.02	0.07
Nakhla	pyrrhotite	-1.0	0.09	-0.55	0.09	-0.03	0.09
Nakhla	pyrrhotite	-2.5	0.11	-1.36	0.08	-0.06	0.08
Nakhla	pyrrhotite	-1.7	0.08	-0.97	0.08	-0.08	0.07
mean		-1.5		-0.87		-0.05	
variance		0.62		0.14		0.00	
Lafayette	pyrite	-13.2	0.10	-6.78	0.09	0.03	0.08
Lafayette	pyrite	-10.1	0.11	-5.51	0.08	-0.26	0.08
Lafayette	pyrite	-10.7	0.30	-5.65	0.19	-0.12	0.24
Lafayette	pyrite	-8.5	0.11	-4.56	0.09	-0.16	0.09
Lafayette	pyrite	-11.1	0.10	-5.72	0.12	0.04	0.11
mean		-10.7		-5.64		-0.09	
variance		2.28		0.49		0.01	
MIL090032	pyrrhotite	7.6	0.08	3.25	0.08	-0.65	0.07
MIL090032	pyrrhotite	9.7	0.08	4.34	0.08	-0.65	0.06
MIL090032	pyrrhotite	9.9	0.10	4.33	0.09	-0.76	0.08
MIL090032	pyrrhotite	15.2	0.11	7.14	0.18	-0.62	0.18
MIL090032	pyrrhotite	10.2	0.08	4.58	0.08	-0.69	0.07
mean		10.5		4.73		-0.67	
variance		6.22		1.66		0.00	
Yamato000749	pyrrhotite	-1.6	0.08	-0.83	0.13	0.00	0.13
Yamato000749	pyrrhotite	-0.9	0.11	-0.59	0.13	-0.08	0.13
Yamato000749	pyrrhotite	-0.9	0.14	-0.71	0.20	-0.23	0.20
mean		-1.1		-0.71		-0.10	
variance		0.09		0.00		0.00	
Yamato000593	pyrrhotite	-0.7	0.07	-0.57	0.07	-0.21	0.05
Yamato000593	pyrrhotite	-2.0	0.08	-1.19	0.10	-0.16	0.09
mean		-1.3		-0.88		-0.18	
variance		0.42		0.09		0.00	

1138 Data on  $\delta^{34}\text{S}$ ,  $\delta^{33}\text{S}$ , and  $\Delta^{33}\text{S}$  values are expressed in permil (‰) and associated  $2\sigma$  standard errors  
 1139 are reported. Uncertainties count statistics. The mean in sulphur isotope abundance for each  
 1140 meteorite is also shown. Sulphur isotope ratios are reported in standard  $\delta$  notation with respect to  
 1141 Canyon Diablo Troilite (CDT), where  $\delta^{34}\text{S} = [({}^{34}\text{S}/{}^{32}\text{S})_{\text{sample}}/({}^{34}\text{S}/{}^{32}\text{S})_{\text{CDT}} - 1] \times 1,000$ ,  $\delta^{33}\text{S} =$   
 1142  $[({}^{33}\text{S}/{}^{32}\text{S})_{\text{sample}}/({}^{33}\text{S}/{}^{32}\text{S})_{\text{CDT}} - 1] \times 1,000$ , and  $\Delta^{33}\text{S} = [({}^{33}\text{S}/{}^{32}\text{S})_{\text{sample}}/({}^{33}\text{S}/{}^{32}\text{S})_{\text{CDT}} -$   
 1143  $[({}^{34}\text{S}/{}^{32}\text{S})_{\text{sample}}/({}^{34}\text{S}/{}^{32}\text{S})_{\text{CDT}}]^{0.515}] \times 1,000$ .

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**Table 2** - Re-Os isotope systematics and HSE abundances (in ppb) for all samples.

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	Sample		
	Lafayette	Nakhla	MIL 090032
<b>Mass (g)</b>	0.417	0.405	0.5
<b>Os (blk %)</b>	0.078 (0.70)	0.012 (4.20)	0.036 (1.3)
<b>Ir (blk %)</b>	0.022 (0.10)	0.009 (0.26)	0.025 (24)
<b>Ru (blk %)</b>	–	0.04 (9.89)	0.27 (3.8)
<b>Pt (blk %)</b>	1.01 (0.40)	1.66 (0.25)	4.54 (1.1)
<b>Pd (blk %)</b>	1.89 (1)	2.24 (0.87)	1.18 (17.5)
<b>Re (blk %)</b>	0.098 (0.49)	0.117 (0.42)	0.065 (8.4)
<b>Rh (blk %)</b>	–	–	0.21 (2.9)
<b>Au (blk %)</b>	–	–	0.081 (24)
<b><sup>187</sup>Re/<sup>188</sup>Os (± 2σ)</b>	6 (6)	49 (49)	–
<b><sup>187</sup>Os/<sup>188</sup>Os (± 2σ)</b>	0.1849 (0.0003)	0.4542 (0.0018)	–
<b>γOs<sub>i</sub> (± 2σ)</b>	-64 (34.3)	-636 (5)	–
<b>Re/Os</b>	1	10	2
<b>Pt/Os</b>	12.9	138.3	126.1
<b>Os/Ir</b>	3.54	1.33	1.44
<b>(Pt/Pd)N</b>	0.35	0.48	2.51
<b>(Pd/Os)N</b>	19.6	131.3	26
<b>ε<sup>143</sup>Nd (± 2σ)</b>	16.3 (0.4)	16	–
<b>Age (Ma) (± 2σ)</b>	1383 (7)	1330 (15)	1392 (10)
<b>Lab</b>	Durham	Durham	Berlin

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1152  $\gamma\text{Os}_i$  is given by  $\gamma\text{Os}_i = 100 \times [({}^{187}\text{Os}/{}^{188}\text{Os}_{\text{sample}(t)})/({}^{187}\text{Os}/{}^{188}\text{Os}_{\text{chondrite}(t)}) - 1]$ . HSE ratios normalized to  
 1153 Orgueil chondrite are denoted by (N). Initial <sup>143</sup>Nd are from Nakamura et al. (1982) and Shih et al.  
 1154 (1998). Ages are from Cohen et al. (2017).

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