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Tracking the volatile and magmatic history of Vesta from chromium stable isotope variations in eucrite and diogenite meteorites

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21 ***Abstract***

22 Although Solar System bodies exhibit large variations in their volatile element
23 abundances, the mechanisms and conditions that lead to these variations remain
24 ambiguous. The howardite-eucrite-diogenite (HED) meteorites that likely sample the
25 asteroid 4 Vesta, provide evidence for extensive volatile depletion on their parent body.
26 Isotopic variations in moderately volatile elements, such as Zn, have been used to track
27 the origin of such volatile loss. Although not nominally volatile, Cr is useful because it
28 has several oxidized gas species that render it volatile under the oxidizing conditions
29 that characterize planetary accretion. As such, volatile loss of Cr has the potential to
30 produce an isotopically light evaporation residue under an equilibrium regime. This
31 contrasts with other moderately volatile elements that show heavy isotope enrichments
32 in the residue following both kinetic or equilibrium fractionation. Here, we report the
33 Cr stable isotope composition of 11 eucrites and four diogenites. The eucrites possess
34 systematically lighter Cr isotope compositions than diogenites, which is onset by the
35 accumulation of isotopically heavy Cr³⁺-rich orthopyroxene and spinel in diogenites
36 during their magmatic evolution. We estimate for the primary eucrite melt with Mg# \approx
37 50, a $\delta^{53}\text{Cr}$ ($^{53}\text{Cr}/^{52}\text{Cr}$ deviation relative to NIST SRM 979 in per mille) of -0.22 ± 0.03 ‰
38 (2SD), lighter than any chondritic meteorite group by ~ 0.1 ‰. This deficit may result
39 from either partial melting with residual Cr³⁺-bearing phases (e.g. chromite) that retain
40 heavy isotopes, or from vapor loss that occurred at equilibrium with a magma ocean on
41 Vesta. Isotopic fractionation during partial melting would necessitate implausibly high
42 Cr contents in the Vestan mantle, and oxygen fugacities high enough to stabilize

43 chromite in the mantle source. Isotopic fractionation during evaporation would require
44 an oxidized vapor and a reduced residue, as predicted by thermodynamic constraints on
45 the composition of the vapor phase above a silicate magma ocean. Therefore, this Cr
46 isotopic deficit between Vesta and chondrites may be caused by Cr loss at relatively
47 high oxygen fugacity in a gas phase at equilibrium with the liquid from which it evolved.
48 Temperatures of volatile loss are estimated to be lower than 2300 K, consistent with
49 loss from a large-scale magma ocean model for formation of Vesta, which may be a
50 common evolutionary stage in accreting planetesimals.

51 ***1. Introduction***

52 Differentiated planetary bodies are characterized by a widespread depletion in their
53 moderately volatile element abundances (e.g. O'Neill and Palme, 2008). The
54 mechanisms and timing of this moderately volatile element depletion observed in the
55 silicate fraction of differentiated bodies is still debated (e.g. O'Neill and Palme 2008;
56 Hans et al., 2013; Day and Moynier, 2014; Siebert et al., 2018; Sossi and Fegley 2018)

57 Recent measurements of the stable isotope compositions of moderately volatile
58 elements (such as Zn, Cl, Ga, K, Rb) in planetary materials have provided new insights
59 into the origin, and conditions of the volatile depletion in Solar System materials (Sharp
60 et al., 2010; Paniello et al., 2012a; Kato et al., 2015; Wang and Jacobsen, 2016; Kato
61 and Moynier, 2017; Pringle and Moynier, 2017; Boyce et al. 2018). These studies have
62 found that, in general, moderately volatile elements were enriched in their heavier
63 isotopes in volatile depleted bodies such as 4 Vesta (e.g. Paniello et al., 2012b; Pringle

64 and Moynier, 2017; Sarafian et al., 2017; Tian et al., 2018) relative to their putative
65 chondritic building-blocks. These results point toward evaporation during planetary
66 processes such as impacts (e.g. Paniello et al., 2012a; Wang and Jacobsen, 2016),
67 degassing during eruption (Sharp et al., 2010) or crystallization of a magma ocean (e.g.
68 Day and Moynier, 2014; Boyce et al., 2015; Kato et al., 2015; Kato and Moynier, 2017)
69 that are absent during chondrite formation.

70 Based on spectroscopic data, the howardite-eucrite-diogenite (HED) clan of
71 meteorites are interpreted as samples of the crust of 4 Vesta, the second largest asteroid
72 in the asteroid belt (McCord et al., 1970; Binzel and Xu, 1993; Beck et al. 2011; Russell
73 et al., 2012). Eucrites are broadly basaltic rocks predominantly composed of pigeonite
74 and plagioclase, derived from Vesta's crust, whereas diogenites are mostly
75 orthopyroxenites, with some olivine-rich variants, and are conventionally viewed as
76 cumulate igneous rocks formed in a magma ocean or during intrusive magmatism on
77 Vesta; howardites are impact-brecciated mixtures of both (Mittlefehldt, 2015).

78 Howardite-eucrite-diogenite meteorites (HEDs) are highly depleted in moderately
79 volatile elements as illustrated by K/U and Rb/Sr ratios ~10 times, and ~100 times lower
80 than in CI chondrites, respectively (Day and Moynier, 2014; Mittlefehldt, 2014). There
81 is limited data available on the stable isotope composition of moderately volatile
82 elements in HEDs, e.g. Zn, Rb, Cl and Li (Magna et al., 2014; Paniello et al., 2012b;
83 Pringle and Moynier, 2017; Sarafian et al., 2017). Zinc and Rb with 50%-nebular
84 condensation temperatures (T_c) of 726 K and 800 K, respectively (Lodders 2003) are

85 enriched in the heavier isotopes in HED meteorites compared to chondrites (Paniello et
86 al., 2012b; Pringle and Moynier, 2017). Chlorine ($T_c = 948$ K, Lodders 2003) isotope
87 ratios correlate with major- (e. g. Mg and Cr) and trace-element (K, Sc and Br) content,
88 which suggests mineral (e. g. olivines and spinel) crystallization and volatile loss (e. g.
89 K and Br) during a magma ocean stage (Sarafian et al., 2017). All of the three isotope
90 systems above point toward volatile depletion due to evaporation from 4 Vesta (Paniello
91 et al., 2012b; Pringle and Moynier, 2017; Sarafian et al., 2017). On the other hand, Li
92 with a T_c of 1142 K, is isotopically similar to chondrites (Magna et al., 2014). The
93 absence of Li isotopic fractionation and limited Li loss would suggest that the
94 temperature under which this occurred was relatively low (Magna et al., 2014). Based
95 on Rb-Sr isotope dating, Hans et al. (2013) suggested that volatile loss occurred under
96 solar nebula conditions, while others have argued for post-nebular loss under more
97 oxidizing conditions (O'Neill and Palme, 2008; Moynier et al., 2012). Since both Zn
98 and Rb have more reduced species (Zn^0 and Rb^0) in the vapor compared to silicate melts
99 (Zn^{2+} and Rb^+) (Lamoreaux and Hildenbrand, 1984; Lamoreaux et al., 1987; Sossi et
100 al. 2019), both equilibrium and kinetic evaporation would enrich these elements in the
101 heavier isotopes in the condensed phase(s), because the vapor (compared to residue)
102 and reduced species (compared to oxidized species) are both enriched in the lighter
103 isotope. It is therefore not presently possible to discern between these two kinds of
104 isotopic fractionation processes based on these isotopic systems. As recently applied by
105 Sossi et al. (2018), Cr isotopes can be used to give insights into the mechanism of
106 volatile depletion. Under oxidizing conditions ($fO_2 > IW+1$), relevant to planetary

107 evaporation (Visscher and Fegley, 2013), Cr may be present in the gas as oxide species
108 CrO(g) , $\text{CrO}_2\text{(g)}$ and $\text{CrO}_3\text{(g)}$ (Chase, 1998) and equilibrium isotopic fractionation
109 (Young et al., 2019) could cause enrichment of the lighter isotopes in the condensed
110 phases, in which Cr is either di- or trivalent, relative to the vapor. This contrasts with
111 its speciation under nebular conditions, in which Cr may be present as Cr^{2+} or Cr metal
112 in the condensed phase and Cr^0 in the gas. Sossi et al. (2018) have shown that the Moon
113 is enriched in the lighter isotopes of Cr compared to Earth's mantle, its likely precursor,
114 a feature ascribed to volatile loss under relatively oxidizing conditions, which cause Cr
115 to be present as CrO_2 in the vapor phase but predominantly as Cr^{2+} in the melt. Because
116 this signature could only have resulted from equilibrium between liquid and gas, they
117 were able to calculate that evaporation must have occurred at temperatures between
118 1600 and 1800 K, implying that loss took place following cooling and accretion of the
119 Moon. This contrasts with models that argue for volatile loss contemporaneous with a
120 very hot (>4000 K) giant impact (Nakajima and Stevenson, 2014). Moreover, relative
121 to other moderately volatile elements such as Zn or K (whose abundances in lunar
122 basalts are ~50 (K) to ~300 (Zn) times lower than those in chondrites; Paniello et al.,
123 2012; Day and Moynier, 2014), the i) higher concentration of Cr (Wänke and Dreibus,
124 1980) and ii) its lower volatility (Sossi et al., 2018) facilitate precise isotopic analysis
125 and make Cr less susceptible to overprinting by possible late accretion on Vesta.

126 Previous studies show that Cr isotopes do not fractionate during core-mantle
127 differentiation, as evidenced by experimental studies (Bonnand et al., 2016b) and the
128 homogeneous Cr isotope composition of chondrites and estimates for the bulk silicate

129 Earth (Bonnand et al., 2016b; Schoenberg et al., 2016; Sossi et al., 2018). Moreover, Cr
130 is not appreciably siderophile (*e.g.*, Rammensee et al. 1983) except under very high
131 temperatures and/or reducing conditions (Wade and Wood, 2001; Mann et al. 2009;
132 Siebert et al. 2013). Therefore, isotopic variations in Cr likely reflect other processes,
133 such as magmatic differentiation and/or volatile depletion instead of core formation.
134 Studying the Cr isotopic composition of HED meteorites may be used to evaluate the
135 redox conditions during volatile loss of the HEDs and to estimate whether the
136 volatilization occurred during equilibrium or kinetic conditions, thereby potentially
137 constraining the temperature of evaporation. While there are no systematic studies of
138 the Cr isotope composition of eucrites and diogenites, the scarce data suggest a hint of
139 a light isotope enrichment in eucrites compared to diogenites and chondrites (Qin et al.,
140 2015; Bonnand et al., 2016b). Here, we report high-precision Cr isotope compositions
141 of 11 eucrites and four diogenites analyzed via double-spike technique by Multi-
142 Collector Inductively-Coupled Plasma Mass Spectrometer (MC-ICP-MS) to better
143 quantify the magmatic and evaporation/condensation process that occurred during
144 Vesta's formation and constrain its physicochemical conditions.

145 ***2. Samples and analytical methods***

146 ***2.1 Samples***

147 Eleven eucrites and four diogenites were studied. The eucrites comprise
148 Pasamonte, Camel Donga, Stannern, Bouvante, Jonzac, Juvinas, EET 87548, Moore
149 County, Pomozdino, Serra de Magé and EET 87542, and the diogenites include EET

150 79002, Tatahouine, LAP 03569 and Shalka. Two different groups of eucrites, Main
151 group and Stannern trend (including Stannern, Pomozdino and Bouvante), have been
152 studied. The Stannern trend eucrites (on basis of their Mg# (molar Mg/(Mg+Fe), Ti and
153 incompatible trace element abundances) may be contaminated by Vestan crustal
154 materials (Barrat et al., 2007). Pasamonte was recognized as an anomalous eucrite
155 based on a different O isotopic composition compared to most HEDs (Greenwood et
156 al., 2009), suggesting that it may not have originated from Vesta or that Vesta is
157 isotopically heterogeneous. Most of the eucrites selected are monomict breccias, and
158 the sample descriptions are summarized in Table 1. Full replicates, including
159 dissolution, spike addition, and chemical purification of Pasamonte, Juvinas and Jonzac
160 were performed in order to test the overall reproducibility of the method. The Cr
161 isotopic composition of three terrestrial geological reference materials, BHVO-2 and
162 DTS-1 and PCC-1 were analyzed to quantify the accuracy of the method.

163 ***2.2 Methods***

164 All sample processing was performed in the clean laboratory at the Institut de
165 Physical du Globe de Paris (IPGP) following the method described in Sossi et al.,
166 (2018). Ten to 20 mg of each meteorite sample were weighed from original powder of
167 ~1g to ensure homogeneity. All eucrites were firstly dissolved in a mixture of HF and
168 HNO₃ (2:1) on a hot plate (130 °C) for **two** days. Subsequently, the samples were
169 dissolved in aqua regia (concentrated HCl and HNO₃ mixture in 3:1 ratio) to ensure
170 complete digestion. The four diogenites were dissolved by the concentrated mixed acid

171 (HCl: HF: HNO₃ = 5:3:2) in Parr Bombs under pressurized steel jackets for four days
172 at 180 °C, and no visible residues were observed. Then, the adequate amount of ⁵⁰Cr-
173 ⁵⁴Cr double spike (28% of the Cr content endemic to the sample) was added and the
174 solution and refluxed in closed PFA beakers at 120 °C overnight. Half of the digested
175 samples were chemically purified for Cr via a two-step cation exchange
176 chromatography adapted from Trinquier et al. (2008), as routinely undertaken at IPGP
177 (Mougel et al., 2017; Mougel et al., 2018). This method has a total procedural yield of
178 60~90% and blank of ~5 ng of Cr. Compared to the total 10-60 µg of Cr, the blank is
179 negligible. The final Cr cut was evaporated in concentrated HNO₃ drops three to five
180 times to convert the HCl medium to HNO₃, and to remove leftover organics (i.e. resin),
181 and then diluted to a concentration of 1 ppm Cr, in 2% (0.317 M) HNO₃ for isotope
182 analysis.

183 The Cr stable isotope compositions of these purified samples were measured on a
184 Thermo Scientific Neptune Plus MC-ICP-MS housed at the IPGP, the details are
185 described in Sossi et al. (2018). The isotopic ratio for samples is compared to NIST
186 SRM 979 and reported in delta notation:

$$187 \quad \delta^{53}\text{Cr}(\text{‰}) = \left(\frac{(^{53}\text{Cr}/^{52}\text{Cr})_{\text{sample}}}{(^{53}\text{Cr}/^{52}\text{Cr})_{\text{NIST SRM 979}}} - 1 \right) \times 1000. \quad (1)$$

188 The Cr isotopic composition of a secondary standard, NIST SRM 3112a, was also
189 measured in each analytical session to monitor the instrumental mass fractionation and
190 the precision of the data. The Cr isotopic composition of every sample was measured

191 twice. Therefore, the Cr isotopic composition of samples for which 2 separate chemical
192 purification procedures were performed (Stannern, Pasamonte, Juvinas and Jonzac)
193 were analyzed four times (in figures, two replicate data for the four samples were
194 combined as one). The uncertainties quoted for individual samples are 2SD of single
195 sample measurements (100 cycles for two times) or 2SD reproducibility of several
196 NIST SRM 979 measurements in the same analytical session (0.04‰), or that of NIST
197 SRM 3112a (0.04‰), whichever is largest.

198 Since, when normalized to the $^{50}\text{Cr}/^{52}\text{Cr}$ ratio, Cr shows non-mass dependent
199 isotopic effects on both the $^{53}\text{Cr}/^{52}\text{Cr}$ (due to the decay of ^{53}Mn) and on $^{54}\text{Cr}/^{52}\text{Cr}$
200 (nucleosynthetic anomalies) ratios in HEDs (Trinquier et al., 2007), a correction must
201 be applied in order to properly perform the double spike reduction. Most samples
202 analyzed here had been previously studied for their ^{53}Cr and ^{54}Cr anomalies. For the
203 samples (Camel Donga, EET 87548, Moore County, Pomozdino, Serra de Magé, EET
204 87542 and EET 79002), which have no available data, we have used the average of the
205 ^{54}Cr anomalies which have been shown to be homogeneous between all HED analyzed,
206 with an average value for $\epsilon^{54}\text{Cr}$ of -0.74. Since ^{53}Cr is produced by the radioactive decay
207 of ^{53}Mn (e.g. Zhu et al., 2019a; Zhu et al., 2019b), one single value cannot be applied
208 and for the samples for which the ^{53}Cr anomalies were not available and the ^{53}Cr
209 anomalies were estimated based on their $^{55}\text{Mn}/^{52}\text{Cr}$ ratio and from the slope of the ^{53}Mn -
210 ^{53}Cr isochron (Trinquier et al., 2008).

211 Pasamonte is anomalous and has heterogeneous O and Cr isotope compositions

212 (Scott et al., 2009; Sanborn and Yin, 2014). Sanborn and Yin (2014) reported $\epsilon^{54}\text{Cr} = -$
213 0.33 ± 0.08 , while Trinquier et al. (2007) reported -0.71 ± 0.08 on a different sample
214 section. However, it should be noted that whichever $\epsilon^{54}\text{Cr}$ values applied in the double
215 spike reduction only changes the calculated $\delta^{53}\text{Cr}$ by 0.02, which is smaller than the
216 2SD error for NIST SRM 979. Furthermore, if the variation for $\epsilon^{53}\text{Cr}$ or $\epsilon^{54}\text{Cr}$ reaches
217 1ϵ (the variation for $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ in HEDs is always less than 0.6ϵ (Sanborn and Yin,
218 2014; Trinquier et al., 2007; 2008) and were not corrected, the final corrected $\delta^{53}\text{Cr}$
219 would only shift by 0.008‰ due to $\epsilon^{53}\text{Cr}$ and 0.038‰ due to $\epsilon^{54}\text{Cr}$ which would fall
220 within the analytical uncertainty (0.04‰). For consistency, we use only the $\epsilon^{54}\text{Cr}$ data
221 from Trinquier et al. (2007) for the samples for which $\epsilon^{54}\text{Cr}$ is unknown.

222 **3 Results**

223 The $\delta^{53}\text{Cr}$ values, Cr contents and Mg# of 11 eucrites (including seven non-
224 cumulate eucrites, three cumulate eucrites and one polymict eucrite) and five diogenites
225 (including one datum, from Bonnand et al. (2016b)) are reported in the Table 1. The
226 $\delta^{53}\text{Cr}$ for eucrite samples ranges from -0.13 to -0.25‰ , with an average value of -0.20
227 $\pm 0.08 \text{‰}$ (2SD, $n=11$), twice as large as the analytical uncertainty. Compared to
228 cumulate eucrites, the non-cumulate eucrites are characterized by lower Cr content,
229 lower Mg# and lower $\delta^{53}\text{Cr}$ than the diogenites. The five diogenite samples display
230 heavier $\delta^{53}\text{Cr}$, with the LAP 03569 sample having the heaviest $\delta^{53}\text{Cr}$ values of $-0.07 \pm$
231 0.04‰ . There is no systematic difference in the Cr isotope composition between the
232 main group and Stannern trend eucrites when comparing the five monomict eucrites:

233 Juvinas, Jonzac, Camel Donga, Stannern and Bouvante. Replicate analyses of the $\delta^{53}\text{Cr}$
234 of Pasamonte, Juvinas, Jonzac and Stannern agree within error (see table 1). The $\delta^{53}\text{Cr}$
235 of the USGS standards, BHVO-2, PCC-1 and DTS-1, are consistent with previously
236 reported values (Schoenberg et al., 2016; Sossi et al., 2018; Chen et al., 2019). When
237 $\delta^{53}\text{Cr}$ values are reported as a function of Cr concentration (and Mg#), diogenites and
238 eucrites are clustered, with eucrites isotopically light and low in Cr (1750 ~ 5673 ppm)
239 compared to the isotopically heavier and Cr-richer diogenites (4404 ~ 6780 ppm)
240 (Figure 1a). The Mg# of the HED meteorites analyzed are also grouped into a high
241 (Mg# \approx 75, diogenites) and a low (Mg# \approx 40, basaltic eucrites) populations, with some
242 cumulate and magnesian eucrites spanning the gap between them (Figure 1b).

243 ***4. Discussion***

244 ***4.1 Heavy Cr isotope enrichment in diogenites***

245 Eucrites and diogenites are samples from the silicate fraction of Vesta (Keil, 2002;
246 Mittlefehldt, 2015). The isotopically heavier diogenites have higher Cr contents and
247 Mg# relative to eucrites. This suggests that magmatic differentiation could have led to
248 the Cr isotopic difference between the two meteorite groups. Small variations on the
249 order of 0.1 ~ 0.2 ‰ are also found in lunar mare basalts and Mg suite cumulates
250 (Bonnand et al., 2016a; Sossi et al., 2018). Fractionation is generally more limited in
251 Earth's mantle (-0.11 ± 0.06 ‰; Schoenberg et al., 2008; Sossi et al., 2018), except
252 during metasomatic processes (Xia et al., 2017; Shen et al., 2018). Therefore, utilizing
253 the eucrites and diogenites to reconstruct the Cr isotopic composition of Vesta requires

254 assessment of any isotopic fractionation that may have occurred during processes such
255 as partial melting and fractional crystallization.

256 Partial melting on Earth involves isotopic exchange between both Cr²⁺- and Cr³⁺-
257 bearing phases. In typical mantle peridotites that have equilibrated near the Fayalite-
258 Magnetite-Quartz (FMQ) buffer, the majority of Cr is present in its trivalent form in
259 spinel and clinopyroxene (Li et al., 1995). At the same fO_2 , basaltic melts have a greater
260 proportion of Cr²⁺, about $Cr^{2+}/\sum Cr = 0.3$ at 1400°C (Berry et al., 2006). The difference
261 in Cr redox states (Cr²⁺ and Cr³⁺) between residual mantle and melt thereby provides a
262 mechanism for inducing Cr isotope fractionation (the heavier Cr³⁺ is highly compatible
263 in some refractory minerals; e.g. chromite), in which the residue becomes isotopically
264 heavier and the complementary liquids are relatively lighter. Shen et al. (2018)
265 calculated the magnitude of this effect, and found a $\Delta^{53}Cr_{Mantle-Melt} = +0.05 \text{ ‰}$ for
266 degrees of melting around 15% (i.e., melts should be isotopically lighter than their
267 sources). Nevertheless, observational evidence points to limited Cr isotope
268 fractionation during partial melting near the FMQ buffer (Schoenberg et al., 2008) on
269 the basis that both terrestrial basaltic rocks and peridotites have similar compositions.

270 On Vesta, basaltic eucrites have assemblages that reflect equilibration at lower fO_2
271 relative to terrestrial magmas, ≈ 1 log unit below the Iron-Wüstite buffer (e.g. Righter
272 et al., 2016) yielding $Cr^{2+}/\sum Cr \approx 0.9$ in the melt using the calibration of Berry et al.
273 (2006). Mineral phases in equilibrium with eucritic liquids (pyroxene-plagioclase \pm
274 spinel \pm metal; Bartels and Grove, 1991; Stolper, 1977) have the majority of their Cr

275 hosted in pyroxene and spinel. Even at IW-1, these phases will contain predominantly
276 Cr^{3+} (Karner et al., 2007). Should these minerals be present as residual phases during
277 partial melting to produce eucrites, then the large $\text{Cr}^{2+}/\sum\text{Cr}_{\text{melt}} > \text{Cr}^{2+}/\sum\text{Cr}_{\text{source}}$ should
278 enhance fractionation relative to terrestrial environments. The $\text{Cr}^{2+}/\sum\text{Cr}_{\text{source}}$ of the
279 Vestan mantle source will depend on the phase assemblage. A peridotitic source at IW-
280 1 and 1400 °C, would contain olivine with $\text{Cr}^{2+}/\sum\text{Cr} \approx 0.8$ to 0.9 (Bell et al. 2014), low-
281 Ca clinopyroxene with exclusively Cr^{3+} (Karner et al. 2007), with orthopyroxene
282 between these two extremes, conferring a weighted average ≈ 0.5 . The net effect is to
283 produce isotopically light partial melts, unless i) spinel is not stable at partial melting
284 temperatures (Li et al., 1995) or ii) spinel and much of the pyroxene is completely
285 dissolved from eucrite parent magma source regions. If the Cr content of the Vestan
286 mantle is ≈ 2300 ppm (see Jones (1984) and discussion below) and given that D_{Cr}
287 between mantle and melt is approximately unity (Hanson and Jones, 1984; Mallmann
288 and O'Neill, 2009), then the relatively high Cr content of main group eucrites (≈ 2000
289 ppm which mainly resides in spinel and pyroxene; Barrat et al., 2000) compared to
290 terrestrial basalts (≈ 300 ppm) suggests it behaved as a moderately incompatible
291 element during partial melting on Vesta, implying spinel was not an important residual
292 phase. This is also borne out in the increasing Cr contents with progressive fractional
293 crystallization among main group eucrites (see Barrat et al., 2000). Importantly, the
294 melt phase thus leverages the Cr isotope composition of the system for eucrites, whereas
295 the majority of the Cr remains in the mantle during partial melting on Earth. However,
296 the effect of partial melting cannot be excluded, and would produce partial melts with

297 lighter Cr isotope compositions than their sources (Figure 2).

298 To interpret the causes of Cr isotope variations in eucrites and diogenites requires
299 understanding of their petrogenesis. One prevailing hypothesis states that diogenites
300 and eucrites originated from an early Vestan magma ocean, and melts parental to
301 eucrites were formed followed by crystallization of cumulate pyroxenes, which would
302 imply that diogenites and eucrites were cogenetic (Mason, 1967; Righter and Drake,
303 1997; Mandler and Elkins-Tanton, 2013). However, the diversity in diogenite
304 compositions have been used as evidence to preclude a direct link to eucrites (Stolper,
305 1977; Barrat et al. 2008). Therefore, in order to determine the Cr isotope composition
306 of Vesta, the effects of fractional crystallization in fractionating Cr isotopes must first
307 be understood.

308 The majority of diogenites are coarse-grained ultramafic rocks dominated by
309 magnesian orthopyroxenes and minor olivine, silica and spinel (Bowman et al., 1997;
310 Beck and Mcsween, 2010), while eucrites are mainly comprised of orthopyroxene,
311 pigeonite, low-Ca pyroxenes, plagioclases and minor silica, ilmenite and spinel
312 (Delaney et al., 1984; Mittlefehldt, 2015). Among these minerals, pyroxene (both
313 orthopyroxenes and clinopyroxenes) and chromite are the main carrier phases for Cr,
314 and together account for more than 98% of the Cr budget in eucrites and diogenites, as
315 will be discussed below. In detail, the pyroxenes, which account for 40~60% in mass
316 of eucrites (including orthopyroxene, pigeonite and high-Ca pyroxene), contain an
317 average of 0.32 wt% Cr₂O₃, while plagioclase (~40% of eucrites) are mostly Cr-free

318 (Mayne et al., 2009). Despite spinel being a minor mineral in eucrites (0.3% in mode),
319 it can contain ~45 wt% of Cr₂O₃, and is therefore an important Cr contributor to bulk
320 eucrites. Ilmenite is another Cr-bearing mineral (~0.4 wt% of Cr), but its proportion in
321 eucrites is only ~0.7% (Mittlefehldt, 2015), of which Cr contribution to bulk rock is
322 less than 1%. Relative to eucrites, diogenites have different mineral modes and
323 compositions. Most diogenites comprise 85~99% orthopyroxene, which have on
324 average 0.41 wt% of Cr₂O₃, and 0.7% spinels that can hold up to 55 wt% of Cr₂O₃ in
325 diogenites (Beck and McSween, 2010; Day et al., 2012). In both eucrites and diogenites,
326 the ratio, [Cr]_{pyroxene}: [Cr]_{spinel}, is close to 1 : 1.

327 Chromite (Cr-spinel) hosts exclusively Cr³⁺ in octahedral coordination that confers
328 a normal site distribution on spinel. Its formation from the melt can be described
329 following Roeder and Reynolds (1991) as:



331 The activity of CrO_{1.5} in the melt is related to *f*O₂ by homogeneous equilibrium with
332 CrO:



334 As reaction (3) is associated with a strongly negative change in entropy, Δ*S*^o₍₃₎ (Li
335 et al. 1995), the crystallization of Mg-rich, Cr-spinel is favoured at i) high *f*O₂ and ii)
336 low temperatures. Trivalent Cr is also preferentially incorporated into pyroxene
337 (Mallmann and O'Neill, 2009), that is to say, Cr³⁺/Cr²⁺_{px,spinel} > Cr³⁺/Cr²⁺_{melt}. Chromium

338 isotope fractionation occurs between the Cr²⁺- and Cr³⁺-containing melt, and
339 predominantly Cr³⁺-bearing phases due to differences in bonding environment between
340 the two phases. Trivalent Cr has high octahedral site preference energy (OSPE) and
341 hence is found solely in VI-fold sites in both minerals and melt (e.g., Berry and O'Neill,
342 2004). The coordination chemistry of divalent Cr is dictated by its tendency for Jahn-
343 Teller distortions, therefore preferring irregular bonding environments (e.g. Burns,
344 1975). Indeed, Cr²⁺ is distributed subequally on the M1 and M2 sites of olivine, due to
345 its competing preferences for the larger M2 site and the more distorted M1 site (Li et
346 al., 1995). However, in pyroxenes, the M2 site is both larger and more distorted than
347 the M1, meaning Cr²⁺ is strongly partitioned onto the M2 site (Angel et al., 1989). Its
348 coordination in silicate melts is uncertain, though it may be coordinated by six oxygens
349 in a square planar arrangement (O'Neill and Berry, 2006). Since Cr³⁺ ($r = 0.615 \text{ \AA}$)
350 exists as 6-fold coordination in all minerals (olivine, pyroxene and spinel) and has
351 shorter M-O distances as compared to Cr²⁺ ($r = 0.80 \text{ \AA}$), which exists in larger, more
352 distorted geometries, the Cr³⁺ phases should be isotopically heavier. The preferential
353 incorporation of Cr³⁺ into orthopyroxene and Cr-spinel relative to the melt leads to
354 isotope fractionation between them and provides a mechanism to explain the heavier
355 isotopic composition of diogenites compared to the eucrites. In terrestrial peridotites,
356 chromites (which host entirely Cr³⁺) are isotopically heavier compared to the bulk
357 (Farkaš et al., 2013; Schoenberg et al., 2008), which is further confirmed by the
358 following general $\delta^{53}\text{Cr}$ order: chromite-free peridotites ($-0.21\text{‰} \sim -0.11\text{‰}$) <
359 chromite-bearing peridotite (-0.07‰) \leq chromite (-0.06‰) (Shen et al., 2015) and by

360 ab initio calculations (Moynier et al., 2011). If a primary melt from the Vestan mantle
361 formed at IW-1, it should only possess ~10% Cr³⁺ (Berry et al., 2006; Wadhwa, 2008).
362 Therefore, the isotopically heavy pyroxenes and spinels in diogenites rapidly uptake
363 most of the limited budget of Cr³⁺ compared to those in eucrites, producing isotopically
364 heavier diogenites.

365 ***4.2 The Cr isotopic composition of the bulk Vesta***

366 HED meteorites are likely direct samples from Vesta (McCord et al., 1970; Binzel
367 and Xu, 1993; Russell et al., 2012), but their chemical variation means that estimating
368 the isotopic composition of the Vestan mantle hinges upon identifying samples that have
369 undergone minimal isotopic fractionation relative to their mantle sources. Samples that
370 are most likely to fulfil these criteria are those that represent primary melts, i.e., those
371 in equilibrium with their mantle sources. Among eucrites, the cumulate varieties
372 (including EET 87548) with high Mg#s (54), have accumulated Cr³⁺-bearing minerals
373 (chromite, pyroxene), that have resulted in an increase in Cr content relative to their
374 parent magma. Because this accumulation could cause Cr isotope fractionation (*cf.* Fig.
375 1 and section 4.1.), these samples are excluded from the determination of the Vestan
376 mantle composition.

377 In order to quantify the magnitude of this effect, the *ab-initio* calculations of
378 Moynier et al. (2011) are used to show that chromite should be isotopically heavier than
379 co-existing Cr²⁺-bearing silicates by about 0.15 ‰ at magmatic temperatures
380 (1200~1400°C; Moynier et al., 2011). The heaviest diogenites have δ⁵³Cr of -0.07 ‰

381 (LAP 03569 and Johnstone), which are, at most, 0.15 ‰ heavier relative to eucrites. If
382 one considers that a primary melt of the Vestan mantle contains 90% Cr²⁺ (Berry et al.
383 2006), then the diogenites, as cumulates that contain only Cr³⁺, can represent no greater
384 than 10% by mass of the initial melt. If, in a closed system with a finite Cr budget, the
385 eucrites are complementary to diogenites (which appears not to be the case; Barrat et
386 al. 2008), then they would contain the other 90% of the Cr budget, and the Cr isotope
387 composition of the parental melt would be given by mass balance: $\delta^{53}\text{Cr}_{\text{parental}} =$
388 $\delta^{53}\text{Cr}_{\text{eucrite}} \times 0.9 + \delta^{53}\text{Cr}_{\text{diogenite}} \times 0.1$, which yields -0.20 ‰, within statistical uncertainty
389 of the eucrite average (-0.22 ± 0.03 ‰).

390 Sample EET 87542 (Mg# = 40) is a petrologically anomalous brecciated eucrite
391 with low Fe/Mn-pyroxene, which underwent unusual subsolidus processing
392 (Mittlefehldt et al., 2015; 2016) that could have modified its Cr isotope composition.
393 Pasamonte has anomalous $\Delta^{17}\text{O}$ and hence may not originate from Vesta (Scott et al.,
394 2009), so it cannot be relied upon as a faithful probe of the composition of Vesta. Then,
395 it should be noted that Stannern and Bouvante belong to Stannern Trend, which,
396 although they may indeed be primary Vestan “mantle” melt products, have incorporated
397 crustal material (Barrat et al., 2007) that compromises the degree to which they
398 represent the Vestan mantle and are also excluded. Finally, this leaves three basaltic
399 Main trend basaltic eucrites (Juvinas, Jonzac and Camel Donga, Mg# = 40-42). We
400 assess below whether these samples are representative of their sources.

401 On the basis that many of the main group eucrites’ bulk compositions plot near the

402 1 atm peritectic, saturated in olivine-low Ca pyroxene-plagioclase-spinel-metal, Stolper
403 (1977) made a convincing case for the derivation of these magmas via partial melting
404 of the Vestan mantle. In this model, the most magnesian of these magmas, Sioux County
405 and Juvinas (and similar non-cumulate eucrites with Mg#s \approx 42), are produced by 15-
406 20% melting, whereas more evolved examples, such as Pasamonte and Nuevo Laredo
407 are liquid residues after moderate degrees (<40%) of fractional crystallization. However,
408 later cosmochemical models postulate Mg#s for the Vestan mantle between 75-80
409 (Dreibus and Wänke, 1980; Ruzicka et al., 1997). Whether these magmas are
410 representative of the mantle of Vesta can be assessed using K_D Fe-Mg systematics
411 between mafic minerals and melt:

$$412 \quad K_{D,Min-Melt}^{Fe-Mg} = \frac{\left(\frac{Fe}{Mg}\right)_{Min}}{\left(\frac{Fe}{Mg}\right)_{Melt}}. \quad (4)$$

413 Experimental studies have shown that this value is close to 0.30 for olivine-melt
414 (Toplis, 2005), orthopyroxene-melt and clinopyroxene-melt (Bédard, 2007; Bédard,
415 2010). Application of equation (4) results in the expectation that primary melts of the
416 Vestan mantle should have Mg#s between 45 and 55, that is, slightly higher than any of
417 the non-cumulate eucrites (36~42). This was pointed out by (Bartels and Grove, 1991),
418 who suggested that the non-cumulate eucrites may come from a more iron-rich region
419 of the Vestan mantle. Therefore, in lieu of non-cumulate samples that have Mg#s
420 compatible with their direct derivation from mantle representative of bulk silicate Vesta,
421 we adopt the most magnesian eucrites analyzed, Juvinas, Jonzac and Camel Donga, as
422 most representative of Vesta, though the caveats mentioned above should be

423 considered. From these lines of reasoning we consider bulk silicate Vesta to have $\delta^{53}\text{Cr}$
424 $= -0.22 \pm 0.03\text{‰}$.

425 ***4.3 Difference in the Cr isotope compositions of Vesta and chondrites caused by***
426 ***evaporation under oxidizing conditions.***

427 Chondrites, commonly considered to be the building blocks of planetary bodies,
428 have homogeneous $\delta^{53}\text{Cr}$ within error, with values ranging from -0.05 to -0.15 ‰ (Qin
429 et al., 2015; Bonnand et al., 2016b; Schoenberg et al., 2016) and Cr contents varying
430 from 2650 ppm in CI chondrites to ≈ 3800 ppm in ordinary chondrites (Wasson and
431 Kallemeyn, 1988). Therefore, the choice of a specific chondrite group to represent the
432 composition of Vesta is of secondary importance in discussing the Cr elemental and
433 isotopic disparity between Vesta and its building blocks. However, since ordinary
434 chondrites (OC) possess the closest non-mass dependent Cr and Ti isotopic
435 compositions ($\epsilon^{54}\text{Cr}$ and $\epsilon^{50}\text{Ti}$; Trinquier et al., 2007; 2009; Pedersen et al., 2019) to
436 those of the HED meteorites, it is more logical to treat this group of chondrites as the
437 building blocks of Vesta. Ordinary chondrites with $\delta^{53}\text{Cr} = -0.12 \pm 0.03 \text{‰}$ (2SD, N=6;
438 Bonnand et al., 2016b) are isotopically heavier than the estimate of the composition of
439 the bulk silicate Vesta ($-0.22 \pm 0.03 \text{‰}$).

440 Ordinary chondrites have Cr contents of ~ 3750 ppm (Kallemeyn et al., 1989). The
441 Cr content of Vesta's mantle is a matter of debate, with estimates of ~ 2300 ppm (Jones,
442 1984) to ≈ 7000 ppm (see Mandler et al. (2013)). As touched upon in section 4.1., the
443 estimate of the Cr content of the Vestan mantle hinges upon the role of Cr-spinel in the

444 melting region; Jones (1984) argues that the experiments of Stolper (1977) predict
445 spinel exhaustion at- or near their liquidus temperatures and hence $D_{Cr} \approx 1$. The models
446 estimating higher Cr content in Dreibus and Wanke (1984); Ruzicka et al. (1997) and
447 Mandler et al. (2013) are predicated on determining the composition of Vesta from
448 binary mixtures of eucrites and diogenites and/or finding the point at which refractory
449 lithophile elements are present in chondritic proportions. This approach implicitly
450 neglects elemental fractionation during partial melting (eucrites) or mineral
451 accumulation (diogenites) and should be treated with caution, and only the model of
452 Jones (1984) considered the behaviour of Cr during partial melting. Additionally, Cr
453 contents upwards of those of chondrites (> 4000 ppm) are difficult to justify given the
454 small size of the Vestan core (Russell et al. 2012). We therefore adopt the estimate of
455 Jones (1984), which is similar to Cr contents of the three representative eucrites
456 (Juvinas-2100 ppm, Jonzac-2501 ppm and Camel donga-2232 ppm). Normalized to Al
457 (a refractory element) and OCs, the fraction (f) of Cr in Vesta is ~ 0.43 (Al content for
458 Vesta's mantle and OCs are 16941 ppm and 11900 ppm respectively; $f = Cr_{Vesta}/Al_{Vesta}$
459 $/((Cr_{Vesta}/Al_{Vesta} + Cr_{OC}/Al_{OC})$). The origin of this deficit of Cr and the shift toward and
460 enrichment in the lighter Cr isotopes, with a $\Delta^{53}Cr_{Vesta-OC} = -0.10 \pm 0.04\%$, between
461 Vesta and OC is discussed below (Figure 3).

462 Chromium behaves as a slightly siderophile element under reduced conditions and
463 high temperatures (Wood et al., 2008). Vesta experienced core-mantle differentiation
464 (Russell et al., 2012), which had the potential to cause Cr isotope fractionation (Moynier
465 et al., 2011). Using the parameterization of Siebert et al. (2013), the metal-silicate

466 partition coefficient (D) of Cr at conditions of core formation on asteroid 4-Vesta
467 (~ 2000 K and IW-1; pressure effect on Cr partitioning is negligible) is estimated to be
468 $D_{\text{Cr}} = 0.11 \pm 0.04$. Considering a core mass fraction of 0.18 for Vesta (Russell et al.,
469 2012) and a bulk silicate Vesta Cr content of 2300 ppm (Jones, 1984), this partitioning
470 value results in a Cr-poor Vestan core containing 262 ± 80 ppm of Cr, which represents
471 roughly 1~3% of the Cr budget of Vesta. Accordingly, the formation of Vesta's core was
472 likely ineffective in producing the Cr depletion or isotope fractionation relative to OCs,
473 particularly when considering the small- to negligible Cr isotope fractionation between
474 metal and silicate at 2000 K (Moynier et al., 2011; Bonnand et al., 2016b).

475 Thermodynamic modelling shows that high oxygen fugacity, near the FMQ buffer,
476 should be a ubiquitous feature of any silicate melt-vapour disk at high temperatures
477 (>1800 K) (Visscher and Fegley Jr, 2013). These higher oxygen fugacities relative to
478 those of the solar nebular gas promote the evaporation of Cr (Sossi et al. 2019). At these
479 conditions (near FMQ), Cr in the gas should mainly exist as CrO_2 according to
480 calculations made with thermodynamic data for homogeneous equilibria involving Cr,
481 CrO , CrO_2 and CrO_3 gas species from the JANAF tables (Chase, 1998). If we consider
482 that 90% of the Cr in the condensed phase is divalent, the appropriate evaporation
483 equation is:



485 Sossi et al. (2018) estimated the equilibrium fractionation factor of $^{53}\text{Cr}/^{52}\text{Cr}$
486 between $\text{CrO}(l)$ and $\text{CrO}_2(g)$ using bond valence theory to be:

487
$$\Delta^{53}\text{Cr}_{\text{CrO}(l)-\text{CrO}_2(g)} = (-0.31 \pm 0.16) \times \frac{10^6}{T^2} \text{ (‰)}. \quad (6)$$

488 The composition of the Vestan mantle in equilibrium with a CrO₂-bearing gas
 489 phase can be calculated by mass balance in which:

490
$$\delta^{53}\text{Cr}_{\text{vapour}} = \frac{\delta^{53}\text{Cr}_{\text{system}} - \delta^{53}\text{Cr}_{\text{silicate Vesta}} \times f_{\text{silicate Vesta}}^{\text{Cr}}}{(1 - f_{\text{silicate Vesta}}^{\text{Cr}})}. \quad (7)$$

491 As explained above, $\delta^{53}\text{Cr}_{\text{system}}$ is taken to be the average of ordinary chondrites
 492 ($-0.12 \pm 0.03 \text{ ‰}$), $\delta^{53}\text{Cr}_{\text{silicate Vesta}}$ is $-0.22 \pm 0.03 \text{ ‰}$, and $f_{\text{silicate Vesta}}^{\text{Cr}}$ is ~ 0.43 ,
 493 yielding $\delta^{53}\text{Cr}_{\text{vapour}} = -0.04 \pm 0.03 \text{ ‰}$ and $\Delta^{53}\text{Cr}_{\text{CrO}(l)-\text{CrO}_2(g)} = -0.18 \pm 0.04 \text{ ‰}$.
 494 Solving Equation (6) for temperature and propagating uncertainties yields a
 495 temperature of $1300 \pm 500 \text{ K}$. A similar rationale can be applied using another type of
 496 chondrite as representative of bulk Vesta. For example, the most extreme case, using CI
 497 chondrites with Cr and Al content of 2630 ppm and 8600 ppm respectively (Wasson
 498 and Kallemeyn, 1988) and $\delta^{53}\text{Cr}$ value of -0.15 ± 0.01 (Bonnand et al., 2016b) gives a
 499 $f_{\text{silicate Vesta}}^{\text{Cr}} = \sim 0.44$, $\delta^{53}\text{Cr}_{\text{vapour}} = -0.09 \pm 0.03 \text{ ‰}$ and $\Delta^{53}\text{Cr}_{\text{CrO}(l)-\text{CrO}_2(g)} = -$
 500 $0.13 \pm 0.04 \text{ ‰}$. According to equation (6), the temperature range is $1550 +750/-600 \text{ K}$
 501 (Figure 4). These two extreme models show that the volatile loss of Vesta occurred
 502 under relatively cool conditions ($<2300 \text{ K}$) and likely near the liquidus of basaltic
 503 magma ($\approx 1500 \text{ K}$).

504 These relatively low temperatures for Vesta's volatile loss can be reconciled with
 505 a degassing process during a magma ocean stage instead of a high-temperature giant
 506 impact ($\approx 4000 \text{ K}$; Nakajima and Stevenson, 2014). Volcanic eruptions and magmatic

507 fire fountains may also contribute to volatile loss on a local scale (Day and Moynier,
508 2014). However, the three basaltic eucrites with homogeneous $\delta^{53}\text{Cr}$ and distinct trace
509 element abundance (Barrat et al., 2000) and different cosmic ray exposure ages (9.5 Ma
510 for Juvinas, 31.4 Ma for Jonzac and 38.5 Ma for Camel Donga; Eugster and Michel,
511 1995) most probably come from different regions of Vesta, so localized degassing
512 processes are not consistent with the Cr isotopic data. Furthermore, considering that the
513 volatile degassing process must occur before Vestan crust formation, magmatic
514 degassing should predate the magmatic differentiation of the HEDs that lead to co-
515 variations between $\delta^{53}\text{Cr}$ and Mg# between eucrites and diogenites.

516 The homogeneous oxygen isotope compositions in HEDs suggests a widespread
517 magma ocean on Vesta (Greenwood et al., 2005; 2014), which is consistent with the Cr
518 isotopic evidence in this study. Al-Mg and Mn-Cr ages for bulk HED meteorites
519 indicate that Vesta differentiated very early, 1~3 Ma after CAIs (the first solids formed
520 in the Solar System), and these old Al-Mg and Mn-Cr ages should reflect the crust-
521 mantle differentiation after early magma ocean (Trinquier et al., 2008; Schiller et al.,
522 2011; Day et al., 2012; Hublet et al., 2017; Schiller et al., 2017). An early-formed
523 carapace or shell formed via radiative cooling from the surface could effectively shut-
524 off evaporation, however, numerical calculations show that these skins are of the order
525 of a few centimeters thick and prone to foundering (Hin et al. 2017), and therefore do
526 not restrict outgassing from small rocky bodies. As such, the late formation of the
527 Vestan crust shows that the volatile depletion on Vesta must have occurred before the
528 crystallization of the magma ocean, which is consistent with volatile loss ages, within

529 1 My after CAI, suggested from Rb-Sr dating (Hans et al., 2013) and with the heavy
530 Mg isotope enrichment observed (Hin et al., 2017; Dhaliwal et al., 2018). However, the
531 magma ocean model is challenged by considering the physical principles of planetary
532 accretion and geochemical and petrological evidence from meteorites (Lunning et al.,
533 2015; Wilson and Keli, 2017), which suggest that magma oceans are not ubiquitous
534 occurrence during planetary formation. If so, then the volatile depletion of Vesta may
535 have been imposed by accretion of material depleted in the solar nebula (Bloom et al.,
536 2018). However, the nebular gas is very reduced (with $\log fO_2 = -18.1$ at 1500 K, or IW-
537 6.8; Grossman et al. 2008), and under such conditions, neither Mn nor Cr are
538 appreciably volatile. It would therefore be difficult to explain the super-chondritic
539 Mn/Na of Vesta (O'Neill and Palme, 2008). Furthermore, Cr in condensed phases
540 would be expected to be, on average, more oxidized (a combination of Cr^{2+} and Cr
541 metal) relative to the gas phase (Cr^0), such that equilibrium isotope fractionation would
542 result in heavy Cr in the solid residue. In this way, Cr in Vesta should be isotopically
543 heavier than chondrites, which is not consistent with the light Cr isotope compositions
544 in HEDs. As highlighted above, it cannot be excluded that the eucrites come from a
545 fractionated, Fe-rich part of the Vestan mantle, or that there is resolvable Cr isotope
546 fractionation during partial melting. Finally, the Cr isotopic study in eucrites and
547 diogenites supports the large-scale magma ocean caused the volatile depletion, and
548 magma oceans should play a critical role in determining the volatile element contents
549 of bodies formed in the early Solar System (Hin et al. 2017; Dhaliwal et al. 2018; Young
550 et al. 2019).

551 **5 Conclusions**

552 This work reports high-precision Cr stable isotope compositions of bulk eucrites
553 and diogenites. It shows that eucrites are isotopically lighter than diogenites, and that
554 their Cr isotope compositions are correlated with the Cr content and Mg#, which
555 suggests crystallization modified the Cr isotope composition of magmas on Vesta. This
556 systematics is reconciled with isotopically heavy Cr³⁺ entering orthopyroxene that
557 characterizes diogenites, whereas the eucrites represent both parental partial melts of
558 the Vestan mantle, and some later differentiates that contain predominantly Cr²⁺.

559 Based on their high Mg#s and lack of accumulated minerals, the non-cumulate
560 eucrites likely provide the best indication as to the composition of the mantle of Vesta.
561 However, the Cr isotope composition deduced for Vesta based on these samples (-0.22
562 ± 0.03 ‰) is lighter than that of its potential building blocks, ordinary chondrites (-0.12
563 ± 0.03 ‰). This deficit may arise due to *i*) partial melting in which residual Cr³⁺-bearing
564 phases in the Vestan mantle sequester the heavy isotopes or *ii*) vapor loss during
565 equilibrium with a magma ocean on Vesta. The former requires very high Cr contents
566 in the Vestan mantle, and that partial melting occurred at oxygen fugacities high enough
567 to stabilize chromite in the mantle source. By contrast, equilibrium fractionation of Cr
568 isotopes necessitates an oxidized vapor and reduced residue, consistent with
569 thermodynamic constraints of the composition of the vapor phase above a silicate
570 magma ocean. If correct, this model suggests a relatively low temperature for the
571 volatile degassing process (< 2300 K) that lead to the impoverishment and light isotope

572 composition of Cr. This result argues that magma ocean degassing may be ubiquitous
573 during the accretionary stages of small telluric bodies.

574

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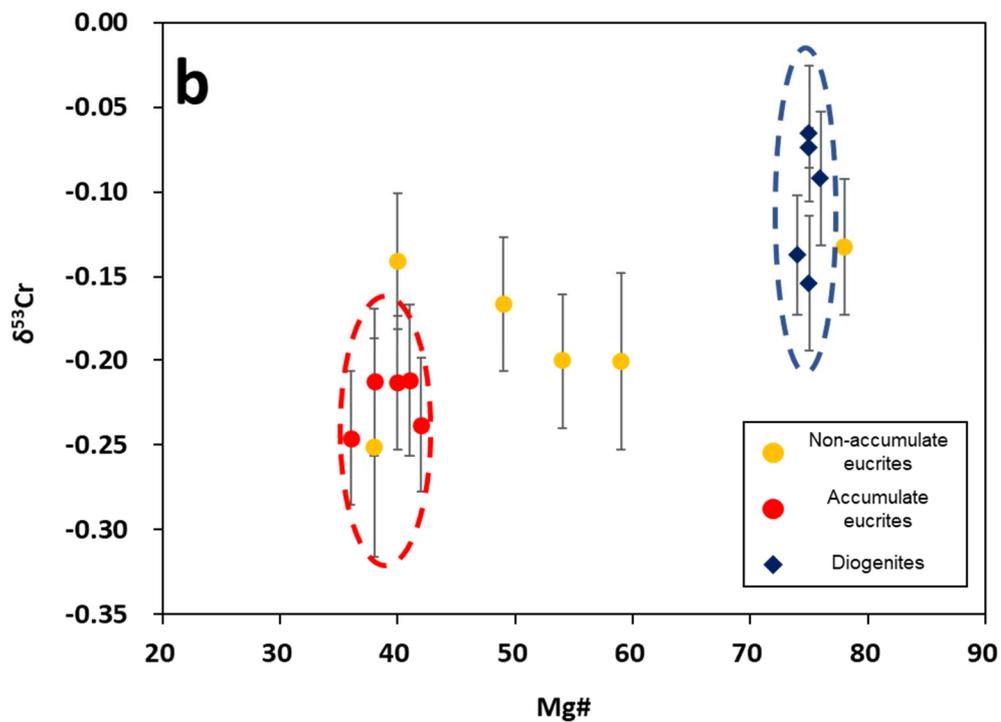
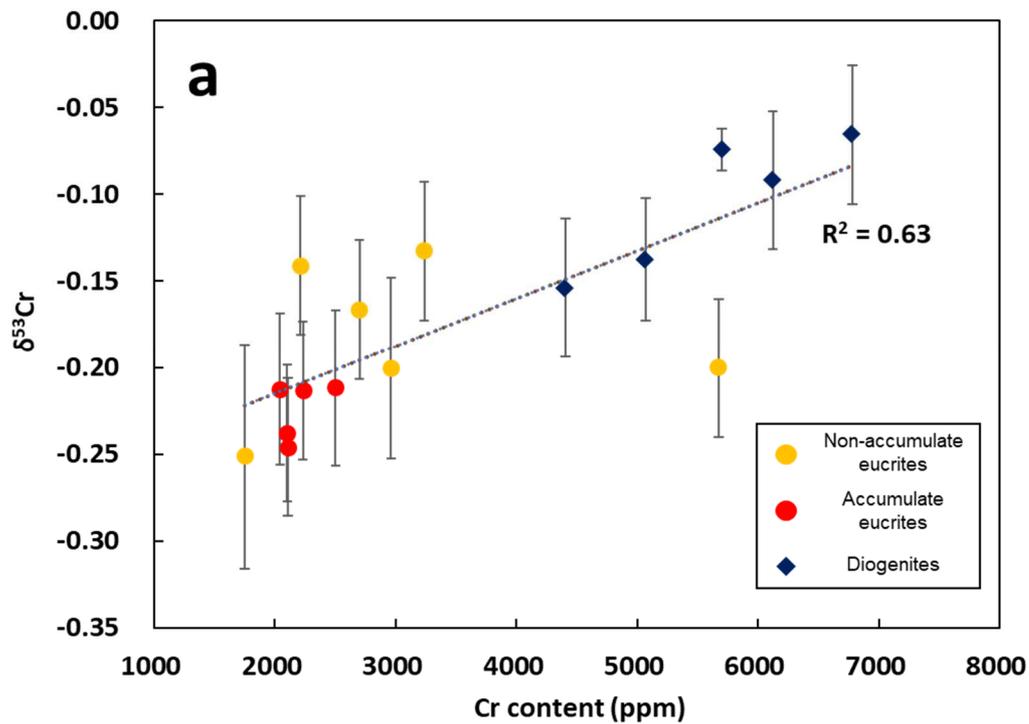
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594 Figure 1 a. Chromium isotope composition vs. Cr content in HED samples. b. Cr

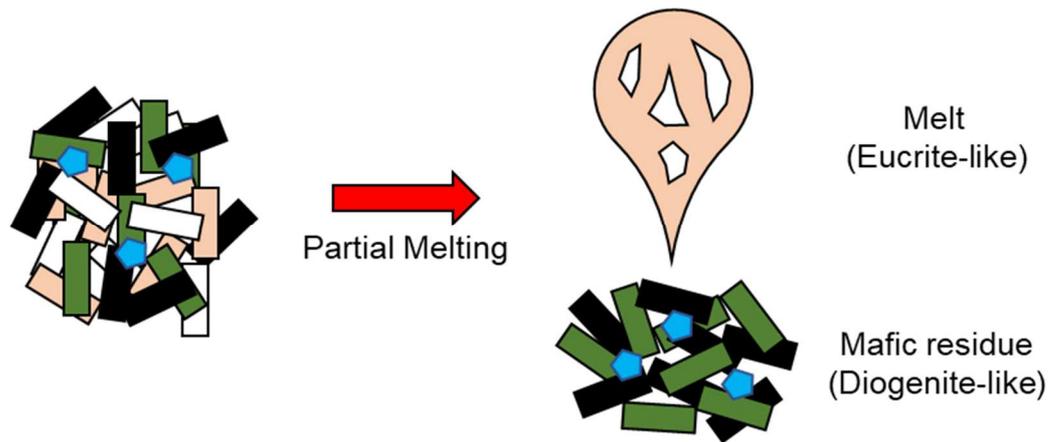
595 isotopes composition vs. Mg# in HED samples. Red circles: non-accumulate eucrites,

596 yellow circles: cumulate eucrites and blue diamonds: diogenites. The red circle

597 indicates the reservoir for basaltic eucrites with low Mg# and light Cr, while the blue

598 circle is for the diogenites with high Mg# and isotopically heavy Cr.

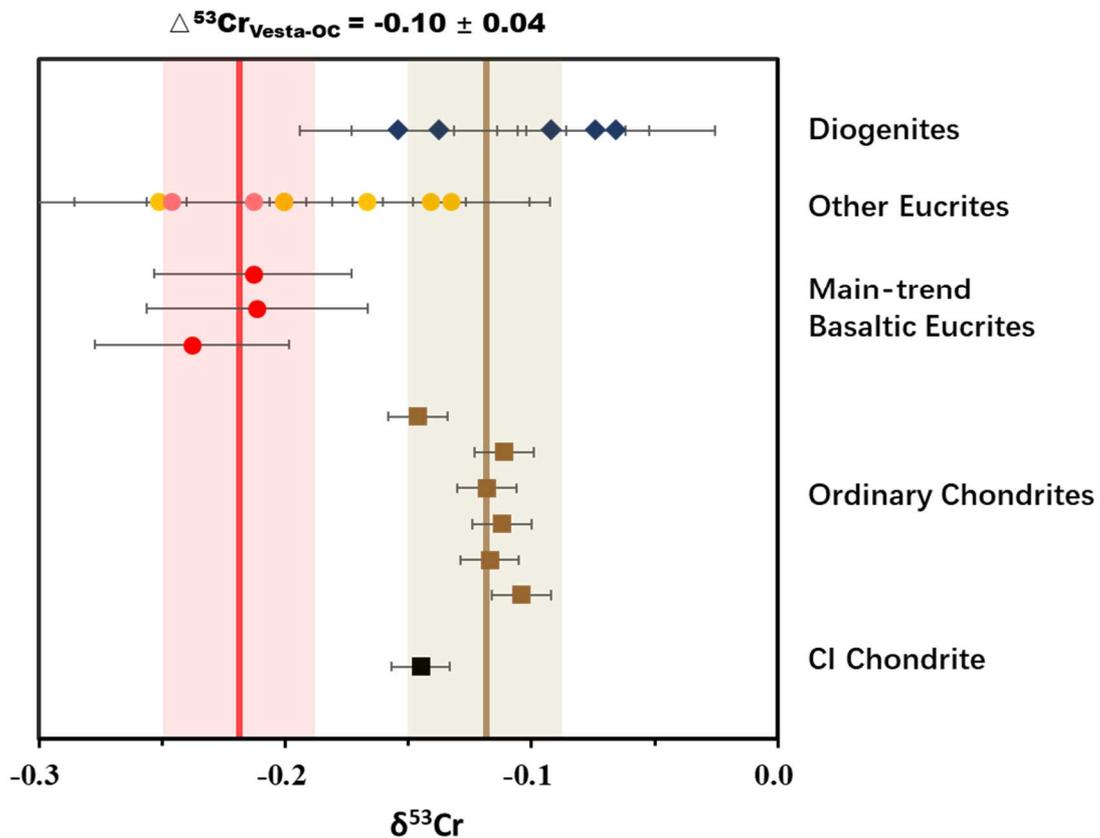
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601 Figure 2 Schematic diagram illustrates the effect of partial melting on the Cr stable
 602 isotope composition of Vesta. The white and light pink bars are felsic composition,
 603 while the green and black bars represent the mafic composition. The blue pentagons are
 604 chromites (Cr-spinels). After partial melting, the felsic composition would mainly go
 605 to the melt while the mafic composition would stay in the residues. It should be noted
 606 that, the pyroxenes and chromites which are compatible to isotopically heavy Cr^{3+} in
 607 the residues would make the residue have higher $\text{Cr}^{3+}/\text{Cr}_{\text{Total}}$ and isotopically heavy for
 608 Cr isotopes. Complementarily, the melt part would be dominated in Cr^{2+} and
 609 isotopically light for Cr. However, the diogenites are not necessarily complementary to
 610 eucrites, but some other range of Vestan melts.

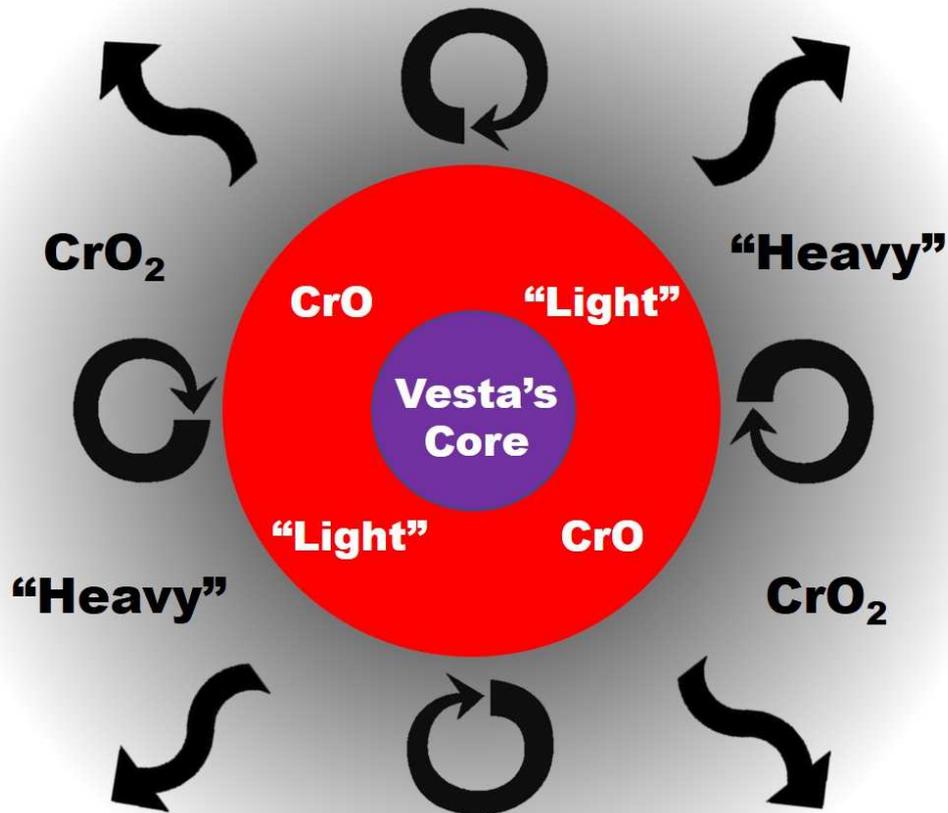
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613 Figure 3 Comparison of the Cr isotope compositions of Diogenites (blue diamond),
 614 Eucrites (yellow and red circles). The red is for main-trend basaltic eucrites, and the
 615 pink is for Stannern-trend basaltic eucrites and yellow for other eucrites). Ordinary
 616 chondrites are shown as brown squares and CI chondrite is shown as a black square.
 617 The light red shade indicates the 2SD of Cr isotope values for three basaltic eucrites
 618 which may represent the primitive Vesta, while the light brown shade is for that of
 619 ordinary chondrites which may represent the building blocks for Vesta. The $\delta^{53}\text{Cr}$ deficit
 620 between primitive Vesta and ordinary chondrites is $\Delta^{53}\text{Cr}_{\text{Vesta-OC}} = -0.10 \pm 0.04$, which
 621 should be equilibrium fractionation during the Cr loss or caused by partial melting effect
 622 at a large-scale magma ocean stage.

623



625

626 Figure 4 Schematic diagram illustrating the effect of volatile loss on the Cr stable
 627 isotope composition of Vesta (average radius of 262.7 km; Russell et al., 2012). In this
 628 model, within 1 Myr after CAI (dated by the volatile-sensitive ⁸⁷Rb-⁸⁷Sr chronometer;
 629 Hans et al., 2013), the ²⁶Al-to-²⁶Mg decay system released sufficient heat to melt Vesta
 630 globally (Schiller et al., 2011). The temperature at the surface of the magma ocean is
 631 estimated to have been under 2300 K. Under such conditions, the *f*O₂ during silicate-
 632 vapor equilibrium should approach the FMQ buffer. Modeling in Young et al. (2019)
 633 support near-equilibrium isotope fractionation between a magma ocean and its vapour
 634 atmosphere during planetesimal evaporation. At this *f*O₂, Cr in the vapour (CrO₂) is
 635 more oxidized than in the melt at equilibrium (CrO). Accordingly, equilibrium
 636 fractionation produces a residual melt isotopically lighter than the vapour. The core only
 637 contains 1~3% of Vesta's Cr budget, and core formation likely did not induce Cr isotope
 638 fractionation.

639

640

Table 1 Cr stable isotope, Cr content and Mg# data of HED meteorites

Sample	Fall/Find	Type	Cr (ppm)	Mg#	$\delta^{53}\text{Cr}$	2SD	N
Pasamonte	fall	Eucrite-pmict	1750	38	-0.27	0.06	2
replicate					-0.23	0.05	2
average					-0.25	0.06	4
Stannern	fall	Eucrite-mmict	2041	38	-0.22	0.04	2
replicate					-0.21	0.04	2
average					-0.21	0.04	4
Jonzac	fall	Eucrite-mmict	2501	41	-0.21	0.04	2
replicate					-0.22	0.04	2
average					-0.21	0.04	4
Juvinas	fall	Eucrite-mmict	2100	42	-0.26	0.04	2
replicate					-0.22	0.04	2
average					-0.24	0.04	4
Bouvante	find	Eucrite-mmict	2106	36	-0.25	0.04	2
Camel Donga	find	Eucrite-mmict	2232	40	-0.21	0.04	2
Moore County	fall	Eucrite-cm	2699	49	-0.17	0.04	2
Pomozdino	find	Eucrite-cm	3237	78	-0.13	0.04	2
Serra de Magé	fall	Eucrite-cm	2962	59	-0.20	0.05	2
		Eucrite-Mg					
EET 87548	find	rich	5673	54	-0.20	0.04	4
EET 87542	find	Eucrite-br	2212	40	-0.14	0.04	2
EET 79002	find	Diogenite	5068	74	-0.14	0.04	2
Tatahouine	fall	Diogenite	6122	76	-0.09	0.04	2
LAP 03569	find	Diogenite	6780	75	-0.07	0.04	2
Shalka	fall	Diogenite	4404	75	-0.15	0.04	4
Johnstown*	fall	Diogenite	5700	75	-0.07	0.01	1
BHVO-2		Basalt	280		-0.13	0.04	1
DTS-1		Dunite	3990		-0.08	0.04	2
PCC-1		Peridotite	2730		-0.10	0.04	2

642 Note: the Cr content and Mg# (the ratio of Mg to the sum of Mg and Fe on an atomic
643 basis) data are in these literature (Barrat et al., 2000; 2008; Bonnand et al., 2016b;
644 Lugmair and Shukolyukov, 1998; Schoenberg et al., 2016; Warren et al., 2009). One
645 data marked * (Johnstone) is from Bonnand et al. (2016b).
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