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Evidence from Tm anomalies for non-CI refractory lithophile element proportions in terrestrial planets and achondrites

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► **To cite this version:**

Jean-Alix J-A Barrat, N. Dauphas, P. Gillet, Claire Bollinger, J. Etoubleau, et al.. Evidence from Tm anomalies for non-CI refractory lithophile element proportions in terrestrial planets and achondrites. *Geochimica et Cosmochimica Acta*, 2015, 176, pp.1-17. insu-01244242

HAL Id: insu-01244242

<https://insu.hal.science/insu-01244242>

Submitted on 15 Jan 2016

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38 **Abstract**

39 Thulium is a heavy rare earth element (REE) whose geochemical behavior is intermediate
40 between Er and Yb, and that is not expected to be decoupled from these elements during accretion of
41 planetary bodies and geological processes. However, irregularities in REE volatilities at higher
42 temperature could have decoupled the REEs relative to one another during the early stages of
43 condensation of the solar nebula. Indeed, positive Tm anomalies are found in some refractory
44 inclusions from carbonaceous chondrites, and it is possible that large scale nebular reservoirs
45 displaying positive or negative Tm anomalies were formed during the early history of the solar system.
46 We analyzed a series of meteorites and terrestrial rocks in order to evaluate the existence of Tm
47 anomalies in planetary materials. Relative to CIs (Ivuna-type carbonaceous chondrites), carbonaceous
48 chondrites display unresolved or positive Tm anomalies, while most of the noncarbonaceous
49 chondrites show slightly negative Tm anomalies. Quantification of these anomalies in terrestrial
50 samples is complicated when samples display fractionated heavy REE patterns. Taking this effect into
51 account, we show that the Earth, Mars, Vesta, the aubrite and ureilite parent bodies display small
52 negative anomalies ($Tm/Tm^* \approx 0.975$), very similar to those found in ordinary and enstatite chondrites.
53 We suggest that a slight negative Tm anomaly relative to CI is a widespread feature of the materials
54 from the inner solar system. This finding suggests that CI chondrites may not be appropriate for
55 normalizing REE abundance patterns of most planetary materials as they may be enriched in a high-
56 temperature refractory component with non-solar composition. The presence of Tm anomalies at a
57 bulk planetary scale is, to this day, the strongest piece of evidence that refractory lithophile elements
58 are not present in constant proportions in planetary bodies.

59

60 **1. Introduction**

61 Rare Earth Elements (REEs) are a group of elements whose geochemical properties are very
62 similar to each other. They are generally trivalent with ionic radii decreasing smoothly from La to Lu.
63 The coherence of their behaviors makes them prime elements for geochemical modeling. Their
64 abundances are classically shown with “Masuda-Coryell plots”, where the ratio of each REE
65 concentration to the corresponding value in a reference is plotted as a function of atomic number
66 (Masuda, 1962; Coryell et al., 1963). The references most commonly used in this normalization
67 scheme are a CI chondrite average (e.g., Anders and Grevesse, 1989; Pourmand et al., 2012; Barrat et
68 al., 2012; Palme et al., 2014) and post Archean Australian shale (PAAS; e.g., Nance and Taylor, 1976;
69 Taylor and McLennan, 1985; Pourmand et al., 2012). The resulting curves, known as REE patterns,
70 became one of the most widely used tools to trace geological processes (e.g., Frey et al., 1978;
71 Hanson, 1980; Taylor and McLennan, 1981). These diagrams provide a means of assessing the REE
72 abundances of many samples at a glance, and to detect easily the decoupling of some elements relative

73 to their neighbors, when the conditions that prevail in the system compel them to a different valence.
74 On Earth for example, Eu and Ce anomalies are found in many magmatic rocks and in aqueous surface
75 environments, respectively when Eu and Ce are present in their 2+ or 4+ valence states while other
76 lanthanides are in their 3+ valence state.

77

78 REEs are refractory elements, meaning that their temperatures of condensation during cooling
79 of a solar gas composition at conditions relevant to the formation of the solar system are higher than
80 those of major elements such as Mg or Si (e.g., Boynton, 1975; Davis and Grossman, 1979, Lodders,
81 2003). Their temperatures of condensation vary from one REE to another, so they can be fractionated
82 from each other at high temperature during evaporation or condensation processes (e.g., Pack et al.,
83 2004 and references therein). This is best illustrated with refractory inclusions found in chondrites,
84 which are the first solids formed in the solar system, that display distinctive volatility-controlled REE
85 patterns with a variety of Ce, Sm, Eu, Tm and Yb anomalies (e.g., Tanaka and Masuda, 1973; Mason
86 and Taylor, 1982; MacPherson, 2003; Fegley and Ireland, 1991; Hiyagon et al., 2011 and references
87 therein).

88

89 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is established as a premier
90 technique for the determination of trace element abundances in rocks. Unlike previous analytical
91 procedures such as neutron activation or isotope dilution-thermo-ionization mass spectrometry, ICP-
92 MS can simultaneously measure the concentrations of all the REEs present in a given sample. Thus,
93 ICP-MS can allow us to detect small anomalies that were previously not accessible using earlier
94 techniques.

95

96 Until recently, it was thought that the REE patterns of terrestrial rocks could only display Eu
97 or Ce anomalies. Thus, the discovery of slight negative Tm anomalies in shales when normalized to CI
98 chondrite was surprising (Pourmand et al., 2012). This observation was subsequently confirmed in
99 some other terrestrial samples and extended to ordinary chondrites, enstatite chondrites, samples from
100 Mars, Moon and Vesta (Bendel et al. 2011, 2012a,b; Dauphas and Pourmand, 2015). Because the
101 negative Tm anomalies obtained in planetary materials by previous workers are small (a few percent),
102 one may argue that they could be at the limit of the precision of the analytical methods, or artifacts
103 produced by an overestimation of the Tm abundance in the chondritic reference. In this paper, we
104 report on analyses obtained on 87 terrestrial and meteoritic samples using a well-established ICP-MS
105 procedure (e.g., Barrat et al., 2012). Our aim is firstly to confirm the Tm abundance in average CI
106 chondrites, secondly to evaluate the diversity of Tm anomalies in differentiated planetary bodies such
107 as Mars and Vesta, which were not investigated in the recent study of Dauphas and Pourmand (2015),
108 which focused on chondrites and Earth, and finally to determine the Tm anomaly of the bulk Earth.

109

110 **2. Samples and analytical methods**

111 Seventeen chondrites, seven eucrites (from asteroid 4 Vesta), six shergottites (from Mars), one
112 lunar meteorite, nine other achondrites (ureilites, aubrites, one angrite and one ungrouped achondrite),
113 forty-six samples from the Earth (including reference materials), and one olivine fraction from a
114 pallasite, were selected in order to capture the diversity of chondrites and magmatic rocks from Earth,
115 Mars and asteroids. These samples were obtained during the last twenty-five years from various
116 sources including the Muséum National d'Histoire Naturelle de Paris (MNHN), Ifremer (Plouzané,
117 France), Université de Rennes 1 (France), Université de Paris VI (France), Université de Bretagne
118 Occidentale (Brest), the National Institute of Polar research (Tokyo), the Natural History Museum,
119 Vienna, the Smithsonian Institution, the Meteorite Working Group (NASA), the Institute for
120 Meteoritics, Albuquerque, the Northern Arizona University, Flagstaff, and meteorite collectors. The
121 details of the meteorite samples used in this study are given in supplementary Table S1.

122
123 Most of the samples were previously characterized extensively for their chemical and
124 mineralogical compositions. The concentrations of some REEs were previously determined in various
125 laboratories using different analytical techniques but with a few exceptions, mono-isotopic Tm was
126 not analyzed. In this study, REE abundances were determined using a Thermo Element 2 ICP-mass
127 spectrometer at Institut Universitaire Européen de la Mer (IUEM), Plouzané, following a well-
128 established procedure first developed at the University of Southampton and Université Joseph Fourier
129 (Barrat et al., 1996), and regularly improved since then (e.g., Barrat et al., 2012). The methodology is
130 briefly summarized below.

131
132 Samples were finely powdered using a boron carbide mortar and pestle. Typically, 120 mg of
133 the powder were dissolved in closed screw-top teflon vessels (Savillex) at about 130 °C for three days
134 using 5 ml of concentrated HF and 2 ml of concentrated HNO₃. The vessels were then opened. After
135 evaporation to dryness of the acid mixture, approximately 2 ml of HNO₃ was added, and the vessels
136 were capped and put back on the hot plate and left overnight. The samples were then dried again, and
137 taken up in about 20 g of 6 M HCl (“mother solutions”). No residual grains were observed in the
138 mother solutions except for ureilites, which contained some carbon grains (low REE concentration
139 graphite and diamond) having no impact on the results. Only reagents double-distilled in quartz or
140 teflon sub-boilers were used. For each sample, the abundances of REEs were determined using two
141 aliquots of the mother solution.

142
143 A first aliquot of the mother solution was dried and the residue was taken up and dissolved in
144 diluted HNO₃ (2 %) containing traces of HF. This sample solution (solution 1) was analyzed in
145 triplicate, in a sequence containing a procedural blank, a BHVO-2 reference solution (prepared like the

146 samples), and a series of solutions for the corrections of oxide and hydroxide interferences (pure
 147 water, Ba+Ce, Pr+Nd, and Sm+Eu+Gd+Tb solution, see Barrat et al. (1996) for more details). One
 148 BHVO-2 reference solution was analyzed every three samples and used for both calibration and drift
 149 corrections. The raw data were first corrected for drift, procedural blank and interferences. $[X]_1$, the
 150 raw concentration of a given element X in sample was calculated using the corrected data for the
 151 BHVO-2 and sample solutions. Then, the three analyses obtained for each sample were averaged.

152

153 A second aliquot of the mother solution was spiked with a pure solution of Tm, and processed
 154 like the previous one. The spiked sample solution (solution 2) was analyzed using a separate sequence
 155 similar to that used for unspiked samples. The REE abundances (except Tm) in the sample are
 156 calculated with the following equation (Barrat et al., 1996):

157

$$158 \quad [X]_2 = (C_x / C'_{Tm1}) (M_{Tm} / M) / [(C_{Tm} / C'_{Tm1}) - 1] \quad (1)$$

159

160 Where $[X]_2$ and C_x are the concentrations of the element X in the sample and in the solution
 161 2, respectively. C_{Tm} and C'_{Tm1} are respectively the concentration of Tm in solution 2 and the estimated
 162 concentration of Tm in this solution without the contribution of the spike. C'_{Tm1} was directly
 163 calculated using the Tm/Er and Tm/Yb ratios previously obtained for the unspiked solution (solution
 164 1). M is the mass of sample contained in the aliquot of the mother solution used to prepare solution 2,
 165 and M_{Tm} is the amount of Tm added. Note that the choice of a Tm-spike here is not specific to the
 166 present study but corresponds to the routine procedure used by the first author in Brest.

167

168 REE abundances obtained with solutions 1 and 2 are of course very similar, but Tm
 169 abundances cannot be determined using solution 2. However, the concentrations obtained with
 170 solution 2 are considered more robust, because less affected by the errors on the dilution factors, and
 171 less prone to the instrumental drift (Barrat et al., 1996) than the concentrations calculated with solution
 172 1. On the other hand, REE ratios determined with the unspiked solution (solution 1) are more accurate
 173 because the solution was run in triplicate. Therefore, $[X]$, the final REE concentrations were calculated
 174 combining $[X]_1$ and $[X]_2$, the results for both solutions as follow:

175

$$176 \quad [X] = K [X]_1 \quad (2)$$

177

178 where $K = ([La]_2/[La]_1 + [Ce]_2/[Ce]_1 + [Pr]_2/[Pr]_1 + [Nd]_2/[Nd]_1 + [Sm]_2/[Sm]_1 + [Eu]_2/[Eu]_1 + [Gd]_2/[Gd]_1 +$
 179 $[Tb]_2/[Tb]_1 + [Dy]_2/[Dy]_1 + [Ho]_2/[Ho]_1 + [Er]_2/[Er]_1 + [Yb]_2/[Yb]_1 + [Lu]_2/[Lu]_1) / 13$

180

181 Two samples (NWA 7325, and an olivine separate from the Brenham pallasite) display very
 182 low heavy REE abundances ($< 0.1 \times CI$). Their REEs were concentrated and separated from the major

183 elements before analysis following the method described by Barrat et al. (1996). These two samples
184 were previously analyzed without REE separation and Tm abundances were not available (Greenwood
185 et al., 2015; Barrat et al., 2015). The new analyses now include Tm, and the other REE abundances are
186 in excellent agreement with the previous ones (the previous and new analyses usually agree within
187 4%).

188

189 The results for international reference materials are given in Table 1, relative to our working
190 values for the USGS basalt BHVO-2. The latter were derived from the isotope dilution results
191 obtained by Raczek et al. (2001) for La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb and Lu, and from our
192 previous ICP-MS analyses for Pr, Tb, Ho, and Tm (Barrat et al., 2012). In the event of future change
193 to these BHVO-2 values, the data need only to be corrected by the ratio of the new and old values.
194 Based on replicate analyses of standard reference materials and samples (Barrat et al., 2012, 2014), the
195 precision for REE abundances is much better than 3 % (one relative standard deviation - RSD).

196

197 The accuracy of our results is of course directly linked to the accuracy of our working values
198 for BHVO-2. At present, BHVO-2 is one of the best characterized reference materials for REEs, and
199 our working values are very similar to the GEOREM's preferred values (georem.mpch-
200 mainz.gwdg.de). Furthermore, the results obtained for other well-characterized reference materials
201 (e.g., Bayon et al., 2009; Barrat et al., 2012, 2014) confirm that the BHVO-2 working values are
202 accurate and validate our calibration, as exemplified here by the results obtained for BIR-1 and BCR-2
203 (Table 1 and Fig. 2), which are other well-known reference materials.

204

205 The Tm anomalies can be estimated using the Tm/Tm^* ratio, where Tm^* is the interpolated
206 Tm concentration for a smooth CI-normalized REE pattern and X_n is the concentration of element X
207 normalized to chondrite:

208

$$209 \quad Tm/Tm^* = (Tm_n) / (Er_n \times Yb_n)^{1/2} \quad (3)$$

210

211 The relative standard deviations of Tm/Tm^* values based on replicate BCR-2 and BIR-1 are
212 better than 0.6 % and 0.3 %, respectively (Table 1). From the results obtained for both reference
213 materials and sample replicates, we estimate that the precision of Tm/Tm^* measurements is better than
214 0.7 % (1 RSD).

215

216 Dauphas and Pourmand (2015) used different equations to estimate the Tm anomalies. In a
217 first equation, Tm^* is interpolated linearly using the logarithm of the CI-normalized abundances
218 against ionic radius of Er and Yb:

219

220
$$(Tm/Tm^*)_{D\&P}=(Tm_n)/(Er_n^{0.55} \times Yb_n^{0.45}) \quad (4)$$

221

222 As shown in Figure 1, the Tm anomalies obtained using this equation are similar to those
 223 obtained with equation (3). Moreover, Dauphas and Pourmand (2015) proposed a second estimation of
 224 the Tm anomalies using Er and Lu, because Yb can be decoupled from the other REEs in highly
 225 reducing conditions (e.g., Pack et al., 2004):

226

227
$$(Tm/Tm^{**})_{D\&P}=(Tm_n)/(Er_n^{0.66} \times Lu_n^{0.34}) \quad (5)$$

228

229 Finally, they noticed that the curvature of the REE patterns could affect the Tm anomalies
 230 when based on simple linear interpolations. They proposed a third approach for normalizing Tm by
 231 using a Lagrangian (3rd order polynomial) interpolation between four REEs, Dy, Ho, Er and Lu:

232

233
$$(Tm/Tm^{***})_{D\&P}=(Tm_n)/(Dy_n^{0.33} \times Ho_n^{-1.29} \times Er_n^{1.85} \times Lu_n^{0.11}) \quad (6)$$

234

235 The enstatite meteorites that we have analyzed do not display negative Yb anomalies. The
 236 $(Tm/Tm^{**})_{D\&P}$ and Tm/Tm^* ratios are very similar (Fig. 1), and consequently the use of equation 5 is
 237 not necessary to compare our enstatite chondrites (EC) samples with the other chondrites. Although
 238 the $(Tm/Tm^{**})_{D\&P}$ and $(Tm/Tm^{***})_{D\&P}$ ratios have their advantages, they will not be used here. In the
 239 rest of the paper, we will use the Tm/Tm^* ratios calculated using equation 3 because these ratios
 240 provide a precise estimate of the Tm-anomalies, are coherent with the inter-element distance in usual
 241 REE plots, and provide in most cases, the same information as the $(Tm/Tm^*)_{D\&P}$ and $(Tm/Tm^{***})_{D\&P}$
 242 ratios. In order to better discuss the curvature effect (CE) of the REE pattern, an additional equation is
 243 preferred. We use a Lagrangian interpolation like Dauphas and Pourmand (2015), but with two
 244 elements at each side of Tm (Ho, Er, Yb, Lu):

245

246
$$Tm/Tm^*_{CE} = Tm_n / [(Yb_n \times Er_n)^4 / (Lu_n \times Ho_n)]^{1/6} \quad (7)$$

247

248 As shown in Figure 1, the Tm/Tm^*_{CE} ratios are more strongly correlated with Tm/Tm^* than
 249 the $(Tm/Tm^{***})_{D\&P}$ ratios, suggesting that the effect of the shape of the REE pattern is more correctly
 250 taken into account with equation 7. The effect of the curvature of the pattern on the calculated
 251 Tm/Tm^* ratio for each sample can be discussed using the CE# number, defined here as the Tm^*_{CE}
 252 $/Tm^*$ ratio:

253

254
$$CE\# = Tm^*_{CE} / Tm^* = [(Yb_n \times Er_n) / (Lu_n \times Ho_n)]^{1/6} \quad (8)$$

255

256 If $CE\# \approx 1$ (i.e., in the range 0.99-1.01), the curvature effect is negligible, and the Tm anomaly
257 estimated using equation 3 is reliable. If $CE\# < 1$, the Tm/Tm* ratio amplifies the negative Tm
258 anomalies and reduces the positive ones. If $CE\# > 1$, the opposite effects are obtained. As we will see
259 for terrestrial lavas, the shapes of the REE patterns can have a significant effect on the Tm/Tm* ratios.
260 Although, these shapes do not generate anomalous or aberrant Tm anomalies, the curvature effects
261 must be taken into account when the Tm/Tm* ratios of samples with very different REE patterns are
262 compared.

263

264 The choice of the normalizing values (i.e., CI concentrations) has an important impact on the
265 values of the calculated Tm/Tm* ratios. However, it has no effect on the offsets between samples of
266 various types. Here we have adopted the CI average recommended by Barrat et al. (2012) because this
267 average was obtained from five “large” samples prepared from distinct stones of Orgueil, which
268 comprise ca. 4 g of this meteorite. *More importantly, the Orgueil analyses were obtained using the*
269 *same procedure and the same calibration strategy as the analyses presented here, minimizing any*
270 *possible systematic bias.* We have reanalyzed aliquots of our Orgueil samples (see below), and the
271 new results confirm the results from Barrat et al. (2012), so that revision of the normalizing values is
272 not necessary.

273

274 The Tm anomalies reported in this study are small ($< 15\%$), but significant as illustrated by
275 the reference materials (Table 1): BIR-1 (Tm/Tm*=0.978, $1\sigma = 0.003$, Table 1) and BCR-2
276 (Tm/Tm*= 0.970, $1\sigma = 0.006$, Table 1) have Tm/Tm* ratios that are respectively 7σ and 5σ below
277 the mean CI value. Comparison with literature results is not straightforward because systematic biases
278 between laboratories are present (Fig. 2). To mitigate this problem, we have adjusted the results
279 obtained by Pourmand et al. (2012, 2014), Stracke et al. (2012), Dauphas and Pourmand (2015) to our
280 calibration using BIR-1, BCR-2, and BHVO-2, and Khan et al. (2015) using the Smithsonian
281 Institution Allende powder (USNM 3529) as follow:

282

$$283 \quad (Tm/Tm^*)_{\text{sample,corrected}} = (Tm/Tm^*)_{\text{standard,Brest}} \times (Tm/Tm^*)_{\text{sample,measured}} / (Tm/Tm^*)_{\text{standard,measured}} \quad (9)$$

284

285 where Tm* is calculated using the average CI abundances obtained by Barrat et al. (2012), and
286 (standard refers to BHVO-2, BIR-1, BCR-2 or USNM 3529 depending on the study considered).
287 When the literature data were accompanied by two or more standards, the corrected Tm/Tm* ratios
288 were averaged. The corrections were small and similar when two or more standards were considered:
289 about 3 % for the data obtained by Dauphas and Pourmand (2015) and about 2 % for the data obtained
290 by Stracke et al. (2012). All values reported or discussed in this paper are relative to our BHVO-2
291 working values.

292

293 **3. Results**

294 Results are given in Tables 1 to 4. The REE abundances of the meteorites and terrestrial rocks
295 analyzed here, are discussed extensively in the literature, and in depth discussions concerning the
296 shape of the REE patterns will not be repeated here. Instead, our study is focused on Tm anomalies,
297 which are small and not always discernable in the REE patterns, as demonstrated in Figure 3. The
298 Tm/Tm* ratios are presented in Figure 4 along with selected literature data. A synthesis of the
299 Tm/Tm* ratios in meteorites and bulk planetary bodies is given in Table 5.

300 **3.1 Tm abundance in the CI reference**

301 Large chips of Orgueil and Ivuna were previously analyzed, and the average of five Orgueil
302 samples was recommended for normalization purposes (Barrat et al., 2012). In order to check the
303 normalization values for the heavy REEs, we dissolved 30 mg splits of the previous CI powders
304 (previous analyses of the same samples were obtained using about 120-150 mg of powders). The
305 results display a limited range of Tm/Tm* ratios from 0.991 to 1.003 (Table 2), with a mean = 0.999
306 ($\sigma=0.005$, $n=10$). These results indicate that our CI average used for normalization does not require
307 revision at the present level of precision. Pourmand et al. (2012) obtained Tm/Tm* ratios ranging from
308 0.999 to 1.043, and consequently a CI average with a small positive anomaly relative to our results
309 (Tm/Tm*=1.022 after correction of the interlaboratory bias). This small discrepancy could be at least
310 partially explained by the small size of most of the chips analyzed by these authors, totaling ca. 2.14 g
311 for Orgueil, Alais and Ivuna, since it is well known that CI chondrites are heavily brecciated and
312 chemically heterogeneous at the sub-mm scale (*e.g.*, Morlok et al., 2006). It is also conceivable that
313 CIs contain rare refractory inclusions (or their remnants after aqueous alteration) which could have
314 affected their Tm abundances (Bendel et al., 2012a,b). Although one small CAI was found in Ivuna
315 (Frank et al., 2011), the limited range of Tm/Tm* ratios shown by our samples is not consistent with
316 the occurrence of heterogeneously dispersed refractory inclusions.

317

318 **3.2 Tm anomalies in other chondrites**

319 The abundance of Tm in chondrites has been measured in a large number of samples by
320 Bendel et al. (2011, 2012a, b), Stracke et al. (2012), Khan et al. (2015), Pourmand et al. (2012) and
321 Dauphas and Pourmand (2015). CM chondrites (Paris, Nogoya and Boriskino), enstatite chondrites (3
322 EH and 3 EL) and ordinary chondrites (Chelyabinsk and Braunschweig) have been analyzed here (Fig.
323 4 and Tables 2-3). Because all these chondrites have CE#-numbers very close to 1 (=0.995-1.006,
324 Table 2), their Tm/Tm* ratios are unaffected by curvature in REE patterns and are faithful measures of
325 Tm anomalies. The three CM samples display Tm/Tm*>1 (*i.e.*, from 1.009 to 1.036) contrary to the
326 two ordinary (average Tm/Tm*= 0.972, $n=2$) and the six enstatite chondrites (average Tm/Tm*=

327 0.983, $\sigma = 0.003$, $n=6$) which all show small negative Tm anomalies. For all these types of chondrites,
328 the new results are in good agreement with data obtained by Dauphas and Pourmand (2015). However,
329 our results for enstatite chondrites appear much more homogeneous than the previously published data
330 (Fig. 4 and Table 5).

331

332 3.3 *Tm anomalies in achondrites and pallasite*

333 Except for the Brenham olivine and NWA 7325, all our achondrite samples have CE#-numbers
334 very close to one ($=0.991-1.003$, Table 3), indicating again that their Tm/Tm* ratios are faithful
335 measures of Tm anomalies. The Tm/Tm* ratios measured on seven eucrites (four main group - Nuevo
336 Laredo trend eucrites: Bereba, Juvinas, NWA 049 and Nuevo Laredo; three Stannern trend eucrites:
337 Stannern, Bouvante, and NWA 2061) are very homogeneous, and range from 0.972 to 0.978. Their
338 average Tm/Tm* ratio ($= 0.974$, $\sigma = 0.002$) is similar to the average of ordinary chondrites ($=0.977$, σ
339 $= 0.006$, $n=22$, see Table 8).

340

341 Similar negative Tm anomalies were obtained for the angrite NWA 1296, and for five aubrites
342 including the samples analyzed by Dauphas and Pourmand (2015). Moreover, the four ureilites
343 analyzed here display analogous negative Tm anomalies (Tm/Tm* $=0.964-0.983$), like the value
344 measured previously for an Almahata Sitta trachyandesite (Tm/Tm* $=0.972$) from the same parent-
345 body (Bischoff et al., 2014). These results strengthen the “noncarbonaceous pedigree” of the ureilite
346 parent body despite the high C contents of the ureilites, as previously suggested by Yamakawa et al.
347 (2010) and Warren (2011a) from isotopic anomalies.

348

349 The REE pattern of the Brenham olivine is enriched in light REEs, with a slightly convex heavy
350 REE distribution (see Fig. 7 in Greenwood et al., 2015). Indeed, the CE#-number is low ($=0.976$) and
351 the curvature of the pattern cannot be ignored. Although its Tm/Tm* ratio ($=0.975$) is similar to those
352 of other achondrites, the Tm/Tm*_{CE} ratio is 0.999 indicating that no Tm anomaly is present in this
353 pallasite. Other pallasites samples are necessary to determine the Tm/Tm* ratio of the main-group and
354 Eagle Station pallasite parent bodies.

355

356 NWA 7325 is an ungrouped achondrite, and it is the sole sample available on Earth from its parent
357 body. It was suggested to have originated from Mercury (Irving et al., 2013), but it is too old to be a
358 sample from the surface of this planet (4562.5 ± 4.4 Ma, Amelin et al., 2013; 4562.8 ± 0.3 Ma, Dunlap
359 et al., 2014). It formed from an unusual melt characterized by very low REE abundances and a very
360 large positive Eu anomaly, generated by the remelting of an ancient gabbroic lithology. NWA 7325 is
361 a remnant of one of the earliest crusts formed on a differentiated body recognized at present (Barrat et
362 al., 2015). It displays the largest negative Tm anomaly analyzed so far in a magmatic rock (Fig. 3). Its

363 Tm/Tm* ratio (=0.855) is too distinct to be explained solely by a curvature effect of the REE pattern
364 despite a low CE#-number (=0.983). Indeed, its Tm/Tm*_{CE} ratio is similarly low (=0.868). A possible
365 explanation for this low value could be an analytical artifact. NWA 7325 displays a huge positive Eu
366 anomaly, and consequently is characterized by a high Eu/Tm ratio of 313. In the case of Eu-rich rocks,
367 the determination of Tm abundances could possibly be hampered by a ¹⁵³Eu¹⁶O interference on the
368 ¹⁶⁹Tm peak, but the former is generally insignificant. This interference is monitored and corrected for
369 in our procedure (e.g., Barrat et al., 1996). A negative Tm anomaly could be obtained if the Eu oxide
370 interference was overcorrected. We have spiked a sample of BIR-1 with a solution of pure Eu, in order
371 to check this effect. Although the Eu/Tm ratio of the spiked BIR-1 sample (Eu/Tm = 205 instead of 2
372 in an unspiked sample) is very high, its Tm/Tm* ratio is identical to the results obtained for unspiked
373 samples (Table 1). We conclude that the low Tm/Tm* ratio obtained for NWA 7325 is real.

374

375 **3.4 Tm anomalies in Martian meteorites**

376 Six shergottites selected for this study range in composition from strongly light-REE depleted
377 (Tissint and Dar al Gani 476) to enriched types (NWA 1669 and Los Angeles), including NWA 1950,
378 one of the rare lherzolic shergottites (Gillet et al., 2005). Their CE# numbers range between 0.992
379 and 0.997, and indicate that the effects of the curvature of the patterns are insignificant. Indeed, the
380 Tm/Tm* ratios fall within a restricted range from 0.974 to 0.983 (average Tm/Tm* = 0.977, σ =
381 0.003), nearly identical to the eucrite and ordinary chondrite values.

382 **3.5 Tm anomalies in terrestrial and lunar rocks**

383 Three types of samples were selected: recent lavas (n=42 including reference materials),
384 mainly basalts, from all the oceans and from different geological settings (mid ocean ridge basalts,
385 ocean island basalts, continental alkali basalts, island arc lavas), tektites (two indochinites and two
386 Libyan Desert glasses) formed from the melting of sedimentary protoliths (e.g., Koeberl, 1992, Barrat
387 et al., 1997), and a lunar meteorite.

388

389 Terrestrial lavas display a wide range of compositions, with a large diversity of REE patterns.
390 Our sampling encompasses a large variety of lavas ranging from light-REE depleted oceanic basalts
391 with no important curvature for the heavy REEs to alkali lavas with strongly fractionated patterns
392 (e.g., lavas from Tubuai or from the French Massif Central). The curvature of the REE patterns is
393 significant for some samples: the CE#-numbers of the lavas range from 0.978 to 0.999. All lavas
394 display a slight negative Tm anomaly and the Tm/Tm* ratios show a significant range of variability,
395 from 0.946 to 0.988 (Fig. 4). The mean Tm/Tm* ratio (=0.965, σ =0.011, n=42) for all lavas including
396 the reference materials BE-N, BIR-1, BHVO-2, JA3, and JB2, is slightly lower than the Vestan and
397 Martian means. The spread of the Tm/Tm* ratios is chiefly explained by a curvature effect of the REE

398 patterns. Indeed, the samples with the lowest CE#-numbers exhibit among the lowest Tm/Tm* ratios
399 (Fig. 5). A more limited range of values is obtained if Tm/Tm*_{CE} ratios are considered (Fig. 5).

400

401 Although the number of high quality Tm analyses of upper crustal rocks available at present is
402 limited, their Tm/Tm* ratios overlap and extend the range obtained for basaltic lavas to lower values
403 (Fig. 4). The REE patterns of the two indochinites are nearly identical, with slight negative Tm
404 anomalies (0.975-0.981) similar to those observed in shales (Figures 4 and 6). A Tm/Tm* as low as
405 0.933 was measured by Dauphas and Pourmand (2015) for G3 granite, a reference material. These
406 authors interpreted the scatter in Tm/Tm* anomalies among terrestrial rocks to reflect the curvature of
407 REE patterns and G3 is indeed a sample that displays a strong curvature (CE# = 0.981). The two
408 Libyan Desert glasses show parallel REE patterns but with slightly more pronounced negative Tm
409 anomalies than shales (Tm/Tm*=0.947-0.954), and these may not totally explained by the curvature of
410 the patterns (Fig. 6). Volatilization of Tm during impact is a possible explanation. However, Libyan
411 Desert glasses display unfractionated isotope compositions of Zn and Cu in comparison to the
412 terrestrial crust (Moynier et al., 2009, 2010). Because these elements are much more volatile than Tm,
413 preferential volatilization of Tm during impact melting is unlikely. More high quality Tm
414 measurements for upper crustal rocks (including granites and sediments), are necessary to evaluate a
415 possible decoupling of Tm during geological processes.

416

417 Dhofar 460, a lunar feldspathic granulitic breccia paired with Dhofar 026, displays a small
418 negative Tm anomaly (Tm/Tm* = 0.969), within error of the terrestrial lava mean.

419

420 **4. Discussion**

421

422 **4.1 Origin of the Tm/Tm* anomalies in chondrites**

423 The dichotomy of Tm anomalies between carbonaceous and non-carbonaceous chondrites is
424 confirmed by our new analyses. All carbonaceous chondrites analyzed so far display unresolved to
425 positive Tm anomalies relative to CI, while most of the non-carbonaceous chondrites exhibit negative
426 Tm anomalies. These negative anomalies are subtle, on the order of just a couple of percent (Tm/Tm*
427 typically close to 0.975), and less marked than those calculated by Dauphas and Pourmand (2015)
428 (Tm/Tm* typically close to 0.96), due to the different CI averages used for normalization.

429

430 Large positive Tm anomalies in some carbonaceous chondrites are well known since a long
431 time, notably in Allende for which they have been interpreted as fingerprints of the presence of group
432 II CAIs (Fig. 6, e.g., Mason and Taylor, 1982; Shinotsuka et al., 1995; Stracke et al., 2012). Thus, it
433 can be inferred that the range of Tm/Tm* ratios in chondrites is mostly controlled by the distribution

434 of refractory inclusions or other refractory components. Indeed, Dauphas and Pourmand (2015)
435 pointed out that there is a relationship between Tm anomalies and Ca isotopic fractionation in bulk
436 meteorites. The reason is that CAIs with type II REE patterns also have fractionated Ca isotopic
437 compositions (Huang et al., 2012). Ordinary and enstatite chondrites have slight negative Tm
438 anomalies and $\delta^{44}\text{Ca}$ values close to the terrestrial composition, while carbonaceous chondrites have
439 positive Tm anomalies and heavy $\delta^{44}\text{Ca}$ values relative to Earth. The data plot on mixing trends
440 defined by type II CAIs and by the terrestrial composition as endmembers (Fig. 7). This general
441 pattern is confirmed by the present study but in order to make progress on this topic, one would need
442 to measure Ca isotopes and Tm anomalies in the same aliquots, as carbonaceous chondrites are likely
443 to be heterogeneous at the sampling scale. Some of the carbonaceous chondrites with high Tm/Tm*
444 values relative to inner solar system bodies are devoid of CAIs (e.g., CIs). The carriers of Tm
445 anomalies need not be in the form of grains that aggregated to form CAIs, however. They could also
446 be in the form of disseminated refractory dust grains that carry the same chemical signature but were
447 obliterated by parent-body processes such as aqueous alteration on the CI parent-body. This means
448 that a simple correlation between the modal abundance of CAIs and Tm anomalies is neither expected
449 nor observed.

450

451 **4.2 *Tm/Tm* ratios of the bulk achondrite parent bodies, Mars and Earth***

452 Because melting and fractional crystallization most likely do not fractionate Tm abundances
453 from those of Er and Yb, the Tm/Tm* ratios of magmatic rocks or mantle restites from a given
454 planetary body provide a picture of the heterogeneity of the body for this parameter. The restricted
455 ranges of Tm/Tm* ratios exhibited by aubrites, ureilites, eucrites and shergottites indicate that their
456 parent bodies accreted from homogeneous building blocks, or were efficiently homogenized by
457 differentiation processes. Consequently, their mean Tm/Tm* ratios are certainly very good estimates
458 of the Tm/Tm* of their parent bodies (Table 5).

459

460 The determination of the Tm anomaly of the bulk Earth is not as straightforward as for those
461 of other telluric bodies, because terrestrial rocks, including lavas and continental rocks, display a
462 puzzling range of Tm/Tm* ratios, from 0.93 to 0.99, which is chiefly explained by the diversity and
463 curvature of their REE patterns (also see Dauphas and Pourmand, 2015). The mean Tm/Tm* ratios of
464 all lavas cannot provide a correct estimate for the bulk Earth because this mean is certainly biased by
465 the alkali lavas, which display the lowest CE#-numbers and Tm/Tm* ratios, and comprise about half
466 of our database. Instead, we estimate the Tm/Tm* ratio of the bulk Earth using only lava samples for
467 which the curvature effect is negligible, in other words those samples with CE# numbers in the range
468 0.99-1.00. Thus, the Tm/Tm* ratio of our planet is certainly very close to 0.976 (Table 5). This ratio is
469 similar to the mean of the shales (Tm/Tm*=0.974, Table 5) whose CE# numbers are all in the range

470 0.996-1.003 (Fig. 5). The mean of the shales certainly mirrors the upper continental crust value, and
471 suggests that Tm was not decoupled from other heavy REEs during the formation of the continental
472 crust or sedimentary processes. The lower Tm/Tm* ratio (= 0.963, n=25) displayed by the mean of the
473 aeolian dust analyzed by Pourmand et al. (2014) is not explained at present (Fig. 5), but a slight
474 analytical bias cannot be excluded (Fig. 5).

475

476 **4.3 *Tm/Tm* ratios and non-CI refractory lithophile element abundances***

477 An important observation that emerges from our work is that the Tm/Tm* ratios of the Earth,
478 Mars, Vesta, the UPB, and the aubrite parent body are indistinguishable and close to 0.975 (Fig. 4 and
479 Table 5). This may be a characteristic signature of inner solar system solids (Dauphas and Pourmand,
480 2015). This inference is strengthened by the results obtained on one angrite, and on ordinary and
481 enstatite chondrites, which all display similar Tm/Tm* ratios as Earth, Mars, and Vesta. The unique
482 achondrite NWA 7325, which crystallized from an impact melt, is the sole sample with a much lower
483 Tm/Tm* ratio. Its parent body could have formed from a minor reservoir with distinctly lower
484 negative Tm anomalies.

485

486 The homogeneity of the Tm/Tm* ratios in the bulk Earth, Mars and other small differentiated
487 bodies has important implications. Tm/Tm* ratios are very sensitive to the proportions of group II
488 CAIs in primary materials. Using the mean of the group II CAIs analyzed by Huang et al. (2012) and
489 CI abundances, calculations indicate that Tm/Tm* ratios ranging from 0.97 to 0.98 can be explained
490 by variations in the proportion of Group II CAI-like dust in the order of ± 0.035 wt% only. Thus the
491 materials that formed the Earth and Mars, and much smaller differentiated bodies like Vesta or the
492 aubrite parent body, were extremely homogeneous with respect to heavy REE fractionation, despite a
493 strong heterogeneity in terms of volatile depletions (Fig. 8).

494

495 Refractory lithophile elements (RLEs; Ca, Al, Ti, REEs) are usually assumed to be in CI-like
496 proportions in planetary materials, reflecting the fact that they cannot easily be fractionated at a bulk
497 planetary scale by nebular processes. This assumption is very difficult to put to the test because these
498 elements can be fractionated by magmatic and aqueous processes that overprint earlier signatures. The
499 first line of evidence that the Earth may have non-chondritic RLE ratios came from high precision
500 ^{142}Nd isotope measurements which revealed that the accessible Earth may have a Sm/Nd ratio higher
501 than chondritic (Boyet and Carlson, 2005). Nebular processes cannot readily explain this
502 fractionation and it was suggested that either a hidden early formed enriched reservoir with a low
503 Sm/Nd is present in the deep Earth (i.e., a recycled protocrust; Boyet and Carlson, 2005) or a
504 protocrust with low Sm/Nd was lost to space by impact erosion (Caro et al. 2008). Either way, the
505 Earth would have started with a chondritic Sm/Nd ratio. Interpretation of ^{142}Nd is still a matter of
506 contention as subsequent measurements showed that ^{142}Nd variations could be partly explained by the

507 presence of nucleosynthetic anomalies (Gannoun et al., 2011), so that the silicate Earth may still have
508 chondritic Sm/Nd ratio. The finding of Tm anomalies in bulk planetary materials relative to CIs (this
509 study; Dauphas and Pourmand 2015) demonstrates that the assumption that RLEs are present in CI
510 proportions in Earth and other terrestrial planets is not valid. CIs are enriched in a highly refractory
511 dust component with fractionated RLE abundances relative to inner solar system objects.

512

513 Finally, the contribution of carbonaceous chondrites during the main stages of the accretion of the
514 terrestrial planets has been a matter of debates. Many models have been put forward ranging from the
515 involvement of essentially non-carbonaceous chondrites for the Earth and Mars to various proportions
516 of carbonaceous and non-carbonaceous chondrites for the Earth, Mars and Vesta (Sanloup et al., 1999;
517 Lodders, 2000; Burbine and O'Brien, 2004; Warren, 2011b; Javoy et al., 2010; Toplis et al., 2013;
518 Siebert et al., 2013; Dauphas et al., 2014 and references therein). In principle, the Tm anomalies in
519 extraterrestrial materials could offer new constraints for estimates of the proportions of carbonaceous
520 chondrites in terrestrial bodies. Unfortunately the Tm/Tm* ratio is not very sensitive to the
521 contributions of such material: for example a 75% ordinary chondrite + 25% CM mixture [calculated
522 with Chelyabinsk (Tm/Tm*=0.975) and Paris (Tm/Tm*=1.009)] displays a Tm/Tm*=0.983 just
523 slightly higher than the mean ordinary chondrite value, at the limit of the present level of precision.
524 However, the homogeneity of the Tm/Tm* ratios for the Earth, Mars and Vesta strongly suggests that
525 carbonaceous chondrites were not the main planetary building materials in the Inner Solar System, in
526 agreement with the systematics of O, Ca, Ti, Cr, and Ni isotopes (*e.g.*, Warren, 2011b; Dauphas et al.,
527 2014).

528

529 **5. Conclusions**

530 Our analyses of chondrites confirm the dichotomy between carbonaceous and non-carbonaceous
531 chondrites reported by previous studies. Relative to CIs, carbonaceous chondrites display Tm/Tm*
532 ratios equal to, or higher than one, while the vast majority of the non-carbonaceous chondrites display
533 negative Tm/Tm* anomalies (Fig. 4). All achondrites and planetary samples analyzed so far display
534 small negative Tm anomalies relative to CIs (Tm/Tm*=0.975), similar to non-carbonaceous chondrites
535 (Fig. 4). Terrestrial rocks show variable Tm/Tm* ratios that reflect the fact that the use of Er and Yb
536 abundances for normalization to determine Tm anomalies can lead to misleading results if REE
537 patterns display some curvature. Accounting for this curvature effect, we show that the Earth has a
538 Tm/Tm* ratio of 0.976. One of the most important observations that emerges from our work is that the
539 mean Tm/Tm* ratios of the Earth, Mars, 4-Vesta, and possibly of most of the parent bodies of
540 achondrites (angrites, ureilites, aubrites) are similar. This suggests that small negative Tm anomalies
541 (typically Tm/Tm*=0.975) were a widespread feature of inner solar system solids. Our data agree with
542 isotope studies, which suggest that carbonaceous chondrites represent a minor fraction of Earth's

543 building blocks. The presence of negative Tm anomalies in bulk planetary materials (Earth, Mars,
544 Vesta, other achondrite parent bodies) relative to CIs demonstrates that the assumption that refractory
545 lithophile elements are present in CI proportions in planets is unwarranted as CIs are seemingly
546 enriched in a refractory component with a distinct RLE signature.

547

548 **Acknowledgements**

549 The samples analyzed during the course of this study were kindly provided to the first author during
550 the last 25 years by the Muséum National d'Histoire Naturelle (Paris), Ifremer, the Université Pierre et
551 Marie Curie, the Université de Rennes 1, the Institute for Meteoritics, Albuquerque, the National
552 Institut of Polar Research, Tokyo, the Natural History Museum, Vienna, the Smithsonian Institution,
553 the Meteorite Working Group (NASA), Patrick Bachelery, Ted Bunch, Alain et Louis Carion, Martial
554 Caroff, Bruno and Carine Fectay, Luc Labenne, Robert Roccia, Don Simptson, and our late colleagues
555 Theodore Monod and Jean-Louis Cheminée. US Antarctic meteorite samples are recovered by the
556 Antarctic search for Meteorites (ANSMET) program which has been funded by NSF and NASA, and
557 characterized and curated in the department of Mineral Sciences of the Smithsonian Institution and
558 Astromaterials Curation Office at NASA Johnson Space Center. Special thanks to Frederik Paulsen
559 who kindly provided a large sample of Chelyabinsk. We thank Marc Norman and Mark Rehkämper
560 for the editorial handling and their helpful comments which greatly improved the manuscript,
561 Christine Floss, Herbert Palme, two anonymous reviewers for their constructive comments and
562 Pascale Barrat for her help. This work was supported by the "Laboratoire d'Excellence" LabexMER
563 (ANR-10-LABX-19) and co-funded by grants from the French government under the program
564 "Investissements d'Avenir" and from the Programme National de Planétologie (CNRS-INSU) to the
565 first author.

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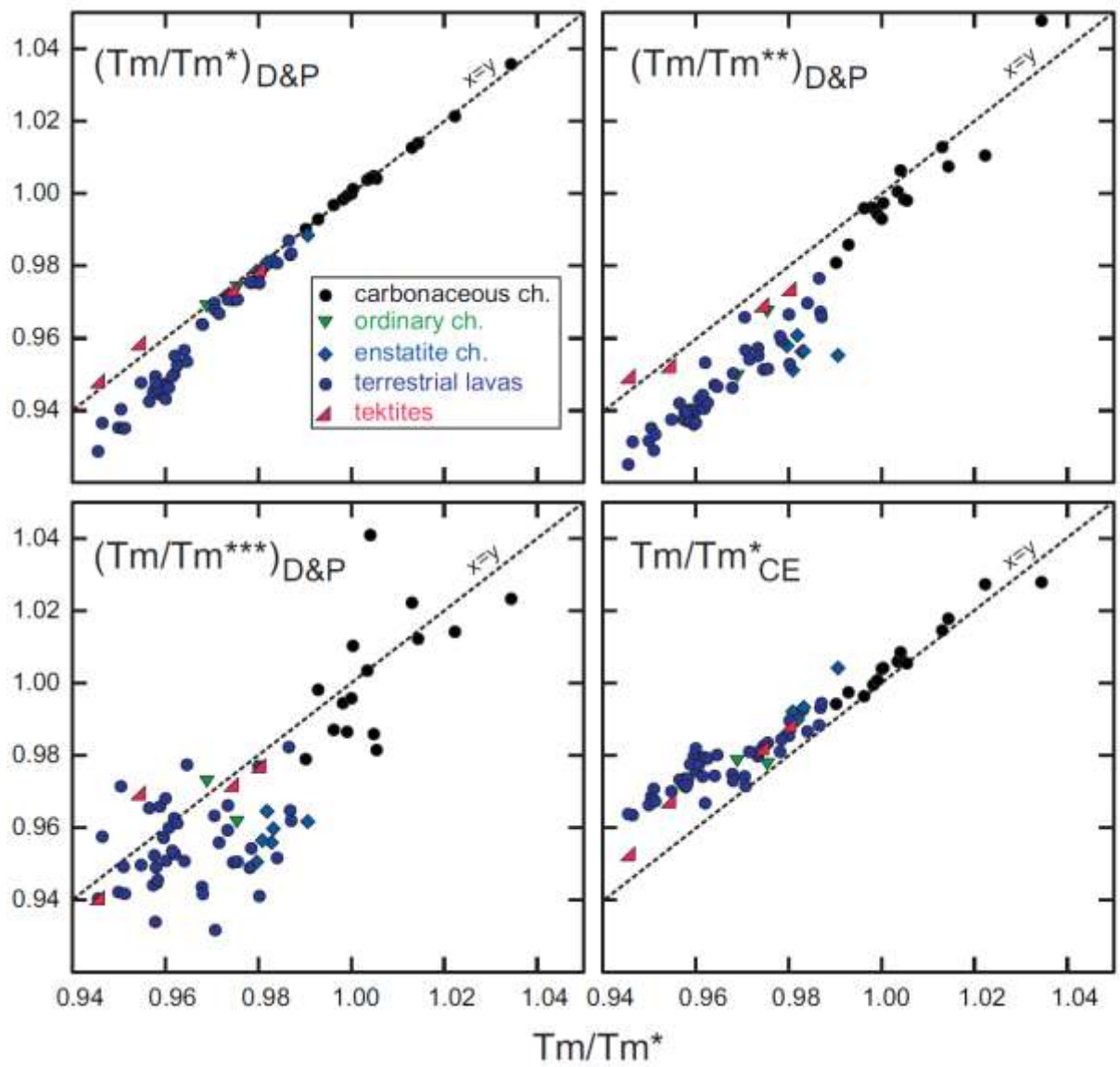


Fig. 1. Comparison of the Tm/Tm^* , Tm/Tm^{**} , Tm/Tm^{***} ratios calculated using the equations given by Dauphas and Pourmand (2015), and Tm/Tm^*_{CE} with the Tm/Tm^* ratios proposed in this study, for a selection of chondrites and terrestrial rocks.

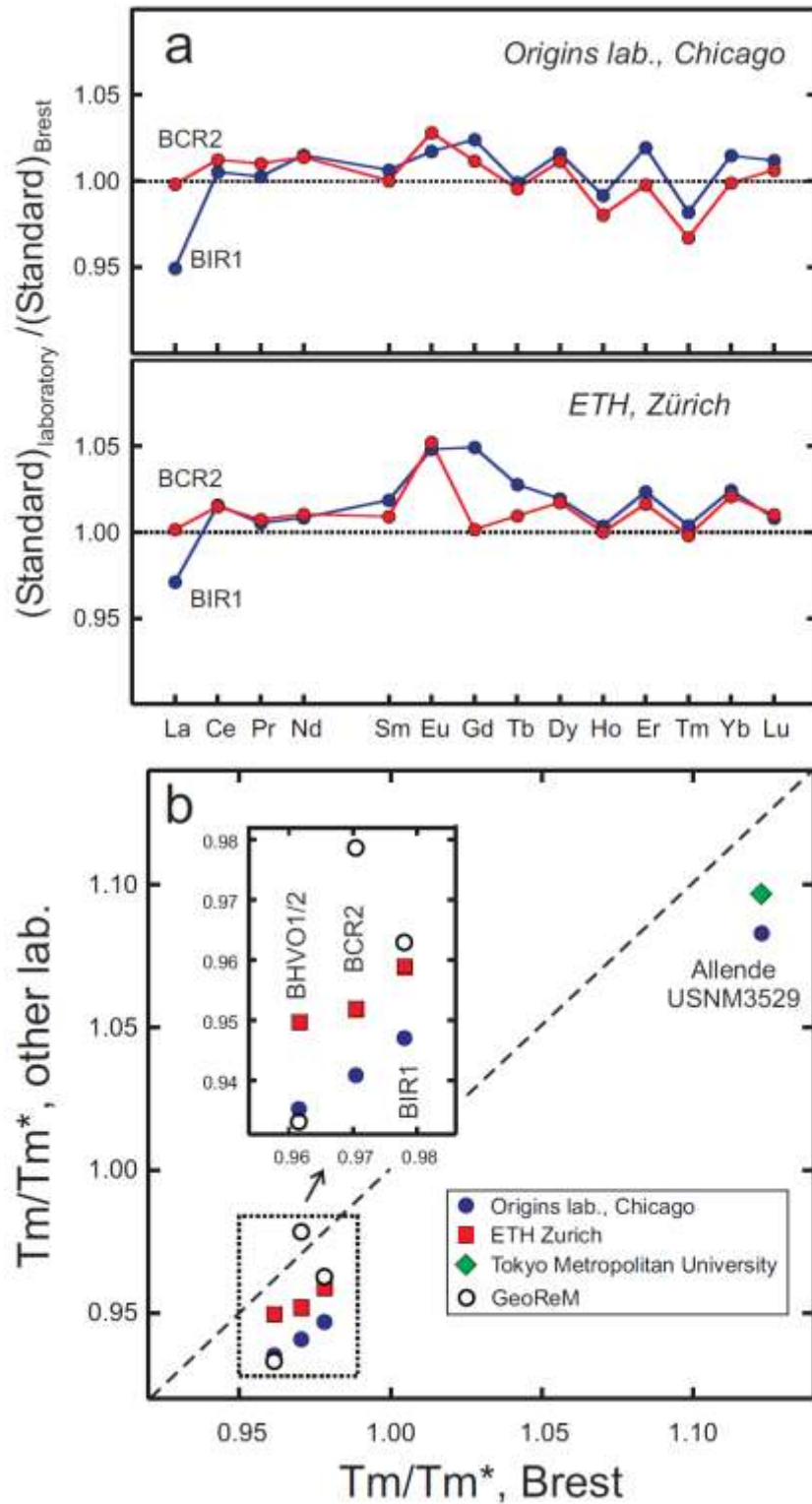


Fig. 2. Comparison of the REE abundances (a), and the Tm/Tm* ratios for reference materials obtained during the course of this study in Brest, with those, uncorrected, obtained at ETH (Stracke et al., 2012), Origins laboratory (Pourmand et al., 2012), Tokyo Metropolitan University (Khan et al., 2015) and the GEOREM's preferred values (georem.mpch-mainz.gwdg.de). Tm/Tm* ratios are relative to the CI data recommended by Barrat et al. (2012). Although the Tm/Tm* values obtained in the different laboratories vary slightly, the results are highly coherent.

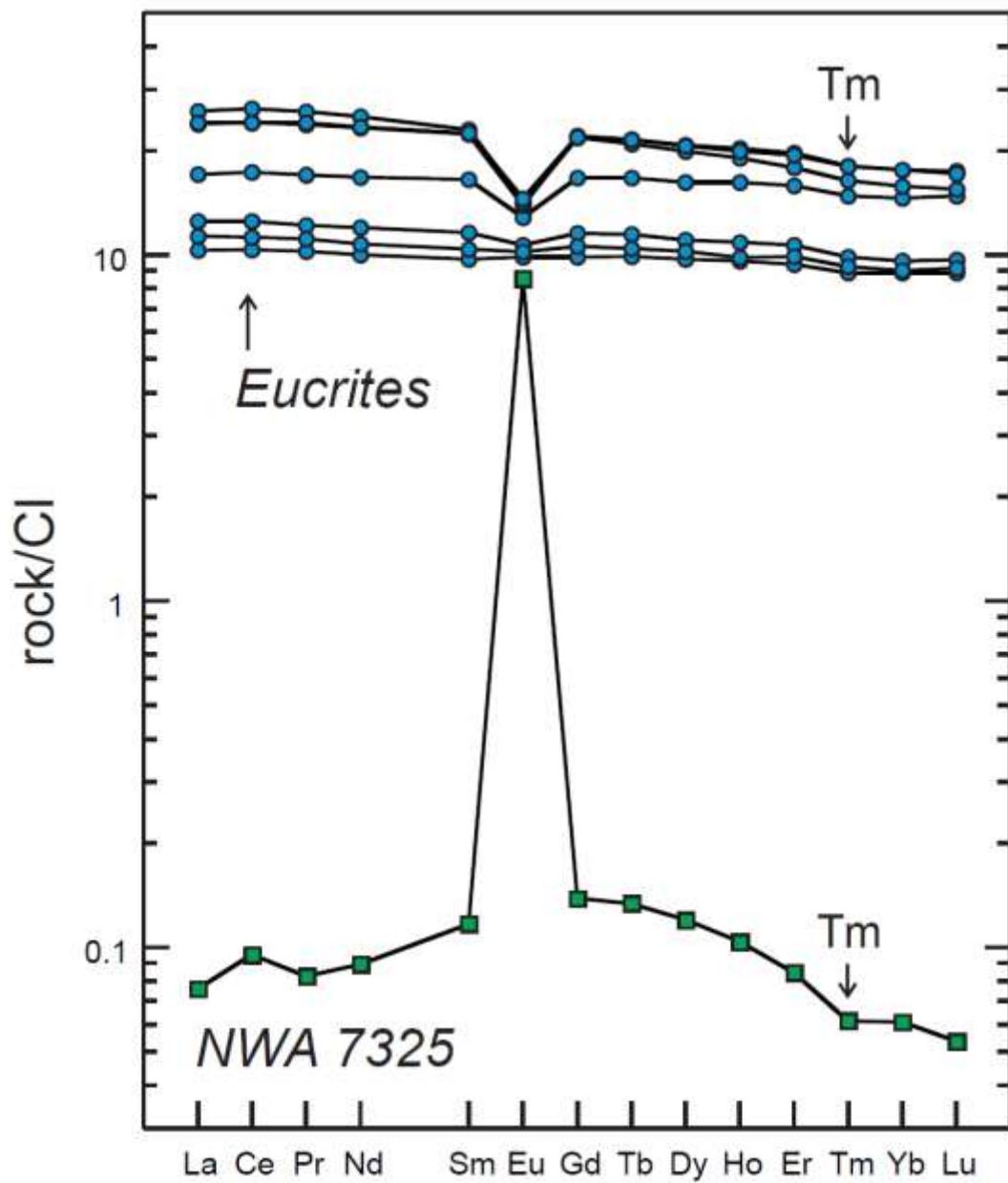


Fig. 3. REE patterns for eucrites and the ungrouped achondrite NWA 7325 normalized to CI chondrite (Barrat et al., 2012). The negative Tm anomalies are generally too small to be easily discerned on the REE patterns of achondrites or planetary samples, excepted for NWA 7325.

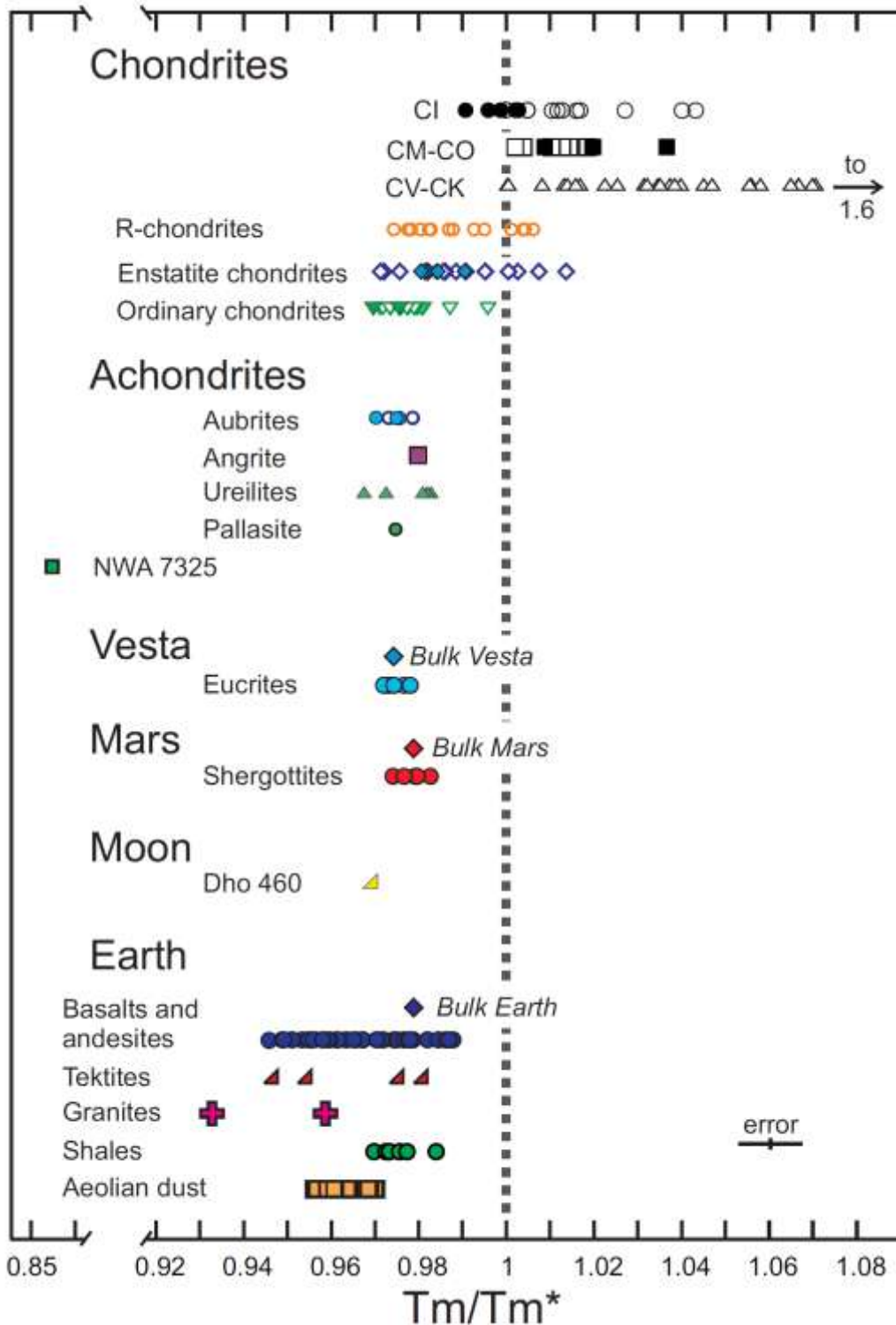


Fig. 4. Tm/Tm^* ratios relative to CI among meteorites and planetary samples (open symbols: Pourmand et al., 2012; Stracke et al., 2012; Bischoff et al., 2012; Dauphas and Pourmand, 2015; Khan et al., 2015; filled symbols: this study). Literature data are adjusted to the Brest BIR-1 and BCR-2 values and Tm/Tm^* ratios are relative to the CI data recommended by Barrat et al. (2012).

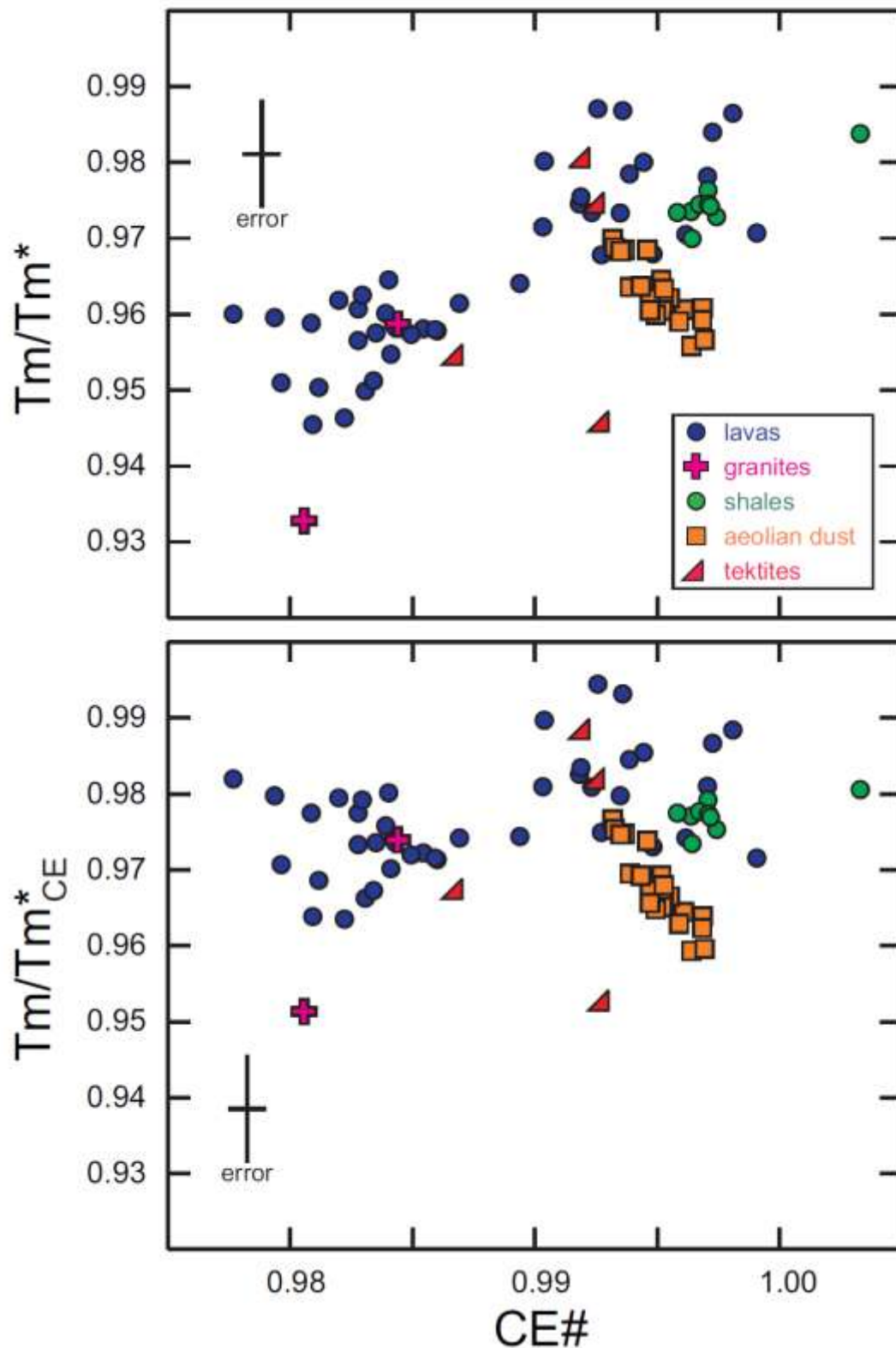


Fig. 5. Tm/Tm^* and Tm/Tm^*_{CE} vs. CE# plots for terrestrial samples (Pourmand et al., 2012, 2014; this study). Literature data are adjusted to the Brest BIR-1 and BCR-2 values and Tm/Tm^* ratios are relative to the CI data recommended by Barrat et al. (2012).

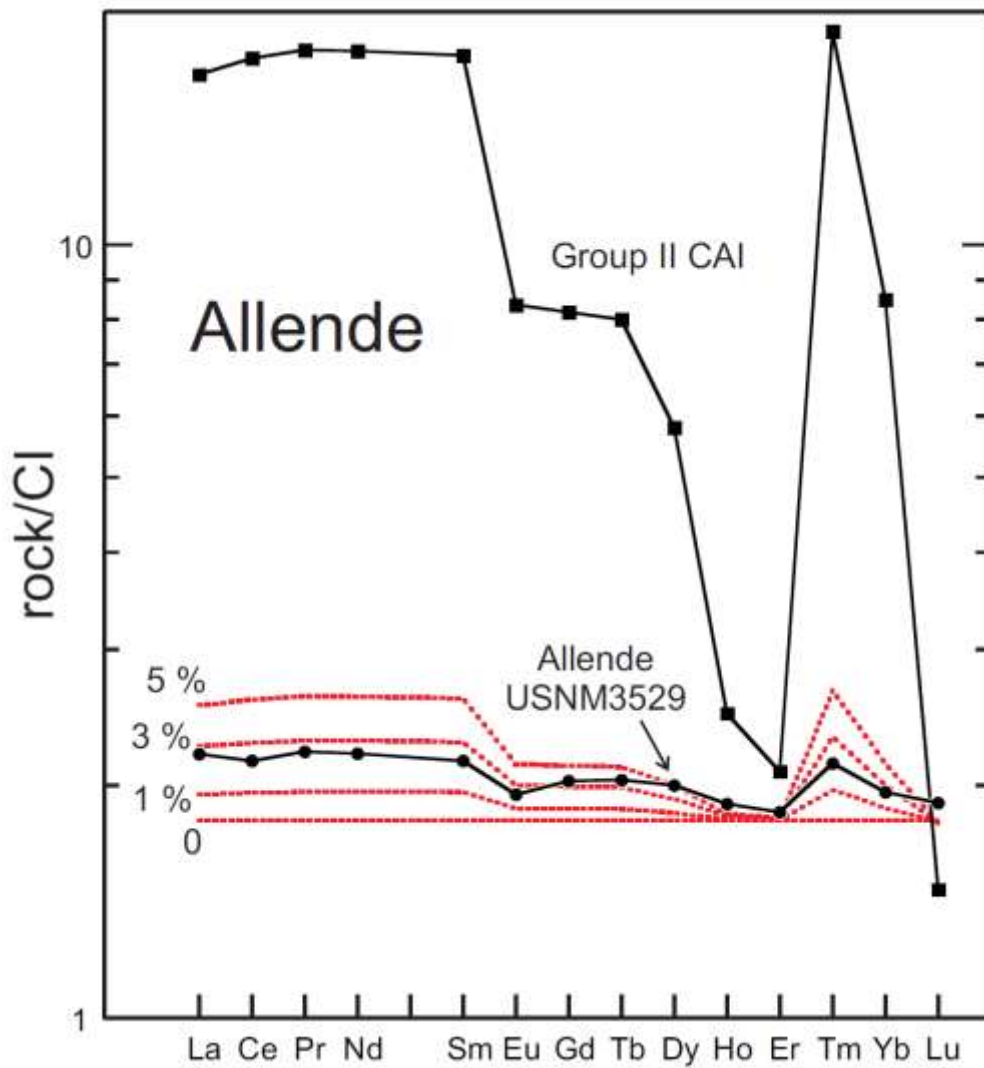


Fig. 6. REE patterns for the Allende CV chondrite (USNM3529, Barrat et al., 2012) and the mean of two group II CAIs obtained by Huang et al. (2012). The REE abundances of this chondrite can be easily reproduced by an addition of 2-3 wt% of this type of CAIs in a chondritic material with REE concentrations = 1.8 x CI abundances.

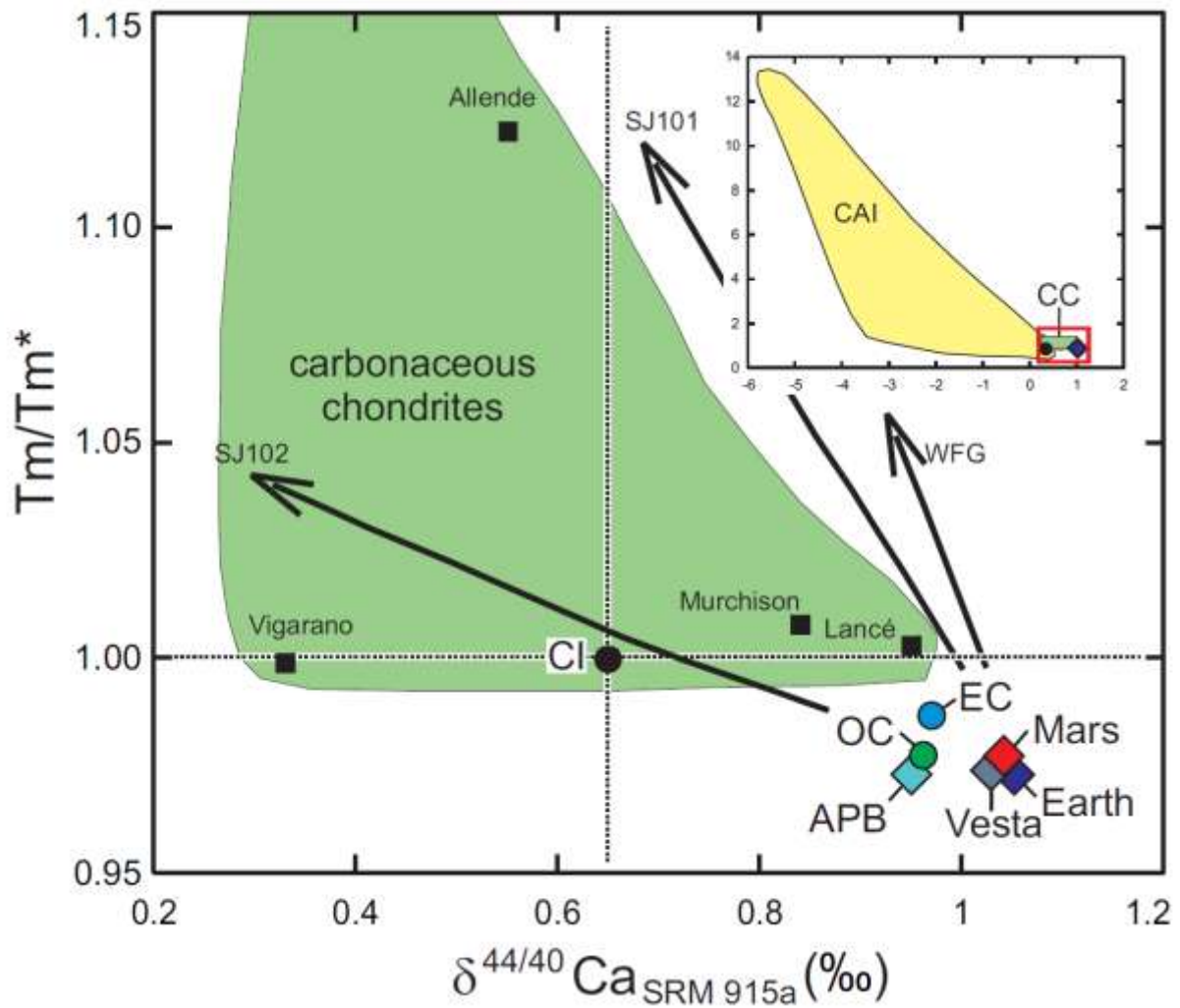


Fig. 7. Relationship between Tm/Tm^* ratios and Ca isotopic composition in chondrite groups, Earth, Mars, Vesta and the aubrite parent body (APB). The black arrows indicate mixing between a bulk silicate Earth composition and selected refractory inclusions analyzed by Huang et al. (2012). The labels on the curves correspond to the names of the inclusions used in the calculations. Tm/Tm^* values for Murchison, Lance, and Vigarano are from Dauphas and Pourmand (2015). Ca isotopic compositions are from Valdes et al. (2014) and Magna et al. (2015).

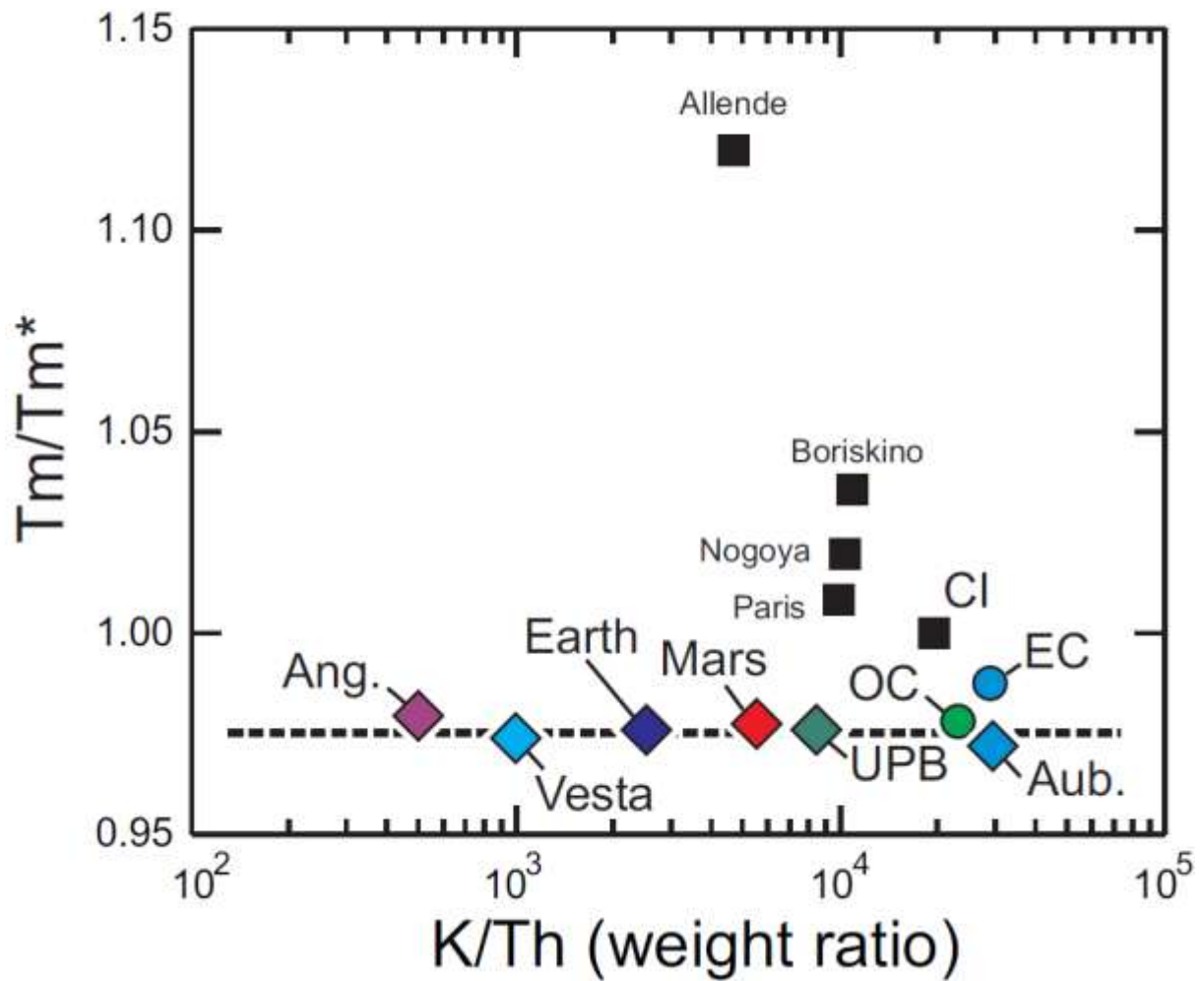


Fig. 8. Plot of T_m/T_m^* vs. K/Th ratios for bulk differentiated bodies and chondrites. The angrite parent body (Ang.) is inferred from NWA 1296, the sole angrite analyzed in this study. The aubrite parent body (Aub.) and enstatite chondrites are assumed to share the same K/Th ratio. The K/Th ratio of the ureilite parent body (UPB) is inferred from the ALMA trachyandesite (Bischoff et al., 2014). Data for carbonaceous chondrites (black squares) are from Barrat et al. (2012), Hewins et al. (2014) and this study.

Table1. REE abundances in basaltic (BHVO-2, BCR-2, BIR-1, BE-N, JB2) and andesitic (JA3) reference materials (in $\mu\text{g/g}$). A to F are replicates from different dissolutions of the same reference material.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Tm/Tm*	CE#
BHVO-2																
working values	15.2	37.5	5.31	24.5	6.07	2.07	6.24	0.94	5.31	1.00	2.54	0.34	2.00	0.27	0.962	0.987
BCR-2 A	25.28	53.32	6.89	28.82	6.51	1.86	6.63	1.05	6.38	1.31	3.63	0.528	3.34	0.483	0.965	0.990
BCR-2 B	25.39	53.44	6.75	28.88	6.58	1.90	6.67	1.04	6.43	1.30	3.63	0.536	3.36	0.476	0.979	0.995
BCR-2 C	24.81	52.92	6.69	28.41	6.55	1.91	6.77	1.06	6.36	1.32	3.65	0.527	3.34	0.481	0.963	0.990
BCR-2 D	24.28	52.67	6.69	28.32	6.52	1.93	6.75	1.05	6.35	1.31	3.67	0.537	3.36	0.492	0.974	0.990
BCR-2 E	24.72	52.38	6.68	28.35	6.52	1.93	6.72	1.05	6.33	1.31	3.66	0.534	3.37	0.489	0.969	0.991
BCR-2 F	24.65	52.19	6.68	28.20	6.46	1.94	6.72	1.05	6.36	1.31	3.68	0.536	3.36	0.492	0.972	0.990
BCR-2 (n=6)	24.86	52.82	6.73	28.5	6.52	1.91	6.71	1.05	6.37	1.31	3.65	0.533	3.35	0.486	0.97	0.991
RSD%	1.67	0.95	1.27	1.00	0.63	1.56	0.75	0.67	0.55	0.38	0.57	0.83	0.35	1.33	0.60	0.19
BIR-1 A	0.624	1.92	0.371	2.37	1.09	0.518	1.81	0.359	2.56	0.583	1.70	0.257	1.65	0.24	0.981	0.997
BIR-1 B	0.627	1.93	0.373	2.37	1.08	0.515	1.8	0.359	2.56	0.579	1.71	0.256	1.63	0.242	0.977	0.996
BIR-1 C	0.626	1.87	0.373	2.38	1.07	0.521	1.84	0.361	2.57	0.573	1.70	0.255	1.64	0.244	0.973	0.997
BIR-1 D	0.628	1.89	0.374	2.38	1.08	0.518	1.84	0.361	2.56	0.574	1.69	0.256	1.64	0.241	0.979	0.997
BIR-1 E	0.612	1.89	0.367	2.37	1.08	0.517	1.82	0.36	2.56	0.581	1.71	0.259	1.65	0.244	0.982	0.996
BIR-1 F	0.613	1.89	0.368	2.35	1.08	0.522	1.83	0.364	2.57	0.573	1.72	0.257	1.63	0.245	0.978	0.997
BIR-1 (n=6)	0.622	1.90	0.371	2.37	1.08	0.518	1.82	0.361	2.56	0.577	1.71	0.257	1.64	0.243	0.978	0.997
RSD%	1.17	1.24	0.80	0.52	0.38	0.46	0.84	0.53	0.23	0.74	0.63	0.57	0.54	0.8	0.29	0.06
Eu-spiked BIR-1	0.618	1.90	0.37	2.36	1.08	52.39	1.84	0.363	2.55	0.575	1.71	0.256	1.64	0.244	0.974	0.997
BE-N A	84.81	155.4	17.06	65.77	12.01	3.67	10.17	1.30	6.39	1.09	2.56	0.320	1.81	0.235	0.949	0.980
BE-N B	84.77	154.9	17.26	66.04	11.98	3.61	9.56	1.26	6.34	1.08	2.55	0.318	1.81	0.235	0.946	0.981
JB2	2.35	6.81	1.17	6.40	2.24	0.791	3.18	0.583	3.92	0.864	2.52	0.381	2.47	0.368	0.972	0.993
JA3	9.84	21.9	2.94	12.94	3.17	0.771	3.29	0.548	3.43	0.728	2.10	0.319	2.09	0.303	0.970	0.996

Table 2. REE abundances in chondrites (in $\mu\text{g/g}$). A and B correspond to duplicates of the same solutions obtained during different sessions.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Tm/Tm*	CE#
<i>Recommended CI,</i> <i>Barrat et al. (2012)</i>	0.235	0.6	0.091	0.464	0.153	0.0586	0.206	0.0375	0.254	0.0566	0.166	0.0262	0.168	0.0242	1	1
Carbonaceous chondrites																
Orgueil 1 (CI)	0.240	0.600	0.0907	0.450	0.145	0.0554	0.196	0.0359	0.238	0.0532	0.155	0.0243	0.157	0.0231	0.991	0.995
Orgueil 2-A (CI)	0.257	0.641	0.098	0.488	0.158	0.0616	0.213	0.0394	0.262	0.0576	0.169	0.0267	0.172	0.0250	0.999	0.999
Orgueil 2-B (CI)	0.257	0.640	0.0971	0.488	0.156	0.0602	0.216	0.0392	0.265	0.0582	0.170	0.027	0.173	0.0252	1.005	0.997
Orgueil 3-A (CI)	0.241	0.605	0.0915	0.457	0.148	0.0556	0.203	0.0365	0.245	0.0535	0.158	0.025	0.161	0.0236	1.000	0.998
Orgueil 3-B (CI)	0.240	0.604	0.0911	0.458	0.146	0.0564	0.201	0.0368	0.245	0.0537	0.158	0.0247	0.16	0.0237	0.992	0.996
Orgueil 4-A (CI)	0.249	0.624	0.0938	0.473	0.153	0.0588	0.210	0.0381	0.258	0.0560	0.165	0.0261	0.169	0.0245	0.996	1.000
Orgueil 4-B (CI)	0.246	0.618	0.094	0.469	0.153	0.0583	0.208	0.0387	0.259	0.0568	0.166	0.0262	0.168	0.0247	1.001	0.996
Orgueil 5-A (CI)	0.250	0.621	0.0953	0.472	0.152	0.0592	0.209	0.0379	0.258	0.0573	0.167	0.0266	0.172	0.0252	1.003	0.996
Orgueil 5-B (CI)	0.250	0.620	0.0946	0.471	0.153	0.0581	0.210	0.0385	0.259	0.0569	0.169	0.0268	0.171	0.0251	1.003	0.999
Ivuna (CI)	0.253	0.635	0.0946	0.479	0.155	0.0588	0.209	0.0387	0.260	0.0571	0.169	0.0265	0.167	0.0243	1.002	1.000
Boriskino 1 (CM)	0.418	1.01	0.141	0.687	0.212	0.0789	0.279	0.0508	0.342	0.0734	0.218	0.0361	0.227	0.0319	1.036	1.006
Nogoya A (CM)	0.318	0.782	0.119	0.606	0.193	0.0726	0.266	0.0486	0.324	0.0719	0.210	0.0335	0.211	0.0309	1.016	0.997
Nogoya B (CM)	0.316	0.777	0.12	0.601	0.193	0.0728	0.268	0.0486	0.325	0.0719	0.210	0.0336	0.209	0.0309	1.023	0.995
Paris A (CM)	0.339	0.848	0.129	0.647	0.206	0.0789	0.283	0.0521	0.350	0.0788	0.224	0.0356	0.228	0.0327	1.006	0.996
Paris B (CM)	0.339	0.847	0.128	0.645	0.207	0.0792	0.283	0.0524	0.350	0.0780	0.226	0.0360	0.227	0.0326	1.011	0.998
Ordinary chondrites																
Chelyabinsk (LL)	0.336	0.849	0.127	0.629	0.200	0.0676	0.281	0.0507	0.337	0.0742	0.217	0.0329	0.213	0.0310	0.975	0.998
Braunschweig (L)	0.351	0.912	0.134	0.662	0.216	0.0775	0.302	0.056	0.366	0.0843	0.247	0.0377	0.249	0.0380	0.969	0.990
Enstatite chondrites																
EET 87746 (EH4)	0.222	0.593	0.0863	0.434	0.141	0.0539	0.196	0.0359	0.245	0.0547	0.163	0.0249	0.161	0.0245	0.980	0.994
EET96135 (EH4/5)	0.247	0.658	0.0955	0.482	0.156	0.0581	0.217	0.0402	0.274	0.0612	0.181	0.0276	0.177	0.0272	0.983	0.991
Abee (EH5)	0.260	0.705	0.102	0.508	0.161	0.0563	0.227	0.0418	0.285	0.0641	0.189	0.0287	0.184	0.0285	0.980	0.989
MAC 02747 (EL4)	0.266	0.698	0.102	0.515	0.167	0.0647	0.229	0.0422	0.29	0.065	0.192	0.0295	0.191	0.0291	0.981	0.992
NWA 4780 (EL4)	0.307	0.808	0.118	0.591	0.19	0.0693	0.262	0.049	0.335	0.075	0.221	0.0338	0.214	0.0336	0.989	0.987
NWA 3134 (EL6)	0.292	0.975	0.156	0.804	0.265	0.0432	0.365	0.0673	0.461	0.1029	0.303	0.0462	0.296	0.0455	0.983	0.990

Table 3. REE abundances in achondrites (in $\mu\text{g/g}$ or in ng/g for aubrites, ureilites, Brenham and NWA 7325). A and B correspond to duplicates of the same solutions obtained during different sessions.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Tm/Tm*	CE#
Angrite																
NWA 1296 A	4.82	12.10	1.82	8.99	2.82	1.08	3.84	0.697	4.68	1.04	3.01	0.446	2.79	0.419	0.982	0.991
NWA 1296 B	4.74	12.01	1.80	9.00	2.86	1.08	3.87	0.700	4.66	1.03	2.99	0.451	2.86	0.413	0.983	0.998
NWA 1296 C	4.73	11.96	1.79	8.95	2.85	1.09	3.9	0.704	4.68	1.03	2.99	0.447	2.86	0.415	0.974	0.997
Aubrites (in ng/g)																
LAR 04316	169	552	95.2	517	178	31.1	256	46.6	313	68.3	197	28.8	180	26.1	0.973	0.996
Norton County	358	1140	200	1040	329	36.9	442	77.4	502	108	311	45.0	280	41.0	0.973	0.994
Pena Blanca Spr.	170	466	67.3	348	128	28.7	190	34.5	229	50.2	143	21.2	136	19.7	0.969	0.994
Ureilites (in ng/g)																
ALH 82130	8.3	33.6	7.3	53.4	31.9	3.97	66.7	14.7	115	29.1	94.4	16.0	115	19.3	0.979	0.991
EET 83225.	1.3	4.9	1.6	19.5	21.5	1.71	58.8	13.8	111	28.2	91.1	15.0	108	18.1	0.964	0.991
MET 01085	8.3	33	6.9	52.6	34.9	6.48	84.3	20.6	175	46.3	15.9	27.7	203	33.7	0.981	1.003
Y-791538	1.4	5.5	1.3	11.6	11.6	1.46	34.2	8.8	77.8	21.2	75.0	13.5	101	17.7	0.983	0.999
Ungrouped (ng/g)																
NWA 7325	17.9	57.2	7.50	41.5	17.9	500	28.6	5.01	30.5	5.88	14.0	1.60	10.2	1.32	0.855	0.983
Pallasite (in ng/g)																
Brenham olivine	51.4	91.6	11.2	38.3	6.5	1.29	6.09	0.962	6.03	1.3	3.9	0.648	4.6	0.782	0.975	0.976
Eucrites																
Bereba	2.66	6.73	1.01	4.98	1.59	0.596	2.18	0.391	2.60	0.555	1.64	0.242	1.51	0.225	0.978	0.996
Bouvante A	5.66	14.45	2.19	10.89	3.43	0.85	4.50	0.802	5.23	1.13	3.21	0.471	2.97	0.423	0.973	0.997
Bouvante B	5.64	14.42	2.19	10.88	3.44	0.853	4.52	0.806	5.24	1.13	3.23	0.472	2.94	0.42	0.976	0.997
Juvinas	2.93	7.48	1.11	5.56	1.77	0.624	2.37	0.429	2.80	0.614	1.77	0.258	1.61	0.238	0.972	0.993
NWA 049	2.42	6.21	0.93	4.64	1.48	0.577	2.03	0.371	2.47	0.543	1.56	0.232	1.49	0.218	0.972	0.994
NWA 2061	6.12	15.87	2.36	11.6	3.51	0.829	4.48	0.783	5.06	1.08	2.96	0.429	2.65	0.381	0.977	0.989
Nuevo Laredo	4.01	10.4	1.55	7.77	2.52	0.750	3.43	0.625	4.11	0.915	2.63	0.387	2.45	0.364	0.973	0.992
Stannern	5.61	14.46	2.16	10.8	3.40	0.817	4.53	0.807	5.28	1.15	3.26	0.473	2.95	0.429	0.973	0.993
Shergottites																
DAG 476	0.124	0.314	0.063	0.456	0.37	0.194	0.889	0.192	1.37	0.306	0.874	0.130	0.811	0.119	0.983	0.993
EETA79001litho.A	0.363	0.87	0.146	0.953	0.668	0.368	1.36	0.281	1.95	0.416	1.17	0.169	1.04	0.146	0.974	0.997
Los Angeles	2.36	5.73	0.815	4.13	1.65	0.874	2.67	0.513	3.45	0.74	2.06	0.298	1.85	0.261	0.970	0.995
NWA 1950	0.61	1.54	0.235	1.35	0.745	0.341	1.39	0.269	1.76	0.366	0.984	0.138	0.815	0.113	0.979	0.992
NWA 1669 A	1.95	4.77	0.700	3.54	1.40	0.560	2.24	0.427	2.86	0.601	1.67	0.240	1.45	0.204	0.981	0.995
NWA 1669 B	1.92	4.64	0.674	3.40	1.35	0.558	2.23	0.430	2.85	0.606	1.68	0.245	1.52	0.216	0.977	0.993
Tissint	0.301	0.93	0.193	1.37	0.863	0.410	1.67	0.329	2.25	0.468	1.31	0.189	1.16	0.163	0.980	0.996
Lunar meteorite																
Dhofar 460 A	2.41	6.37	0.819	3.75	1.05	0.745	1.28	0.23	1.49	0.323	0.919	0.135	0.859	0.121	0.969	0.999
Dhofar 460 B	2.42	6.35	0.822	3.71	1.05	0.745	1.28	0.228	1.49	0.32	0.919	0.135	0.866	0.122	0.968	1.000

Table 4. REE abundances in terrestrial lavas, indochinites and Libyan Desert Glasses (in $\mu\text{g/g}$). A, B correspond to duplicates of the same solution analyzed during different sessions.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Tm/Tm*	CE#
Mid Atlantic Ridge																
MAPCO/CH98 DR11	2.75	9.18	1.65	9.42	3.44	1.26	4.85	0.906	6.02	1.32	3.81	0.571	3.57	0.526	0.986	0.994
FAMOUS/CH31-DR2	7.55	17.06	2.40	11.31	3.30	1.14	4.26	0.757	4.98	1.09	3.14	0.463	2.92	0.434	0.974	0.992
FAMOUS/CH31-DR5	4.41	10.42	1.46	7.07	2.18	0.81	2.93	0.53	3.5	0.766	2.21	0.324	2.06	0.305	0.966	0.993
A127 299 DR55	2.85	7.58	1.19	6.34	2.19	0.835	3.15	0.588	3.98	0.891	2.57	0.384	2.46	0.365	0.975	0.992
E Pacific Ridge																
SEARISE/SR1 DR04	5.14	15.32	2.62	14.07	4.76	1.68	6.45	1.16	7.66	1.66	4.79	0.719	4.50	0.667	0.988	0.993
E Rift, Easter plate																
PI 18-06	0.504	2.13	0.464	3.00	1.30	0.582	2.18	0.432	3.16	0.743	2.23	0.349	2.28	0.34	0.987	0.998
PI 19-02	1.46	5.20	0.970	5.65	2.17	0.842	3.20	0.592	3.94	0.883	2.54	0.382	2.43	0.355	0.978	0.994
PI 19-09	4.67	12.77	2.00	10.56	3.57	1.27	4.81	0.871	5.57	1.22	3.50	0.513	3.21	0.475	0.977	0.992
Pacific-Antarctic Ridge																
PC1/DR03-1	5.59	15.30	2.42	12.45	3.99	1.46	5.28	0.944	6.14	1.33	3.83	0.56	3.55	0.518	0.967	0.995
Tadjoura Gulf																
CY84/103-1	5.73	13.62	1.99	9.74	3.04	1.11	4.09	0.733	4.88	1.07	3.11	0.465	2.95	0.437	0.979	0.994
A3D3	1.93	5.06	0.805	4.34	1.54	0.635	2.31	0.429	2.99	0.652	1.93	0.287	1.84	0.269	0.972	0.999
E Indian Ridge																
HYAMS/DR3-10	41.64	88.40	11.22	43.97	10.91	3.09	11.85	1.96	12.07	2.54	7.28	1.07	6.65	0.992	0.982	0.990
HYAMS/DR9-7	4.01	11.64	1.96	10.41	3.51	1.3	4.84	0.869	5.75	1.24	3.62	0.544	3.43	0.500	0.984	0.997
French Massif Central																
Gergovie	50.30	90.28	10.19	38.69	7.37	2.32	6.46	0.908	4.89	0.906	2.25	0.303	1.84	0.251	0.950	0.981
Cantal, IC3	125.6	201.3	20.39	69.34	10.67	3.07	8.31	1.13	5.89	1.08	2.84	0.393	2.41	0.339	0.958	0.986
Cantal, IC6	26.81	52.37	6.22	25.42	5.54	1.80	5.41	0.788	4.32	0.814	2.09	0.280	1.66	0.229	0.958	0.985
Cantal, IC11	105.4	186.6	20.30	72.52	12.23	3.60	9.90	1.33	6.99	1.28	3.20	0.431	2.63	0.360	0.946	0.982
Cantal, SC2	71.14	134.8	15.42	58.78	10.65	3.26	9.03	1.23	6.48	1.17	2.91	0.388	2.29	0.310	0.958	0.984
Cantal, SC4	24.88	51.46	6.44	26.76	5.93	1.89	5.61	0.808	4.44	0.808	2.02	0.269	1.57	0.213	0.960	0.984
Cantal, SC5	59.00	112.2	13.15	51.02	9.54	2.89	8.13	1.09	5.75	1.02	2.49	0.329	1.92	0.261	0.960	0.979
Tubuai (Austral Islands, French Polynesia)																
TB1	60.41	115.4	13.19	50.26	9.18	2.83	7.95	1.09	5.71	1.01	2.42	0.315	1.81	0.239	0.959	0.981
TB24	70.51	138.4	15.99	61.49	11.30	3.45	9.73	1.33	7.00	1.24	3.00	0.391	2.24	0.296	0.961	0.983
TB60	136.2	243.6	26.25	92.41	15.27	4.53	12.33	1.66	8.61	1.50	3.64	0.468	2.70	0.356	0.950	0.983
TB113	132.6	237.9	25.60	89.77	14.86	4.45	11.95	1.62	8.44	1.49	3.59	0.468	2.71	0.355	0.957	0.983
TB131	75.66	144.9	16.62	62.71	11.61	3.53	9.97	1.35	7.00	1.21	2.86	0.362	2.06	0.272	0.951	0.980
TB140	113.3	212.0	23.75	86.52	14.83	4.41	12.16	1.64	8.52	1.46	3.49	0.442	2.51	0.325	0.951	0.983
TB207	50.74	98.64	11.57	44.68	8.51	2.65	7.61	1.07	5.82	1.06	2.68	0.356	2.09	0.284	0.957	0.985
TB220	41.11	80.54	9.60	37.59	7.28	2.26	6.47	0.911	4.91	0.909	2.27	0.305	1.79	0.246	0.962	0.982
TB228	42.40	83.60	9.94	38.90	7.50	2.33	6.73	0.941	5.14	0.939	2.37	0.314	1.85	0.251	0.958	0.984
TB237	43.29	84.38	9.91	38.62	7.43	2.31	6.60	0.929	5.14	0.965	2.46	0.337	2.02	0.281	0.963	0.983
TB244	38.57	79.44	9.55	38.04	7.58	2.36	6.94	0.989	5.48	1.03	2.66	0.360	2.16	0.297	0.958	0.986
Other basalts																
Kaiserstühl, KS3	56.45	102.8	11.52	43.86	7.97	2.41	6.57	0.850	4.30	0.743	1.73	0.220	1.23	0.161	0.960	0.978
Jan Mayen, JM47	92.66	178.6	20.31	74.45	12.29	3.64	9.59	1.33	7.24	1.36	3.56	0.498	3.10	0.440	0.955	0.984
Erta Ale, ER13 A	20.85	41.66	5.25	21.87	4.78	1.59	4.92	0.745	4.56	0.901	2.43	0.341	2.10	0.298	0.963	0.989
Erta Ale, ER13 B	20.39	41.34	5.17	21.74	4.82	1.61	4.91	0.765	4.48	0.901	2.43	0.344	2.12	0.298	0.967	0.990
Réunion, Chisny	21.99	46.07	6.01	26.15	6.05	2.01	6.12	0.934	5.22	1.01	2.55	0.346	2.05	0.28	0.965	0.984
Svalbard, WF27	14.45	29.60	3.71	15.56	3.66	1.17	3.99	0.653	3.91	0.805	2.20	0.311	1.93	0.267	0.961	0.995
Indochinites																
Muong Nong, Thailand	44.34	83.77	9.38	35.15	6.8	1.26	5.95	0.915	5.42	1.10	3.10	0.471	3.06	0.443	0.975	0.993
Splash form, China	42.84	82.89	9.03	34.45	6.74	1.32	6.11	0.932	5.52	1.12	3.15	0.480	3.09	0.448	0.981	0.992
Libyan Desert glasses																
LDG 7	8.78	18.94	1.95	6.97	1.24	0.219	0.974	0.14	0.78	0.152	0.431	0.0677	0.474	0.0715	0.954	0.987

Table 5. T_m/T_m^* ratios in various types of chondrites and in differentiated bodies (only bodies for which at least five samples were analyzed, are considered here). Literature data are adjusted to the Brest BIR-1 and BCR-2 values, and T_m/T_m^* ratios are relative to the CI recommended by Barrat et al. (2012).

	n	minimum	maximum	mean	σ	References
Carbonaceous chondrites						
CI	6	0.991	1.003	0.999	0.005	This work
CI	7	0.999	1.043	1.015	0.014	Dauphas and Pourmand (2015)
CM	4	1.003	1.019	1.012	0.007	Dauphas and Pourmand (2015)
CM	5	1.006	1.036	1.018	0.012	This work
CM	9	1.003	1.036	1.015	0.010	Dauphas and Pourmand (2015), this work
CV	45	1.000	1.602	1.096	0.112	Stracke et al. (2012), Dauphas and Pourmand (2015)
Other chondrites						
Enstatite chondrites	6	0.980	0.989	0.983	0.003	This work
Enstatite chondrites	16	0.971	1.013	0.989	0.012	Dauphas and Pourmand (2015)
Enstatite chondrites	22	0.971	1.013	0.987	0.011	Dauphas and Pourmand (2015), this work
Ordinary chondrites	2	0.969	0.975	0.972		This work
Ordinary chondrites	20	0.971	0.995	0.978	0.006	Dauphas and Pourmand (2015)
Ordinary chondrites	22	0.969	0.995	0.977	0.006	Dauphas and Pourmand (2015), this work
R-chondrites	15	0.975	1.007	0.989	0.011	Khan et al. (2015)
Differentiated bodies						
Aubrite parent body	5	0.969	0.979	0.973	0.003	Dauphas and Pourmand (2015), this work
Ureilite parent body	5	0.964	0.983	0.976	0.008	Bischoff et al. (2014), this work
Vesta (eucrites)	7	0.972	0.978	0.974	0.002	This work
Mars (Shergottites)	6	0.970	0.983	0.977	0.005	This work
Earth						
Bulk Earth (selected lavas)	18	0.962	0.987	0.976	0.007	This work
Basalts and andesites	42	0.946	0.987	0.965	0.011	This work
Post-archean shales	9	0.969	0.983	0.974	0.004	Pourmand et al. (2012)
Aeolian dust	25	0.956	0.970	0.963	0.004	Pourmand et al. (2014)

Supplementary Table 1. Details of meteorite samples studied (IOM: Institute of Meteoritics, Albuquerque; MPI: Max Planck Institute, Mainz; MNHN : Muséum National d'Histoire Naturelle (Paris) ; MWG : Meteorite Working Group, NASA; NHM: National History Museum, Wien).

	type	source	homogenized mass (g)	dissolved mass (g)
Chondrites				
Orgueil 1	CI	MNHN, Paris	1	0.025
Orgueil 2	CI	MNHN, Paris	0.62	0.027
Orgueil 3	CI	MNHN, Paris	0.61	0.032
Orgueil 4	CI	MNHN, Paris	0.84	0.031
Orgueil 5	CI	MNHN, Paris	0.96	0.028
Ivuna	CI	MNHN, Paris	0.71	0.034
Boriskino 1	CM2	MNHN, Paris	0.5	0.124
Nogoya	CM2	MNHN, Paris	0.5	0.092
Paris	CM2	MNHN, Paris	13	0.153
Chelyabinsk	LL5	F. Paulsen	2	0.124
Braunschweig	L6	U. Münster	0.35	0.119
EET 87746	EH4	MWG	1	0.224
EET 96135	EH4/5	MWG	1	0.221
Abee	EH5	MNHN, Paris	1	0.133
MAC 02747	EL4	MWG	1	0.159
NWA 4780	EL4	MNHN, Paris	1	0.106
NWA 3134	EL6	J.A. Barrat	2	0.173
Achondrites				
Bereba	euclite (main group)	MNHN, Paris	2.1	0.102
Bouvante	euclite (Stannern)	MNHN, Paris	1.5	0.105
Juvinas	euclite (main group)	MNHN, Paris	2.8	0.098
NWA 049	euclite (main group)	ENS, Lyon	1.5	0.107
NWA 2061	euclite (unbr., Stannern)	NAU, Flagstaff	0.5	0.122
Nuevo Laredo	euclite (Nuevo Laredo)	Smithsonian Inst.	1	0.115
Stannern	euclite (Stannern)	NHM, Wien	1	0.101
DAG 476	shergottite	MPI, Mainz	5	0.138
EETA 79001litho.A	shergottite	MWG	1	0.162
Los Angeles	shergottite	B. & C. Fectay	0.04	0.040
NWA 1950	shergottite	ENS, Lyon	0.326	0.123
NWA 1669	shergottite	B. & C. Fectay	0.5	0.142
Tissint	shergottite	U Paris VI	0.5	0.109
Dhofar 460	lunar meteorite	L. Labenne, Paris	0.15	0.150
NWA 1296	angrite	U. Paris VI	0.12	0.120
LAR 04316	aubrite	MWG	2	0.153
Norton County	aubrite	IOM, Albuquerque	5	0.122
Pena Blanca Spr.	aubrite	IOM, Albuquerque	3.5	0.157
ALH 82130	ureilite	MWG	0.84	0.204
EET 83225.	ureilite	MWG	0.81	0.202
MET 01085	ureilite	MWG	0.71	0.179
Y-791538	ureilite	NIPR, Tokyo	0.5	0.184
NWA 7325	ungrouped achondrite	S. Ralew	0.6	0.102
Brenham olivine	main group pallasite	D. Stimpson	1	0.152