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# Calculation of cerium and lanthanum anomalies in geological and environmental samples

by

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17 **Abstract**

18           The determination of La and Ce anomalies in natural waters, biological samples and  
19 sedimentary rocks can provide unique information on biogeochemical processes in Earth  
20 surface environments. Over the last decades, several approaches have been used for calculating  
21  $La/La^*$  and  $Ce/Ce^*$ , based on the comparison between measured and theoretical abundances  
22 ( $La^*$  and  $Ce^*$ ) extrapolated from neighboring rare earth element concentrations normalized to  
23 chondritic or shale reference values. These extrapolations can be achieved either linearly or  
24 semi-logarithmically ("geometrically"), both methods being used in the literature in the absence  
25 of any consensus. We show here, using a database of rocks exhibiting no La and Ce anomaly,  
26 that the linear extrapolation of La and Ce abundances can result in markedly different results  
27 depending on whether chondritic or shale values are used for normalization. The geometric  
28 extrapolation allows consistent calculation of La and Ce anomalies for the entire compositional  
29 range tested in this study, regardless of whether data are normalized to chondritic or shale  
30 reference values. The differences between linear and geometric extrapolations are illustrated by  
31 a few selected examples from the literature, including various carbonate rock and seawater  
32 samples, further demonstrating that linear extrapolation can result in erroneous estimates of La  
33 and Ce anomalies. We thus propose that  $La/La^*$  and  $Ce/Ce^*$  ratios in all geological and  
34 environmental samples should be determined using the geometric extrapolation only.

35

36 **Key words**

37 Rare earth elements, La anomaly, Ce anomaly, linear extrapolation, geometric extrapolation

38

## 39 1/ Introduction

40 Over the last sixty years, rare earth elements (REE) have become one of the most studied  
41 groups of elements in Earth sciences. These elements have the particularity of having an  
42 extremely coherent geochemical behavior that can be classically described with the famous  
43 "Masuda-Coryell plots" (Masuda, 1962; Coryell et al., 1963), known today as "rare earth  
44 patterns". The principle of these diagrams is simple. Rare earth elements are ordered by  
45 increasing atomic number, and their abundances in any given sample are normalized to a set of  
46 reference values that generally correspond to average concentrations for chondrites (e.g.,  
47 Anders and Grevesse, 1989; Pourmand et al., 2012; Barrat et al., 2012; Palme et al., 2014) or  
48 shales (e.g., Nance and Taylor, 1976; Pourmand et al., 2012; Bau et al., 2018). The first  
49 advantage of these diagrams is that the Oddo-Harkins effect (i.e. chemical elements with even  
50 atomic numbers are more abundant than adjacent odd atomic number elements) disappears with  
51 normalization. Smooth REE patterns are generally obtained for most geological and  
52 environmental samples, mostly because all REE are trivalent and not significantly decoupled  
53 from each other under relevant physico-chemical conditions. There are notable exceptions,  
54 however. For instance, europium ( $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ ) and cerium ( $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ ) can be found in  
55 two valence states in geological samples. During particular magmatic or environmental  
56 processes, these two elements can be significantly decoupled from their neighboring REE,  
57 thereby producing specific elemental depletion or enrichment in normalized REE patterns.  
58 Additionally, significant anomalies in La, Sm, Gd and Tm can be also found in terrestrial rocks  
59 or natural waters, unrelated to any effect of valence. The occurrence of Tm anomalies in  
60 terrestrial rocks are thought to be inherited from the building blocks that formed our planet  
61 (Dauphas and Pourmand, 2015; Barrat et al., 2016). The origin of other anomalies is not always  
62 well understood, except when they are the result of environmental pollution (e.g., Bau and  
63 Dulski, 1996b; Kulaksiz and Bau, 2007, 2013; Merschel and Bau, 2015; Ma et al., 2019; Le  
64 Goff et al., 2019, Valdés-Vilchis, 2021).

65 Among these anomalies, Ce anomalies have received considerable interest. The  
66 distinctive behavior of Ce in the marine environment was discovered more than 50 years ago  
67 (e.g., Goldberg et al., 1963). The first reliable REE analyses of seawater, various authigenic  
68 phases, and ichthyoliths showed very early on that aqueous phases, marine carbonates and other  
69 seawater archives could display pronounced negative Ce anomalies (e.g., Piper, 1974;  
70 Elderfield and Pagett, 1986 and references therein). The role of Fe and Mn oxides in the  
71 development of these anomalies was subsequently proposed because Mn-rich nodules and

72 crusts displayed complementary positive anomalies in Ce (e.g., Goldberg et al., 1963; Piper,  
73 1974). Today, it is generally well accepted that the decoupling of Ce from other REEs in the  
74 oceans, or more generally in aqueous environments, mainly results from oxidative scavenging  
75 of Ce by Fe and Mn hydroxides (e.g., Bau and Koschinsky, 2009). The occurrence of Ce  
76 anomalies in natural waters and in the biogenic or authigenic phases that precipitate from them  
77 is used as a proxy for oxidative conditions in Earth surface environments (e.g., German and  
78 Elderfield, 1990; German et al., 1991; Bau et al., 1997; Wallace et al., 2017; Bellefroid et al.,  
79 2018). Cerium anomalies are also of interest for magma-related studies, although their  
80 application to basalts and other igneous rocks remains limited. Lavas from subduction zones  
81 and oceanic islands occasionally show negative Ce anomalies, interpreted as reflecting a  
82 recycled sedimentary component in their mantle sources (e.g., Shimizu et al., 1992; Class and  
83 Le Roex, 2008). In contrast, zircons frequently show excess Ce ( $\text{Ce}^{4+}$  having the same ionic  
84 radius as  $\text{Zr}^{4+}$ ), indicating preferential selective incorporation of Ce relative to neighboring REE  
85 during crystal growth. The resulting positive Ce anomalies could reflect the  $\text{Ce}^{4+}/\text{Ce}^{3+}$  ratios of  
86 their parental magmas, and therefore provide constraints on oxygen fugacity (e.g., Burnham  
87 and Berry, 2012; Trail et al., 2012; Smythe and Brenan, 2016).

88 Unlike Ce, the La anomaly in geological and environmental samples has received much  
89 less attention. Lanthanum anomalies represent a common feature in seawater and marine  
90 authigenic phases (e.g., Elderfield, 1988; Tostevin et al., 2016), but remains to date  
91 undocumented in igneous rocks. The cause of these anomalies is still poorly understood but  
92 could relate to the higher stability of La in solution relative to the other light REE (De Baar et  
93 al., 1985, Byrne and Kim, 1990, Byrne et al., 1996). Previous studies have suggested that  
94 marine barite could play a role in the development of La anomalies in seawater (Grenier et al.,  
95 2018). Indeed, Hein et al. (2007) have reported positive La anomalies in this phase. It is likely  
96 that the La excesses they measured, however, are ~~only~~ analytical artefacts generated in the  
97 plasma, notably isobaric interferences from Ba (e.g.,  $^{138}\text{BaH}^+$  on  $^{139}\text{La}^{+2}$ ), and need to be  
98 confirmed. Recently, a number of pioneering studies have demonstrated that biological activity  
99 can also fractionate light-REE (e.g., Pol et al., 2014; Semrau et al., 2018; Bayon et al., 2020a).  
100 Wang et al. (2020) reported positive La anomalies in methanotrophic mussels at submarine  
101 methane seeps, interpreted as resulting from microbial enzymatic activity related to aerobic  
102 methane oxidation. These results ~~have suggested~~ that the La anomaly could ~~be~~ serve as a  
103 diagnostic tool for tracing past biological activity related to aerobic methanotrophy. Moreover,  
104 La also represents an emerging pollutant in modern environments due to its widespread

105 industrial use in ~~the industry~~ in magnetic alloys and ~~or~~ catalysts for gasoline engines (Kulaksiz  
106 and Bau, 2013; Merschel and Bau, 2015). The emergence of anthropogenic La issues in Earth  
107 surface environments calls for a better understanding of the mechanisms that control the  
108 decoupling of La from neighboring REE in aquatic environments.

109 Over the last few decades, different methods have been proposed for calculating La and  
110 Ce anomalies in geological and environmental samples, yet no consensus exists among  
111 geochemists on best practices for these calculations. In the literature, historical conventions  
112 ~~usages~~ or habits prevail. These anomalies are calculated from normalized concentrations and  
113 by interpolating or extrapolating La and Ce concentrations ( $La^*$  and  $Ce^*$ ) assuming smooth  
114 REE patterns with linear or logarithmic scales. This results in anomaly values that can be very  
115 different from one study to another, and cannot be compared. Here we show that that some  
116 commonly used approaches for calculating La and Ce anomalies can lead to aberrant results,  
117 hence our call for a standardization of the calculation.

118

## 119 **2/ The different ways to calculate La and Ce anomalies**

### 120 **2.1/ Normalization values**

121 The patterns of average CI chondrites and average shales do not show significant  
122 anomalies in La and Ce when normalized to each other. Therefore, one would expect to  
123 calculate similar  $La/La^*$  or  $Ce/Ce^*$  values in any given sample following normalization to  
124 either chondritic or shale reference values. We will see below that this is not necessarily the  
125 case. In this work, we used the average of the Orgueil chondrite concentrations measured by  
126 Barrat et al. (2012), and the Post Archean Australian Shale (PAAS) average obtained by  
127 Pourmand et al. (2012), which was recalculated relative to our standard values to correct for a  
128 slight calibration bias (Barrat et al., 2020). These preferred normalization values are given in  
129 Table 1. In the following,  $X_{CI}$  and  $X_{SN}$  corresponds to the element X concentrations normalized  
130 to chondritic or shales values, respectively.

131

### 132 **2.2/ The calculation of Ce and La anomalies**

133 By definition, an anomaly visualized in a normalized-REE diagram for an element (X)  
134 can be quantified by dividing its measured abundance by its theoretical concentration in the

135 absence of any anomaly ( $X^*$ ). This latter can be calculated by interpolation or extrapolation  
136 using the normalized abundances of ~~for~~ neighboring elements, assuming a smooth REE pattern.  
137 The measured/theoretical ~~ratio~~ elemental ratio ( $X/X^*$ ) thus makes it possible to quantitatively  
138 measure a positive ( $X/X^*>1$ ) or a negative ( $X/X^*<1$ ) anomaly for this element.

139 Many approaches to calculating  $Ce^*$  and  $La^*$  have been proposed in the last few  
140 decades. In the case of magmatic rocks or zircons, which are devoid of La anomalies,  $Ce^*$  is  
141 given by the geometric mean of the normalized concentrations of La and Pr, or interpolated  
142 "semi-logarithmically" between La and Nd when Pr abundances are not determined:

$$143 \quad Ce/Ce^* = Ce_{Cl} / (La_{Cl} \times Pr_{Cl})^{1/2} \quad (1)$$

144 or

$$145 \quad Ce/Ce^* = Ce_{Cl} / (La_{Cl}^{2/3} \times Nd_{Cl}^{1/3}) \quad (2)$$

146

147 The choices of a geometric mean or the semi-log interpolation are justified here by the  
148 fact that the REE patterns are plotted in semi-log diagrams, where linear abscissa corresponds  
149 to the number of protons ( $Z$ ) of REE and ordinates refer to normalized concentrations  
150 conventionally displayed in logarithmic scale.

151 During the 1970s, new developments in sedimentary geochemistry were accompanied  
152 by ~~with~~ increasing use of reference shale values for normalizing measured REE abundances  
153 (e.g., Piper, 1974). In these early studies,  $Ce^*$  was interpolated as described above (e.g., Piper  
154 (1974) with Equation 2) but also linearly, ~~hence~~ considering that shale-normalized REE patterns  
155 were sometimes plotted using linear scales for both ordinates and abscissae. Additionally, prior  
156 to the 1990s and the advent of ICP-MS, REE abundances were mostly measured by INAA and  
157 Pr concentrations were rarely determined, meaning that  $Ce^*$  was generally interpolated between  
158 La and Nd (e.g., Elderfield and Greaves, 1981), and occasionally between La and Sm (Toyoda  
159 et al., 1990):

$$160 \quad Ce/Ce^* = 3 Ce_{SN} / (2 La_{SN} + Nd_{SN}) \quad (3)$$

$$161 \quad Ce/Ce^* = 5 Ce_{SN} / (4 La_{SN} + Sm_{SN}) \quad (4)$$

162 It was only with the development of plasma source mass spectrometry in the mid-1980's  
163 that the simultaneous determination of the concentrations of all the REE's in ~~the~~ a given samples  
164 ~~was greatly facilitated~~ became routine, and the number of analyses that also included ~~ing~~ Pr

165 increased considerably. The calculation of the Ce anomaly with Ce\* linearly interpolated  
 166 between La and Pr, is given by the following equation (e.g., De Baar et al., 1983):

$$167 \quad \text{Ce/Ce}^* = 2 \text{Ce}_{\text{SN}} / (\text{La}_{\text{SN}} + \text{Pr}_{\text{SN}}) \quad (5)$$

168 However, many natural waters, biogenic or authigenic precipitates, and sediments  
 169 display La anomalies, thereby biasing the determination of the Ce anomaly using the above  
 170 formula. With this approach, the calculation of Ce\* calculated with La abundances using either  
 171 linear or geometrical interpolations (Fig. 1) resulted in biased results, generating for instance  
 172 Ce/Ce\* ratios < 1 even in the case of samples devoid of any Ce anomaly. For this reason, Bau  
 173 and Dulski (1996a) developed a Ce/Ce\* vs. Pr/Pr\* diagram (Fig. 2, with Ce\* linearly  
 174 interpolated between La and Pr (equation 5), and Pr\* linearly interpolated between Ce and Nd,  
 175  $\text{Pr}^*_{\text{SN}} = (\text{Ce}_{\text{SN}} + \text{Nd}_{\text{SN}}) / 2$ ). This plot can be used to identify whether La anomalies are present or  
 176 not, and whether Ce/Ce\* ratios < 1 correspond to true negative Ce anomalies or not. This  
 177 diagram, which was also popularized by Webb and Kamber (2000), is frequently used today.  
 178 We will come back to it later.

179 Since one cannot properly interpolate Ce\* using La with Pr or Nd abundances, one can  
 180 instead extrapolate Ce\* and La\* with Pr and Nd abundances (Fig. 1). To avoid ambiguity, we  
 181 use here the symbols X\*<sup>g</sup> and X\*<sup>l</sup> for the geometric (semi-log) and linear extrapolations,  
 182 respectively, of the theoretical concentrations of X. The following equations give La<sub>SN</sub>\*<sup>g</sup>,  
 183 Ce<sub>SN</sub>\*<sup>g</sup>, La<sub>SN</sub>\*<sup>l</sup>, and Ce<sub>SN</sub>\*<sup>l</sup> [e.g., Bolhar et al. (2004) for the linear interpolations and Lawrence  
 184 et al. (2006) for the geometric interpolations], and of course similar equations can be written  
 185 for the chondritic normalization:

$$186 \quad \text{La}_{\text{SN}}^{*g} = \text{Pr}_{\text{SN}}^3 / \text{Nd}_{\text{SN}}^2 \quad (6)$$

$$187 \quad \text{Ce}_{\text{SN}}^{*g} = \text{Pr}_{\text{SN}}^2 / \text{Nd}_{\text{SN}} \quad (7)$$

$$188 \quad \text{La}_{\text{SN}}^{*l} = 3 \text{Pr}_{\text{SN}} - 2 \text{Nd}_{\text{SN}} \quad (8)$$

$$189 \quad \text{Ce}_{\text{SN}}^{*l} = 2 \text{Pr}_{\text{SN}} - \text{Nd}_{\text{SN}} \quad (9)$$

190

191 These are the equations used by most teams working today on sedimentary rocks or  
 192 natural waters, without consensus on whether geometric or linear interpolations should be used  
 193 or not. Questions arise about whether linear or geometric extrapolation allows for a better



194 estimation of the anomalies. Additionally, do the normalization values (chondrite or shale) lead  
195 to different estimates of La and Ce anomalies?

196

### 197 **2.3/ Which type of extrapolation to select?**

198 An ideal extrapolation should meet the following criteria:

199 - To allow for the best estimation of La\* and Ce\* concentrations;

200 - To be universal, i.e. to correctly estimate La\* and Ce\* over the ~~whole~~ entire compositional  
201 range encountered in Earth systems;

202 - To be independent of normalization values; in other words, the type of extrapolation must be  
203 able to calculate consistent La/La\* or Ce/Ce\* ratios even if the data are normalized to chondritic  
204 or shale values.

205 We have built a database including a total of 286 magmatic rocks, covering a large range  
206 of light-REE depletion or enrichment, in order to evaluate the ~~utility~~ ability of both linear and  
207 geometric extrapolations to meet these requirements (Hamelin et al., 2009, 2010; Cordier et al.,  
208 2010; Daoud et al., 2010; Pelleter et al., 2014; Barrat et al., 2016; Caroff et al., 2021, Pelleter  
209 et al., 2014). The chosen suite of igneous rocks ranges from highly-depleted MORBs to highly-  
210 enriched alkaline rocks through lamprophyres, and some evolved rocks  $[(La/Sm)_{CI} = 0.24 -$   
211  $13.4]$ . All of these rocks were analyzed using the same procedure and calibration to avoid any  
212 potential analytical bias (e.g., Barrat et al., 2012). Finally, and obviously most importantly,  
213 these rocks do not have Ce, nor La anomalies: their “correct” La/La\* or Ce/Ce\* ratios are hence  
214  $\sim 1$ .

215 We calculated the Ce/Ce\* ratio with Ce\* interpolated geometrically between La and Pr  
216 (equation 1) for the rocks in our database. This ratio varies from 0.92 to 1.11 only, with most  
217 of the samples exhibiting Ce/Ce\* between 0.95 and 1.05, confirming the lack of significant Ce  
218 anomaly (Fig. 2a). The curvature of some of the patterns ~~explains mostly~~ is largely responsible  
219 for this range. In the  $Ce_{SN}/Ce_{SN}^*$  vs.  $Pr_{SN}/Pr_{SN}^*$  plot of Bau and Dulski (1996), where Ce\* and  
220 Pr\* are linearly interpolated, only half of studied rock samples ~~is~~ are located in the panel  
221 attributed to samples having no Ce and La anomalies; the other half being scattered in an area  
222 corresponding to positive anomalies in Ce with either positive or negative La anomaly. This  
223 discrepancy is somewhat surprising, as one would have expected the vast majority of studied

224 rocks to fall within the area corresponding to samples having no anomalies. This can be  
 225 explained by the fact that the rocks used in our database display a much greater LREE  
 226 compositional range relative to those used by Bau and Dulski (1996).

227 Next, we use Ce/Nd vs. Pr/Nd plots to compare linear or semi log extrapolations for Ce,  
 228 normalizing ratios to either chondritic (Fig. 3a) or PAAS values (Fig. 3b). Indeed, the Ce<sup>\*g</sup>/Nd  
 229 and Ce<sup>\*l</sup>/Nd ratios define parabolas and straight lines in these plots, respectively:

$$230 \quad Ce_{CI}^{*g}/Nd_{CI} = (Pr_{CI}/Nd_{CI})^2 \text{ and } Ce_{SN}^{*g}/Nd_{SN} = (Pr_{SN}/Nd_{SN})^2 \quad (10)$$

$$231 \quad Ce_{CI}^{*l}/Nd_{CI} = 2 (Pr_{CI}/Nd_{CI}) - 1 \text{ and } Ce_{SN}^{*l}/Nd_{SN} = 2 (Pr_{SN}/Nd_{SN}) - 1 \quad (11)$$

232 *In eq. 10 and 11, I just removed some extra spaces.*

233 The rocks of our database having no Ce anomaly, they can be directly compared to these  
 234 curves or lines. Figure 3 shows directly that the parabolas calculated using a geometric  
 235 extrapolation reproduce very satisfactorily the Ce/Nd ratios of the rocks over the whole range  
 236 of Pr/Nd ratios considered in this study. On the other hand, the lines corresponding to the linear  
 237 extrapolation allow for an acceptable approximation of Ce\* in a given range of values only.  
 238 Note that in each diagram the parabola and the line are tangent to the point (1,1). If we consider  
 239 that both interpolations give acceptable results when Ce<sup>\*g</sup>/Ce<sup>\*l</sup> is between 1 and 1.05, we can  
 240 easily calculate that we can then use indifferently one or the other extrapolation only when  
 241 (Pr/Nd)<sub>CI</sub> or (Pr/Nd)<sub>SN</sub> are between 0.82 and 1.28. Whenever (Pr/Nd)<sub>CI</sub> or (Pr/Nd)<sub>SN</sub> plot outside  
 242 this range of values, the Ce/Ce<sup>\*l</sup> and Ce/Ce<sup>\*g</sup> ratios diverge, due to a clear underestimation of  
 243 Ce<sup>\*l</sup>. The choice of normalization values is not without consequence if linear extrapolation is  
 244 used. The use of shales instead of chondritic reference values results in a shift towards the left  
 245 of the diagram [because (Pr/Nd)<sub>SN</sub> < (Pr/Nd)<sub>CI</sub>], and, as a consequence, the Ce<sub>CI</sub>/Ce<sub>CI</sub><sup>\*l</sup> and  
 246 Ce<sub>SN</sub>/Ce<sub>SN</sub><sup>\*l</sup> ratios may be very different depending on the Pr/Nd ratios. In this study, this is  
 247 strikingly illustrated by the fact that the Ce<sub>CI</sub>/Ce<sub>CI</sub><sup>\*l</sup> ratio varies from 0.91 to 1.24 only, while  
 248 Ce<sub>SN</sub>/Ce<sub>SN</sub><sup>\*l</sup> varies from 0.96 to 5.11. On the other hand, the Ce<sub>SN</sub>/Ce<sub>SN</sub><sup>\*g</sup> and Ce<sub>CI</sub>/Ce<sub>CI</sub><sup>\*g</sup> ratios  
 249 are perfectly proportional, with (Ce<sub>SN</sub>/Ce<sub>SN</sub><sup>\*g</sup>)/(Ce<sub>CI</sub>/Ce<sub>CI</sub><sup>\*g</sup>) being equal to the PAAS  
 250 Ce<sub>CI</sub>/Ce<sub>CI</sub><sup>\*g</sup> ratio.

251 In Fig. 4, we show the Ce/Ce<sup>\*g</sup> and Ce/Ce<sup>\*l</sup> ratios obtained after normalization to either  
 252 chondritic or PAAS values. The diagrams not only indicate that the ranges of values obtained  
 253 are different, but that the correlations are poor: Ce anomalies calculated in different ways are  
 254 not comparable.

255 We followed the same approach for La anomalies. In La/Nd vs. Pr/Nd plots, the  $La^{*g}/Nd$   
256 and  $La^{*l}/Nd$  ratios define cubic curves and straight lines, respectively:

$$257 \quad La_{CI}^{*g}/Nd_{CI} = (Pr_{CI}/Nd_{CI})^3 \text{ and } La_{SN}^{*g}/Nd_{SN} = (Pr_{SN}/Nd_{SN})^3 \quad (12)$$

$$258 \quad La_{CI}^{*l}/Nd_{CI} = 3 (Pr_{CI}/Nd_{CI}) - 2 \text{ and } La_{SN}^{*l}/Nd_{SN} = 3 (Pr_{SN}/Nd_{SN}) - 2 \quad (13)$$

259 As shown above, the curves corresponding to the geometric extrapolation superimpose  
260 well on the correlation trends displayed by the rock data used in this study (Fig. 5). The straight  
261 lines corresponding to the linear extrapolation only allow a good estimation of the La/Nd ratios  
262 for the patterns exhibit little REE decoupling (i.e., when  $(Pr/Nd)_{CI}$  or  $(Pr/Nd)_{SN}$  close to 1).  
263 Calculation of La anomalies using the linear extrapolation even appears to be inconsistent for  
264 many samples. When the data are normalized to chondritic reference values, the linear  
265 extrapolation underestimates considerably  $La^*$  values, leading to anomalously high  $La/La^{*l}$   
266 ratios. The situation is much more problematic when data are normalized to PAAS values,  
267 especially for the most light-REE depleted samples. Not only does Equation 8 underestimate  
268  $La_{SN}^*$ , but when  $(Pr/Nd)_{SN} \leq 2/3$ ,  $La_{SN}^{*l} \leq 0$  and the  $La_{SN}/La_{SN}^{*l}$  ratio becomes negative or  
269 tends toward  $-\infty$  when  $(Pr/Nd)_{SN}$  is just below  $2/3$ . The  $La_{SN}/La_{SN}^{*l}$  ratio also tends toward  $+\infty$   
270 when  $(Pr/Nd)_{SN}$  is just above  $2/3$ . These cases are not uncommon on Earth: the  $La_{SN}/La_{SN}^{*l}$   
271 ratios calculated with our database range from -216.3 to 103.5, while much smaller ranges  
272 around 1 are obtained with other  $La/La^*$  calculations (Fig. 6). As for the Ce anomaly, the ratios  
273  $La_{SN}/La_{SN}^{*g}$  and  $La_{CI}/La_{CI}^{*g}$  are perfectly proportional, and the  $La/La^{*g}$  and  $La/La^{*l}$  ratios are  
274 not strongly correlated, even when the latter ratios are not aberrant. The range of  $(Pr/Nd)_{SN}$   
275 ratios for which La anomaly calculations are similar for linear or geometric interpolations  
276 ( $La^{*g}/La^{*l} < 1.05$ ) is narrow and only between 0.9 and 1.16.

277 These results demonstrate that La and Ce anomalies calculated using linear  
278 extrapolation can lead to biased or even aberrant values in many cases. Moreover, the calculated  
279 anomalies are very dependent on the type of normalization used. On the other hand, the results  
280 obtained with our database indicate that the use of geometric extrapolation results in more  
281 reliable estimates of La and Ce anomalies, ~~whatever~~ regardless of whether chondrite or shale  
282 are used for normalization, and this applies for the whole range of compositions tested in this  
283 study.

284

### 285 **3/ Some examples**

286 The theoretical ground discussed above is illustrated below for a few examples taken  
287 from the literature (Table 1). It is not our goal here to discuss the differences obtained between  
288 the anomalies calculated for each type of rocks or waters, normalizations and extrapolations.  
289 We have chosen to discuss in more detail the ~~case-study~~ specific cases of seawater samples and  
290 biogenic carbonates, in order to show how the choice of extrapolation can affect data  
291 interpretation.

292

### 293 3.1. Carbonates

294 We selected 5 series of carbonate samples corresponding to microbialites or  
295 stromatolites of different ages: the 3.45-Ga-old Strelley Pool stromatolites (Van Kranendonk et  
296 al., 2003); the 2.84-Ga-old Mushandike stromatolites (Kamber et al, 2004); the 2.52-Ga-old  
297 Campbellrand stromatolites (Kamber and Webb, 2001); the late Devonian reefal carbonates  
298 from the Lennard Shelf (Nothdurft et al., 2004); and the Holocene microbialites from the Heron  
299 Reef (Webb and Kamber, 2000). All data used here were obtained in the same laboratory  
300 (ACQUIRE, Brisbane) following similar analytical procedures, and are of excellent quality.  
301 These series of samples do not of course cover the full compositional range existing for such  
302 these types of carbonates, but nevertheless display important variations in various REE  
303 signatures.

304 We plotted these analyses in the Ce/Ce\* vs. Pr/Pr\* diagram of Bau and Dulski (1996a),  
305 which can be used, as discussed above, to identify the presence of Ce and La anomalies (Fig.  
306 7a). In this diagram, Ce\* and Pr\* are linearly interpolated between La and Pr and Ce and Nd  
307 respectively. All but 2 samples have a Ce/Ce\* ratio < 1 when calculated in ~~that~~ this way, but only  
308 those with a Pr/Pr\* ratio > 1 have a true negative Ce anomaly, due to the bias introduced by the  
309 La anomalies. We calculated the Ce and La anomalies using both geometrical and linear  
310 extrapolation from PAAS-normalized concentrations. The obtained  $Ce_{SN}/Ce_{SN}^{*g}$  and  
311  $Ce_{SN}/Ce_{SN}^{*l}$  ratios are very similar (Fig. 8a) for most samples. Only 4 samples from Strelley  
312 Pool deviate significantly from the trend, their  $Ce_{SN}^{*l}$  certainly being underestimated. The  
313  $La_{SN}/La_{SN}^{*g}$  and  $La_{SN}/La_{SN}^{*l}$  ratios are for most samples reasonably well correlated, but the  
314 Holocene samples markedly deviate from the trend with  $La_{SN}/La_{SN}^{*l}$  ratios greater than  
315  $La^{SN}/La_{SN}^{*g}$ , and 4 Strelley Pool samples display outlier  $La_{SN}/La_{SN}^{*l}$  values (=-27.7 to -4.6).  
316 These calculations show that in many cases, one can use either linear or geometric  
317 extrapolations to estimate La or Ce anomalies, without detecting an anomaly. This is

318 particularly the case when the patterns are little or not fractionated, but linear extrapolation can  
319 nevertheless generate artifacts or even aberrant values. To avoid the latter, we recommend using  
320 only the geometrical extrapolation to calculate La or Ce anomalies.

321 Although the Ce/Ce\* vs. Pr/Pr\* diagram proposed by Bau and Dulski (1996a) can bring  
322 useful insights for discussing REE patterns and the origin of La and Ce anomalies, it also suffers  
323 from inherent drawbacks that are briefly described below:

324 - The Ce/Ce\* ratio used in this diagram depends on a Ce\* value linearly interpolated  
325 between La and Pr. This ratio does not allow a correct quantification of the anomaly, because  
326 in addition to the problems related to the linear interpolation, it can be largely biased for the  
327 samples with an anomaly in La, as already reported by these authors

328 - the Pr/Pr\* ratio allows for the detection of samples with positive or negative anomalies  
329 in La, but the diagram does not allow the quantification of the latter.

330 For all the above-mentioned reasons, we propose using instead the Ce/Ce\*<sup>g</sup> vs. La/La\*<sup>g</sup>  
331 diagram, which is ~~best~~ better suited for illustrating whether any given sample displays La or Ce  
332 anomalies, and which also provides direct quantification of these anomalies. Additionally, the  
333 use of the geometric extrapolation ensures that calculated anomalies in this diagram are  
334 independent of the type of reference used for normalization, ~~but~~ and above all it avoids the  
335 calculation of erroneous Ce/Ce\* or La/La\* ratios due to artifacts linked to linear extrapolation.  
336 For the carbonate samples selected here, the Ce/Ce\*<sup>g</sup> vs. La/La\*<sup>g</sup> diagram shows that these  
337 carbonates exhibit a wide range of positive La anomalies, but also allows one to identify a clear  
338 distinction between those Archean samples characterized by the absence of marked negative  
339 Ce anomalies ( $Ce/Ce^{*g} \geq 1$ ), in contrast with the Devonian or Holocene carbonates.

340

### 341 3.2. Seawater

342 We employ ~~used~~ here a previously published REE database for seawater samples  
343 (n=1649; Bayon et al., 2020b). We normalized the concentrations with PAAS and examined  
344 ~~reported~~ (Ce/Nd)<sub>SN</sub> and (La/Nd)<sub>SN</sub> vs. (Pr/Nd)<sub>SN</sub> plots systematics (Fig. 9). The (Pr/Nd)<sub>SN</sub> ratios  
345 range from 0.49 to 1.19: 62% of the analyses have (Pr/Nd)<sub>SN</sub> ratios <0.82, and thus have Ce/Ce\*<sup>1</sup>  
346 and Ce/Ce\*<sup>g</sup> ratios that differ by more than 5%; 97% of the analyses have (Pr/Nd)<sub>SN</sub> ratios <0.9,  
347 and thus have La/La\*<sup>1</sup> and La/La\*<sup>g</sup> ratios that differ by more than 5%. The position of the  
348 points with respect to the calculated curves and lines shows unambiguously that the choice of

349 the extrapolation method is critical here, as the  $\text{La}^{*1}$  or  $\text{Ce}^{*1}$  concentrations are most often  
350 underestimated by the calculation, or even aberrant ( $\text{La}^{*1} < 0$  for many samples).

351 In order to illustrate the pitfalls of using the linear extrapolation for the case of seawater  
352 samples, we chose two hydrographic stations from the China Sea (Alibo and Nozaki, 2000) and  
353 the Kerguelen Plateau (Grenier et al., 2018), and ~~calculated~~ examined the vertical profiles of  
354 La anomalies calculated by normalizing the data with respect to both CI-chondrite and PAAS,  
355 extrapolating  $\text{La}^*$  linearly or geometrically (Fig. 10). For both stations,  $\text{La}_{\text{SN}}/\text{La}_{\text{SN}}^{*1}$  ratios are  
356 always much larger than those estimated geometrically by normalizing with PAAS or with CI-  
357 chondrite: for the first station,  $\text{La}_{\text{SN}}/\text{La}_{\text{SN}}^{*1}$  ratios are 1.30 to 1.42 times larger than  $\text{La}_{\text{SN}}/\text{La}_{\text{SN}}^{*g}$   
358 ratios, and for the second station they are 1.54 to 3.71 times larger. The La anomalies estimated  
359 with the  $\text{La}_{\text{SN}}/\text{La}_{\text{SN}}^{*1}$  ratios are obviously strongly exaggerated, and these calculations must be  
360 rejected. Note that the  $\text{La}_{\text{CI}}/\text{La}_{\text{CI}}^{*1}$  ratios are very close to the  $\text{La}_{\text{CI}}/\text{La}_{\text{CI}}^{*g}$  or  $\text{La}_{\text{SN}}/\text{La}_{\text{SN}}^{*g}$  ratios,  
361 and similar or identical profiles are obtained with these three ratios. These results adds further  
362 support that the use of geometric extrapolation is best suited for calculating La and Ce  
363 anomalies relative to the linear extrapolation. The fact that the  $\text{La}_{\text{CI}}/\text{La}_{\text{CI}}^{*1}$  ratios are correct here  
364 is fortuitous, and is easily explained. The  $(\text{Pr}/\text{Nd})_{\text{CI}}$  ratios are higher than the  $(\text{Pr}/\text{Nd})_{\text{SN}}$  ratios,  
365 and are then in the range of values for which geometric and linear extrapolations give equivalent  
366 results.

367

#### 368 **4/ Conclusion**

369 An extended REE database for a suite of igneous rocks devoid of La and Ce anomalies,  
370 was used to investigate the effects of linear and geometric extrapolations for calculating  $\text{La}/\text{La}^*$   
371 and  $\text{Ce}/\text{Ce}^*$  ratios in geological and environmental samples, based on Pr and Nd concentrations.  
372 We show that the linear extrapolation only provides reliable estimates of  $\text{La}^*$  and  $\text{Ce}^*$  for a  
373 limited range of REE compositions. These calculations can lead in many cases to biased  $\text{La}/\text{La}^*$   
374 and  $\text{Ce}/\text{Ce}^*$  values, which are also critically dependent on the type of normalization used (i.e.  
375 chondritic versus shale reference values). The artifacts generated when using the linear  
376 extrapolation are illustrated with examples from the literature for seawater and biogenic  
377 carbonates, demonstrating that it can lead to misleading interpretations regarding the presence  
378 and/or significance of La and Ce anomalies. Finally, we show that the use of geometric  
379 extrapolation ensures reliable quantitative calculation of Ce and La anomalies in all samples,  
380 which remain unaffected by the type of normalization used. We propose that linear

381 extrapolations be discontinued ~~here~~, and instead recommend the exclusive use of geometric  
382 extrapolations to quantify La and Ce anomalies.

383

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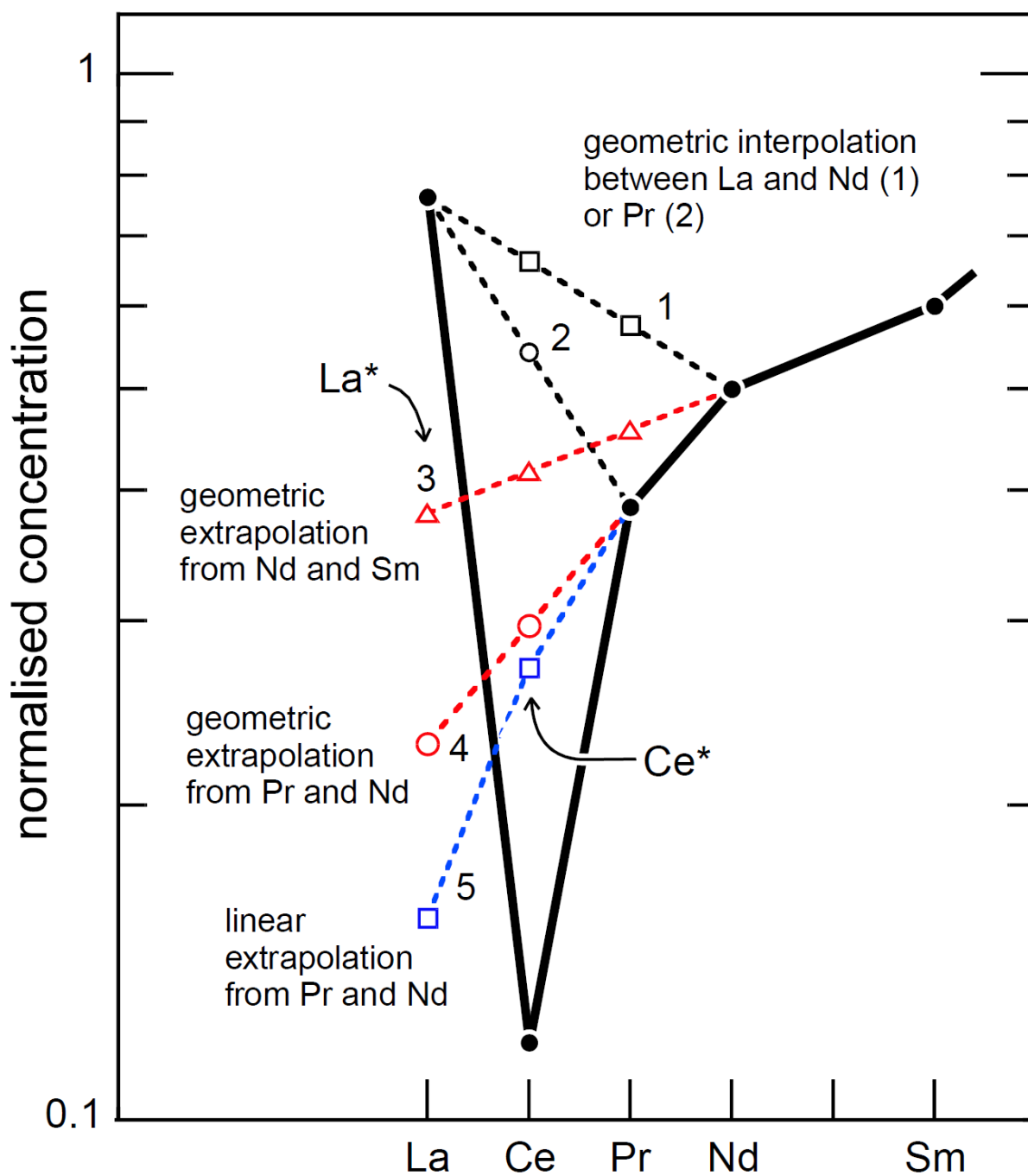
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596 Table 1. Preferred normalization values and examples of calculation. (References: 1: Barrat et al., 2012; 2: Pourmand et al., 2012; 3: Barrat et al., 2016 ; 4 :  
597 Bau et al., 2003 ; 5 : Charles et al., 2021 ; 6 : Van Kranendonk et al., 2003).

	CI-chondrite	CI-chondrite	PAAS	PAAS	MORB	fluorite	Mn-nodule	stromatolite	BIF
ref.	1	1	2	2	3	4	5	6	6
#					PI 18-06	CT2a	GSMC-1	2-9-11a	IF-G
unit	$\mu\text{g/g}$	$\mu\text{mol/kg}$	$\mu\text{g/g}$	$\mu\text{mol/kg}$	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	$\text{ng/g}$	$\text{ng/g}$
Y	1.56	17.55	32.2	362		35.6	259	1014.2	9135
La	0.235	1.692	44.75	322.2	0.504	0.54	326	56.3	2706
Ce	0.600	4.28	87.29	623.0	2.13	0.89	1246	85.9	3902
Pr	0.091	0.646	10.1	71.68	0.464	0.23	68.74	14	430
Nd	0.464	3.22	36.98	256.4	3.00	1.42	283	77.7	1731
Sm	0.153	1.018	6.908	45.94	1.30	0.57	58.4	45.9	399
Eu	0.0586	0.386	1.188	7.818	0.582	0.18	14.36	27.1	362
Gd	0.206	1.31	5.958	37.89	2.18	1.33	61.68	89.6	667
Tb	0.0375	0.236	0.894	5.625	0.432	0.23	9.53	13.6	112
Dy	0.254	1.563	5.272	32.44	3.16	1.71	56.48	70	791
Ho	0.0566	0.343	1.078	6.536	0.743	0.4	11.58	17.7	207
Er	0.166	0.992	3.094	18.50	2.23	1.15	31.93	54.8	619
Tm	0.0262	0.155	0.468	2.770		0.13			
Yb	0.168	0.971	3.028	17.50	2.28	0.61	29.2	48	580
Lu	0.0246	0.141	0.438	2.503	0.34	0.07	4.26	8.6	90.4
$\text{La}_{\text{CI}}/\text{La}_{\text{CI}}^{*\text{g}}$	1	1	0.88	0.88	0.68	1.33	1.20	1.84	1.52
$\text{Ce}_{\text{CI}}/\text{Ce}_{\text{CI}}^{*\text{g}}$	1	1	0.94	0.94	0.88	0.71	2.22	1.01	1.09
$\text{La}_{\text{CI}}/\text{La}_{\text{CI}}^{*\text{l}}$	1	1	1.10	1.10	0.91	1.57	1.33	1.89	1.71
$\text{Ce}_{\text{CI}}/\text{Ce}_{\text{CI}}^{*\text{l}}$	1	1	1.02	1.02	0.95	0.74	2.31	1.02	1.14
$\text{La}_{\text{SN}}/\text{La}_{\text{SN}}^{*\text{g}}$	1.13	1.13	1	1	0.76	1.51	1.35	2.09	1.72
$\text{Ce}_{\text{SN}}/\text{Ce}_{\text{SN}}^{*\text{g}}$	1.06	1.06	1	1	0.94	0.75	2.36	1.08	1.15
$\text{La}_{\text{SN}}/\text{La}_{\text{SN}}^{*\text{l}}$	2.71	2.71	1	1	-0.46	-1.42	1.42	-28.69	1.77
$\text{Ce}_{\text{SN}}/\text{Ce}_{\text{SN}}^{*\text{l}}$	1.26	1.26	1	1	2.27	1.43	2.40	1.47	1.17



600

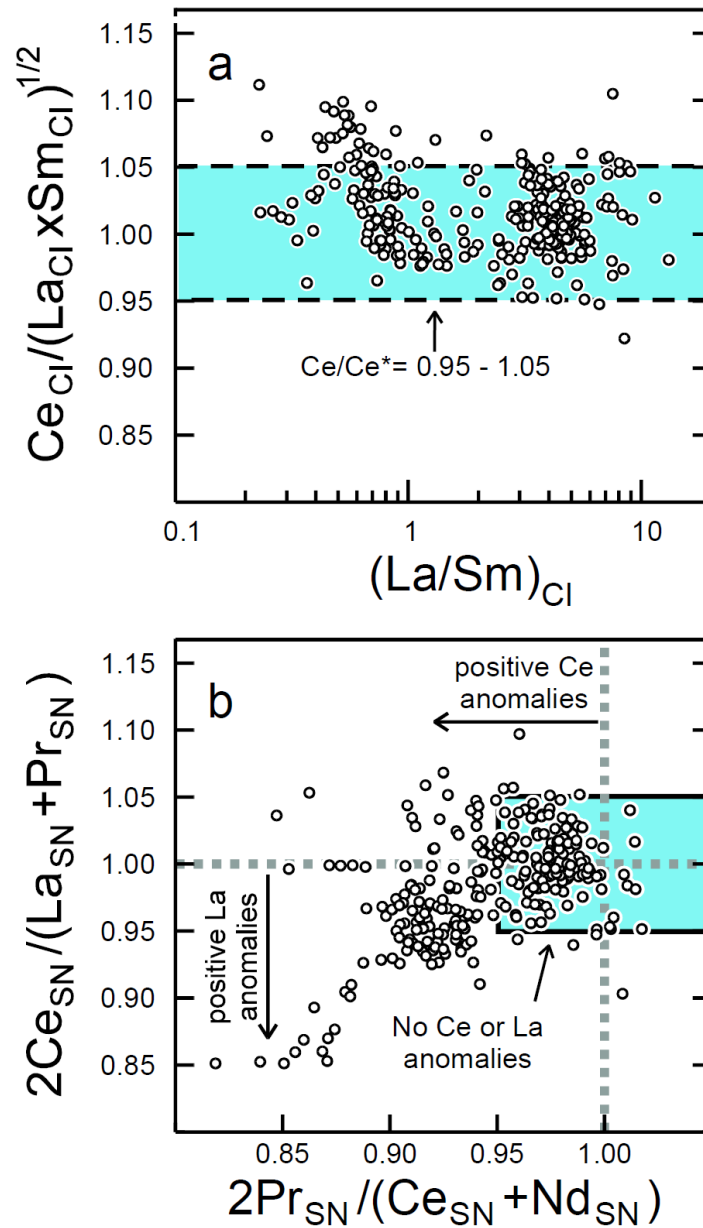
601

602 Figure 1. The different ways of calculating La\* and Ce\*.

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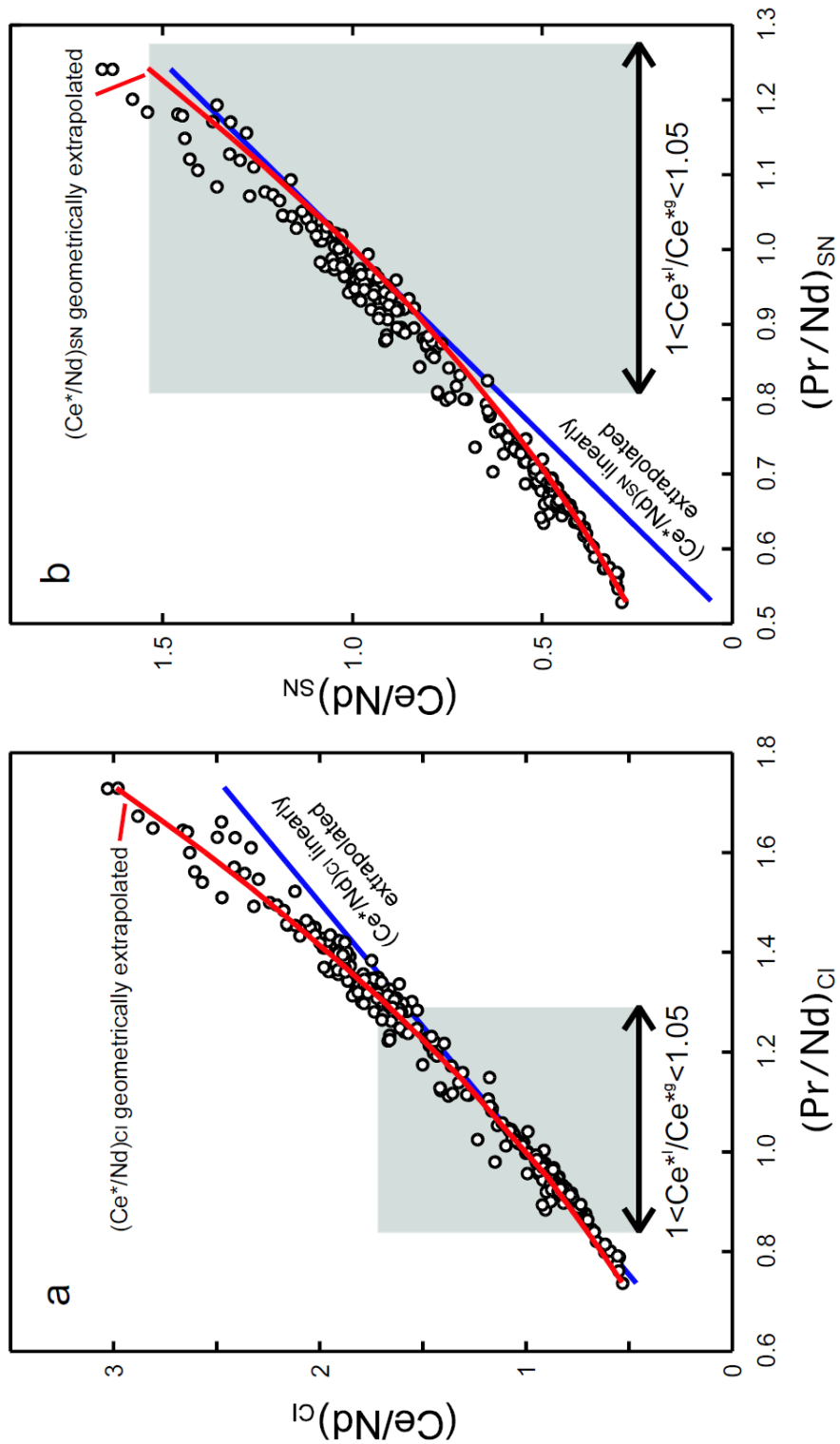
607 Figure 2. The 286 samples devoid of true La and Ce anomalies of the database used to compare  
608 linear and geometric extrapolations for calculating  $La^*$  and  $Ce^*$ , are plotted in a  $Ce/Ce^*$  vs.  
609  $La/Sm$  plot (a) and in the  $Ce/Ce^*$  vs.  $Pr/Pr^*$  plot of Bau and Dulski (1996a) (b).  $Ce^*$  is  
610 geometrically interpolated in (a) and linearly interpolated in (b).

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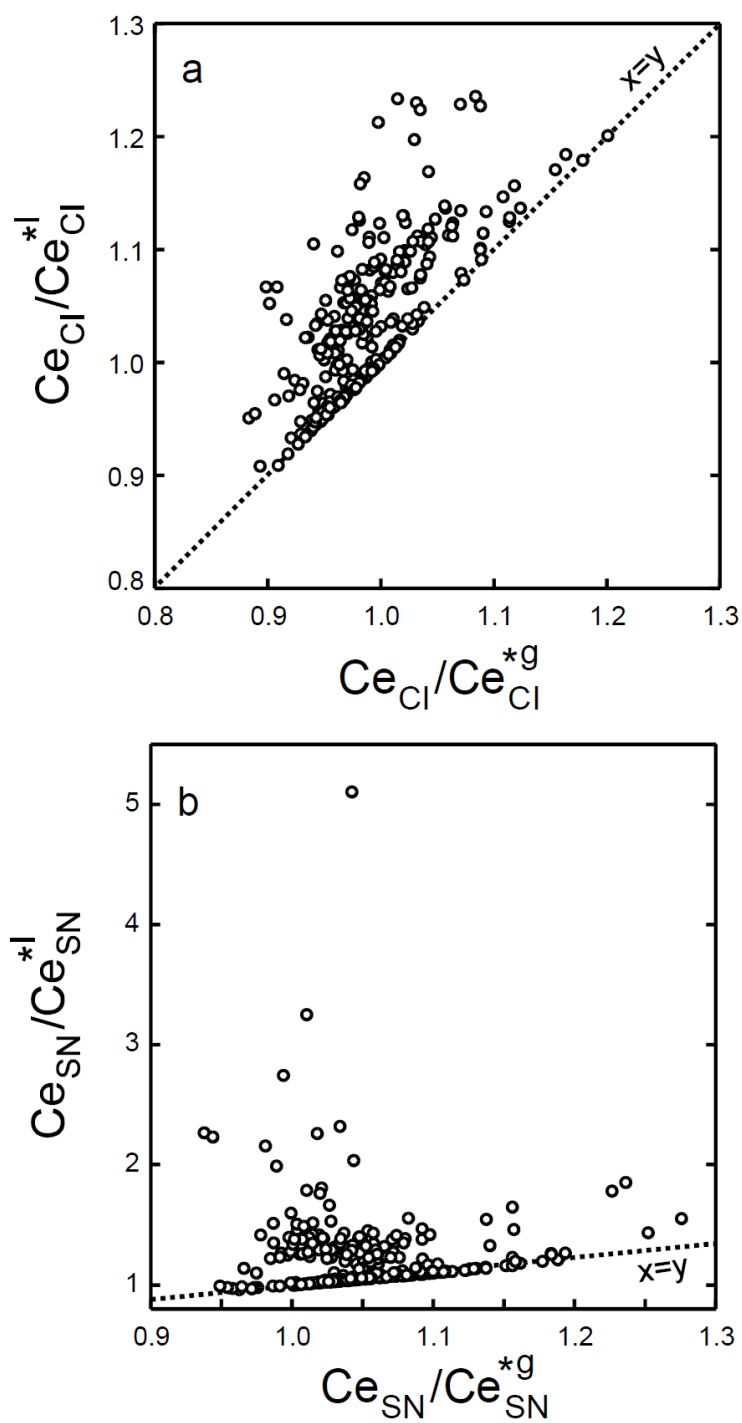
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615

616 Figure 3. Ce/Nd vs. Pr/Nd plots for the samples devoid of true La and Ce anomalies of our  
617 database, used here to compare linear (blue line) and geometric (red parabola) extrapolations  
618 for Ce\*. The data are normalized with CI chondrite (a) or with PAAS (b).



620

621 Figure 4.  $Ce_{Cl}/Ce_{Cl}^{*l}$  vs.  $Ce_{Cl}/Ce_{Cl}^{*g}$  (a) and  $Ce_{SN}/Ce_{SN}^{*l}$  vs.  $Ce_{SN}/Ce_{SN}^{*g}$  (b) plots for the  
 622 samples devoid of true Ce anomalies used to test the different extrapolations. Notice the ranges  
 623 of values obtained.

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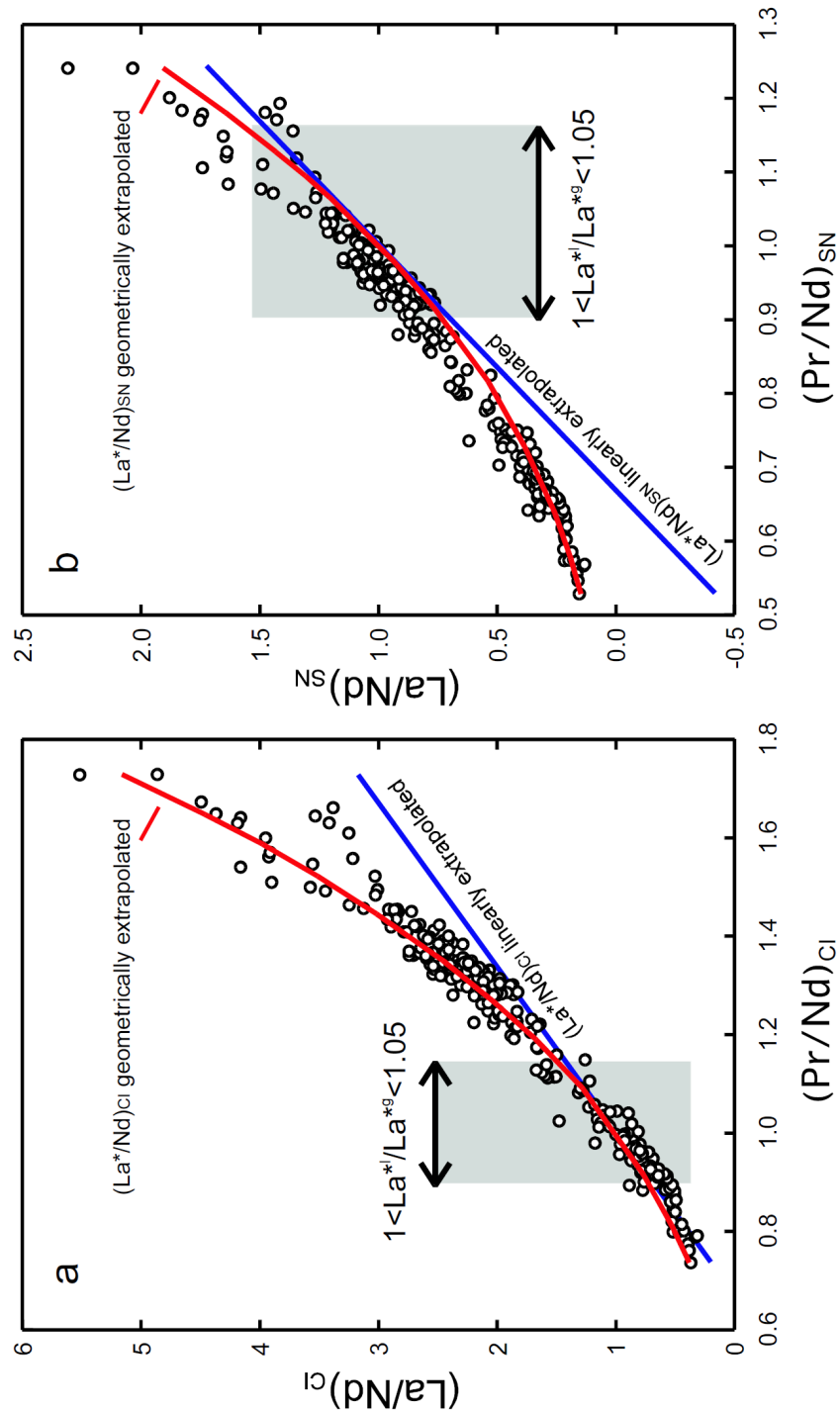
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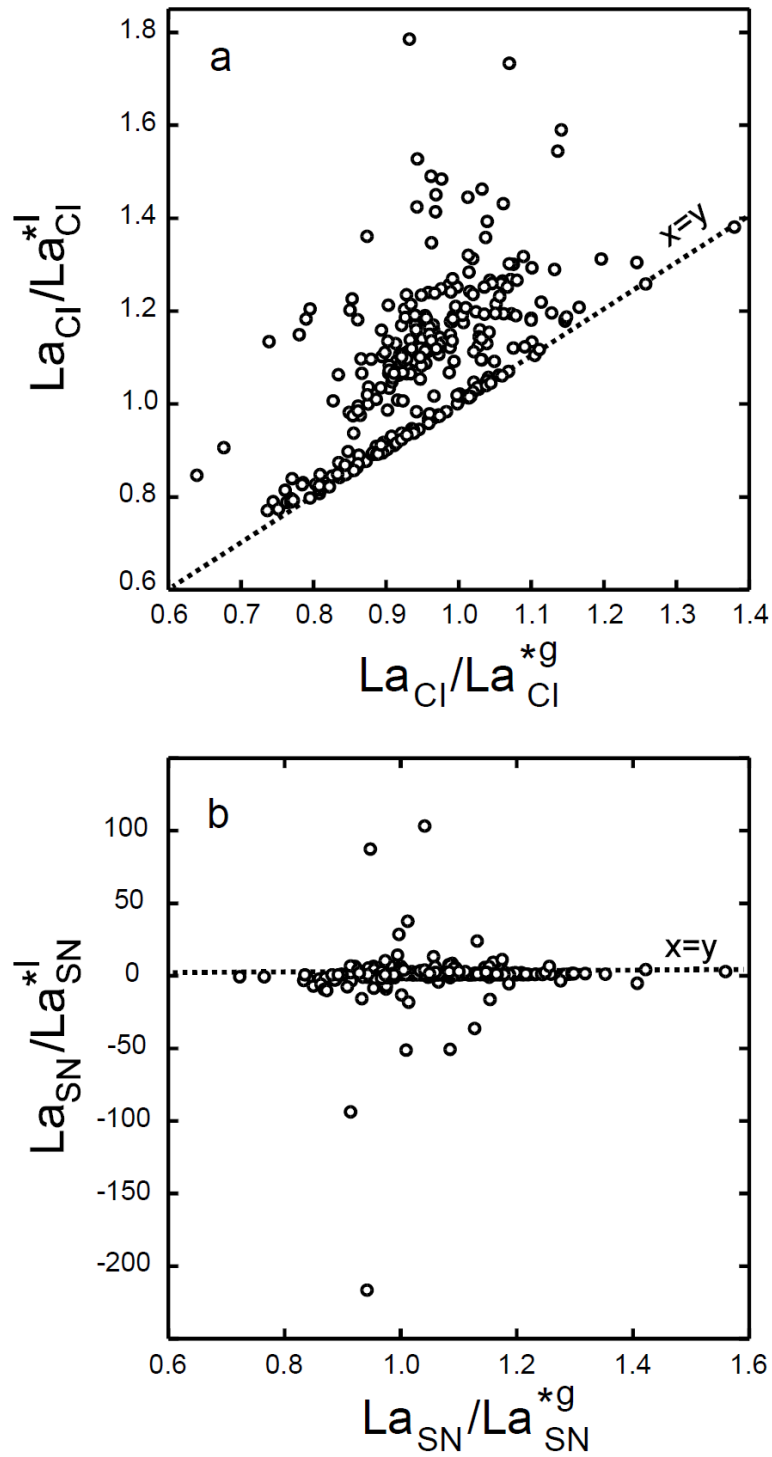
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631 Figure 5. La/Nd vs. Pr/Nd plots for the samples devoid of true La and Ce anomalies of our  
632 database used to compare linear (blue line) and geometric (red cubic) extrapolations for Ce\*.  
633 The data are normalized with CI chondrite (a) or with PAAS (b).

634



635

636 Figure 6.  $La_{Cl}/La_{Cl}^{*l}$  vs.  $La_{Cl}/La_{Cl}^{*g}$  (a) and  $La_{SN}/La_{SN}^{*l}$  vs.  $La_{SN}/La_{SN}^{*g}$  (b) plots for the  
 637 samples devoid of true La anomalies used to test the different extrapolations. Notice the ranges  
 638 of values obtained.

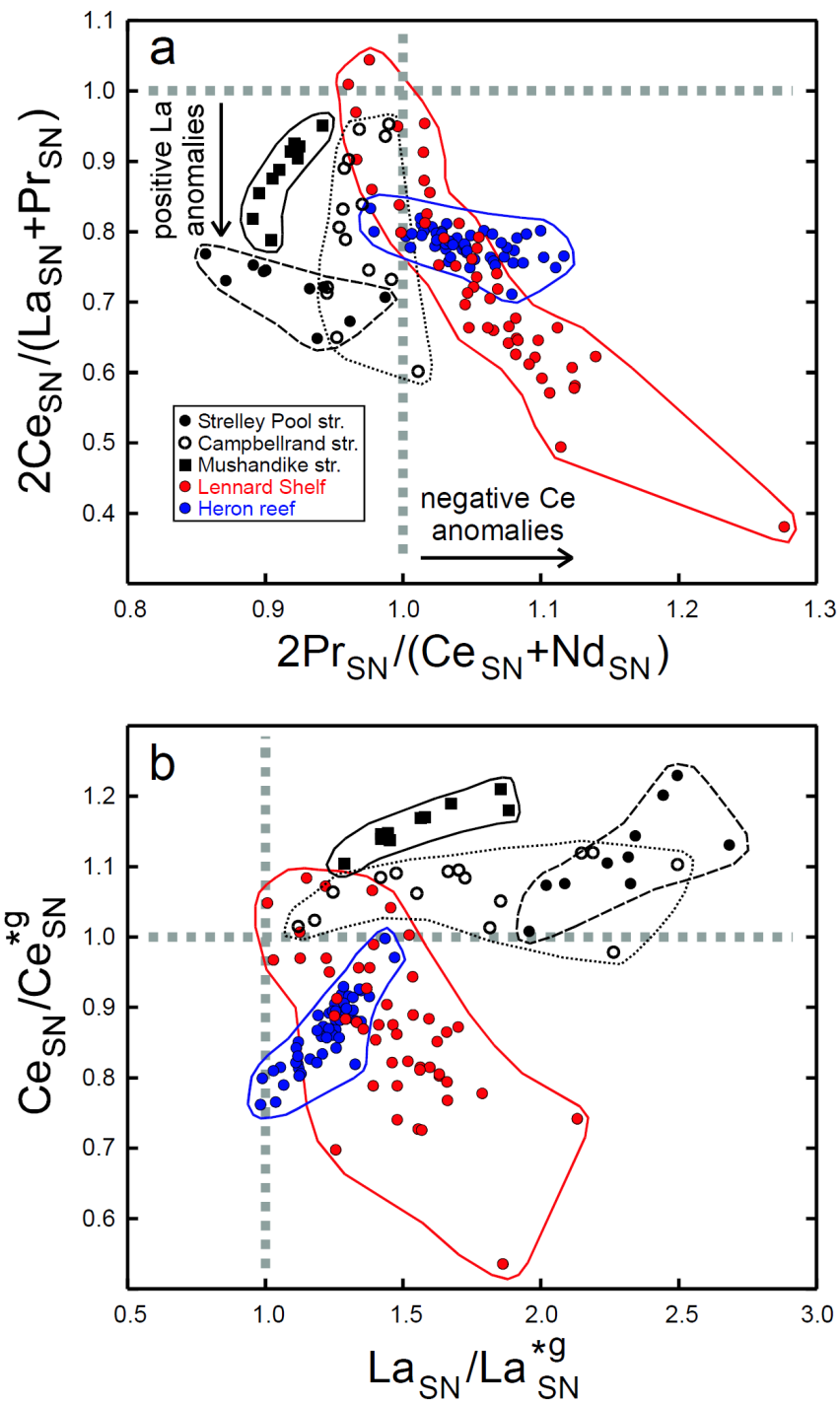
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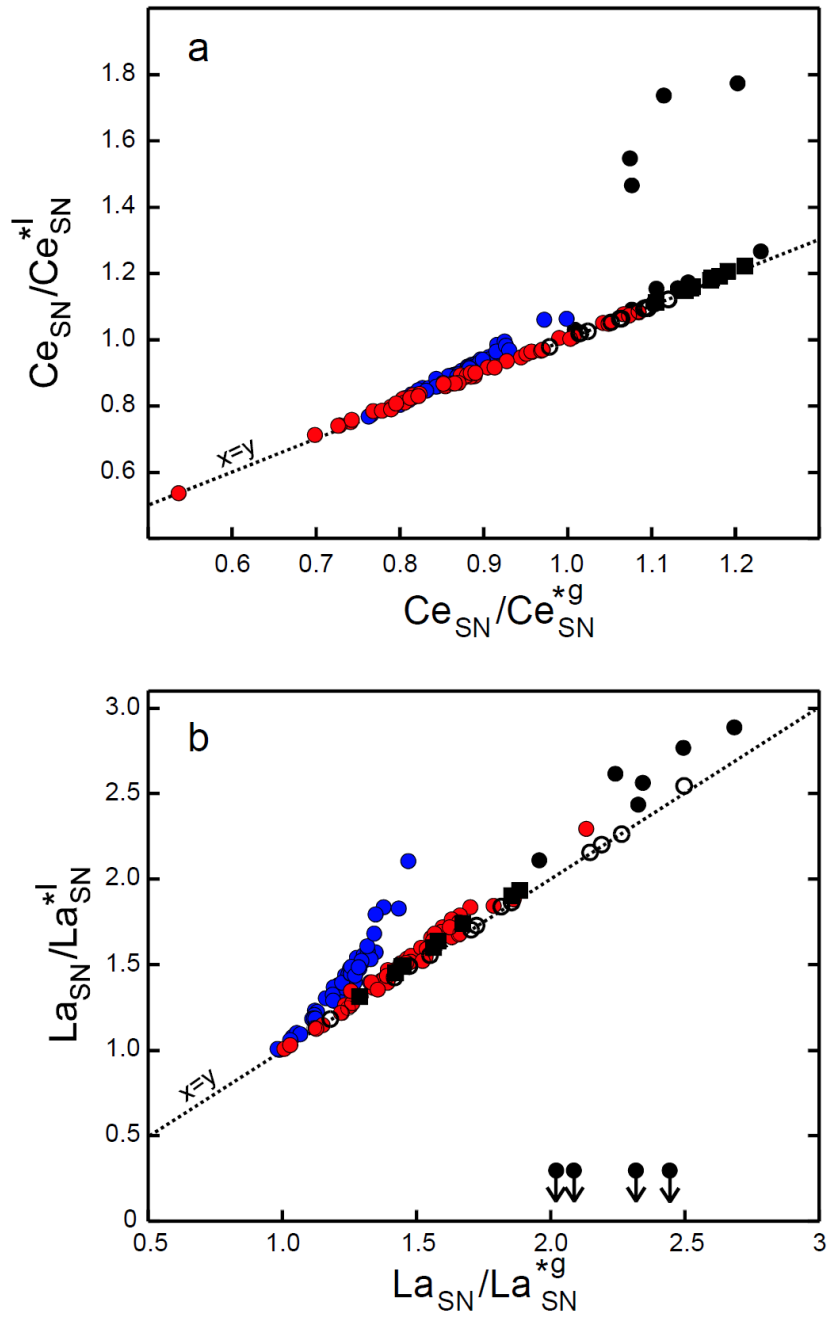
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645 Figure 7. Selected carbonates are plotted in the Ce/Ce\* vs. Pr/Pr\* plot of Bau and Dulski  
646 (1996a) (a) where Ce\* and Pr\* are linearly interpolated, and in a Ce/Ce\* vs. La/La\* where Ce\*  
647 and La\* are geometrically interpolated. Notice the different Ce/Ce\* ranges obtained. See text  
648 for more details.



649

650 Figure 8.  $Ce_{SN}/Ce_{SN}^{*l}$  vs.  $Ce_{SN}/Ce_{SN}^{*g}$  (a) and  $La_{SN}/La_{SN}^{*l}$  vs.  $La_{SN}/La_{SN}^{*g}$  (b) plots for the  
 651 selected carbonates used to test the different extrapolations (same caption as Fig. 7).

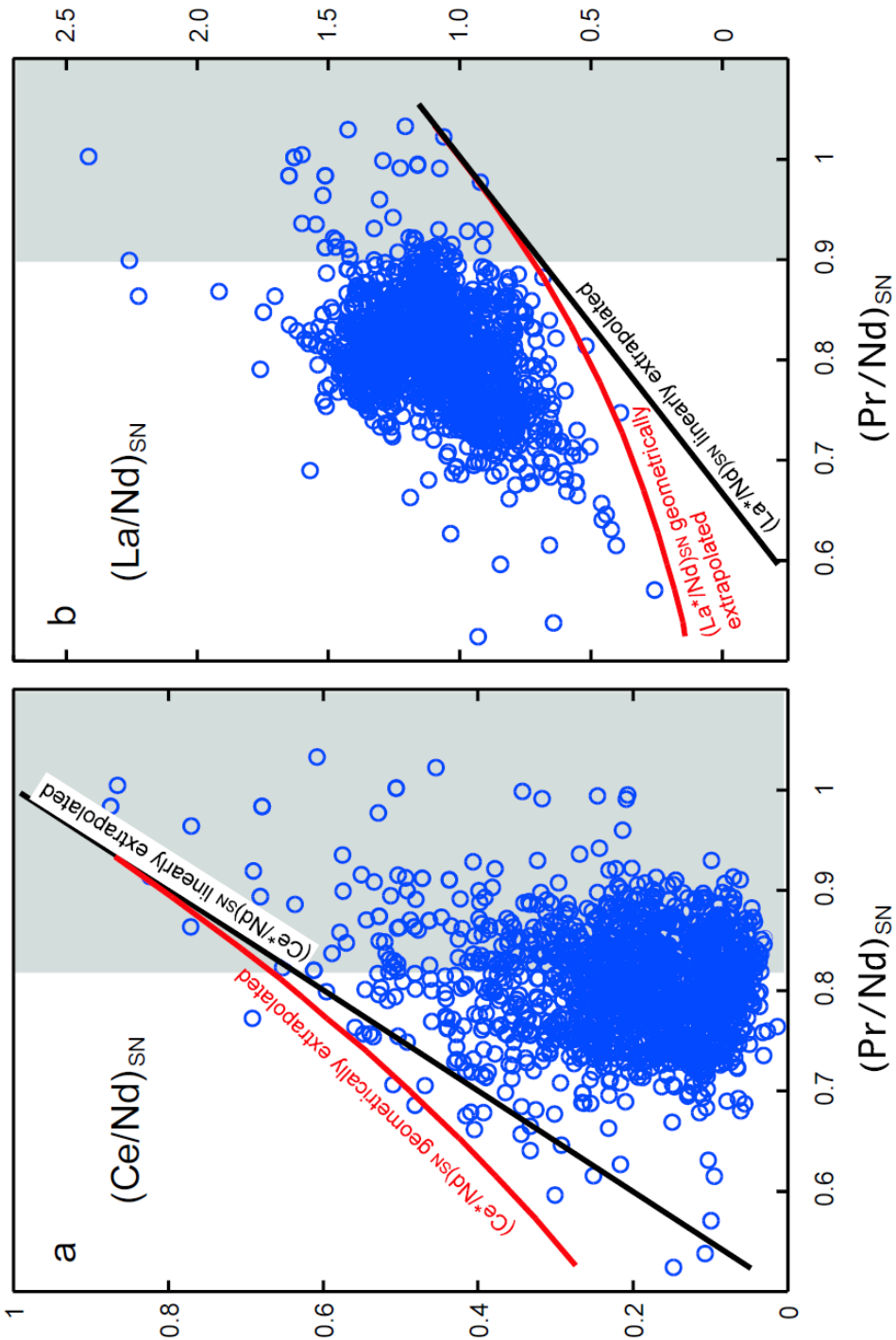
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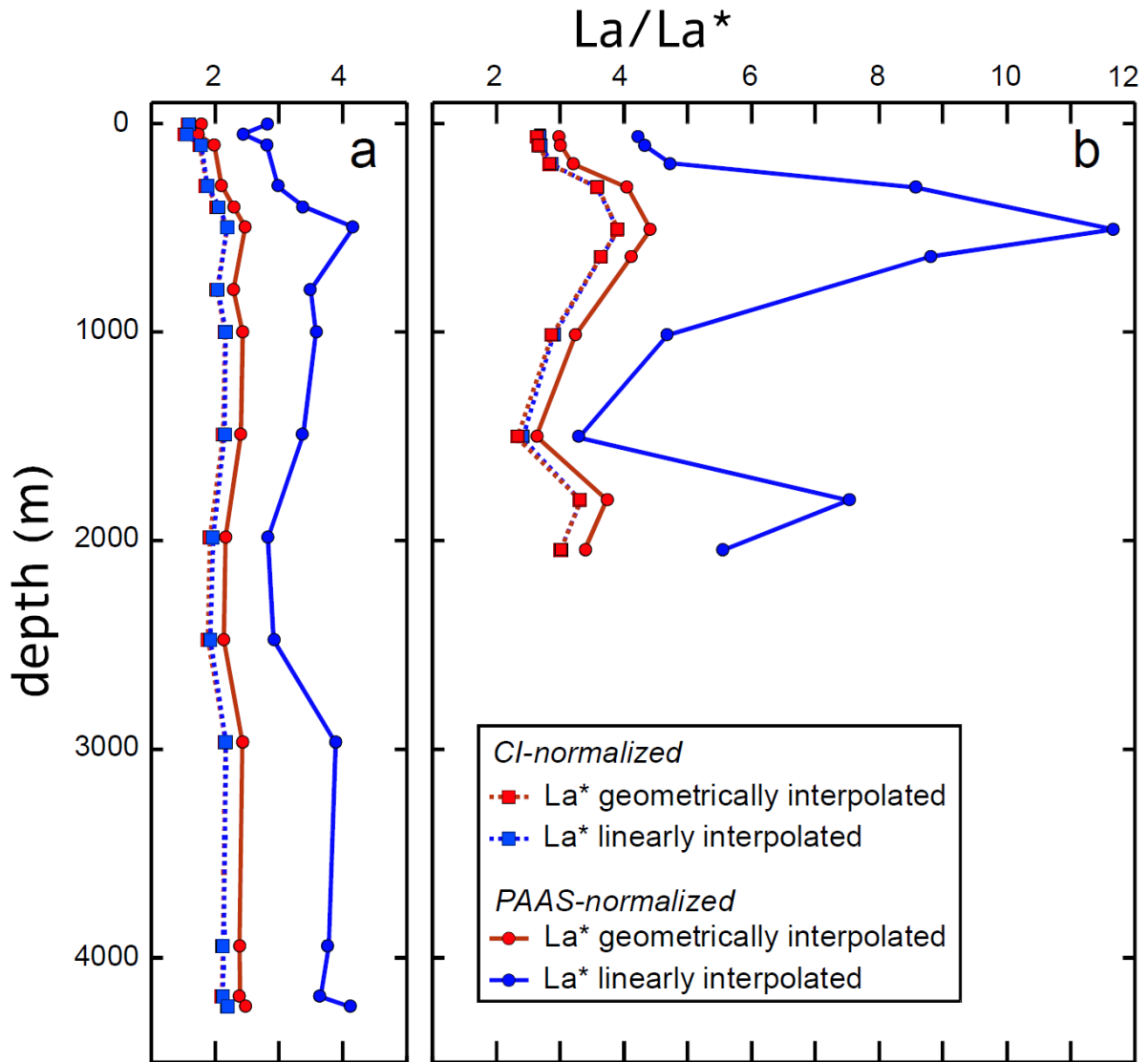


657

658 Figure 9.  $(\text{Ce}/\text{Nd})_{\text{SN}}$  (a) and  $(\text{La}/\text{Nd})_{\text{SN}}$  (b) vs.  $(\text{Pr}/\text{Nd})_{\text{SN}}$  plots for seawater. The shaded areas  
659 correspond to the range in  $\text{Pr}/\text{Nd}$  ratios for which the linear and geometric extrapolations are  
660 similar ( $1 < X^*/X^*_g < 1.05$ ), correspond to the areas that have been shaded. A large proportion  
661 of the samples are outside the ranges where the linearly extrapolated  $\text{Ce}^*$  or  $\text{La}^*$  are equivalent  
662 to the geometrically extrapolated ones.

663

664



665

666 Figure 10. Vertical profiles of La anomaly ( $\text{La}/\text{La}^*$ ) at (a) station PA-11, South China Sea  
 667 (February 11 and 12, 1997;  $15^\circ 22' \text{N}$ ,  $115^\circ 17' \text{E}$ ; depth: 4240 m ; Alibo and Nozaki, 2000) and  
 668 at (b) the meander core station E1, Kerguelen Plateau (October 30, 2011;  $72.178^\circ \text{E}$ ,  $48.498^\circ \text{S}$ ;  
 669 depth: 2058 m, Grenier et al., 2018).  $\text{La}/\text{La}^*$  was calculated linearly and geometrically with  
 670 data normalized with chondrite or with PAAS. The  $\text{La}_{\text{SN}}/\text{La}_{\text{SN}}^{*1}$  values are always much larger  
 671 than the other  $\text{La}/\text{La}^*$  estimates, and is an artifact.