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2 **Quadrivalent praseodymium in planetary materials**

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8 **Abstract**

9 Praseodymium is capable of existing as Pr³⁺ and Pr⁴⁺. Although the former is dominant across
10 almost all geological conditions, the observation of Pr⁴⁺ by XANES and Pr anomalies (both
11 positive and negative) in multiple light rare earth element minerals from Nolans Bore,
12 Australia and Stetind, Norway, indicates that quadrivalent Pr can occur under oxidizing
13 hydrothermal and supergene conditions. High-temperature REE partitioning experiments at
14 oxygen fugacities up to more than 12 log units more oxidizing than the fayalite-magnetite-
15 quartz buffer show negligible evidence for Pr⁴⁺ in zircon, indicating that Pr likely remains as
16 Pr³⁺ under all magmatic conditions. Synthetic Pr⁴⁺-bearing zircons in the pigment industry
17 form under unique conditions which are not attained in natural systems. Quadrivalent Pr in
18 solutions has an extremely short lifetime, but may be sufficient to cause anomalous Pr in
19 solids. Because the same conditions that favors Pr⁴⁺ also stabilize Ce⁴⁺ to a greater extent,
20 these two cations have similar ionic radii, and Ce is more than six times as abundant as Pr, it
21 seems that Pr-dominant minerals must be exceptionally rare, if they occur at all. We identify
22 cold, alkaline, and oxidizing environments such as oxyhalide-rich regions at the Atacama
23 Desert or on Mars as candidates for the existence of Pr-dominant minerals.

24 Introduction

25 The lanthanides (La to Lu) and yttrium are known as the rare earth elements (REE), a group
26 which exhibits strikingly similar geochemical properties, stemming from their electronic
27 structure. They form trivalent cations whose radius decreases with increasing Z because of
28 weak shielding of the other electrons by the 4f shell (e.g. ${}_{58}\text{Ce}^{3+} = [\text{Xe}]4f^1$, ${}_{59}\text{Pr}^{3+} = [\text{Xe}]4f^2$,
29 ..., ${}_{71}\text{Lu}^{3+} = [\text{Xe}]4f^{14}$). For example, the diameter of La^{3+} is 116 pm whereas that of Lu^{3+} is
30 97.7 pm (Fig. 1), a phenomenon known as the lanthanide contraction. The combination of
31 identical ionic charge and smoothly varying radius makes the geochemistry of the REE
32 mostly simple and predictable. However, under oxidizing conditions, Ce loses four electrons
33 instead of three resulting in a closed shell (${}_{58}\text{Ce}^{4+} = [\text{Xe}]4f^0$).

34 Although the crustal abundance of Ce is only ~60 ppm (Rudnick and Gao, 2014),
35 fractionating processes can concentrate it to the point where Ce-dominant minerals
36 crystallize. Indeed, there are more than 150 known minerals with essential Ce in their
37 formulas. The majority of these minerals contain Ce^{3+} as expected and their names contain
38 the “-(Ce)” Levinson suffix when Ce dominates relative to the other REE (e.g. monazite-
39 (Ce)- $\text{Ce}^{3+}\text{PO}_4$, fluocerite-(Ce)- Ce^{3+}F_3 , or bastnäsite-(Ce)- $\text{Ce}^{3+}\text{CO}_3\text{F}$, when considering their
40 ideal chemical formulas), but there are three known exceptions: stetindite-(Ce) ($\text{Ce}^{4+}\text{SiO}_4$),
41 cerianite-(Ce) (Ce^{4+}O_2), and dyraesite-(La) ($\text{Na}_8\text{Ce}^{4+}(\text{La},\text{REE})_2(\text{PO}_4)_6$). Other minerals such
42 as zircon and baddeleyite similarly exhibit a strong preference for Ce^{4+} over Ce^{3+} , resulting in
43 a deviation of REE patterns from the aforementioned smooth behavior expected for purely
44 trivalent REE (Burnham and Berry, 2012, 2014). Accurate modelling of REE in geological
45 systems requires knowledge of the likely REE anomalies arising from redox variability.
46 Therefore, it is important to establish whether, and to what extent, other REE change their
47 oxidation states. Europium is the best known, occurring as Eu^{2+} under reducing conditions
48 (Burnham et al., 2015), with Ingrao et al. (2019) showing that Sm and Yb can also be

49 divalent under ultra-reducing conditions such as those observed in some extraterrestrial
50 materials.

51 After Ce, the most likely candidate to undergo oxidative redox changes is Pr. On Earth's
52 surface, pure Pr oxide is stable as commercially available mixed-valence oxide: Pr_6O_{11} :
53 $4\text{Pr}^{4+}\text{O}_2 \cdot \text{Pr}_2^{3+}\text{O}_3$ (Martin, 1974; Suzuki et al., 2009). Pure quadrivalent Pr is not known so far
54 from natural materials and is uncommon in synthetic materials (Willauer et al., 2020). This
55 raises the question of whether Pr^{4+} exists in nature, to what degree, and can any anomalous
56 behavior stemming from the higher oxidation state be detected or predicted.

57 In this study we examine the known Ce^{4+} -bearing minerals, which are obvious candidates for
58 inclusion of other quadrivalent REE. We assess whether their chemical composition shows
59 evidence for the presence of Pr^{4+} . We show experimental evidence from zircon, a common
60 mineral which demonstrates Ce anomalies. We then discuss the possibility of Pr^{4+} occurring
61 in nature and compare them to REE^{3+} minerals in the context of mineral evolution (Hazen
62 and Ausubel, 2016; Hazen et al., 2015).

63 **Methods**

64 We conducted two zircon synthesis experiments. The P-free starting mix used in the
65 experiments of Burnham and Berry (2012) was decarbonated at 1000 °C. The resulting
66 powder was loaded into two capsules to achieve oxidizing and reducing conditions. In the
67 “oxidized” experiment the mix was placed in a 3.5 mm diameter Pt capsule between two
68 layers of PtO_2 . In the “reduced” experiment the mix was placed inside a graphite capsule (2.5
69 mm inner diameter) within a 5 mm diameter Pt capsule. The capsules were crimped, welded
70 and placed at the center of 1/2” MgO–graphite–Pyrex–NaCl assemblies in an end-loaded
71 piston cylinder apparatus. The pressure was raised to 1.0 GPa and the temperature was
72 monitored by Type-B thermocouple and was raised at 6 °C/min to 1380 °C and held for 4

73 hours, cooled at 2 °C/hr to 1300 °C and held for 1 hour prior to quenching to room
74 temperature by cutting the power to the heater. The capsules were recovered, and the contents
75 exposed for analysis by grinding and polishing with SiC and diamond powders. Specimens of
76 REE-rich minerals from Stetind (Norway) and Nolans Bore (Australia) were mounted in
77 epoxy and prepared in the same way as the experimental samples.

78 REE patterns were calculated from REE concentrations acquired using LA-ICP-MS. We used
79 a 193 nm ArF excimer (Coherent CompexPro 110) laser ablation system, and an Agilent
80 7700 quadrupole ICP-MS with dual-mode discrete dynode electron multiplier detector. The
81 ablation was conducted in a custom-built “HeEx” two-volume vortex sampling cell in an
82 atmosphere of He and Ar. Material was ablated at a frequency of 5 Hz and transported to the
83 ICP-MS in this gas mixture, with a small amount of H₂ added during sample introduction for
84 interference minimization. The laser energy was 80 mJ, with an operating fluence at the
85 sample surface of ~9.25 J/cm², and a spot size of 28 μm. The following isotopes are reported
86 in this study: ²⁹Si, ⁴³Ca, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ^{155, 156, 157}Gd, ¹⁵⁹Tb, ¹⁶³Dy,
87 ¹⁶⁵Ho, ^{166, 167}Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu. Multiple isotopes of Gd and Er were measured to assess
88 and correct for the oxide interferences ¹³⁹La+¹⁶O=¹⁵⁵Gd, ¹⁴⁰Ce+¹⁶O=¹⁵⁶Gd and
89 ¹⁵⁰Nd+¹⁶O=¹⁶⁶Er. Data were processed in Iolite 2.5 using Si as an internal standard (Paton et
90 al., 2011; Woodhead et al., 2007). Silicon contents were measured by calibrated energy-
91 dispersive spectroscopy (EDS) in a Hitachi 4300 SE/N field emission scanning electron
92 microscope equipped with an Oxford Instruments INCA X-MAX system. The primary
93 reference material was NIST-610 using GeoReM recommended values from Jochum et al.
94 (2011). Analyses of zircon with Ca > 50 ppm were excluded as being contaminated because
95 of the extreme incompatibility of this element (Burnham and Berry, 2012). Chondrite
96 normalization values were taken from O'Neill (2016). Analytical results are available in the
97 supplementary online information.

98 X-ray absorption spectra at the Pr L₃-edge (5964 eV) were collected in fluorescence mode
99 using a 100-element germanium array detector (Canberra Industries) at the XAS beamline at
100 the Australian Synchrotron. The excitation energy was selected using a Si(111) double crystal
101 monochromator, which was calibrated at the Cr-K absorption edge using an inline Cr metal
102 foil (first maximum of the first derivative at 5989 eV).

103 Samples were analysed with a count time of 4 seconds for each energy step, with 3 eV steps
104 in the pre-edge region of the XAS spectra (5764–5944 eV), 0.25 eV steps in the XANES
105 region (5944–6014 eV), and in the EXAFS region spectra were collected in steps of 0.2 k to a
106 maximum of 8 k (6209 eV).

107 The X-ray beam was focused at a glass harmonic rejection mirror upstream of the sample,
108 and slits (0.2 mm horizontal, 0.3 mm vertical) were used to reduce the beam size to a ≈1 mm
109 spot at the sample. A mask of 50 μm thick aluminium foil was applied to the front of the
110 sample, with a small window cut around the area of interest (approximately 2 mm high, 3 mm
111 wide). Scans were conducted at ten locations within this area.

112 Reference materials were (1) commercially available Pr₆O₁₁ powder (Aldrich, 99.9%) diluted
113 to ~2000 ppm Pr by mixing with BN, and (2) silicate glass containing ~5000 ppm each of La
114 and Pr³⁺ prepared by mixing the above-mentioned Pr₆O₁₁ powder, La₂O₃ (BDH, 99.9%) and a
115 eutectic CMAS silicate composition, followed by melting in a graphite crucible at 1500 °C
116 for 20 minutes and quenching in air. Data was pre-processed using the in-house Sakura
117 program and the Athena program was used for background subtraction and edge-height
118 normalization (Ravel and Newville, 2005).

119

Results

120 **Zircon**

121 The zircon synthesis experiments produced crystals with similar shapes and sizes to those
122 reported in Burnham and Berry (2012). The ratios of zircon/melt partition coefficients
123 between the oxidized run (PtO₂) and reduced run (graphite), which we define as the
124 parameter Δ_{\sim} , are given in Figure 2. As expected, there is a strong positive Ce-anomaly, with
125 Ce enriched by a factor of ~ 100 in the oxidized experiment (where Ce⁴⁺ comprises a
126 significant fraction of Ce) relative to the reduced experiment (almost exclusively Ce³⁺).
127 Likewise, Eu is more compatible in zircon in oxidized conditions (as Eu³⁺) relative to
128 reduced conditions (with a higher proportion as Eu²⁺). The non-redox sensitive REE should
129 plot as a horizontal line at $\Delta_{\sim}=1$, as they are not influenced by the oxygen buffer. Their
130 deviation from unity is likely to result from zircon sector-zoning (Burnham and Berry, 2012).
131 Praseodymium plots slightly above its expected position on a La–Nd interpolation line
132 (hereafter Pr*, where $Pr^* = \sqrt[3]{(La \times Nd^2)}$ on a chondrite-normalized basis), but this enrichment
133 is not completely resolved from the measurement uncertainty and so there is no evidence for
134 Pr⁴⁺ at the high-temperature, high-*f*O₂ conditions of this experiment.

135 **Stetindite-(Ce)**

136 We measured REE patterns of stetindite-(Ce) from two localities: the type locality at Stetind
137 pegmatite in Tysfjord, Norway (Fig. 3a; Schlüter et al., 2009), and the second known
138 occurrence at Nolans Bore, Northern Territory, Australia (Fig. 3b; Anenburg et al., 2018;
139 Huston et al., 2016).

140 Stetindite-(Ce) from Stetind (Fig. 4a) shows a positive Pr-anomaly (evident by Pr plotting
141 higher than the expected position at Pr*). This anomaly is negligible in the most LREE-rich
142 analyses, but becomes more significant with decreasing LREE, reaching a $\sim 30\%$ enrichment
143 in the most LREE-poor stetindite-(Ce). These LREE-poor stetindite-(Ce) occur as fine-

144 grained feather-like coating on the LREE-rich, euhedral, stetindite-(Ce) (Schlüter et al.,
145 2009).

146 Stetindite-(Ce) from Nolans Bore shows an apparent positive Pr-anomaly (Fig. 4b), but it
147 might be misleading as it is an alteration phase of fluorapatite, which commonly exhibits
148 curved LREE patterns with a maximum at Pr (Anenburg et al., 2018; Schoneveld et al.,
149 2015). Therefore, REE contents from the Nolans Bore stetindite-(Ce) has been normalized to
150 the average precursor unaltered fluorapatite (Fig. 5a), which modifies the shape of the pattern
151 but nevertheless reveals a positive Pr-anomaly representing ~10% enrichment over Pr*. An
152 as-yet-undescribed La-rich silicate–phosphate (Fig 3c; see Anenburg et al., 2018), which
153 occurs in association with stetindite-(Ce), exhibits a complementary negative Ce anomaly
154 (Fig. 4c). When normalized to the precursor unaltered fluorapatite, it additionally exhibits a
155 negative Pr-anomaly amounting to a ~30% depletion relative to Pr* (Fig. 5b). The
156 morphology of the Nolans Bore stetindite-(Ce) is anhedral, but the associated La-silicate–
157 phosphate shows a fine-grained boytroidal habit characteristic of supergene environments
158 (Anenburg et al., 2018).

159 XANES spectra obtained for the stetindite-(Ce) sample from Stetind, Norway, is given in
160 Figure 6 together with reference spectra for Pr⁴⁺-containing material (Pr₆O₁₁) and Pr⁴⁺-absent
161 material (silicate glass). A hump-like feature in the Pr⁴⁺ region is clearly observed in the
162 stetindite-(Ce) spectrum. This is the first spectroscopic evidence for Pr⁴⁺ in a naturally
163 occurring material.

164 **Cerianite-(Ce)**

165 A REE pattern of cerianite-(Ce) from Kerimasi, Tanzania (Zaitsev et al., 2011) is given in
166 Fig. 7a. As expected, it is dominated by Ce, whereas the rest of the pattern is mostly flat,
167 varying by less than a factor of two. Nonetheless, Pr plots above the rest of the trivalent REE.

168 Kerimasi is a carbonatite volcano, and like the carbonatite-related Nolans Bore (Anenburg
169 and Mavrogenes, 2018; Anenburg et al., 2020), it is possible that the Pr-enrichment results
170 from a curved LREE pattern. However, none of the published REE patterns of Kerimasi
171 rocks and minerals show any curvature (Church, 1996; Guzmics et al., 2015). Zaitsev et al.
172 (2011) interpreted the Kerimasi cerianite-(Ce) as alteration of apatite, but REE analyses of
173 Kerimasi apatite given by Chakhmouradian et al. (2017) show a consistently decreasing REE
174 pattern from La to Nd (Fig. 7a). Therefore, the positive Pr-anomaly observed in the Kerimasi
175 cerianite-(Ce) pattern does not represent inherited curvature, but instead represents a true
176 enrichment.

177 REE patterns of an additional cerianite-(Ce) from Sushina Hill, India (Chakrabarty et al.,
178 2013) show a clear positive Pr-anomaly (Fig. 7b). Like Kerimasi, there is no evidence for a
179 pre-existing LREE curvature from which the anomaly can be inherited (Chakrabarty et al.,
180 2018).

181 **Dyrnaesite-(La)**

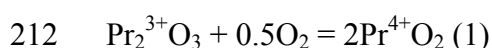
182 Dyrnaesite-(La) compositions given by Rønsbo et al. (2017) are given in Fig. 8. Even though
183 it reportedly contains quadrivalent Ce (Balić-Žunić, 2017), no Ce anomaly is observed.
184 Therefore, dyrnaesite-(La) cannot contain a Pr-anomaly, since in any case it would be much
185 weaker than that of Ce.

186 **Discussion**

187 The above results show that small positive Pr anomalies accompany the Ce⁴⁺ minerals
188 cerianite-(Ce) and stetindite-(Ce). Moreover, a negative Pr anomaly was found in a Ce-free
189 mineral coexisting with stetindite-(Ce) in Nolans Bore. Synthetic zircon at extremely
190 oxidizing conditions did not have an obvious Pr anomaly.

191 Our XANES spectra show that the white line is narrower and more intense in our stetindite-
192 (Ce) samples than in the Pr-doped glasses (Fig. 6). This is likely due to the smaller number of
193 local environments around Pr in the mineral structure than in the silicate glass. As a result,
194 the absolute peak height at the energy that is characteristic of Pr³⁺ is not a reliable indicator of
195 the redox state of Pr when comparing between materials with such different structures. The
196 feature in the stetindite-(Ce) spectrum at 5982 eV is similar to that observed in the mixed-
197 valence oxide Pr₆O₁₁, and is characteristic of Pr⁴⁺ (Dumschat et al., 1995; Ocaña et al., 1998;
198 Ogier et al., 2019). The slight shift of the position of the Pr⁴⁺ peak between Pr₆O₁₁ and
199 stetindite-(Ce) is not considered significant; This feature has been observed to shift by ~2.5
200 eV between PrBaO₃ and PrO₂, attributed to crystal field effects (Dumschat et al., 1995).
201 Similar differences are noted in the XANES spectra for Ce, in which the two characteristic
202 peaks of Ce⁴⁺ vary in energy by 0.8–0.9 eV, and in their relative intensities, between
203 reference compounds (Takahashi et al., 2002; Trail et al., 2015). The few, comparatively
204 broad features in these XANES spectra are known to arise from a large number of transitions
205 from 2p_{3/2} to 5d orbitals that are highly sensitive to the electronic configuration of the
206 lanthanide atom, and not just oxidation state (Kvashnina et al., 2011; Suzuki et al., 2009).
207 Although the overlap of the La L₂-edge with the Pr L₃-edge could conceivably result in
208 EXAFS oscillations from La appearing in the region of the Pr⁴⁺ peak, the complete absence
209 of any such features in the spectrum of the La–Pr³⁺-doped glass indicates that this is not an
210 adequate explanation for our observations (Fig. 6).

211 Praseodymium oxidation can be formulated as:



213 Thus, the presence of Pr⁴⁺ is preferred at higher oxygen fugacities (*f*O₂). Additionally, high
214 temperature stabilizes the higher entropy side of the reaction (with the O₂ component),

215 promoting Pr³⁺. Therefore, Pr⁴⁺ is strongly preferred at oxidizing, low-temperature
216 conditions. This is in agreement with the observation of a Pr-anomaly in supergene formation
217 environments of cerianite-(Ce) and Pr-anomalous stetindite-(Ce). In contrast, Pr⁴⁺ is unlikely
218 to be stable at igneous temperatures, even at oxidizing conditions. The graphite-buffered run
219 is equilibrated at conditions that closely approach FMQ, in which all Pr is trivalent. The Pt–
220 PtO₂ oxygen buffer with which our synthetic zircons equilibrated is not quantitatively
221 calibrated yet, but it is known to be more oxidizing than Ir–IrO₂, the most oxidizing solid-
222 state oxygen buffer known so far ($fO_2 = \sim 12$ bar at 1300 °C and 1 atm, or 60 times more
223 oxidizing than air; Belonoshko and Saxena (1991)) and close to the fugacity of pure
224 supercritical O₂ at 1 GPa ($fO_2 = 10^{4.73}$ bar at 1300 °C). Evidently, at this combination of
225 temperature and fO_2 , no statistically significant Pr-anomaly was observed. Since such
226 oxidizing conditions are unrealistically high for any plausible igneous process on Earth or
227 elsewhere in the solar system, we conclude that Pr⁴⁺ is not stable in any high-temperature
228 igneous conditions.

229 **Lessons from materials science—zircon**

230 Praseodymium-doped zircon is an excellent yellow pigment, noted for its brilliant color and
231 thermal stability (Badenes et al., 2002; Chen et al., 2018; Montoya et al., 2011). The yellow
232 color results from crystal field splitting (Kar et al., 2005), where Pr⁴⁺ substitutes Zr⁴⁺ on the
233 dodecahedral site (Hill et al., 2000; Trojan, 1988). The existence of this mixed (Zr,Pr⁴⁺)SiO₄
234 compound seems to be at odds with our failure to incorporate Pr⁴⁺ in our experimental
235 zircons, but there are several factors that appear to stabilize it.

236 **Suitable combination of temperature and fO_2 .** Pr-bearing zircons are usually prepared in
237 temperatures below 1100 °C, sometimes as low as 750 °C (Chen et al., 2018). Oxygen
238 fugacity is buffered to atmospheric oxygen ($fO_2 = 10^{-0.7}$ bar), so lower temperatures cause the
239 zircon synthesis to occur at conditions more oxidizing relative to a specific buffer. For

240 example, at 1000 °C, fO_2 of Ir–IrO₂ roughly equals that of air, and at 900 °C air is more
241 oxidizing (fO_2 constrained by Ir–IrO₂ equals 10^{-1.59} bar). Therefore, under the assumption that
242 Pr⁴⁺/Pr³⁺ ratios are similar along a fO_2 –temperature curve relative to an oxygen buffer, lower
243 temperatures at a fixed atmospheric fO_2 will promote oxidation of Pr³⁺ to Pr⁴⁺. Pr-zircons
244 synthesized at high temperatures (> 1300 °C) lose some color or become green by reduction
245 of Pr⁴⁺ to Pr³⁺, which exsolves as a separate Pr³⁺ phase (e.g. Pr³⁺₄Si₃O₁₂, Pr³⁺₂Si₂O₇,
246 NaPr³⁺₄(SiO₄)₃F, or Pr³⁺₂Zr₂O₇ (Badenes et al., 2002; Chen et al., 2018; Del Nero et al., 2004;
247 Ocaña et al., 1999). Thus, the general observations stemming from reaction (1) hold in this
248 case.

249 **The use of sodic fluxes.** Pr-doped zircons are prepared in the presence of a “mineralizer”—a
250 flux that promotes the reaction between ZrO₂, SiO₂ and Pr₆O₁₁, and promotes crystallization.
251 The most common flux is NaF, although other alkali or alkali-earth halides are occasionally
252 used (Badenes et al., 2002; Chen et al., 2018; Del Nero et al., 2004; Hill et al., 2000; Ocaña et
253 al., 1999; Ocaña et al., 1998). The commonly cited explanation for the mineralizer
254 effectiveness is volatile transport of the reactants and lowering of crystallization temperature
255 stabilizing Pr⁴⁺ (Badenes et al., 2002; Hill et al., 2000; Ocaña et al., 1999), but in the case of
256 Pr-doped zircon an additional factor may be high optical basicity of the flux (Duffy, 1993;
257 Moretti, 2005; Wagner, 1975). Cations with a high optical basicity (such as Na⁺) tend to
258 stabilize higher oxidation states of various metals as is often seen in silicate melts or solids
259 (Anenburg and Le Losq, 2019; Balić-Žunić, 2017; Burnham and Berry, 2014; Ernst, 1962;
260 Giuli et al., 2012; Markl et al., 2010). The cationic component of NaF is pure Na⁺,
261 maximizing the stabilization of Pr⁴⁺ relative to Pr³⁺, making it available for incorporation into
262 zircon.

263 Zirconium-bearing minerals in terrestrial peralkaline silicate melts do not contain any Pr
264 anomalies. Agpaitic melts are usually equilibrated at reducing conditions (at values between

265 the IW and FMQ buffers; Marks and Markl, 2017), which are not sufficient to form Ce
266 anomalies, let alone Pr anomalies, including in the hyperagpaitic Ce⁴⁺-mineral dynaesite-
267 (La) (Rønso et al., 2017). Zircons in nepheline syenites, on the other hand, contain some of
268 the strongest Ce anomalies known from any igneous rock type, but no Pr anomalies
269 (Belousova et al., 2002). Additionally, REE minerals formed in fluoride melt systems contain
270 no anomalies (Vasyukova and Williams-Jones, 2016), or very weak Ce anomalies (Kynicky
271 et al., 2019). Thus, stabilization by Na⁺ is unlikely to affect the oxidation state of Pr in natural
272 systems, because fO_2 is not as high as that reached when preparing synthetic Pr-zircon
273 pigments.

274 Considering the combined effect of temperature, atmospheric fO_2 , and stabilization by Na⁺, it
275 is not surprising that Pr⁴⁺ can be incorporated into synthetic zircon. However, these zircons
276 usually contain a mix of both Pr³⁺ and Pr⁴⁺ (Badenes et al., 2002; Chen et al., 2018; Del Nero
277 et al., 2004; Guo et al., 2018; Montoya et al., 2011; Ocaña et al., 1998), indicating incomplete
278 oxidation of Pr. For example, Guo et al. (2018) showed miscibility of up to 9% Ce⁴⁺SiO₄ into
279 zircon, but Pr also exists in a separate NaPr³⁺F₄ phase when Pr>2%. As Pr⁴⁺ has a smaller
280 ionic radius, closer to Zr⁴⁺ than Ce⁴⁺, it is expected to be even more compatible in zircon than
281 Ce⁴⁺. Therefore, the formation of NaPrF₄ suggests an abundance of Pr³⁺ in Pr-zircon
282 formation systems. The absence of other Pr⁴⁺ phases from such experiments suggests that the
283 incorporation of quadrivalent Pr into zircon may be promoted by crystal chemical effects, but
284 limited by the overall Pr⁴⁺/Pr³⁺ at these fO_2 conditions.

285 **Lessons from materials science—cerium and praseodymium oxides**

286 Cerium oxide (ceria: Ce⁴⁺O₂ and its natural analogue cerianite-(Ce)) and praseodymium
287 oxide (Pr₆O₁₁, or PrO_{1.83}) adopt fluorite-like structures (Borchert et al., 2008; Burnham and
288 Eyring, 1968; Graham, 1955; Hull et al., 2009; Matović et al., 2013; Yashima et al., 2006),
289 which differs from the hexagonal or monoclinic crystal structures typical for other trivalent

290 REE (including $\text{Ce}^{3+}_2\text{O}_3$). In moderately reducing conditions, which are not sufficient to form
291 the ultra-reduced hexagonal Ce_2O_3 , ceria adopts a lower symmetry crystal structure and
292 becomes a mixed $\text{Ce}^{4+}\text{-Ce}^{3+}$ oxide with the general formula CeO_{2-x} ($0 \leq x \leq 0.25$), where the
293 lower valence Ce^{3+} is charge balanced by oxygen vacancies (Hull et al., 2009; Matsukawa et
294 al., 2018; Ray et al., 1975; Sørensen, 1976). The stable form of Pr-oxide (Pr_6O_{11}) similarly
295 contains oxygen vacancies (Sinev et al., 1996). Stabilization of pure PrO_2 requires strong
296 oxidants, and it will readily revert to Pr_6O_{11} (Sieglaff and Eyring, 1957; Yidong and Yuan,
297 1980). Both Ce and Pr oxides (including intermediate solid solutions) are highly reactive and
298 will readily gain or lose the oxygen vacancies (Gazulla et al., 2019; Hyde et al., 1966),
299 leading to their many industrial applications as catalysts (Artini, 2018; Borchert et al., 2008).

300 As both CeO_2 and Pr_6O_{11} adopt closely-related crystal structures and contain similarly sized
301 cations with the same valence and close electronic properties, they can form solid solutions
302 (Chun et al., 2006; Ftikos et al., 1993; Knauth and Tuller, 1999; Logan and Shelef, 1994;
303 Michel et al., 2017; Stefanik and Tuller, 2004; Takasu et al., 1984). Knauth and Tuller (1999)
304 studied a mixed $\text{Pr}_{0.7}\text{Ce}_{0.3}\text{O}_{2-x}$ oxide between 470 and 640 °C and $f\text{O}_2$ of 0.2 to 10^{-3} and found
305 that Ce was tetravalent in all conditions, but the $\text{Pr}^{4+}/\text{Pr}^{3+}$ ratio (manifested by oxygen
306 vacancies) was increasing with higher $f\text{O}_2$ and lower temperatures. $\text{Pr}^{4+}/\text{Pr}^{3+}$ in these oxides is
307 positively correlated with $1/T$ (Knauth and Tuller, 1999; Stefanik and Tuller, 2004), meaning
308 that lowering temperature stabilizes Pr^{4+} at a rate that is enhanced at lower temperatures. The
309 speciation is also affected by kinetic effects and cooling rate (Gazulla et al., 2019).

310 Because trivalent Ce or Pr can substitute in the $(\text{Ce,Pr})\text{O}_2$ structure, charge balanced by
311 oxygen vacancies, other trivalent REE such as La, Nd, Sm, etc. can likewise be
312 accommodated (Artini, 2018; Biswas et al., 1997; Chockalingam et al., 2014; Lin et al.,
313 2015). This leads to a two-fold mechanism for Pr incorporation in CeO_2 . First, Pr will
314 partition to CeO_2 as part of a smoothly changing partitioning pattern for all REE^{3+} . However,

315 this will not cause an anomaly to form. An anomaly requires a second mechanism: the
316 presence of Pr^{4+} in the fluid the mineral is crystallizing from. The amount does need not be
317 large if one oxidation state is much more compatible than the other. For instance, Burnham
318 and Berry (2012) showed that $\text{Ce}^{4+}/\text{Ce}^{3+}=0.0001$ in the melt was sufficient to produce a
319 measurable Ce anomaly in zircon, a mineral which strongly partitions Ce^{4+} . Therefore, a
320 small amount of Pr^{4+} in the crystallizing medium should be sufficient to form a Pr anomaly in
321 cerianite-(Ce) or stetindite-(Ce), minerals that presumably strongly partition Pr^{4+} .

322 **Stabilization of Pr^{4+} in fluids**

323 In order to preferentially partition Pr to Ce^{4+} -minerals relative to other REE, some amount of
324 Pr^{4+} has to exist in the fluid the minerals are crystallizing from. This was empirically
325 observed by the Pr anomalies detected in cerianite-(Ce) and stetindite-(Ce) (Fig. 5, 7).

326 In general, it is more difficult to stabilize REE^{4+} in solutions than it is in solids. For example,
327 Heidt and McMillan (1954) succeeded in converting only 0.14% of Ce^{3+} to Ce^{4+} by
328 photochemical oxidation in an oxidizing perchlorate solution. Praseodymium is more
329 challenging, because Pr^{4+} has an oxidation potential high enough to decompose H_2O to O_2
330 and H_2 (Nugent et al., 1973). Nonetheless, Pr^{4+} has been stabilized in water for periods of
331 milliseconds by pulse radiolysis (Faraggi and Feder, 1972), or for longer by electrochemical
332 oxidation in an alkaline solution (Hobart et al., 1980). These decomposition reactions are
333 kinetically controlled, and trace amounts of Pr^{4+} might persist for long enough to cause Pr
334 anomalies in Ce^{4+} -dominant minerals.

335 **Formation of Pr-dominant minerals**

336 Because Pr is approximately an order of magnitude less abundant than neighboring Ce or Nd
337 (Rudnick and Gao, 2014), making a Pr-dominant mineral by regular REE fractionating
338 methods requires an unlikely REE pattern with a strong curvature and maximum at Pr, ideally

339 mixed with a negative Ce anomaly (Anenburg, 2020). Although the lower-abundance REE
340 sometimes end up as the dominant element (e.g., monazite-(Sm), florencite-(Sm), samarskite-
341 (Yb) or xenotime-(Yb); Buck et al., 1999; Masau et al., 2002; Repina et al., 2011; Simmons
342 et al., 2006), the necessary enrichment factor for Pr over Nd is unprecedented (Anenburg,
343 2020). Nevertheless, the quadrivalent oxidation state of Pr opens a pathway for it to
344 predominate in a mineral (e.g., Christy, 2015). To produce a Pr-dominant mineral, Ce would
345 have to be removed first. Some minerals contain strong negative Ce anomalies, such as the
346 La-silicate–phosphate found in Nolans Bore (Fig. 4c; Schoneveld et al., 2015), and former
347 bridgmanite and “new aluminous phase” inclusions from Transition Zone diamonds
348 (Thomson et al., 2016). However, these minerals are expected to be found adjacent to
349 complementary Ce⁴⁺-rich minerals that can absorb any Pr⁴⁺ that may form. Therefore, we
350 suggest two paths that lead to Pr-mineral crystallization:

- 351 1. Differential sedimentary transport which physically separates the Ce-absent minerals
352 from the rest. For example, the La-silicate–phosphate at Nolans Bore commonly
353 resides in open cavities, whereas stetindite-(Ce) completely fills space. This could
354 lead to preferential fragmentation of the rock during weathering along grain
355 boundaries containing open cavities, releasing more Ce-depleted material to a
356 sedimentary system. Strong oxidation at low temperatures could then cause
357 exsolution of Pr⁴⁺ phases out of REE³⁺ minerals, similar to the formation cerianite-
358 (Ce) exsolution out of REE-bearing apatite at Kerimasi (Zaitsev et al., 2011), or as
359 demonstrated experimentally for monazite by Trail (2018).
- 360 2. Limited interaction with low temperature and oxidizing fluids could cause in-situ
361 oxidation of Pr hosted in Ce-absent minerals. Too much interaction might mobilize
362 the Pr into the adjacent Ce⁴⁺ minerals to form a solid solution. The transport fluid has
363 to sustain oxidizing conditions long enough to separate Pr from its source, which can

364 be at the micrometer scale. The lifetime of Pr^{4+} in solutions is short (Suming and
365 Rudong, 1983; Yidong and Yuan, 1980), so most likely any new minerals would be
366 Pr^{3+} dominated. If the system retains its high oxidation state, it would be possible to
367 form Pr_6O_{11} or another Pr^{4+} mineral. This becomes more likely in the presence of Na
368 and F as they are known to stabilize Pr^{4+} compounds. For example, Asprey and
369 Keenan (1961) synthesized crystalline NaPrF_5 and Na_2PrF_6 by reacting Na–Pr
370 solutions and F_2 gas at 400 °C, and Mazej (2002) synthesized PrF_4 by reacting Pr_6O_{11}
371 with UV-photolyzed F_2 gas at room temperature. Pure F_2 gas is unlikely to exist in
372 nature, but it is possible that a less strong oxidizer can suffice to form these solid
373 phases at lower temperatures.

374 Fluids containing Pr^{4+} may not even be required: Estevenon et al. (2019) demonstrated that,
375 counterintuitively, low-temperature hydrothermal CeSiO_4 preferentially forms from Ce^{3+}
376 precursors relative to Ce^{4+} . By analogy, the extreme difficulty of stabilizing Pr^{4+} in solution
377 may not be a hindrance to formation of Pr^{4+} -bearing minerals, so long as the conditions are
378 sufficiently cold and oxidizing to stabilize it in the solid state.

379 **Terrestrial candidate—Atacama Desert, Chile**

380 The Atacama in Chile is a dry desert plateau in which temperatures occasionally reach below
381 0 °C (Wörner et al., 2018b). It is host to many evolved granitoids (Wörner et al., 2018a),
382 several of which contain elevated REE contents. The Mindat.org database lists several REE
383 minerals known from the Atacama region: kimuraite-(Y), a hydrous carbonate; agardite-(Y),
384 a hydrous arsenate (Morrison et al., 2013); florencite-(Ce) and florencite-(La), hydrous
385 phosphates (Deyell et al., 2005); and most importantly, cerianite-(Ce). These minerals
386 indicate REE exposure to supergene environments in the Atacama. Additionally, some
387 hydrothermal ore deposits in Chile contain allanite, indicating some degree of REE mobility
388 and enrichment (Marquardt et al., 2015; Rieger et al., 2010; Veloso et al., 2017). The

389 Atacama is well known for the occurrence of strong oxidizing salts: nitrates, perchlorates and
390 iodates (Lybrand et al., 2016; Reich and Bao, 2018). The aridity of the Atacama can lead to
391 conditions of metastable or local equilibrium, which could lead to separation of Ce-absent
392 and other REE minerals, followed by formation of Pr-dominant minerals.

393 **Are extraterrestrial Pr minerals possible?**

394 A Pr-dominant mineral is likely to form from another REE-rich mineral precursor, and
395 previous studies discussed the various degrees of REE-enrichments possible on other
396 planetary bodies (Bonin, 2012; McLeod and Shaulis, 2018). However, as noted above, any
397 detectable Pr⁴⁺ requires low temperatures and high fO_2 , leading to Mars being the prime
398 candidate. REE-minerals have been observed in Martian meteorites (Liu et al., 2016), and the
399 Martian surface experienced prolonged low-temperature alteration under oxidizing conditions
400 (Guitreau and Flahaut, 2019).

401 The Atacama surface conditions are commonly considered as analogues for the Martian
402 surface (Lybrand et al., 2016), which contains all the basic ingredients which may be required
403 for formation of Pr-dominant minerals. Recent observations suggest the presence of felsic or
404 fractionated magmatism on Mars (Cousin et al., 2017; Meslin et al., 2013; Sautter et al.,
405 2014; Wray et al., 2013), which could lead to local REE enrichment sufficient to form REE
406 minerals. Additionally, oxidizing salts were detected by the Phoenix Lander and Curiosity
407 Rover (Clark and Kounaves, 2016; Hecht et al., 2009; Leshin et al., 2013; Ming et al., 2014;
408 Stern et al., 2015) and in Martian meteorites (Kounaves et al., 2014). The temperature of the
409 Martian surface is lower than that of Earth, and it has abundant evidence for the former flow
410 of liquid water. Low-temperature hydrothermal alteration of relatively evolved potassic rocks
411 was observed by Curiosity (Thompson et al., 2016). Therefore, it possible that at some point
412 in the Martian geological history a REE-rich mineral was exposed to oxidizing brines on the
413 surface (e.g., Gough et al., 2011; Quinn et al., 2013), which allowed fractionation of Ce,

414 followed by another fractionation of Pr with the outcome of producing a Pr-dominant
415 mineral.

416 **A note on terbium**

417 Like Pr, Tb is also stable as a mixed-valance oxide Tb_4O_7 ($2Tb^{4+}O_2 \cdot Tb_2^{3+}O_3$). However, due
418 its low chondritic abundance and moderate compatibility, it does not reach levels which can
419 be analyzed precisely by EPMA. Furthermore, Tb has only one isotope: ^{157}Tb , which has an
420 oxide interference from $^{141}Pr^{16}O$, increasing uncertainty and obscuring any possible
421 anomalies when analyzed by mass spectrometry. Finally, Tb_4O_7 has Tb^{4+}/Tb^{3+} of 2, whereas
422 Pr_6O_{11} has Pr^{4+}/Pr^{3+} of 4. Taken together with the higher 4th ionization energy for Tb
423 compared to Pr (3839 and 3761 kJ/mol, respectively), the stability of Tb^{4+} is expected to be
424 lower than Pr^{4+} . Therefore, any Tb anomalies would be smaller in magnitude and more
425 challenging to detect.

426 **Implications**

427 Praseodymium anomalies are unlikely to exist in any high temperature igneous, metasomatic,
428 or hydrothermal process on Earth, or elsewhere in the solar system. Praseodymium anomalies
429 only become apparent in low temperature and oxidizing conditions. Stetindite-(Ce) from
430 Stetind only exhibits the Pr anomalies on supergene late-stage coating on pegmatitic
431 stetindite-(Ce), and Pr-anomalous stetindite-(Ce) from Nolans Bore coexists with a La-
432 silicate–phosphate of supergene origin. The fact that Pr-dominant minerals have not been
433 found in close to 100 known localities of cerianite-(Ce) and in the two known stetindite-(Ce)
434 localities puts a strong doubt on the existence of Pr-dominated minerals on Earth.
435 Other than earth, the only other solar system body with conditions conducive to the presence
436 of Pr^{4+} is Mars. With its overall low temperature and local accumulations of perchlorate, it is
437 possible that Pr^{4+} exists or has existed in the past on the surface of Mars. However,

438 enrichment of Pr such that it will become abundant enough to form its own mineral, and
439 dominate relative to Ce requires (1) fractionated, REE-rich igneous rocks, (2) supergene
440 alteration and formation of Ce-free and Ce⁴⁺ minerals, (3) separation of the two types of
441 minerals by sedimentary processes, and (4) strong oxidation of the Ce-free minerals. It is
442 extremely unlikely for all four processes to have occurred on same place on Mars, thus we
443 doubt the presence of Pr-dominated minerals on Mars.

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Figure Captions

782 Figure 1. Ionic radii for cations of interest from Shannon (1976).

783 Figure 2. Ratios of zircon/melt REE partition coefficients for Pt–PtO₂ and graphite-buffered
784 runs. Error bars indicate 1 sd of several analyses on zircon and glass, propagated through the
785 division stages.

786 Figure 3. Backscattered electron images of (a) stetindite-(Ce) from Stetind, (b) stetindite-(Ce)
787 from Nolans Bore, and (c) La-silicate–phosphate from Nolans Bore. Oval craters are laser
788 ablation spots. Scale bar is 50 μm. Abbreviations: stet–stetinite-(Ce); stet*–supergene
789 stetindite-(Ce); fap–fluorapatite; lsp–La-silicate–phosphate.

790 Figure 4. Chondrite-normalized REE patterns of (a) stetindite-(Ce) from Stetind, (b)
791 stetindite-(Ce) from Nolans Bore, and (c) La-silicate–phosphate from Nolans Bore. Error bars
792 indicate analytical uncertainty at 2 se. Uncertainties smaller than the symbol size are not
793 plotted.

794 Figure 5. REE patterns of (a) stetindite-(Ce) and (b) La-silicate–phosphate, normalized to
795 unaltered Nolans Bore fluorapatite. Error bars indicate 1 se of analytical uncertainty,
796 propagated through division. Uncertainties smaller than the symbol size are not plotted.

797 Figure 6. XANES spectra of a mixed Pr³⁺–Pr⁴⁺ oxide Pr₆O₁₁, a synthetic La–Pr³⁺ silicate
798 glass, and stetindite-(Ce) from Stetind, Norway. The vertical gray band indicates the Pr⁴⁺-
799 peak region. The contribution of Pr⁴⁺ in stetindite-(Ce) is indicated by the arrow.

800 Figure 7. Chondrite-normalized REE patterns of cerianite-(Ce) from (a) Kerimasi, and (b)
801 Sushina Hill. LREE patterns of unaltered Kerimasi apatite are shown for comparison. Dashed
802 lines are interpolations for elements with no data available.

803 Figure 8. Chondrite-normalized LREE pattern of dynaesite-(La) from the type locality.

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