

1 **On the compositional variability of dalyite,  $K_2ZrSi_6O_{15}$ : a new**  
2 **occurrence from Terceira, Azores**

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16

17 **Running title:** A new occurrence of dalyite, Azores

18

## 19 **Abstract**

20 The rare potassium zirconium silicate dalyite has been identified for the first time  
21 on Terceira, Azores, within syenitic ejecta of the Caldeira-Castelinho Ignimbrite  
22 Formation. New quantitative analyses of this dalyite are combined with the small  
23 number of published analyses from various locations worldwide to evaluate the  
24 mineral's compositional variability. Additionally, solid-state modelling has been  
25 applied to assess the site allocations of substituting elements. The new analyses  
26 yield the average formula  $(K_{1.84}Na_{0.15})_{\Sigma=1.99}(Zr_{0.94}Ti_{0.012}Hf_{0.011}Fe_{0.004})_{\Sigma=0.967}Si_{6.03}O_{15}$ .  
27 Model results predict the placement of substituting Hf and Ti in the octahedral site,  
28 and highlight the overall difficulty in the incorporation of Fe, Mg and Ba. The  
29 combined dataset reveals that dalyite found within peralkaline granites and  
30 syenites is generally defined by higher Na $\leftrightarrow$ K substitution and lower Ti $\leftrightarrow$ Zr  
31 substitution relative to dalyite from highly potassic rocks. The Terceira dalyite  
32 exhibits a bimodal variation in the degree of Na $\leftrightarrow$ K substitution which is attributed  
33 to a K-enrichment trend induced by late stage pore wall crystallisation and  
34 albitization, coupled with the control of pore size upon the degree of  
35 supersaturation required to initiate nucleation of dalyite in pores of varying size.

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38 Key words: Dalyite, Peralkaline, Syenite, Oceanic island magmatism, Terceira,  
39 Azores

40

## 41 **Introduction**

42 Dalyite is a rare potassium zirconium silicate, with the empirical formula  $K_2ZrSi_6O_{15}$ .  
43 It was first identified in peralkaline granitic ejecta found within the pyroclastic  
44 sequences of Green Mountain and Middleton Peak, Ascension Island (Van Tassel,  
45 1952). Since its discovery, it has been identified as an accessory phase in a variety  
46 of rocks, including peralkaline granites and syenites, late-stage pegmatites,  
47 charoitites, lamproites, lamprophyres, fenites and carbonatites (e.g. Furnes et al.,  
48 1982; Robins et al., 1983; Harris & Rickard, 1987; Linthout et al., 1988; Konev et

49 al., 1996). Having been established as a general indicator of peralkaline conditions,  
50 silica-oversaturation, and high chemical potential of  $K_2O$  ( $\mu K_2O$ ) (e.g. Marks et al.,  
51 2011), the presence and composition of dalyite may provide important insights into  
52 the evolution of these magmatic systems.

53 Here, we report the first known occurrence of dalyite from the mildly  
54 peralkaline rocks of Terceira, Azores. We apply solid-state modelling to investigate  
55 various proposed substituting elements, and complement the existing global  
56 database with new high quality quantitative chemical analyses of dalyite from  
57 Terceira. Using these analyses, alongside whole rock major element analyses of  
58 the host syenites, we discuss the geochemical variability of dalyite, based on  
59 previously published compositions from both similar and contrasting rock types.

60

## 61 **Background**

### 62 *Dalyite occurrences*

63 Following the initial discovery of dalyite (Van Tassel, 1952), it was next identified in  
64 peralkaline syenitic ejecta from Agua de Pau volcano, São Miguel, Azores (Cann,  
65 1967; Widom et al., 1993); where it was observed as an entirely intercumulus  
66 phase and therefore inferred by Ridolfi et al. (2003) to be the last mineral to  
67 crystallise (alongside quartz). Lazebnik & Makhotko (1982) identified dalyite in the  
68 Murun Complex, Siberia, Russia, also providing additional quantitative analyses.  
69 Furnes et al. (1982) and Robins et al. (1983) noted the presence of dalyite within a  
70 highly potassic lamprophyric dyke in Sunnfjord, Norway. Raade & Mladeck (1983)  
71 reported dalyite within a peralkaline granite pluton at Gjerdingen, Norway, where it  
72 was typically found in close contact with janhaugite  $Na_3Mn_3Ti_2Si_4O_{15}(OH,F,O)_3$ .  
73 Harris and Rickard (1987) recorded the occurrence of dalyite, alongside eudialyte,  
74 in a peralkaline granitic dyke that cross-cuts the nepheline syenites of the  
75 Straumsvola Complex, Antarctica. In 1988, an enstatite-sanidine-phlogopite  
76 lamproite in south-eastern Spain was reported to contain the mineral's first known  
77 occurrence in an extrusive rock (Venturelli et al., 1984; Linthout et al., 1988). Soon  
78 afterwards, dalyite was observed within fenites from the Serra Negra and Salitre –  
79 carbonatite alkaline igneous complex, Brazil (Mariano & Francis, 1989; Mariano &

80 Marchetto, 1991; Brod, 1999). Dalyite was later identified in the Strange Lake  
81 peralkaline granite complex, Canada, and noted to have nucleated  
82 heterogeneously onto older zircon crystals (Birkett et al., 1992; Salvi & Williams-  
83 Jones, 1995). Subsequent reported occurrences include the Amis peralkaline  
84 granite intrusion of the Brandberg Complex, Namibia (Schmitt et al., 2000), the  
85 various lithologies of the Murun Complex, Siberia, Russia (e.g. Dolivo-  
86 Dobrovol'skiy & Yevdokimov, 1991; Konev et al., 1996; Reguir, 2001), the Gordon  
87 Butte pegmatites, Montana, USA (Chakhmouradian & Mitchell, 2002), peralkaline  
88 granite dykes to the north of the Zargat Na'am ring complex, Egypt (Saleh, 2006),  
89 more unusually, a nepheline-bearing pegmatite, Langesundfjord, Norway  
90 (Andersen et al., 2010) and the alkali syenites and metasomatites of the  
91 Shibanovsky Massif, Russia (Stepnova et al., 2013) (Fig. 1).

92         The occurrence documented here is within quartz syenite ejecta sampled  
93 from the Caldeira-Castelinho Ignimbrite Formation (CCI) on Terceira Island, Azores  
94 (Gertisser et al., 2010). The nine Azorean islands straddle the Mid-Atlantic Ridge in  
95 the central North Atlantic Ocean and mark a triple junction between the American,  
96 Eurasian and African plates (e.g. Krause & Watkins, 1970). All nine islands are  
97 volcanic in origin and represent the subaerial manifestation of a large submarine  
98 plateau, itself interpreted to have originated from the interaction of a mantle plume  
99 with the Mid-Atlantic Ridge (e.g. Gente et al., 2003). The CCI is one of at least  
100 seven ignimbrite formations found within the stratigraphy of Terceira (Self, 1974,  
101 1976; Gertisser et al., 2010) and can be readily distinguished from its counterparts  
102 by its relative abundance of quartz syenite ejecta (Gertisser et al., 2010). The  
103 discovery of dalyite within these ejecta marks the mineral's second known  
104 occurrence within the Azores archipelago.

105

#### 106 *Mineral properties*

107 Van Tassel (1952) provided the first description of the physical properties,  
108 chemical composition, unit cell and x-ray powder diffraction data of dalyite. It is a  
109 triclinic, colourless mineral of moderate positive relief, exhibiting up to second order  
110 interference colours. The unit cell was defined as  $K_2ZrSi_6O_{15}$ , though the potential

111 substitutions of Na for K, and Hf for Zr, were suggested. The chemical similarity  
112 between dalyite and wadeite ( $K_2ZrSi_3O_9$ ) was also noted. The original quantitative  
113 chemical analysis of dalyite is reported in Table 1 (analysis 1).

114 The crystal structure of dalyite was determined by Fleet (1965), who  
115 defined it as a phyllosilicate comprising four-, six- and eight-membered rings of  
116  $SiO_4$  tetrahedra. These sheets are linked by regular  $ZrO_6$  octahedra and irregular  
117  $(K,Na)O_8$  polyhedra. Robins et al. (1983) provided 10 quantitative chemical  
118 analyses of dalyite from Sunnfjord, Norway and presented evidence for the  
119 substitution of Zr with Ti, and K with Fe, suggesting the more accurate empirical  
120 formula  $(K,Na,Fe)_2(Zr,Ti)Si_6O_{15}$ . They also highlighted the compositional similarity  
121 between dalyite and darapiosite,  $KNa_2LiMnZnZrSi_{12}O_{30}$ , sogdianite,  $(K,Na)$   
122  $_2Li_2(Li,Fe,Al,Ti)_2Zr_2(Si_2O_5)_6$  and zektzerite,  $LiNaZrSi_6O_{15}$ . Further chemical analyses  
123 of dalyite were reported by Harris et al. (1982), Lazebnik & Makhotko (1982),  
124 Harris & Rickard (1987), Linthout et al. (1988), Birkett et al. (1992), Konev et al.  
125 (1996), Reguir (2001), Chakhmouradian & Mitchell (2002) and Ridolfi et al. (2003)  
126 (Table 1).

127

## 128 **Methods**

### 129 *Analytical procedure*

130 Whole rock major element analyses of the syenite ejecta were undertaken at  
131 Acme Analytical Laboratories Ltd, Canada, using x-ray fluorescence (XRF)  
132 spectrometry (samples TER 30-1, TER 30-6, TER35-1), and inductively coupled  
133 plasma atomic emission spectroscopy (ICP-AES) (TER 30-7). Weathered surfaces  
134 were removed and samples were crushed in an agate mill, prior to drying for 2  
135 hours at 110 °C and a  $LiBO_2$  fusion. Loss-on-ignition (LOI) was reported as the  
136 weight difference after ignition for 2 hours at 1,000 °C.

137 Semi-quantitative analyses and element maps were produced using a  
138 Hitachi TM-3000 scanning electron microscope (SEM) equipped with a Bruker  
139 Quantax 70 energy dispersive system (EDS) at Keele University, U.K. Quantitative  
140 major element analyses of dalyite were achieved for samples TER 30-1 and TER

141 30-7 using a JEOL JXA 8900 RL electron microprobe at the Georg-August  
142 Universität Göttingen, Germany. Peak counting times were 15 seconds for Si, Ti,  
143 Al, Fe, Mg, Ca, Na and K, and 30 seconds for Cr, Zr, Hf, Mn and Ba, using an  
144 acceleration voltage of 15 kV, a beam current of 15 nA and a 20 µm defocused  
145 beam. The following natural silicate minerals and synthetic materials (denoted as  
146 formulae) were used as primary standards: olivine (Si, Mg), albite (Na), sanidine  
147 (K), TiO<sub>2</sub> (Ti), haematite (Fe), anorthite (Al), wollastonite (Ca), Cr<sub>2</sub>O<sub>3</sub> (Cr), rhodonite  
148 (Mn), celsian (Ba), ZrSiO<sub>4</sub> (Zr) and HfSiO<sub>4</sub> (Hf). Detection limits and errors (Table  
149 2) were calculated at a confidence level of two-sigma from the raw background  
150 noise and the signal/background counting, respectively, following the Gaussian law  
151 of error propagation. The intensities were converted into concentrations by taking  
152 the matrix corrections into account.

153

#### 154 *Solid state modelling*

155 Solid state modelling calculations were carried out to investigate the substitution of  
156 a number of potential substituting cations (Ti, Hf, Fe, Ba and Mg). This was  
157 undertaken using the GULP code (Gale, 1997). This code uses effective  
158 interatomic potentials to model the interactions between atoms, and has been  
159 widely used to calculate the structure and properties of inorganic materials. The  
160 Buckingham potential, supplemented by an electrostatic term, is used:

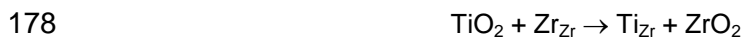
161

$$162 \quad V(r) = A \exp(-r/\rho) - Cr^{-6} + q_1q_2/r$$

163

164 In this equation, the parameters A, ρ and C are fitted to structures and properties of  
165 related materials; here they have been transferred from studies on zircon (Akhtar &  
166 Waseem, 2001). The charges of the interacting ions are q<sub>1</sub> and q<sub>2</sub>. The  
167 experimental and calculated lattice parameters for dalyite are given in Table 3  
168 below, using the experimental structure from Fleet (1965) for comparison. It is seen  
169 that the lattice parameters agree to within a few percent, which gives confidence in  
170 using this transferred potential. The calculations reported here have been used to  
171 obtain the energies involved when various ions are substituted into the dalyite

172 lattice. The calculation of substitutional and solution energies for dopant ions in  
173 materials has been widely described elsewhere; see, for example, a recent study  
174 of Nd, Gd and Yb ions in BaF<sub>2</sub> (Mujaji et al., 2014). However, a brief summary will  
175 be given here. In the case of the substitution of Ti<sup>4+</sup> into the dalyite lattice, the  
176 following reaction (solution scheme) is considered, assuming substitution at the  
177 Zr<sup>4+</sup> site:



179

180 The energy of this reaction (the solution energy), E<sub>sol</sub>, is then calculated, as follows:

181

$$182 \quad E_{\text{sol}} = [E_{\text{latt}}(\text{ZrO}_2) + E(\text{Ti}_{\text{Zr}})] - E_{\text{latt}}(\text{TiO}_2)$$

183

184 In this case no charge compensation is needed, but considering substitution at the  
185 K<sup>+</sup> site, the following scheme was assumed (with charge compensation by K<sup>+</sup>  
186 vacancies):

187



189

190 The solution energy for this reaction is:

191

$$192 \quad E_{\text{sol}} = [E(\text{Ti}_{\text{K}}^{\bullet\bullet\bullet}) + 3E(\text{V}_{\text{K}}') + 2E_{\text{latt}}(\text{K}_2\text{O})] - E_{\text{latt}}(\text{TiO}_2)$$

193

194 In each case, a similar procedure is adopted, and a single solution scheme is  
195 assumed. More complex solution schemes, such as coupled substitutions, cannot  
196 be ruled out. Note that in the above expressions, Kröger-Vink notation has been  
197 used (Kröger & Vink, 1956).

## 198 **Results**

### 199 *Petrography of the Caldeira-Castelinho Ignimbrite ejecta*

200 Mineral assemblages of the CCI syenite ejecta include sodic alkali-feldspar, Na-  
201 pyroxene, Na-Ca to Na amphibole, quartz, aenigmatite and fayalite with accessory

202 Ti-magnetite, ilmenite, apatite, dalyite, an unspecified eudialyte group phase and  
203 biotite. Significant grain-size variation exists between nodules, allowing the broad  
204 distinction of two groups; fine to medium (~ 0.5 to 1.5 mm) grained nodules (Fig.  
205 2a), and medium to coarse (~ 1.0 to 6.0 mm) grained nodules (Fig. 2b). Typically,  
206 the fresher samples are more friable, whereas the more altered samples appear  
207 more indurated. Some samples exhibit patches of granular texture, comprising  
208 predominantly alkali-feldspar and quartz of finer grain size than the surrounding  
209 material. Rarely, samples exhibit mineral modal and/or grain size layering at the  
210 cm-scale.

211 Alkali-feldspar is by far the most abundant phase in all of the nodules and  
212 ranges from fresh and unaltered crystals, to heavily altered, perthitic crystals.  
213 Pyroxenes and amphiboles are the dominant intercumulus phases. Quartz is also  
214 an intercumulus phase and is generally found as large rounded grains or  
215 aggregates. Aenigmatite is typically present in small amounts and often exhibits a  
216 complex reaction relationship with pyroxene, amphibole and Fe-Ti oxides. When  
217 not associated with the apparent breakdown of aenigmatite, Fe-Ti oxides are  
218 usually observed as inclusions within other phases (primarily alkali-feldspar).  
219 Apatite exists as small, acicular inclusions within alkali-feldspars and varies in  
220 abundance between samples. Dalyite is typically present as small (< 0.5 mm) sub-  
221 to anhedral crystals (Fig. 2c-e), though can reach sizes of 1 to 1.5 mm (Fig. 2f). It is  
222 almost exclusively anhedral and confined to the interstices, either filling or partially  
223 filling void spaces. It is often associated spatially with quartz, and in some cases  
224 can be found as inclusions within larger interstitial quartz crystals. An unspecified  
225 eudialyte-group mineral is rarely found as frequently zoned anhedral crystals that,  
226 like dalyite, appear to totally or partially infill interstitial pore spaces, and are often  
227 spatially associated with clinopyroxene. Biotite is uncommon and, where present,  
228 exists as small inclusions within alkali-feldspars.



229 *Whole rock and mineral compositions*

230 *Whole rock*

231 Four whole rock major element analyses of dalyite-bearing syenite nodules are  
232 given in Table 4. Major element compositions are relatively uniform between  
233 samples, with the variation of individual elements generally being restricted to less  
234 than 1 wt. %. Peralkalinity indices and Na<sub>2</sub>O/K<sub>2</sub>O ratios range from 1.08 to 1.14  
235 and 1.42 to 1.51, respectively. Calculated CIPW norms yield quartz, albite,  
236 orthoclase, diopside, hypersthene, acmite, ilmenite, apatite and sodium  
237 metasilicate. All samples are silica-oversaturated, with between 1.0 and 3.3 wt. %  
238 normative quartz.

239

240 *Dalyite chemistry*

241 New chemical analyses of the CCI syenite dalyite (samples TER 30-1 and TER 30-  
242 7) are reported in Table 5. The data reveal that the CCI syenite dalyite does not  
243 deviate substantially from the empirical formula, with Na being the most significant  
244 substituting element (~ 0.10 to 0.20 apfu), substituting for K. The combined totals  
245 of atomic Na and K are close to the ideal total of 2 cations, and Fe contents are  
246 often below detection limit (0.038 wt. %, average error = 0.052 wt. %), highlighting  
247 limited incorporation of Fe in the dalyite structure. The low contents of Ti and Hf  
248 (up to 0.030 and 0.013 apfu, respectively), indicate that replacement of Zr with Ti  
249 and Hf is limited. These analyses suggest that the CCI dalyite corresponds to the  
250 more precise formula (K<sub>1.79-1.87</sub>Na<sub>0.12-0.19</sub>)(Zr<sub>0.90-0.96</sub> Ti<sub>0.004-0.030</sub>Hf<sub>0.010-0.013</sub>)(Si<sub>6.01-</sub>  
251 <sub>6.06</sub>O<sub>15</sub>). Calculated alkalinity moduli (Khomyakov 1995) values range from 21.90 to  
252 22.39. In addition to Na, Fe Ti and Hf, the data suggest that trace amounts of Al,  
253 Ba, Mg, and Mn may be present, though these are all very close to the detection  
254 limit. This is supported by their occurrence in trace amounts in various literature  
255 analyses (Table 1).

256

257 *Solid state modelling*

258 Calculated solution energies ( $E_{\text{sol}}$ ) for a number of potential substitutions are  
259 presented in Table 6. In each instance, the lowest  $E_{\text{sol}}$  value is considered to  
260 highlight the most likely substitution. Model results for Ti indicate Ti↔Si substitution  
261 as the most energetically favourable ( $E_{\text{sol}} = - 0.98$  eV), though Ti↔Zr substitution is  
262 also likely ( $E_{\text{sol}} = - 0.25$  eV). Modelling of Hf is more conclusive, with Hf↔Zr  
263 substitution representing the most likely scenario ( $E_{\text{sol}} = - 0.31$  eV). The  
264 incorporation of the  $R^{2+}$  cations  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Ba}^{2+}$  was also modelled, but charge  
265 balancing necessitates the presence of site vacancies, in this case assumed to be  
266 a single O vacancy. Results indicate that, in the case of  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  the lowest  
267 energy scenario is replacement of K. Nevertheless, the calculated  $E_{\text{sol}}$  values of  
268 8.86 eV and 9.61 eV, respectively, highlight the overall difficulty of their inclusion  
269 within the dalyite structure. Modelling of Ba yields a similar result, though the  
270 calculated  $E_{\text{sol}}$  value of 4.94 eV for Ba↔K substitution is noticeably lower than  
271 other  $R^{2+}$  cations.

272 **Discussion**

273 *Variations in dalyite chemical composition*

274 To facilitate a wider discussion of the compositional variability of dalyite, all  
275 available analyses are divided into two groups: 1) those found within peralkaline  
276 syenitic or granitic rocks and 2) those found within other lithologies, including  
277 lamproites, lamprophyres and charoitites. As such, the dalyite analyses from  
278 Terceira, São Miguel, Ascension, Straumsvola, Strange Lake and Gordon Butte  
279 are included in group 1, whereas analyses from Sunnfjord, Murun and Cancarix  
280 occupy group 2. All analyses were tested for quality using the following criteria: a)  
281 analysis total = 100 wt. %  $\pm$  1.5, b) total cations = < 9.05 apfu, c) cation total for the  
282 tetrahedral site = 6 apfu  $\pm$  0.05, d) cation total for the octahedral site = 1 apfu  $\pm$   
283 0.05. Only those analyses which passed all four criteria were applied to the  
284 following discussion, reducing the size of dataset from 43 to 25 analyses.

285 The overall average calculated  $K_{\text{alk}}$  for the combined dataset is 21.94, with  
286 minimum and maximum values of 20.90 and 22.51, respectively. This shows

287 essentially no variation between groups 1 and 2, with average values of 21.98 and  
288 21.91, respectively.

289 Figure 3a shows the available dalyite analyses in K–Na space. The data  
290 typically lie within 0.05 apfu of the one-to-one line, indicating the role of one-to-one  
291  $K \leftrightarrow Na$  substitution within the polyhedral sites. Group 1 analyses are characterised  
292 by a relative abundance of Na (0.12 to 0.19 apfu) and a corresponding paucity of K  
293 (1.79 to 1.87 apfu), though two analyses from Straumsvola and Strange Lake  
294 (analyses 3 & 4, Table 1) exhibit Na concentrations below the detection limit,  
295 alongside a slight deficiency in K. This discrepancy in older dalyite analyses may  
296 indicate Na loss during analysis, as suggested by Birkett et al. (1992). The dalyite  
297 from Strange Lake may also have been subject to alteration, as it is described as  
298 being frequently rimmed by elpidite or vlasovite.

299 In contrast to group 1, group 2 analyses are closer to the ideal dalyite  
300 formula, with significantly lower concentrations of Na (< 0.015 to 0.03 apfu). The  
301 relatively sodic nature of group 1 and potassic nature of group 2 dalyite correlates  
302 with the relatively sodic nature of the group 1 rocks and the generally potassic  
303 nature of group 2 rocks. For example, reported whole rock  $Na_2O/K_2O$  ratios of  
304 group 1 typically lie between 1 and 1.5 (Harris and Rickard, 1987; Ridolfi et al.,  
305 2003; this study). In contrast, group 2 whole rock  $Na_2O/K_2O$  is likely to be  
306 significantly lower, given their often highly potassic nature, as is the case for the  
307 Cancarix dalyite ( $Na_2O/K_2O = 0.1$ , Linthout et al., 1988; Salvioli-Mariani &  
308 Venturelli, 1996). Harris & Rickard (1987) made a similar observation, noting that  
309 the dalyite analyses from Sunnfjord (analyses 16 to 25, Table 1) exhibit lower Na  
310 contents than dalyite from Ascension Island (analysis 2, Table 1), which they  
311 attributed to the higher  $Na_2O/K_2O$  ratio of the latter. However, they also noted that  
312 Straumsvola dalyite (analysis 3, Table 1) has essentially no Na, despite a highly  
313 comparable  $Na_2O/K_2O$  ratio to that of group 1 samples (1.35).

314 Another potential control that must be considered is the crystallisation  
315 mechanism of each example, which must also play a role in the composition of  
316 dalyite. For example, the dalyite-bearing, ultrapotassic Sunnfjord dyke is reported  
317 to be heavily hydrothermally-altered (Furnes et al., 1982), suggesting that any  
318 dalyite present may be metasomatic in origin, or a magmatic composition that has

319 been altered by metasomatism. It can be seen in Table 1 that those analyses  
320 which may have been influenced by metasomatism (e.g. Sunnfjord, Murun)  
321 frequently exhibit Na contents below detection. However, although the Straumsvola  
322 analysis (itself an average of three analyses) contains no significant Na, the  
323 peralkaline granite host rock is described as being very fresh (Harris & Rickard,  
324 1987), and so the reported Na-poor dalyite cannot be attributed entirely to the  
325 effects of crystallisation mechanism or alteration.

326           The degree of substitution within the octahedral sites is highlighted in  
327 Figure 3b. Ti and Hf are considered as the most suitable substitutes, though the  
328  $R^{2+}$  cations Mg, Mn and Fe are also considered (where data is available), due to  
329 the similarity of their ionic radii with Zr. In Figure 3b, the data plot within 0.05 apfu  
330 of the one-to-one line, indicating one-to-one cation exchange. In the case of Fe,  
331 Mn and Mg, this would introduce a charge imbalance which can be mitigated by a  
332 single oxygen vacancy. Although solid-state modelling suggests that  $R^{2+} \leftrightarrow K$   
333 substitution should be energetically favourable, the calculated  $E_{sol}$  values are still  
334 too large (8.86 eV & 9.61 eV), and the difference in ionic radii too great, to fully  
335 justify the placement of  $R^{2+}$  cations in the polyhedral sites. The substitutions of  
336  $Hf \leftrightarrow Zr$  and  $Ti \leftrightarrow Zr$  are both supported by solid-state modelling ( $E_{sol} = -0.31$  eV & -  
337 0.25 eV, respectively, though in the latter case, the modelling also indicates the  
338 potential of  $Ti \leftrightarrow Si$  substitution ( $E_{sol} = -0.98$  eV). However, there is no evidence  
339 within the dataset to support such a substitution.

340           Group 1 analyses remain close to the ideal dalyite formula, with 0.91 to  
341 0.98 apfu Zr. Group 2 analyses exhibit a greater degree of substitution, generally  
342 clustering between 0.85 and 0.94 apfu Zr, with 0.05 to 0.12 apfu Ti. It is notable  
343 that one of the two analyses from the charoitites of the Murun Complex is enriched  
344 in the davanite component ( $K_2TiSi_6O_{15}$ ), with 0.21 apfu Ti. This may relate to the  
345 unusual nature of their charoititic host rock, which is typically considered to be  
346 metasomatic rather than magmatic in origin (e.g. Reguir, 2001 and references  
347 therein). This alternative origin may explain the apparent geochemical deviation  
348 from the rest of the dataset.

349           The dataset indicates the presence of small amounts of Ba within Group 2  
350 dalyite. On the basis of solid-state modelling and ionic radii, it is suggested that the

351 most likely mechanism for its inclusion within the dalyite structure is  $Ba \leftrightarrow K$ . The  
352 resulting charge imbalance could be mitigated by a single vacancy in the  
353 polyhedral site, in which case the Ba content may be used as a proxy for the  
354 polyhedral vacancies in each analysis (up to 0.02 apfu). This may, in part, account  
355 for analyses in which the structural total is less than the ideal 9 apfu. Alternatively,  
356 structural deficits may result from the presence of Li. Significant concentrations of  
357 Li have been reported in peralkaline rocks and Li-enrichment can occur via  
358 metasomatic processes (e.g. Borley, 1963; Hawthorne et al., 1996; Brenan et al.,  
359 1998; Hawthorne et al., 2001). Although the mechanisms of Li-substitution in  
360 dalyite are unclear, its inclusion may contribute to the frequently low structural  
361 totals observed within the dataset.

362                 The key geochemical parameters required to stabilise dalyite are  
363 high  $\mu K_2O$  and high  $aSiO_2$  (Marks et al., 2011). For example, an insufficiently high  
364 silica activity will lead to the crystallisation of wadeite ( $K_2ZrSi_3O_9$ ) in place of dalyite  
365 (Marks et al., 2011). Dalyite is therefore limited to silica-saturated to –oversaturated  
366 lithologies, although its occurrence in a nepheline-bearing pegmatite from  
367 Langesundfjord, Norway (Andersen et al., 2010) appears to contradict this. The  
368 additional requirement of high  $\mu K_2O$  is likely due to high  $K_2O$  contents in the melts,  
369 achieved either by slowly increasing  $K_2O$  via fractional crystallisation and/or crustal  
370 assimilation of potassic rocks in the group 1 samples, or by producing melts with  
371 initially high  $K_2O$  values via the more unusual processes suggested to produce  
372 ultrapotassic rocks, such as partial melting of metasomatised mantle lithologies,  
373 (e.g. Mitchell & Bergman, 1991).

374                 The geochemical variations observed between the groups of this study are  
375 likely to represent major element variations in the melts themselves. For example,  
376 the group 2 dalyites generally show elevated Ti and Fe contents relative to the  
377 group 1 dalyites, which may relate to the relatively Ti- and Fe-rich whole rock  
378 compositions of lamproites and lamprophyres, particularly when compared to the  
379 low Ti contents of group 1 whole rock analyses (< 0.7 wt. %). Additionally, group 2  
380 analyses exhibit significantly lower degrees of Na substituting for K, which might be  
381 expected given the  $K_2O$ -rich nature of their whole rock analyses.

382

383 *Dalyite crystallisation on Terceira*

384 Dalyite is generally considered to be a late-stage, magmatic mineral phase (e.g.  
385 Harris & Rickard, 1987; Ridolfi et al., 2003) that may be altered, either during later  
386 magmatic or sub-solidus stages, to minerals such as elpidite,  $\text{Na}_2\text{ZrSi}_6\text{O}_{15}\cdot 3(\text{H}_2\text{O})$   
387 (Cann, 1967), catapleiite,  $\text{Na}_2\text{Zr}(\text{Si}_3\text{O}_9)\cdot 2\text{H}_2\text{O}$  (Birkett et al., 1992; Chakhmouradian  
388 & Mitchell, 2002) and intergrown quartz and zircon (Cann, 1967). Key features of  
389 the Terceira dalyite, notably the dominantly anhedral crystal forms, its restricted  
390 occurrence in interstitial pore spaces and its lack of inclusion within other mineral  
391 phases, all point towards late-stage, post-cumulus, magmatic crystallisation,  
392 though extension of the crystallisation interval into the sub-solidus deuteric stage  
393 cannot be ruled out. Evidence for the alteration of primary dalyite compositions is  
394 lacking. Its textural association and occasional intergrowth with quartz suggests  
395 that the crystallisation of these two phases was largely contemporaneous. This  
396 conclusion is in agreement with that of Ridolfi et al. (2003), who studied similar  
397 parageneses in syenite nodules erupted by Agua de Pau volcano, São Miguel,  
398 Azores.

399         The dalyite analyses from Terceira display two clusters in Na-K space (Fig.  
400 3a), with one cluster of more sodic compositions (0.17 to 0.19 Na apfu), and  
401 another cluster of more potassic compositions (0.12 to 0.13 Na apfu). The  
402 difference between these clusters cannot be entirely accounted for by the  
403 calculated two-sigma errors of  $\pm 0.015$  apfu, and is considered to represent  
404 bimodality in the dataset. Both clusters lie within 0.05 apfu of the one-to-one line  
405 and, as such, the trend of the data likely highlights the role of varying degrees of  
406 one-to-one Na $\leftrightarrow$ K substitution within the Terceira samples. The presence of two  
407 subgroups may imply that two separate populations of dalyite are present, either  
408 derived from multiple processes that each led to the crystallisation of  
409 compositionally distinct dalyite, or a single process that is capable of producing a  
410 heterogeneous dalyite population. No visible correlation exists between dalyite  
411 composition and textural features such as crystal form or size, or the degree to  
412 which they infill pores. Instead, the two clusters of dalyite analyses can be related  
413 to the two separate samples in which dalyite was analysed (TER-30-1 and TER 30-

414 7), with the most sodic dalyite analyses being from TER 30-1. The compositional  
415 variations may therefore reflect random sampling of a syenitic mush in which  
416 geochemical heterogeneity is sufficiently large in scale that it yields 'inter-nodule'  
417 variations in dalyite composition, whilst 'intra-nodule' variations are more limited.  
418 Such heterogeneity may be primary (i.e. derived from original compositional  
419 variations in the melt, perhaps originating from multiple magma batches that  
420 contributed to a single crystal mush body), or secondary, originating from the  
421 variable degree of fluid-feldspar reaction (albitization; e.g. Lee & Parsons, 1997) in  
422 the crystal mush during deuteric alteration. The late stage albitization of the rock  
423 would lead to a bulk rock increase in Na and an enrichment of K in the albitizing  
424 fluids. The prevalence of coarse patchy perthitic feldspars in the Terceira syenites  
425 provides evidence for the prominent role of albitization in their late stage evolution.  
426 Evidence for primary bulk compositions being the underlying control upon dalyite  
427 composition exists in the bimodality of the dataset, with the most sodic dalyites  
428 found in the most sodic whole rock analysis.

429           However, a single analysis from sample TER 30-7 falls within the cluster of  
430 TER 30-1 analyses (Fig. 2a, Table 5), indicating that a simple relationship between  
431 dalyite chemistry and bulk rock composition cannot entirely account for the  
432 observed variation. As such, alternative processes that might influence the degree  
433 of Na $\leftrightarrow$ K substitution are explored. One example that is considered here is the role  
434 of variable pore size in the compositional evolution of interstitial melts. Because  
435 heterogeneous nucleation is energetically favourable compared to homogenous  
436 nucleation, the dominant process that drives the compositional evolution of a melt  
437 within a pore under closed system conditions is the crystallisation of surrounding  
438 cumulus phases, as components that are incompatible in the pore wall minerals  
439 become enriched in the residual melt. In the Terceira syenite nodules, alkali-  
440 feldspar is the most abundant phase, and surrounds the majority of pore spaces,  
441 suggesting that the post-cumulus, heterogeneous nucleation of feldspar onto pore  
442 walls will exert the strongest influence upon interstitial melt compositions. Due to its  
443 albite-rich composition ( $\sim$  Ab<sub>64</sub>, average Na/K = 1.67) (A. J. Jeffery, unpublished  
444 data), this effect is likely to promote the development of depressed Na/K ratios in  
445 the liquid as evolution continues. Petrographic evidence for this process exists in

446 the form of optically distinguishable rims on many of the pore-wall feldspars (e.g.  
447 Fig. 2c). During the sub-solidus deuteric stage, albitization also contributes to the  
448 depression of liquid Na/K ratios via the replacement of alkali feldspar with near end  
449 member albite. Thus, it is suggested that during the late stage magmatic and sub-  
450 solidus deuteric evolution of the syenite, the majority of liquid-filled pores were  
451 evolving towards more potassic compositions.

452 It is proposed that the observed variation in Terceira dalyite composition  
453 could be related to the timing of crystallisation relative to the evolution of the  
454 interstitial melt. The thermodynamics of crystallisation in pore spaces has been  
455 shown to be fundamentally different compared to a free fluid (Bigg, 1953; Melia &  
456 Moffitt, 1964; Putnis et al., 1995; Scherer, 1999). In particular, a fluid confined to a  
457 pore space can achieve greater degrees of supersaturation prior to the onset of  
458 crystallisation compared with an unconfined fluid, thus introducing a nucleation  
459 delay that is more substantial in smaller pores (e.g. Putnis & Mauthe, 2001;  
460 Holness et al., 2007; Holness & Sawyer, 2008). As such, the dalyite crystals that  
461 grew in smaller pores would have nucleated later than those in larger pores, and  
462 would record more evolved compositions. Holness & Sawyer (2008) also cited the  
463 prevalence of single-grain pseudomorphs in small pores and poly-mineralic  
464 aggregate pseudomorphs in larger pores as petrographic evidence for the relative  
465 ease of nucleation in larger pores. This feature can also be observed in the CCI  
466 syenite, where larger pores are frequently filled with aggregates of late-crystallising  
467 phases such as quartz, clinopyroxene, dalyite, and eudalyte (Fig. 2f), whilst small  
468 pores generally contain only a single crystal of one of these phases (Fig. 2d).

469 Considering the previously described evolutionary trend of relative K-  
470 enrichment during both late stage magmatic and sub-solidus stages, dalyite in  
471 smaller pores should therefore have more potassic compositions. To test this  
472 hypothesis, dalyite-bearing pore spaces were digitised and measured using  
473 ImageJ to determine the two-dimensional area. This was then plotted against the  
474 Na content of the dalyite crystal within them (Fig. 4), yielding a positive correlation  
475 that suggests that the size of a pore exerts, at least to some extent, a control over  
476 the composition of the dalyite crystallising within it.



477 A single data point in Fig. 4 appears to deviate from the broadly linear  
478 trend observed in the rest of the data (pore area = 1.07 mm<sup>2</sup>, Na content = 0.18).  
479 Unlike other reported dalyites, this dalyite crystal is found in a pore that is bounded  
480 by a large clinopyroxene crystal, in addition to alkali-feldspar. It is therefore  
481 suggested that this deviation in pore size vs. Na content space may highlight the  
482 influence of other minerals in the evolution of interstitial melts. Given the relatively  
483 high Na contents and negligible K contents of the Terceira clinopyroxene (Na/K = 6  
484 to 2584) (A. J. Jeffery, unpublished data), the pore wall crystallisation of  
485 clinopyroxene would greatly accelerate the described evolutionary trend of K-  
486 enrichment in interstitial melt, leading to dalyite compositions that appear unusually  
487 K-rich when compared with the suggested feldspar-controlled trend (Fig. 4). The  
488 pore wall crystallisation of amphibole would also produce this effect but to a lesser  
489 degree (Na/K = 5.7 to 8.9) (A. J. Jeffery, unpublished data).

490 In summary, it is suggested that the dalyite from Terceira is predominantly  
491 late-stage magmatic in origin, and the observed compositional variability is  
492 influenced by the K-enrichment trend of late stage interstitial melt resulting from  
493 pore wall crystallisation of sodic alkali feldspar. Any continued crystallisation during  
494 a sub-solidus deuteric stage is considered to have been subject to a similar K-  
495 enrichment trend, driven by albitization of alkali feldspar. Variation in Na content is  
496 likely to have been controlled, at least in part, by the larger nucleation delay that is  
497 introduced in smaller pores compared to larger ones.

498

## 499 **Conclusions**

500 A new occurrence of the rare potassium zirconium dalyite is reported from  
501 Terceira, Azores. The detailed study of new quantitative analyses of dalyite from  
502 Terceira, alongside solid state modelling and previously published analyses, allows  
503 the following conclusions to be made regarding the compositional variability of  
504 dalyite:

505 (1) Substitution of Na for K in dalyite is generally more significant in  
506 peralkaline granites and syenites than in highly potassic rock types.

- 507 (2) The incorporation of small amounts of Ba occurs in potassic rocks and is  
508 most likely achieved via Ba $\leftrightarrow$ K substitution..
- 509 (3) The incorporation of Fe into dalyite is minimal in peralkaline granites and  
510 syenites, but becomes more significant in highly potassic lithologies.  
511 Mineral chemical data and solid state modelling suggest that this is most  
512 easily achieved via Fe<sup>2+</sup> $\leftrightarrow$ Zr substitution, though high  $E_{sol}$  values and  
513 charge balancing requirements must hinder this relationship.
- 514 (4) The degree of substitution of Ti for Zr is greater in highly potassic igneous  
515 rocks than in peralkaline granites and syenites, and may be linked to  
516 elevated Ti-contents of the melts.
- 517 (5) The dalyite from Terceira shows variation in the degree of Na $\leftrightarrow$ K  
518 substitution that does not relate obviously to texture, and cannot be entirely  
519 attributed to 'inter-nodule' diversity. This feature is linked to relative K-  
520 enrichment induced by the effects of pore wall crystallisation (during a late  
521 stage magmatic phase) and albitization (during a sub-solidus deuteric  
522 phase), coupled with the variation in nucleation delay that is introduced by  
523 variable pore sizes.

524

## 525 **Acknowledgements**

526 We gratefully acknowledge S. Self, A. Pimentel, J. Pacheco and the Centro de  
527 Vulcanologia e Avaliação de Riscos Geológicos (CVARG) for their invaluable  
528 assistance and logistical support during fieldwork. We are grateful to P. Williams  
529 and R. Mitchell for editorial handling, and F. Ridolfi and G. Gatta for their detailed  
530 and constructive comments, which greatly improved the manuscript. E. Reguir is  
531 thanked for kindly providing a copy of Table 48 from Konev et al. (1996).

532

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## Figure captions

**Figure 1** Reported occurrences of dalyite worldwide. **1)** Ascension Island, South Atlantic Ocean (Van Tassel, 1952) **2)** Agua de Pau volcano, São Miguel, Azores (Cann, 1967) **3)** the Murun Complex, Siberia, Russia (Lazebnik & Makhotko, 1982; Dolivo-Dobrovolskiy & Yevdokimov, 1991; Konev et al., 1996; Reguir, 2001) **4)** Gjerdingen, Norway (Raade & Mladeck, 1983) **5)** Sunnfjord, Norway (Furnes et al., 1982; Robins et al., 1983) **6)** the Straumsvola Complex, Dronning Maud Land, Antarctica (Harris & Rickard, 1987) **7)** Cancarix, South Eastern Spain (Venturelli et al., 1984; Linthout et al., 1988) **8)** the Serra Negra and Salitre Complex, Brazil (Mariano & Francis, 1989; Mariano & Marchetto, 1991) **9)** the Strange Lake Complex, Canada (Birkett et al., 1992; Salvi & Williams-Jones, 1995) **10)** the Brandberg Complex, Namibia (Schmitt et al., 2000) **11)** Gordon Butte, Montana, USA (Chakhmouradian & Mitchell, 2002) **12)** the Zargat Na'am ring complex, Egypt (Saleh, 2006) **13)** Langesundfjord, Norway (Andersen, et al., 2010) **14)** the Shibanovsky Massif, Russia (Stepnova et al., 2013) **15)** Terceira Island, Azores (this study)

**Figure 2 a)** Example of a fine to medium grained, alkali-feldspar dominated nodule. The feldspars appear altered and are often perthitic. A large, optically-continuous quartz crystal is highlighted with a white box in the lower right corner of the image. **b)** A medium to coarse grained nodule with larger crystal sizes and fresher, less-altered feldspars **c)** A large dalyite crystal which partially infills an interstitial void between larger alkali-feldspar crystals. Also visible are small amphibole crystals and stellate clinopyroxene **d)** An anhedral dalyite crystal which partially fills an interstitial void between large alkali-feldspars and a large amphibole crystal **e)** An anhedral dalyite crystal forming an incomplete rim around the edges of an interstitial cavity. A small clinopyroxene crystal appears to have been included within the dalyite. A resorbed, optically distinctive feldspar core is visible within the large feldspar to the lower right of the image **f)** An element map highlighting a large, anhedral dalyite crystal filling an interstitial space, together with intergrown quartz and small amounts of clinopyroxene. Colours used: Red = Fe, Purple = Zr, Blue = Si, Green = Al. Abbreviations used: Qtz = quartz, Fsp = alkali-feldspar, Amp = amphibole, Cpx = Clinopyroxene, Dal = dalyite

**Figure 3** Geochemical variation diagrams highlighting the variable degree of substitution within the dataset. The ideal composition of dalyite is highlighted with a black star symbol. The maximum error is applicable to the new data for Terceira (TER 30-1 and TER 30-7) only and is calculated as described in the text. Group 1 dalyite is denoted by diamonds, group 2 by triangles. Only analyses that passed all of the filtering criteria described in the text are shown

**a)** Bivariate plot showing the degree of  $K \leftrightarrow Na$  substitution in the dataset. **b)** Bivariate plot showing the degree of substitution in the octahedral site. Data for Hf, Mg and Fe is presented where analyses permit

**Figure 4** Bivariate plot of measured pore area against the Na content of dalyite within the pore

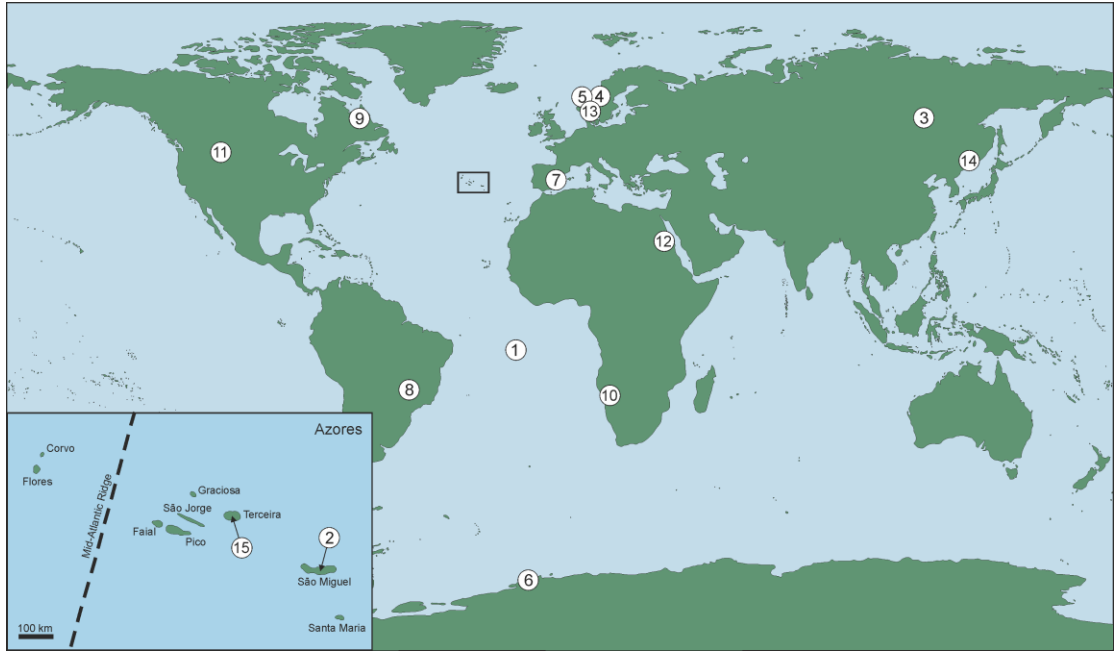


Figure 1

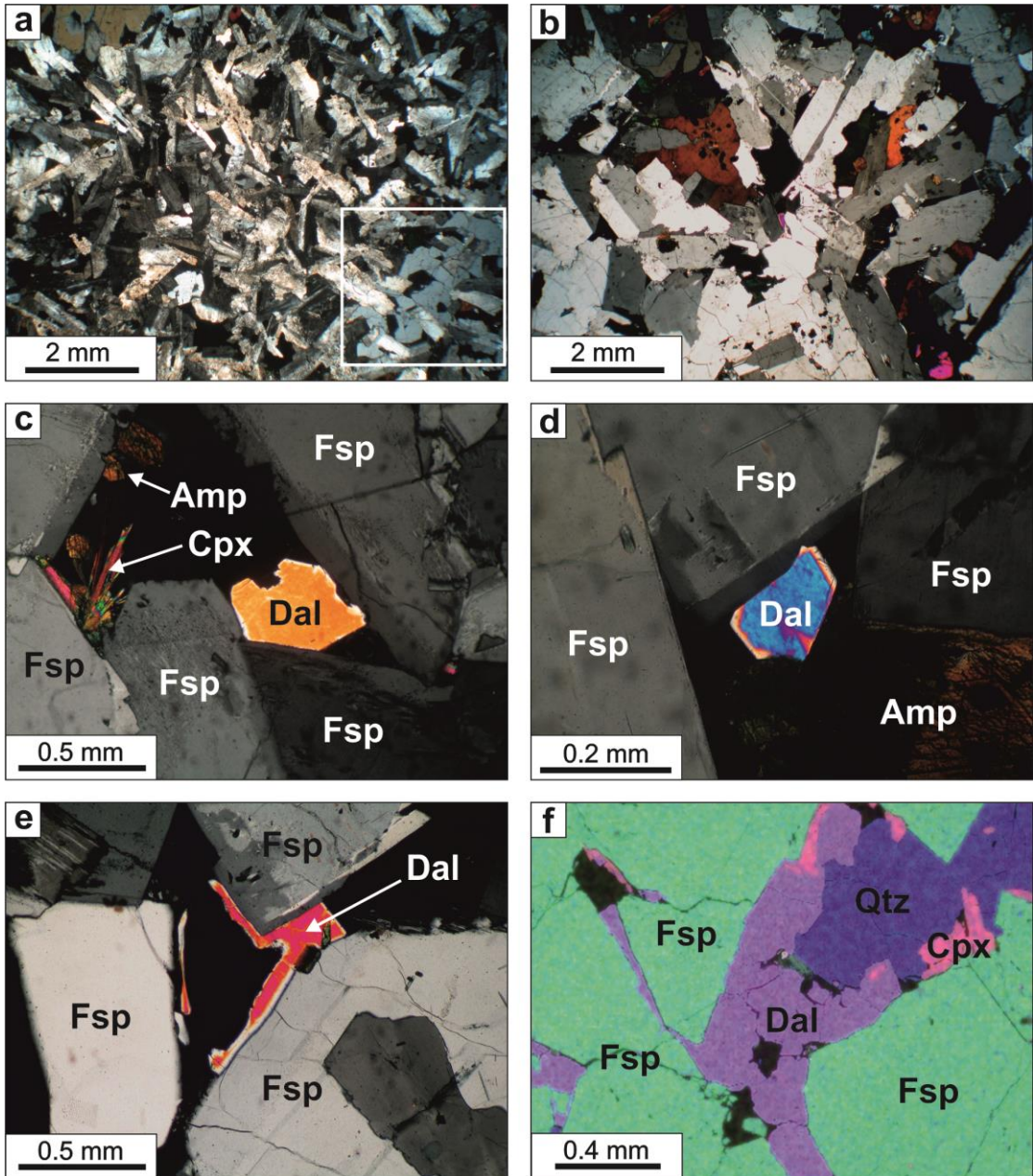


Figure 2

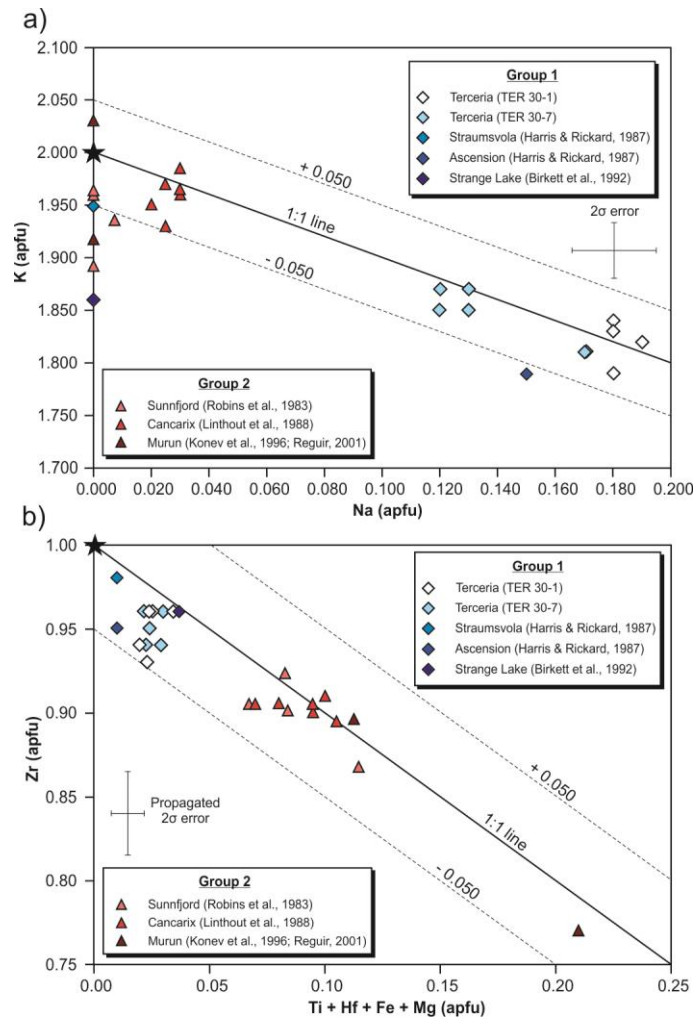


Figure 3

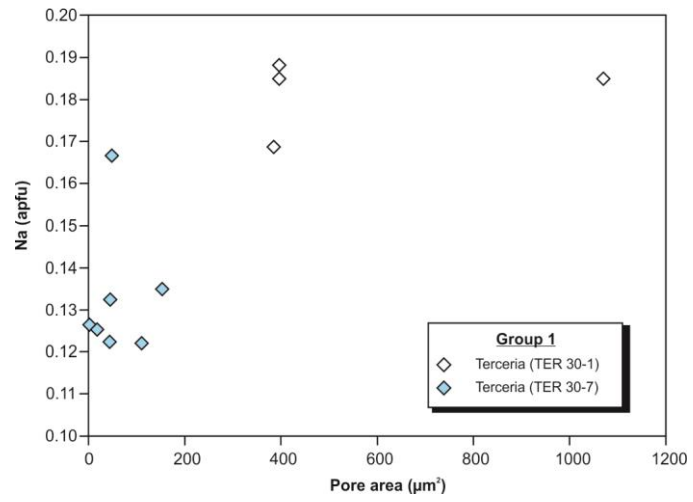


Figure 4

**Table 1** Literature electron microprobe analyses of dalyite

Location Group	Ascension 1	Ascension 1	Straumsvola 1	Strange Lake 1	Gordon Butte 1	Agua de Pau 1	Agua de Pau 1	Agua de Pau 1	Agua de Pau 1
Host rock	Granite ejecta	Granite ejecta	Granite dyke	Granite	Alkaline pegmatite	Syenitic ejecta	Syenitic ejecta	Syenitic ejecta	Syenitic ejecta
Suggested origin	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic
No.	1 <sup>†</sup>	2*	3	4	5	6	7	8	9
SiO <sub>2</sub>	61.85	63.25	62.07	62.55	60.35	62.23	61.35	61.35	61.36
TiO <sub>2</sub>	-	0.12	0.13	0.08	1.78	0.08	0.11	0.14	0.15
Al <sub>2</sub> O <sub>3</sub>	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-
FeO	0.33	0.03	<i>bdl</i>	0.06	0.18	-	-	-	-
MnO	-	<i>bdl</i>	<i>bdl</i>	-	<i>bdl</i>	-	-	-	-
MgO	-	-	-	-	<i>bdl</i>	-	-	-	-
CaO	-	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	-	-	-	-
Na <sub>2</sub> O	1.75	0.79	<i>bdl</i>	<i>bdl</i>	0.02	0.69	0.37	0.44	0.49
K <sub>2</sub> O	14.60	14.63	15.71	15.08	15.34	13.80	14.56	14.60	14.72
ZrO <sub>2</sub>	21.70	20.43	20.63	20.38	18.21	23.72	23.57	23.27	23.49
HfO <sub>2</sub>	-	-	-	0.81	-	-	-	-	-
BaO	-	-	-	-	<i>bdl</i>	-	-	-	-
P <sub>2</sub> O <sub>5</sub>	-	-	-	-	-	-	-	-	-
La <sub>2</sub> O <sub>3</sub>	-	<i>bdl</i>	<i>bdl</i>	0.04	-	-	-	-	-
Ce <sub>2</sub> O <sub>3</sub>	-	<i>bdl</i>	<i>bdl</i>	0.06	<i>bdl</i>	-	-	-	-
Nb <sub>2</sub> O <sub>5</sub>	-	<i>bdl</i>	<i>bdl</i>	-	1.65	-	-	-	-
<b>Total</b>	<b>100.23</b>	<b>99.25</b>	<b>98.54</b>	<b>98.96</b>	<b>97.53</b>	<b>100.52</b>	<b>99.96</b>	<b>99.80</b>	<b>100.21</b>
Si	5.94	6.05	6.03	6.04	5.92	5.94	5.92	5.92	5.91
Ti	-	0.01	0.01	0.01	0.13	0.01	0.01	0.01	0.01
Al	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-
Fe	0.03	0.00	<i>bdl</i>	0.01	0.02	-	-	-	-
Mn	-	<i>bdl</i>	<i>bdl</i>	-	<i>bdl</i>	-	-	-	-
Mg	-	-	-	-	<i>bdl</i>	-	-	-	-
Ca	-	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	-	-	-	-
Na	0.33	0.15	<i>bdl</i>	<i>bdl</i>	0.00	0.13	0.07	0.08	0.09
K	1.79	1.79	1.95	1.86	1.92	1.68	1.79	1.80	1.81
Zr	1.02	0.95	0.98	0.96	0.87	1.10	1.11	1.10	1.10
Hf	-	-	-	0.02	-	-	-	-	-
Ba	-	-	-	-	<i>bdl</i>	-	-	-	-
P	-	-	-	-	-	-	-	-	-
La	-	<i>bdl</i>	<i>bdl</i>	0.00	-	-	-	-	-
Ce	-	<i>bdl</i>	<i>bdl</i>	0.00	<i>bdl</i>	-	-	-	-
Nb	-	<i>bdl</i>	<i>bdl</i>	-	0.07	-	-	-	-
<b>Sum</b>	<b>9.11</b>	<b>8.95</b>	<b>8.97</b>	<b>8.90</b>	<b>8.93</b>	<b>8.86</b>	<b>8.90</b>	<b>8.91</b>	<b>8.92</b>
K <sub>alk</sub>	23.27	21.68	21.74	20.90	21.50	20.43	20.90	21.10	21.30

Analysis 1-2 from Ascension Island, (van Tassel, 1952; Harris & Rickard, 1987), analysis 3 from Straumsvola, Antarctica (Harris & Rickard, 1987), analysis 4 from the Strange Lake complex, Canada (Birkett et al., 1992), analysis 5 from Gordon Butte, USA (Chakhmouradian & Mitchell, 2002), analyses 6-9 from Agua de Pau, São Miguel Island (Ridolfi et al., 2003), analyses 10-15 from the Murun complex, Russia (Lazebnik & Makhotko, 1982; Konev et al., 1996; Reguir, 2001), analyses 16-25 from Sunnfjord, Norway (Robins et al., 1983), , analyses 26-31 from Cancarix, Spain (Linhout et al., 1988). Abbreviations and symbols used: (-) = not analysed; † Analysis includes 0.64 wt. % H<sub>2</sub>O; \* Average of three analyses; *bdl* = below detection limit. K<sub>alk</sub> calculated after Khomyakov, 1995. All structural formulae recalculated from reported weight percent oxide values



Table 1 continued

Location	Murun	Murun	Murun	Murun	Murun	Murun	Sunnfjord	Sunnfjord	Sunnfjord	Sunnfjord	Sunnfjord
Group	2	2	2	2	2	2	2	2	2	2	2
Host rock			Charoitite	Charoitite	Charoitite	Charoitite	Syenite dyke	Syenite dyke	Syenite dyke	Syenite dyke	Syenite dyke
Suggested origin	Magmatic or Metasomatic	Magmatic or Metasomatic	Magmatic or Metasomatic	Magmatic or Metasomatic	Magmatic or Metasomatic	Magmatic or Metasomatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic
No.	10	11	12	13	14	15	16	17	18	19	20
SiO <sub>2</sub>	63.62	60.82	63.44	62.35	61.83	62.25	63.39	61.86	64.94	64.12	64.22
TiO <sub>2</sub>	1.87	0.69	2.92	5.86	0.69	1.56	0.64	1.22	1.59	0.83	0.88
Al <sub>2</sub> O <sub>3</sub>	0.03	<i>bdl</i>	<i>bdl</i>	0.02	<i>bdl</i>	<i>bdl</i>	0.03	0.01	<i>bdl</i>	0.15	0.06
FeO	<i>bdl</i>	<i>bdl</i>	0.01	0.07	<i>bdl</i>	<i>bdl</i>	0.22	0.30	0.26	0.31	0.19
MnO	-	-	-	-	<i>bdl</i>	<i>bdl</i>	0.05	<i>bdl</i>	0.06	<i>bdl</i>	<i>bdl</i>
MgO	-	-	-	-	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.08	<i>bdl</i>	<i>bdl</i>	0.05
CaO	0.02	0.03	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.04	<i>bdl</i>	0.03	<i>bdl</i>	<i>bdl</i>
Na <sub>2</sub> O	0.11	0.03	<i>bdl</i>	0.10	<i>bdl</i>	<i>bdl</i>	0.04	<i>bdl</i>	0.09	<i>bdl</i>	<i>bdl</i>
K <sub>2</sub> O	14.99	15.41	16.75	16.68	15.15	15.65	15.93	16.64	14.08	15.80	16.36
ZrO <sub>2</sub>	21.50	22.16	16.68	14.84	20.60	19.13	19.49	18.83	19.13	20.17	19.68
HfO <sub>2</sub>	-	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-	-
BaO	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.08	0.03	0.11	0.04	0.03
P <sub>2</sub> O <sub>5</sub>	-	-	-	-	<i>bdl</i>	<i>bdl</i>	0.10	0.12	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
La <sub>2</sub> O <sub>3</sub>	-	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-	-
Ce <sub>2</sub> O <sub>3</sub>	-	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-	-
Nb <sub>2</sub> O <sub>5</sub>	-	-	-	-	<i>bdl</i>	0.60	-	-	-	-	-
<b>Total</b>	<b>102.14</b>	<b>99.14</b>	<b>99.79</b>	<b>99.92</b>	<b>98.27</b>	<b>99.19</b>	<b>100.01</b>	<b>99.09</b>	<b>100.29</b>	<b>101.42</b>	<b>101.47</b>
Si	5.94	5.92	6.01	5.89	6.00	5.98	6.04	5.98	6.08	6.02	6.03
Ti	0.13	0.05	0.21	0.42	0.05	0.11	0.05	0.09	0.11	0.06	0.06
Al	0.00	<i>bdl</i>	<i>bdl</i>	0.00	<i>bdl</i>	<i>bdl</i>	0.00	0.00	<i>bdl</i>	0.02	0.01
Fe	<i>bdl</i>	<i>bdl</i>	0.00	0.01	<i>bdl</i>	<i>bdl</i>	0.02	0.02	0.02	0.02	0.01
Mn	-	-	-	-	<i>bdl</i>	<i>bdl</i>	0.00	<i>bdl</i>	0.00	<i>bdl</i>	<i>bdl</i>
Mg	-	-	-	-	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.01	<i>bdl</i>	<i>bdl</i>	0.01
Ca	0.00	0.00	<i>bdl</i>	-	<i>bdl</i>	<i>bdl</i>	0.00	<i>bdl</i>	0.00	<i>bdl</i>	<i>bdl</i>
Na	0.02	0.01	<i>bdl</i>	0.02	<i>bdl</i>	<i>bdl</i>	0.01	<i>bdl</i>	0.02	<i>bdl</i>	<i>bdl</i>
K	1.78	1.91	2.03	2.01	1.88	1.92	1.94	2.05	1.68	1.89	1.96
Zr	0.98	1.05	0.77	0.68	0.98	0.90	0.91	0.89	0.87	0.92	0.90
Hf	-	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-	-
Ba	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.00	0.00	0.00	0.00	0.00
P	-	-	-	-	<i>bdl</i>	<i>bdl</i>	0.01	0.01	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
La	-	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-	-
Ce	-	-	-	-	<i>bdl</i>	<i>bdl</i>	-	-	-	-	-
Nb	-	-	-	-	<i>bdl</i>	0.03	-	-	-	-	-
<b>Sum</b>	<b>8.85</b>	<b>8.94</b>	<b>9.02</b>	<b>9.03</b>	<b>8.91</b>	<b>8.93</b>	<b>8.97</b>	<b>9.05</b>	<b>8.79</b>	<b>8.94</b>	<b>8.98</b>
K <sub>alk</sub>	20.34	21.48	22.51	22.48	21.07	21.47	21.71	22.65	19.34	21.16	21.80

Table 1 continued

Location Group	Sunnfjord 2	Sunnfjord 2	Sunnfjord 2	Sunnfjord 2	Sunnfjord 2	Cancarix 2	Cancarix 2	Cancarix 2	Cancarix 2	Cancarix 2	Cancarix 2
Host rock	Syenite dyke	Syenite dyke	Syenite dyke	Syenite dyke	Syenite dyke	Lamproite	Lamproite	Lamproite	Lamproite	Lamproite	Lamproite
Suggested origin	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic
No.	21	22	23	24	25	26	27	28	29	30	31
SiO <sub>2</sub>	62.75	62.25	62.53	62.58	62.04	62.60	62.45	62.65	62.95	62.65	63.00
TiO <sub>2</sub>	1.08	1.54	1.21	1.61	1.71	1.25	1.10	1.10	0.75	1.15	0.85
Al <sub>2</sub> O <sub>3</sub>	0.01	0.13	0.12	0.07	0.03	0.10	0.10	0.10	0.05	0.05	0.05
FeO	0.60	0.31	0.19	0.15	0.28	0.18	0.18	0.18	0.18	0.09	0.18
MnO	0.04	0.05	<i>bdl</i>	<i>bdl</i>	0.03	<i>bdl</i>	-	-	-	-	-
MgO	0.65	0.10	0.08	0.02	0.06	<i>bdl</i>	<i>bdl</i>	-	0.05	<i>bdl</i>	0.05
CaO	0.04	0.04	0.06	<i>bdl</i>	0.02	<i>bdl</i>	-	-	-	-	-
Na <sub>2</sub> O	<i>bdl</i>	0.19	<i>bdl</i>	<i>bdl</i>	0.07	0.15	0.15	0.15	0.10	0.15	0.15
K <sub>2</sub> O	15.79	15.33	15.98	16.17	13.93	15.75	16.10	16.10	15.95	16.25	16.10
ZrO <sub>2</sub>	18.29	19.22	18.46	20.23	20.16	19.10	19.20	19.35	19.40	19.60	19.70
HfO <sub>2</sub>	-	-	-	-	-	-	-	-	-	-	-
BaO	<i>bdl</i>	0.19	0.21	0.20	0.22	0.45	0.30	0.40	0.15	0.25	0.35
P <sub>2</sub> O <sub>5</sub>	0.04	0.10	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	-	-	-	-	-	-
La <sub>2</sub> O <sub>3</sub>	-	-	-	-	-	-	-	-	-	-	-
Ce <sub>2</sub> O <sub>3</sub>	-	-	-	-	-	-	-	-	-	-	-
Nb <sub>2</sub> O <sub>5</sub>	-	-	-	-	-	-	-	-	-	-	-
<b>Total</b>	<b>99.29</b>	<b>99.45</b>	<b>98.84</b>	<b>101.03</b>	<b>98.55</b>	<b>99.58</b>	<b>99.58</b>	<b>100.03</b>	<b>99.58</b>	<b>100.19</b>	<b>100.43</b>
Si	6.01	5.97	6.02	5.94	5.97	6.00	6.00	6.00	6.02	5.99	6.00
Ti	0.08	0.11	0.09	0.11	0.12	0.09	0.08	0.08	0.05	0.09	0.06
Al	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.05	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Mn	0.00	0.00	<i>bdl</i>	<i>bdl</i>	0.00	<i>bdl</i>	-	-	-	-	-
Mg	0.09	0.01	0.01	0.00	0.01	<i>bdl</i>	<i>bdl</i>	-	0.01	<i>bdl</i>	0.01
Ca	0.00	0.00	0.01	<i>bdl</i>	0.00	<i>bdl</i>	-	-	-	-	-
Na	<i>bdl</i>	0.04	<i>bdl</i>	<i>bdl</i>	0.01	0.03	0.03	0.03	0.02	0.03	0.03
K	1.93	1.87	1.96	1.96	1.71	1.93	1.97	1.97	1.95	1.99	1.96
Zr	0.85	0.90	0.87	0.94	0.95	0.90	0.90	0.91	0.91	0.91	0.91
Hf	-	-	-	-	-	-	-	-	-	-	-
Ba	<i>bdl</i>	0.01	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.01
P	0.00	0.01	0.00	<i>bdl</i>	<i>bdl</i>	-	-	-	-	-	-
La	-	-	-	-	-	-	-	-	-	-	-
Ce	-	-	-	-	-	-	-	-	-	-	-
Nb	-	-	-	-	-	-	-	-	-	-	-
<b>Sum</b>	<b>9.02</b>	<b>8.96</b>	<b>9.00</b>	<b>8.98</b>	<b>8.82</b>	<b>8.99</b>	<b>9.02</b>	<b>9.01</b>	<b>8.99</b>	<b>9.02</b>	<b>9.01</b>
K <sub>alk</sub>	21.42	21.29	21.78	21.80	19.55	21.83	22.20	22.17	21.89	22.28	22.06

**Table 2** Average detection limits and errors for Terceira dalyite analyses

	<b>Detection limit (wt. %)</b>	<b>Oxide error (wt. %)</b>	<b>Formula error (apfu)</b>
SiO <sub>2</sub>	0.034	0.326	0.045
TiO <sub>2</sub>	0.038	0.054	0.004
Al <sub>2</sub> O <sub>3</sub>	0.020	0.027	0.003
Cr <sub>2</sub> O <sub>3</sub>	0.023	bdl	bdl
FeO	0.038	0.052	0.004
MnO	0.022	0.030	0.002
MgO	0.020	0.024	0.003
CaO	0.024	bdl	bdl
Na <sub>2</sub> O	0.046	0.078	0.015
K <sub>2</sub> O	0.021	0.199	0.026
ZrO <sub>2</sub>	0.062	0.524	0.025
HfO <sub>2</sub>	0.032	0.055	0.002
BaO	0.045	0.073	0.003
Total		0.661	

bdl = all values below detection limit

**Table 3** Comparison of experimental and calculated lattice parameters

<b>Lattice parameter</b>	<b>Experimental</b>	<b>Calculated</b>	<b>% difference</b>
a/Å	7.371	7.211	-2.17
b/Å	7.730	7.679	-0.66
c/Å	6.912	6.787	-1.80
$\beta$ /degrees	106.23	104.82	-1.33

**Table 4** Whole rock major element analyses of the CCI syenite ejecta

<b>Sample</b>	<b>TER 30-1</b>	<b>TER 35-1</b>	<b>TER 30-6</b>	<b>TER 30-7</b>
SiO <sub>2</sub>	64.14	64.78	63.90	64.80
TiO <sub>2</sub>	0.58	0.45	0.61	0.41
Al <sub>2</sub> O <sub>3</sub>	15.76	15.51	15.82	16.18
Fe <sub>2</sub> O <sub>3</sub>	5.34	5.29	5.57	4.53
MnO	0.21	0.20	0.22	0.17
MgO	0.36	0.27	0.36	0.27
CaO	0.82	0.44	0.76	0.54
Na <sub>2</sub> O	7.44	7.41	7.36	7.25
K <sub>2</sub> O	4.93	5.11	4.98	5.10
P <sub>2</sub> O <sub>5</sub>	0.08	0.06	0.07	0.05
LOI	0.10	0.30	0.10	0.40
Total	99.76	99.82	99.75	99.70
A.I.	1.12	1.14	1.11	1.08
Na <sub>2</sub> O/K <sub>2</sub> O	1.51	1.45	1.48	1.42
<b>CIPW</b>				
Q	1.52	3.33	1.00	2.42
Or	29.25	30.32	29.55	30.14
Ab	53.76	51.58	53.84	54.83
An	0.00	0.00	0.00	0.00
Di	3.08	1.57	2.88	2.06
Hy	4.40	5.05	4.54	5.55
Ac	6.02	5.64	6.10	2.05
Il	1.10	0.85	1.16	0.78
Ap	0.19	0.14	0.16	0.12
NaS	0.61	1.18	0.41	0.97

**Table 5** Electron microprobe analyses of dalyite from CCI syenite ejecta

Sample Group	TER 30-1 1	TER 30-1 1	TER 30-1 1	TER 30-1 1	TER 30-1 1	TER 30-7 1	TER 30-7 1	TER 30-7 1	TER 30-7 1	TER 30-7 1	TER 30-7 1	TER 30-7 1
Suggested origin	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic	Magmatic
SiO <sub>2</sub>	62.9	62.6	62.4	62.2	62.4	62.9	63.0	62.4	62.6	62.6	63.0	63.0
TiO <sub>2</sub>	0.10	0.23	0.19	0.13	0.11	0.17	0.10	0.12	0.41	0.09	0.06	0.27
Al <sub>2</sub> O <sub>3</sub>	<i>bdl</i>	<i>bdl</i>	0.03	0.03	<i>bdl</i>	<i>bdl</i>	0.04	0.04	0.05	0.03	<i>bdl</i>	<i>bdl</i>
Cr <sub>2</sub> O <sub>3</sub>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
FeO	<i>bdl</i>	0.06	<i>bdl</i>	0.06	0.09	<i>bdl</i>	0.07	0.07	0.11	0.05	0.06	<i>bdl</i>
MnO	<i>bdl</i>	0.03	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.04	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
MgO	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.03	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
CaO	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
Na <sub>2</sub> O	0.99	0.95	0.99	1.00	0.90	0.90	0.67	0.71	0.67	0.72	0.66	0.66
K <sub>2</sub> O	14.6	15.0	14.9	14.8	14.7	14.8	15.0	15.0	15.0	15.2	15.3	15.1
ZrO <sub>2</sub>	20.0	20.5	19.8	20.4	20.4	20.4	19.7	20.3	19.1	20.0	20.6	20.2
HfO <sub>2</sub>	0.46	0.40	0.38	0.40	0.39	0.45	0.39	0.39	0.42	0.42	0.48	0.38
BaO	0.06	0.06	0.08	<i>bdl</i>	<i>bdl</i>	0.05	0.08	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
<b>Total</b>	<b>99.08</b>	<b>99.78</b>	<b>98.81</b>	<b>98.89</b>	<b>98.98</b>	<b>99.72</b>	<b>98.99</b>	<b>99.05</b>	<b>98.33</b>	<b>99.01</b>	<b>100.17</b>	<b>99.57</b>
Si	6.05	6.01	6.03	6.01	6.02	6.03	6.06	6.02	6.05	6.04	6.02	6.04
Ti	0.007	0.016	0.013	0.009	0.008	0.012	0.008	0.009	0.030	0.006	0.004	0.019
Al	<i>bdl</i>	<i>bdl</i>	0.004	0.003	<i>bdl</i>	<i>bdl</i>	0.005	0.004	0.006	0.004	<i>bdl</i>	<i>bdl</i>
Cr	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
Fe	<i>bdl</i>	0.005	<i>bdl</i>	0.004	0.007	<i>bdl</i>	0.005	0.006	0.009	0.004	0.005	<i>bdl</i>
Mn	<i>bdl</i>	0.002	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.004	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
Mg	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	0.004	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
Ca	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
Na	0.18	0.18	0.18	0.19	0.17	0.17	0.13	0.13	0.13	0.13	0.12	0.12
K	1.79	1.84	1.83	1.82	1.81	1.81	1.84	1.85	1.85	1.87	1.87	1.85
Zr	0.94	0.96	0.93	0.96	0.96	0.95	0.92	0.96	0.90	0.94	0.96	0.94
Hf	0.013	0.011	0.010	0.011	0.011	0.012	0.011	0.011	0.011	0.012	0.013	0.010
Ba	0.002	0.002	0.003	<i>bdl</i>	<i>bdl</i>	0.002	0.003	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>	<i>bdl</i>
<b>Sum</b>	<b>8.982</b>	<b>9.026</b>	<b>9.000</b>	<b>9.007</b>	<b>8.986</b>	<b>8.986</b>	<b>8.982</b>	<b>8.994</b>	<b>8.990</b>	<b>9.006</b>	<b>8.992</b>	<b>8.979</b>
K <sub>alk</sub>	21.98	22.34	22.39	22.32	22.06	21.99	21.90	22.03	21.98	22.27	22.13	21.94

**Table 6** Results of computer modelling undertaken using the GULP code (Gale, 1997)

Substitution	Solution scheme	E <sub>sol</sub> (eV)
Ti → Zr	TiO <sub>2</sub> + Zr <sub>Zr</sub> → Ti <sub>Zr</sub> + ZrO <sub>2</sub>	-0.25
Ti → Si	TiO <sub>2</sub> + Si <sub>Si</sub> → Ti <sub>Si</sub> + SiO <sub>2</sub>	-0.98
Ti → K	TiO <sub>2</sub> + 4K <sub>K</sub> → Ti <sub>K</sub> <sup>•••</sup> + 3V <sub>K</sub> <sup>'</sup> + 2K <sub>2</sub> O	30.64
Hf → Zr	HfO <sub>2</sub> + Zr <sub>Zr</sub> → Hf <sub>Zr</sub> + ZrO <sub>2</sub>	-0.31
Hf → Si	HfO <sub>2</sub> + Si <sub>Si</sub> → Hf <sub>Si</sub> + SiO <sub>2</sub>	2.67
Hf → K	HfO <sub>2</sub> + 4K <sub>K</sub> → Hf <sub>K</sub> <sup>•••</sup> + 3V <sub>K</sub> <sup>'</sup> + 2K <sub>2</sub> O	29.09
Fe <sup>2+</sup> → Zr	FeO + Zr <sub>Zr</sub> → Fe <sub>Zr</sub> <sup>''</sup> + V <sub>O</sub> <sup>••</sup> + ZrO <sub>2</sub>	12.52
Fe <sup>2+</sup> → Si	FeO + Si <sub>Si</sub> → Fe <sub>Si</sub> <sup>''</sup> + V <sub>O</sub> <sup>••</sup> + SiO <sub>2</sub>	13.69
Fe <sup>2+</sup> → K	FeO + K <sub>K</sub> → Fe <sub>K</sub> <sup>•</sup> + V <sub>K</sub> <sup>'</sup> + K <sub>2</sub> O	8.86
Mg <sup>2+</sup> → Zr	MgO + Zr <sub>Zr</sub> → Mg <sub>Zr</sub> <sup>''</sup> + V <sub>O</sub> <sup>••</sup> + ZrO <sub>2</sub>	12.97
Mg <sup>2+</sup> → Si	MgO + Si <sub>Si</sub> → Mg <sub>Si</sub> <sup>''</sup> + V <sub>O</sub> <sup>••</sup> + SiO <sub>2</sub>	14.07
Mg <sup>2+</sup> → K	MgO + K <sub>K</sub> → Mg <sub>K</sub> <sup>•</sup> + V <sub>K</sub> <sup>'</sup> + K <sub>2</sub> O	9.61
Ba <sup>2+</sup> → Zr	BaO + Zr <sub>Zr</sub> → Ba <sub>Zr</sub> <sup>''</sup> + V <sub>O</sub> <sup>••</sup> + ZrO <sub>2</sub>	12.54
Ba <sup>2+</sup> → Si	BaO + Si <sub>Si</sub> → Ba <sub>Si</sub> <sup>''</sup> + V <sub>O</sub> <sup>••</sup> + SiO <sub>2</sub>	16.58
Ba <sup>2+</sup> → K	BaO + K <sub>K</sub> → Ba <sub>K</sub> <sup>•</sup> + V <sub>K</sub> <sup>'</sup> + K <sub>2</sub> O	4.94