



Title	The magmatic–hydrothermal transition in rare-element pegmatites from southeast Ireland: LA-ICP-MS chemical mapping of muscovite and columbite–tantalite
Authors(s)	Kaeter, David, Barros, Renata, Menuge, Julian, Chew, David M.
Publication date	2018-11-01
Publication information	Kaeter, David, Renata Barros, Julian Menuge, and David M. Chew. “The Magmatic–Hydrothermal Transition in Rare-Element Pegmatites from Southeast Ireland: LA-ICP-MS Chemical Mapping of Muscovite and Columbite–Tantalite.” Elsevier, November 1, 2018. https://doi.org/10.1016/j.gca.2018.08.024 .
Publisher	Elsevier
Item record/more information	http://hdl.handle.net/10197/10522
Publisher's statement	This is the author’s version of a work that was accepted for publication in <i>Geochimica et Cosmochimica Acta</i> . Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in <i>Geochimica et Cosmochimica Acta</i> (240, (2018)) https://doi.org/10.1016/j.gca.2018.08.024
Publisher's version (DOI)	10.1016/j.gca.2018.08.024

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The magmatic–hydrothermal transition in rare-element pegmatites from southeast Ireland: LA-ICP-MS chemical mapping of muscovite and columbite–tantalite

David Kaeter^{a,b,*}, Renata Barros^b, Julian F. Menuge^{a,b}, David M. Chew^{a,c}

^a*Irish Centre for Research in Applied Geosciences (iCRAG), University College Dublin, Dublin 4, Ireland*

^b*School of Earth Sciences, University College Dublin, Dublin 4, Ireland*

^c*Department of Geology, School of Natural Sciences, Trinity College Dublin, Dublin 2, Ireland*

*Corresponding author. E-mail address: david.kaeter@icrag-centre.org

Abstract

The processes involved in the magmatic–hydrothermal transition in rare-element pegmatite crystallization are obscure, and the role of hydrothermal mechanisms in producing economic concentrations of rare elements such as tantalum remains contentious. To decipher the paragenetic information encoded in zoned minerals crystallized during the magmatic–hydrothermal transition, we applied SEM-EDS and LA-ICP-MS chemical mapping to muscovite- and columbite-group minerals (CGM) from a rare-element pegmatite of the albite-spodumene subtype from Aclare, southeast Ireland.

We present a three-stage model for the magmatic–hydrothermal transition based on petrography, imaging and quantification of rare-element (Li, B, Rb, Nb, Sn, Cs, Ba, Ta, W, U) zoning, integrated with geochemical modeling and constraints from published literature. Stage I marks the end of purely magmatic crystallization from a peraluminous granitic melt. In stage II, polymerized silicic melt and depolymerized alkaline aqueous melt coexist as immiscible media, both of which influence muscovite and CGM crystallization. Stage II also marks the onset of phyllic alteration of primary mineral assemblages. Hydrothermal fluid release causes further resorption of primary minerals and eventual precipitation of fine-grained albite in stage III.

Muscovite and CGM both exhibit trace-element zoning, while CGM also show major-element zoning. Petrographic relationships and geochemical markers such as $Ta\#$ ($=Ta/[Ta+Nb]$) of individual mineral zones reveal that both mineral species crystallized contemporaneously over all three stages. Furthermore, Rayleigh fractional crystallization of muscovite is efficient in fractionating Ta from Nb. Tantalum and Nb are additionally fractionated by halogen-rich aqueous media, which remobilize both elements, but redeposit

37 preferentially Ta-enriched oxides. Columbite–tantalite mineralization is therefore both
38 magmatic and hydrothermal. Albite associated with stage-III muscovite and CGM was likely
39 precipitated from a hydrothermal fluid when pH changed due to hydrolysis of primary
40 minerals. The complex zoning and resorption of minerals indicates that bulk analyses and
41 conventional LA-ICP-MS spot ablation analyses of muscovite in rare element pegmatites
42 may lead to erroneous modelling of element partitioning and fluid evolution.

43 Combined petrographic and high-resolution geochemical analysis of two mineral
44 species (which co-crystallize and incorporate the same elements of interest) is an effective
45 tool to assess the complex processes of crystal–melt–fluid interaction. Our three-stage model
46 may also be applicable to the still not well understood magmatic–hydrothermal transition
47 from fertile granitic melts to formation of Sn-W veins and greisens or porphyry-type deposits.

48

49 **1. Introduction**

50

51 Understanding mineralization processes is essential for the exploration and optimal
52 exploitation of rare-element pegmatites for metals such as lithium (Li) or tantalum (Ta)
53 (Černý and Ercit 1989). While Li can be extracted from other sources like brine deposits, Ta
54 is mainly sourced from rare-element granites and pegmatites or from placer deposits derived
55 therefrom. Even though the growth in Ta demand has waned since 2000 (Nassar, 2017), Ta
56 remains an important strategic raw material widely used in automobile parts, consumer
57 electronics and high-performance alloys (Linnen et al., 2014). However, controls on Ta in
58 pegmatites and the fractionation of Ta from niobium (Nb) as well as the influence of
59 hydrothermal processes are still not well understood (Van Lichtervelde et al., 2008). Based
60 on experimental work (Linnen, 1998) and observations from Li-Cs-Ta-enriched (LCT)
61 pegmatites at Brazil Lake in Nova Scotia, Canada, Kontak (2006) proposed that the main
62 phase of Nb–Ta mineralization crystallized from a sodium-enriched residual melt after
63 crystallization of primary minerals. Tantalum mineralization associated with albitization of
64 alkali feldspar is common in LCT pegmatites and the abundant occurrence of such
65 replacement bodies is used as an indicator for economic Ta potential (Möller and Morteani,
66 1987).

67 Secondary Ta oxides potentially associated with late hydrothermal alteration and
68 formation of quartz and muscovite can be found in several LCT pegmatites worldwide (e.g.
69 Foord and Cook, 1989; Partington et al., 1995; Lumpkin, 1998; Sweetapple and Collins,
70 2002; Van Lichtervelde et al., 2008; Anderson et al., 2013). Many of these studies are based

71 on petrographic observations, but the common textural complexity of pegmatites impedes a
72 clear differentiation of primary from secondary textures (Van Lichtervelde et al., 2008).
73 Nevertheless, the consensus is that the main Ta mineralization stage appears late in the
74 pegmatite-forming process. Most researchers agree that fluid exsolution occurs during
75 pegmatite formation, which is documented by miarolitic cavities, fluid inclusions, as well as
76 stable isotope (H, B, O) fractionation (Thomas et al., 2012; Thomas and Davidson, 2013;
77 London, 2014; Siegel et al., 2016; Thomas and Davidson, 2016). However, the timing of
78 fluid release is still debated. Furthermore, the significance of melt–melt immiscibility and
79 fluid exsolution for rare-element mineralization in pegmatites remains contentious (Thomas
80 et al., 2012; Siegel et al., 2016)

81 Characterizing the chemical variation in zoned minerals using modern *in-situ* micro-
82 analytical methods can yield important constraints on changes in crystallization conditions in
83 magmatic, metasomatic and hydrothermal systems (Ginibre et al., 2007). Micas are ideal for
84 this type of approach. They are the third most common mineral group in granitic pegmatites
85 (Hawthorne and Černý, 1982), are stable over a wide range of physicochemical environments
86 (Tischendorf et al., 1997), and incorporate many rare elements such as Li, Be, B, Rb, Cs, Ba,
87 Sn, Nb and Ta (Fleet et al., 2003), which are indicators of geochemical evolution.
88 Furthermore, muscovite may maintain chemical equilibrium with melt due to fast
89 recrystallization under conditions close to the liquidus (London, 2005). Therefore, mica
90 geochemistry in lithium pegmatites has been studied widely (e.g. Jolliff et al., 1987; Roda-
91 Robles et al., 1995; Wise, 1995; Pesquera et al., 1999; Neiva, 2013; Marchal et al., 2014).

92 Geochemical analysis of mica is also an important exploration tool for Ta-rich
93 pegmatites (Selway et al., 2005) as empirical data show that mean concentrations of >65–
94 70 ppm Ta and >500 ppm Cs in muscovite indicate high potential for economic Ta
95 mineralization (Gordiyenko, 1971; Morteani and Gaupp, 1989; Selway et al., 2005). A
96 decreasing K/Rb ratio over a suite of muscovite samples is a marker for increasing
97 fractionation and typically coupled with increasing concentrations of incompatible elements
98 (Černý and Burt, 1984). However, although trace elements in micas are routinely analyzed in
99 rare-element pegmatite exploration studies, published data for Sn and high-field-strength
100 elements (HFSE: Zr, Nb, Hf, Ta, W, U) are rare, and most studies employ bulk analyses of
101 mica separates. Such analyses cannot detect internal zoning, multiple generations of mica
102 growth or mineral inclusions within mica crystals, and hence high-resolution *in-situ* micro-
103 analytical methods are preferable (see also Van Lichtervelde et al., 2008; Roda-Robles et al.,
104 2012).

105 Columbite group minerals (CGM, columbite–tantalite, $[\text{Mn,Fe}][\text{Ta,Nb}]_2\text{O}_6$), which
106 are the main economic host for Ta in rare-element pegmatites (Linnen et al., 2012), are also
107 potentially useful targets for studying melt evolution. These oxides are usually strongly
108 zoned, exhibiting a wide range of chemical compositions. They typically show signs of
109 partial digestion and later overgrowths, and appear to grow during all stages of pegmatite
110 formation (Černý and Ercit, 1985; Lahti, 1987; Mulja et al., 1996; Tindle and Breaks, 2000).
111 Oscillatory zoning and irregular or patchy zoning are common, and magmatic CGM usually
112 show zoning trends with increasing Mn# ($=\text{Mn}/[\text{Mn}+\text{Fe}]$) and Ta# ($=\text{Ta}/[\text{Ta}+\text{Nb}]$) from core
113 to rim, referred to as normal zoning (Lahti, 1987). Increasing Mn# and Ta# is typically
114 coupled with increasing fractionation of the pegmatite-forming melt (Linnen and Cuney,
115 2005; and references therein). While it is commonly assumed that Ta# is directly coupled to
116 fractional crystallization of CGM, Stepanov et al. (2014) demonstrated that Ta# can be
117 controlled by partial melting and fractional crystallization of mica. Mn# is additionally
118 controlled by the crystallization of Mn-/Fe-bearing minerals (e.g. Linnen and Cuney, 2005;
119 Van Lichtervelde et al., 2006; Neiva, 2013). Besides major element zoning, trace element
120 zoning is also likely, but again *in-situ* trace element analyses of CGM are rare.

121 *In-situ* analysis of major and minor elements is routinely achieved with high spatial
122 resolution ($<5\ \mu\text{m}$) using scanning electron microscopy (SEM) or electron probe
123 microanalysis. Laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS)
124 can achieve significantly better detection limits and is hence preferable for many *in-situ* trace
125 element analyses (Ubide et al., 2015; Sylvester and Jackson, 2016). Conventional LA-ICP-
126 MS spot ablation analyses employ laser pit diameters of 30–50 μm and tens of micrometers
127 depth, often larger than CGM growth zones. This can be circumvented by recent advances in
128 high-resolution spatial LA-ICP-MS chemical mapping (e.g. Ubide et al., 2015).

129 In this study, we applied the quantitative LA-ICP-MS chemical mapping approach to
130 white mica and CGM from a rare-element pegmatite from Aclare, southeast Ireland. We
131 compare intra- as well as inter-grain element patterns and test whether trace element
132 variations in muscovite, which crystallizes during the entire magmatic–hydrothermal
133 transition, can be explained by Rayleigh fractional crystallization. These data are integrated
134 with petrographic information and correlation of white mica and CGM geochemistry to
135 produce a crystallization model for the magmatic–hydrothermal transition in the studied drill
136 core.

137

138 2. Geologic setting, previous studies, and sample material

139

140 The Leinster pegmatite belt is located at the eastern margin of the Caledonian S-type
141 Leinster Batholith in southeast Ireland. The LCT pegmatite dikes are of the albite-spodumene
142 sub-type (Černý and Ercit, 2005) and were intruded along the contact zone between the
143 Leinster Batholith and Ordovician metasedimentary rocks (Fig. 1). The dikes strike NE-SW
144 and were emplaced along the regional East Carlow Deformation Zone (ECDZ). The ECDZ is
145 characterized by dip-slip ductile shear expressed by strong foliation of both granite and
146 schist, parallel to the earlier S_1 regional cleavage (McArdle and Kennedy, 1985). No evidence
147 has been found for significant metamorphic or tectonic overprinting of the Leinster rare-
148 element pegmatites (McArdle and Kennan, 1988), which simplifies interpretation of the
149 pegmatite-forming processes.

150 The Leinster pegmatite belt has been the target of exploration drilling and academic
151 research since the 1970s (e.g. Steiger and von Knorring, 1974; Luecke, 1981; O'Connor et al.,
152 1991). Barros and Menuge (2016) provide a lithological description of the pegmatites and
153 their host rocks at Aclare and Moylisha. However, rare-element and specifically Nb–Ta
154 mineralization has received little attention in earlier studies.

155 Earlier studies have proposed that the pegmatites crystallized from highly fractionated
156 residual melts of Li-enriched granitic magma (O'Connor et al., 1991). However recent
157 geochemical modelling has shown that this mechanism is unlikely and the pegmatite melt
158 probably formed from anatexis of metasediments (Barros and Menuge, 2016). An anatectic
159 origin by partial melting of metasediments in the ECDZ was also postulated by McArdle and
160 Kennan (1992).

161 The samples in this study are from a ~10-m-long drill core interval from Aclare
162 (provided by Blackstairs Lithium Ltd, core ACL13-05, ~60 m in total), where several albite-
163 spodumene pegmatite dikes up to ~20 meters thick intrude foliated granodiorite and
164 andalusite-bearing quartz-mica schist. The albite-spodumene pegmatites at Aclare were
165 examined in hundreds of meter of drill core, in boulders and in over 100 thin sections made
166 from this material. Blackstairs Lithium Ltd provided litho-geochemistry data. Samples for this
167 study were selected based on textural features such as replacement or overprint of early
168 pegmatitic units as well as high concentrations of rare-elements such as Be, Rb, Mn, Sn, Cs,
169 and Ta, characteristic of the most evolved parts of the pegmatite. Albitite associated with
170 CGM and cassiterite is abundant, and albitization of microcline as well as muscovitization of
171 spodumene are evident. Following petrographic and mineralogical characterization (optical

172 microscopy, SEM coupled with energy-dispersive X-ray spectroscopy [EDS]) of 100 μm -
173 thick polished thin sections, two representative thin sections of the albitized parts and one
174 thin section of a coarse-grained quartz–muscovite assemblage were selected for LA-ICP-MS
175 chemical mapping.

176

177 3. Analytical methods

178

179 3.1. SEM-EDS

180

181 Back-scattered electron (BSE) imaging and quantitative major-element analyses of
182 white mica, albite, alkali feldspar, and CGM were carried out at the iCRAG laboratory at
183 Trinity College Dublin (TCD).

184 Silicates were analyzed using a Tescan TIGER Mira III field-emission (FE) SEM
185 equipped with two Oxford X-Max^N 150 mm² EDS detectors. The instrument was calibrated
186 using natural minerals (albite [Na, Al, Si], apatite [Ca, P, F], almandine [Fe, Mg], orthoclase
187 [K], pollucite [Cs]) and synthetic rubidium titanium phosphate (Rb). The reference materials
188 were prepared by Astimex Standards Ltd, Toronto, Canada.

189 Columbite group minerals were analyzed using a Tescan Mira II FE SEM. The
190 microscope is equipped with an Oxford X-Max^N 150 mm² EDS detector. The instrument was
191 calibrated using pyrite (for Fe) and pure metals (Mn, Ta, Nb). The reference materials were
192 prepared by Micro-Analysis Consultants Ltd, Cambridgeshire, United Kingdom.

193 With both instruments, quantitative analyses were performed at 20 kV acceleration
194 voltage and ~ 0.3 nA beam current. Energy-dispersive X-ray spectra with at least 3,000,000
195 total counts per spectrum were acquired using the Oxford Aztec software with a process time
196 setting of 5. The working distances (WD) were 15 mm (TIGER) and 18 mm (Mira II). Before
197 each measurement, samples were focused using the z-control of the SEM stage without
198 changing the WD. Detection limits were below 0.1 wt% for most elements. Beam calibration
199 was performed on cobalt metal. Polished samples, reference materials, and cobalt metal were
200 carbon coated (~ 13 nm) before analysis.

201 Reproducibility of major element silicate analyses using the TIGER SEM was
202 monitored over 6 months using stoichiometric diopside ($n = 8$) and orthoclase ($n = 6$) as
203 quality control materials. The standard deviation (1σ) for SiO_2 in both minerals over this time
204 period is below 1%. The data quality of quantitative SEM-EDS data presented in this study is
205 assessed in more detail in Supplementary Note A.2.

206

207 *3.2. LA-ICP-MS chemical mapping*

208 Trace element mapping was carried out with a Photon Machines Analyte Excite
209 193 nm ArF Excimer laser-ablation system with a Helex 2-volume ablation cell coupled to an
210 Agilent 7900 quadrupole ICP-MS at the iCRAG laboratory at TCD.

211 White mica and alkali feldspar were mapped using a suite of fifteen isotopes (^7Li , ^{11}B ,
212 ^{23}Na , ^{27}Al , ^{28}Si , ^{39}K , ^{47}Ti , ^{55}Mn , ^{71}Ga , ^{85}Rb , ^{93}Nb , ^{118}Sn , ^{133}Cs , ^{137}Ba , ^{181}Ta). A modified set
213 of isotopes (^7Li , ^{11}B , ^{28}Si , ^{39}K , ^{45}Sc , ^{47}Ti , ^{85}Rb , ^{89}Y , ^{93}Nb , ^{118}Sn , ^{133}Cs , ^{137}Ba , ^{181}Ta , ^{182}W ,
214 ^{238}U) was acquired while mapping CGM, which was also used for one white mica
215 experiment. The laser repetition rate was 55 Hz and the fluence was 3.9 J/cm^2 for all
216 experiments. The mass spectrometer was tuned using line scans on NIST612 glass reference
217 material (Jochum et al., 2011) to yield stable Th/U ratios of unity and low oxide production
218 rates at the beginning of each analytical session.

219 Element image maps were created by successively acquiring adjacent lines to produce
220 a rectangular mapped area. A square-shaped laser aperture was used with a laser spot
221 diameter (d_s) of 7, 10, or 18 μm depending on the size of the mineral area of interest. The
222 scan speed was either 10 $\mu\text{m/s}$ ($d_s = 7, 10 \mu\text{m}$) or 30 $\mu\text{m/s}$ ($d_s = 18 \mu\text{m}$). Each individual
223 experiment commenced and finished with two line scans on NIST610 glass (Jochum et al.,
224 2011), which was used as the primary reference material. The ablation depth is very shallow
225 ($< 1 \mu\text{m}$) as indicated in supplementary Fig. A.1 (Supplementary Note A.1), which is
226 assessed in greater detail in Ubide et al. (2015).

227 The Iolite v3 software (Paton et al., 2011) was used for data reduction and production
228 of trace element images. The data was processed using a modified version of Iolite's
229 "Trace_Elements" data reduction scheme (DRS) (Ubide et al., 2015). Besides data reduction
230 for trace element analyses, this modified DRS additionally allows calculation of elemental
231 ratios and generation of images therefrom. Silicon concentrations of white mica and feldspar
232 as determined by SEM-EDS were used as the internal standard for the calibration of silicate
233 LA-ICP-MS data. Due to strong CGM heterogeneity, CGM data was processed without an
234 internal standard element using the semi-quantitative mode of the same DRS. After data
235 reduction, trace element ratios were calculated, and images were created using the "Image
236 from integrations" feature of Iolite. A comprehensive description of the experimental setup
237 and data reduction can be found in Ubide et al. (2015).

238 The resulting semi-quantitative element concentrations in CGM were extracted by
239 defining regions of interest (ROIs), which can be regarded as 'pseudo-laser spots', in the

240 elemental image using the Iolite extension Monocle (Petrus et al., 2017) in small,
 241 homogenous areas (according to BSE imaging), where the major element chemistry had
 242 previously been determined by SEM-EDS. A correction factor was calculated by dividing the
 243 Ta concentration calculated with Iolite by the Ta concentration obtained by SEM-EDS ($f_c =$
 244 $[Ta]_{Iolite}/[Ta]_{SEM-EDS}$). This correction factor was then used to calculate the concentrations of
 245 the remaining elements ($[X] = [X]_{Iolite}/f_c$). Due to the large difference in Ta concentration
 246 between NIST610 (~446 ppm, Jochum et al., 2011) and the CGM in this study (15–40 wt%),
 247 as well as micron-scale inhomogeneities in CGM, these concentrations are regarded as semi-
 248 quantitative, but relative differences in trace element zoning are unaffected.

249 The fully quantitative white mica data was extracted by defining ROIs which
 250 correspond to distinct crystal zones using Monocle. This data was then utilized to compare
 251 the compositions of different growth zones and evaluate fractionation trends within single
 252 crystals, as well as between the three samples. Example muscovite ROIs are shown in
 253 supplementary Fig. A.2 (Supplementary Note A.1) The boundaries of each zone and the outer
 254 portions of the grain rim were avoided to prevent extracting mixed signals from adjacent
 255 zones or the matrix. Additional ROIs were defined to extract whole-grain compositions. The
 256 whole-grain data is compared to K and minor-element data from SEM-EDS in
 257 Supplementary Note A.3. Most deviations between the two data sets can be explained by the
 258 low precision of SEM-EDS for minor elements. However, analyses of the major element K
 259 are more accurate using SEM-EDS. Therefore, the K LA-ICP-MS data used for element
 260 ratios was adjusted by linear regression of the two data sets as described in Supplementary
 261 Note A.3. Errors presented for LA-ICP-MS data are 2 standard errors (2SE) for the average
 262 concentration of individual ROIs.

263

264 **4. Mineralogy**

265

266 The studied drill core interval can be subdivided into three lithologies: a) a coarse
 267 pegmatitic mineral assemblage (Fig. 2a) characterized by variable proportions of centimeter-
 268 scale quartz (20–50%), muscovite (10–50%), spodumene (0–20%) and perthitic microcline
 269 (0–35%); b) a fine-grained (usually < 1 mm) albitite (Fig. 2b) comprising lath-shaped albite
 270 (>85–90%) with quartz and yellow muscovite; and c) assemblages with equal proportions of
 271 coarse dark-green muscovite and dark gray quartz (5–20 mm, Fig. 2c) that comprise ~10% of
 272 the pegmatite drill core intersection, which are typically interfingered with or pervaded by
 273 albitite. Spodumene in (a), muscovite (a, b) and albite (b) are preferentially aligned

274 subparallel to the pegmatite contact and the granodiorite country-rock foliation. Muscovite
275 shows generally very pronounced cleavage planes; violet fluorite along cleavage planes
276 occurs in some grains. Apart from rare fine-grained epitaxial overgrowths, muscovite appears
277 optically homogenous. Accessories in all lithologies include fine-grained (<2 mm) dark blue
278 anhedral to subhedral Mn-rich F-apatite, colorless beryl, orange spessartine garnet, zircon,
279 and interstitial brown sphalerite.

280 A distinct lithological zonation with paragenetic changes from border to center often
281 observed in other granitic pegmatites is absent in this drill core intersection. However,
282 spodumene crystallized early assuming crystallization from the outer contact towards the
283 center of the pegmatite, because the main spodumene-bearing interval (~15% over 2.5 m) is
284 located close to the hanging wall.

285 The term sodic aplite is sometimes used to refer to parts of granitic pegmatites formed
286 by late or secondary albitization (lithology b), but this can lead to confusion with aplites in
287 pegmatite borders. For clarity and consistency, *albitite* will be used in the following to refer
288 to the fine-grained lithology, which is dominated (usually >90%) by platy or lath-shaped
289 albite associated with replacement of primary minerals.

290 In the pegmatitic lithology (a), quartz exhibits undulose extinction and common
291 recrystallization. Microcline shows diffuse crosshatch twinning, albite its typical lamellar
292 twinning and spodumene simple twinning parallel to the long axis of elongate-prismatic
293 crystals. Tabular and anhedral CGM (<2000 μm) occur associated with muscovite and
294 microcline. In albitite (b), lath-shaped, tabular and irregular CGM (20–2000 μm) as well as
295 other Nb–Ta–Sn oxides, such as microlite and wodginite, can occur disseminated or in high
296 local abundance (0–3% total). Albitite is located near the upper and lower margins and is
297 common throughout the whole drill core interval. Replacement textures are preserved
298 especially close to the borders. These textures include albitization and muscovitization of
299 microcline and pseudomorphic replacement of spodumene by fine-grained green muscovite.
300 However, albitite without remnant minerals is also abundant throughout the drill core
301 intersection.

302 Foliated granite shows about 2–3 cm of greisenization at pegmatite contacts. Here,
303 granodiorite feldspar and biotite are increasingly replaced by white mica towards the
304 pegmatite body. The alignment of white mica is parallel to the granodiorite foliation.
305 Additionally, dark brown tourmaline is observed in granodiorite close to the pegmatite
306 contacts.

307 Petrographic features of the three pegmatite samples studied in more detail using LA-
308 ICP-MS are described in the following subsections.

309

310 4.1. *Upper border albitite (UB-A)*

311 Sample UB-A is located near the upper border and consists only of lithology (b). It
312 comprises coarse-grained tabular (~20%, 1000–2000 μm) and fine-grained lath-shaped albite
313 (~50%, 50–500 μm), tabular muscovite (10–15%, 500–2000 μm), anhedral quartz (10%,
314 500–2000 μm) and coarse subhedral spessartine-rich garnet (<1%, ~1500 μm). Albite shows
315 micro-porosity at high SEM magnification (Fig. 3a, inset). Subhedral elongate-prismatic
316 CGM (100–400 μm , Fig. 3a) are commonly associated with albite, while irregular CGM
317 (100–300 μm) are coeval with coarse muscovite. Tantalum-enriched rims as expressed by
318 higher BSE intensity (Fig. 3a, arrow) are observed for most CGM associated with albitite.
319 Furthermore, some CGM exhibit replacement or overgrowth by microlite (Fig. 3b) and
320 wodginite. Additional accessories are interstitial Mn-rich F-apatite and irregularly-zoned
321 sphalerite. Minor chalcopyrite, pyrite, uraninite, zircon and calcite occur especially as fillings
322 of cavities and fractures. Overall alignment of the crystals is subparallel to the pegmatite–
323 granodiorite contact. Several fractures crosscut the sample at a high angle to the primary
324 foliation. Associated with these fractures are quartz, sulfides, and secondary fine-grained
325 rose-colored mica overgrowing coarse-grained muscovite. Three muscovite grains, one of
326 which is coeval with CGM (Fig. 3c), were selected for LA-ICP-MS mapping.

327

328 4.2. *Quartz–muscovite assemblage (QM-A)*

329 Sample QM-A is located in the lower half of the drill core and consists mainly (80%)
330 of lithology (c). It is in contact with albitite at its lower end. Coarse-grained silvery dark-
331 green muscovite (5–20 mm) is embedded in a matrix of irregular translucent grey quartz
332 (~50:50). Opaque elongate inclusions between cleavage planes of muscovite are common.
333 Additional phases are rare anhedral colorless beryl and anhedral to subhedral dark orange
334 spessartine (1–2 mm and <1% each, Fig. 3d–e). Accessories include F-apatite, chalcopyrite,
335 pyrite and sphalerite. Isolated patches of albite laths (0.1–1 mm) occur sporadically on quartz
336 and muscovite grain boundaries. Some mica shows replacement by secondary mica (brighter
337 BSE intensity in Fig. 3d–e, arrows). The albititic part of the sample is similar to the fine-
338 grained portion of UB-A (see above). Muscovite in contact with the albitite (one map) as well
339 as inside the quartz–muscovite assemblage (two maps, one in contact with beryl, Fig. 3d)
340 were selected for LA-ICP-MS mapping.

341

342 *4.3. Lower border albitite (LB-A)*

343 In sample LB-A, which is located close to the footwall contact, coarse perthitic
344 microcline (25%, 3–20 mm) of lithology (a) occurs in a matrix of fine-grained albite laths
345 (50%, 0.1–1.5 mm, Fig. 3f) of lithology (b). Albite shows minute elongate-prismatic apatite
346 inclusions (5–25 μm). Microcline is fractured, with crystallization of a very fine-grained
347 intergrowth of rose-colored mica and quartz (20–40 μm , Fig. 3f, inset) along fractures. This
348 replacement is rarely observed for albite and the fractures often do not advance into adjacent
349 albite.

350 Albite laths are preferentially aligned subparallel to the pegmatite margin. No
351 preferred orientation is observed in albite surrounding microcline. Quartz is absent apart from
352 a patch of massive quartz (approx. 10% of the thin section) showing dynamic recrystallization
353 with grains up to 5 mm, associated with pegmatitic microcline. Coarse muscovite occurs as
354 anhedral crystals (up to 3 mm) between microcline and rarely as smaller anhedral flakes
355 (<1 mm) within the albitite matrix. Some muscovite is overgrown by fine-grained mica
356 (arrows in Fig. 3g). Rare zircon with uraninite-rich cores is associated with albite. Accessory
357 zoned sphalerite occurs interstitially.

358 Columbite–tantallite is common as elongate-prismatic subhedral crystals associated
359 with muscovite and microcline as well as within albitite. Grains associated with albitite
360 appear finer grained (50–150 μm , Fig. 4a) and show oscillatory zoning more distinctly than
361 CGM associated with pegmatitic muscovite and microcline (300–500 μm). Coarse CGM
362 appear more irregular, show patchy zoning and common truncation (Fig. 4c). Irregular zones
363 are also visible in CGM within the albite matrix, often overgrown by a Ta-enriched rim
364 (higher BSE intensity, Fig. 4a, arrow). Zoning seems more complex in CGM in this part of
365 the drill core than in the upper border albitite (UB-A), while microlite and other secondary
366 Nb–Ta–Sn oxides are absent. Two muscovite grains, three CGM, and part of a fractured
367 remnant microcline crystal with secondary mica and quartz were selected for LA-ICP-MS
368 mapping.

369

370 **5. Geochemical data**

371

372 Table 1 summarizes all samples and mineral grains analyzed. Mineral chemistry as
373 determined by SEM-EDS and LA-ICP-MS chemical mapping is presented in the following
374 subsections.

375

376 *5.1. Major element chemistry*

377

378 Individual grains were analyzed in at least three locations and the standard deviation
379 (1σ over n measurements) for major element concentrations over these measurements is
380 generally low (e.g. usually $<0.5\%$ for SiO_2). The standard deviation for minor elements near
381 the detection limit is high, because of low EDS intensities (low signal-to-noise-ratios) as well
382 as potential inhomogeneity for incompatible elements such as Rb and Cs.

383

384 *5.1.1. White mica*

385 Compositions of white mica from all samples are presented in Table 2. Apart from
386 rare alteration rims, which were avoided during analysis, muscovite in all samples is
387 homogenous within analytical precision regarding its major element composition.

388 Besides fine-grained muscovite filling fractures (LB-A-Ms-3), iron and fluorine
389 contents of primary muscovite are high ($\sim 1.4\text{--}3.5$ wt% FeO; $0.4\text{--}1.0$ wt% F). Furthermore,
390 muscovite from the quartz–muscovite assemblage (Q-MA) is richer in Fe and F than
391 muscovite associated with albitite (UB-A, LB-A). All samples are enriched in Rb and show
392 Cs near the EDS detection limit of 0.03 wt% Cs_2O . The secondary mica QM-A-Ms-2b shows
393 highest concentrations of Fe and F (8.81 wt% FeO; 4.37 wt% F) and elevated Mn and Cs.

394 Accuracy of the data for F, is a potential problem, because of a partial overlap of the F
395 $\text{K}\alpha$ peak with the Fe $\text{L}\alpha$ peak in the EDS spectrum. Therefore, we did not undertake
396 quantitative analysis and interpretation of the presented F data. For a detailed discussion, we
397 refer to Supplementary Notes A.2 and A.3.

398

399 *5.1.2. Feldspar*

400 Compositions of albite (Ab) and microcline (Kfs) in sample LB-A are shown in
401 Table 3. Cation totals are close to stoichiometric formulae. Albite (Ab₉₉) shows little
402 variation. Microcline shows higher variability (Or_{91–94}) with up to 0.4 wt% P_2O_5 and
403 detectable amounts of Cs and Rb, but signal-to-noise ratios were too low for quantification.

404

405 *5.1.3. Columbite group minerals*

406 As mentioned in 3.2, data for CGM were derived from sum spectra over small
407 homogenous areas (according to BSE intensity), which are displayed in Fig. 4a–c (circles).
408 Apart from one measurement (LB-A-CGM-3-3), element oxide sums and cation calculations

409 presented in Table 4 are close to the stoichiometric formula of XY_2O_6 . The slightly elevated
410 cation sum for CGM-3-3 (3.05 apfu) might be caused by the presence of Fe^{3+} . Due to likely
411 inhomogeneity even within small areas of crystals, these data need to be handled with
412 caution. These small-scale variations become evident in Fig. 5, which shows a quantitative
413 line scan over LB-A-CGM-1 with $\sim 0.8 \mu m$ point spacing. The oscillatory zoning is clearly
414 defined by Ta# (solid red line), while the pattern for Mn# (dotted blue line) is less distinct.
415 Even within narrow zones that appear homogenous in BSE intensity, Mn# can vary strongly.
416 It is furthermore noticeable that the overall increase of Ta# from core to rim is accompanied
417 by generally decreasing Mn#, which slightly increases again within the rims.

418

419 *5.2 Minor and trace element maps*

420

421 Selected LA-ICP-MS chemical images of muscovite and CGM are shown and
422 described here for each sample while additional LA-ICP-MS images and accompanying
423 descriptions can be found in Supplementary Note B. Individual zones were defined based on
424 high gradients in concentrations of Cs and Sn, and Ta/Nb for muscovite, and Ta/Nb and other
425 HFSE (Sn, W, U) for CGM. The Ta/Nb ratio in muscovite is related primarily to variations in
426 Ta, as variations in Nb are less pronounced. The mean elemental concentrations of each zone
427 in every grain are summarized in supplementary tables ST1 (micas) and ST2 (CGM).

428

429 *5.2.1. Upper border albitite (UB-A)*

430 In muscovite UB-A-Ms-1, four distinct zones can be identified (Fig. 6). Texturally,
431 zone 1 comprises small euhedral triangular flakes, overgrown by zone 2, which shows an
432 irregular contact with subhedral zone 3. The large gradient in Cs concentration between zones
433 3 and 4, and the truncation of zone 3, suggest a hiatus in crystallization. The Ta/Nb ratio is
434 lowest in zone 1 (30 ppm/150 ppm = 0.20) and highest in zone 3 (90 ppm/109 ppm = 0.83).
435 Cesium and Rb are lowest in zone 4 (376 ppm and 3995 ppm) and highest in zone 2
436 (1359 ppm and 6788 ppm). Zoning of Na and Li appears independent of the zone boundaries
437 and varies between 3150–3490 ppm and 711–844 ppm, respectively. However, both are
438 depleted towards the margins, which correspond to the outer parts of zone 4. Ba shows an
439 enrichment in the margins from 46–63 ppm (zones 1–3) to 74 ppm (4).

440

441 5.2.2. *Quartz–muscovite assemblage (QM-A)*

442 Grain QM-A-Ms-2a is coarse-grained green muscovite in contact with beryl showing
 443 four zones (Fig. 7). Zone 1 comprises several grains of platy to elongate-prismatic mica,
 444 which are overgrown by subhedral zone 2, followed by irregular zones 3 and 4, which do not
 445 appear to be in contact with each other. Chemically, zone 1 is enriched in Li (3496 ppm), Rb
 446 (6193 ppm), Mn (3476 ppm), Sn (564 ppm), and especially Cs (2963 ppm). The second zone
 447 is characterized by decreasing concentrations of these elements but elevated Na (2532 ppm).
 448 Zone 3 has low concentrations of Li (2607 ppm), Rb (3545 ppm), Cs (442 ppm), Mn
 449 (2682 ppm) and Sn (433 ppm). The Ba concentration slightly increases from 45–52 ppm
 450 between zones 1 and 3. Zone 4 is similar to zone 3 in most elements, but shows the lowest Ba
 451 concentration (22 ppm). Zone 1 shows the highest Ta/Nb ($51 \text{ ppm}/100 \text{ ppm} = 0.51$) and zone
 452 4 the lowest ($42 \text{ ppm}/91 \text{ ppm} = 0.46$). The LA-ICP-MS data also show that the secondary Fe-
 453 rich mica QM-A-Ms2b, is enriched in Li (8325 ppm), Mn (5170 ppm) and Ta
 454 ($\text{Ta/Nb} = 54 \text{ ppm}/99 \text{ ppm} = 0.55$).

455

456 5.2.3. *Lower border albitite (LB-A) – White mica and microcline*

457 Muscovite LB-A-Ms-2 (Fig. 8) is a coarse grain in contact with remnant high-Ba
 458 microcline, secondary albite (low in all trace elements) and LB-A-Ms-CGM-3 (high Sc, Ti,
 459 Sn, W). It exhibits at least six distinct zones. Texturally, the core zone (zone 1) is anhedral
 460 and truncated by the subsequent zones. Zones 2–4 appear subhedral to euhedral, while zone 5
 461 shows an anhedral boundary. Zone 6 is a sub-epitaxial overgrowth of very fine-grained
 462 muscovite.

463 Geochemically, zone 1 is rich in Cs (1197 ppm) and low in Ti (169 ppm) and B
 464 (124 ppm). It shows a high Ta/Nb ratio ($69 \text{ ppm}/141 \text{ ppm} = 0.49$) associated with elongated
 465 inclusions parallel to the cleavage. Inclusions of plagioclase and quartz occur at the margin of
 466 zone 1, in the upper center of each image. Zones 2–4 are characterized by oscillating
 467 concentrations of B, Ti, Sn, Ba, Ta and W. Boron and Ba are high in zones 2 and 4 (143–
 468 175 ppm B, 9–16 ppm Ba), while Sn, W and Ta are depleted in these zones and are enriched
 469 in zone 3 (909 ppm Sn, 5.8 ppm W, $\text{Ta/Nb} = 118 \text{ ppm}/169 \text{ ppm} = 0.70$). Rb and Cs show
 470 progressive increase from 6356 ppm and 958 ppm in zone 2 to 6487 ppm and 1073 ppm in
 471 zone 4, respectively. Zone 5 is characterized by a drop in B (80 ppm), Rb (3323 ppm) and Cs
 472 (391 ppm), while Sc (~1 ppm), Ti (365 ppm), Ba (32 ppm), Ta (90 ppm) and W (4.8 ppm) are
 473 all elevated compared to zone 4. The Ba image shows that zone 5 appears in direct contact
 474 with microcline. Zone 6 is low in most elements except B (113 ppm). Lithium seems largely

475 independent of the zoning. However, it is highest in the core (928 ppm) and lowest along
 476 fractures as well as in zone 6 (603 ppm). Concentrations of Ta and to a lesser extent W are
 477 elevated in close proximity to LB-A-CGM-3, which is clearly visible in the Ta/Nb ratio
 478 (Fig. 8), possibly caused by diffusion along the steep concentration gradient between the two
 479 minerals. This area and high-Ta inclusions elsewhere were avoided when extracting the data.
 480 U and Y (not shown) are low and close to their detection limits. Slight enrichment in both
 481 elements is visible along fractures and grain boundaries.

482 Microcline LB-A-Kfs-1 (Fig. B.6a, Supplementary Note B) has low trace element
 483 contents, except for enrichment in Rb (~4200 ppm, K/Rb = 35) and Cs (~430 ppm).
 484 Furthermore, the analyzed grain is low in Li (17 ppm), B (12 ppm), Mn (~100 ppm), Ga
 485 (19 ppm), Sn (3.5 ppm) and Ba (90 ppm). Ta and Nb are below 1 ppm (Ta/Nb = 1.4).
 486 Secondary mica associated with fractures crosscutting microcline (LB-A-Ms-3), is too fine-
 487 grained to extract quantitative data. Furthermore, the concentrations are likely to be diluted
 488 because of the intimate intergrowth with quartz. Nevertheless, its composition can be
 489 described qualitatively based on the LA-ICP-MS images (Fig. B.6b): it is similar to zone 6 of
 490 LB-A-Ms-2 with 2000–2500 ppm Na, up to 200 ppm Ti, 50–70 ppm Ga, and 2000–
 491 3000 ppm Rb. However, it is poorer in Li (<200 ppm), Mn (<300 ppm), Nb (<10 ppm), Sn
 492 (<150 ppm) and Ta (<10 ppm).

493

494 5.2.4. Lower border albitite (LB-A) – Columbite–tantalite

495 The extensive zoning of CGM, visible in the BSE images (Fig. 4), is also observed in
 496 the minor- and trace-element maps (Fig. 9). For LB-A-CGM-1 (Fig. 9a), Ta/Nb corresponds
 497 well with intensity variations observed in the BSE image. Five zones were identified in
 498 CGM-1: zone 1 is high in Y (5 ppm), Ti (3130 ppm), Sn (1515 ppm), W (2175 ppm) and U
 499 (4890 ppm). Concentrations of these elements drop progressively towards zone 3, where they
 500 are lowest. Zone 4 is enriched again in Sn (1065 ppm) and Ti (1700 ppm). Zone 5 shows an
 501 enrichment in K (93 ppm), Sc (~9 ppm), and Y (1.5 ppm) and is enriched in Ti (1760 ppm)
 502 and W (575 ppm, up to 800 ppm) in the inner part of the zone. The Ta/Nb ratio increases in
 503 steps alternating with local minima from zone 2 to 5 as seen in the SEM-EDS data. Strong
 504 enrichment in K (>1400 ppm) at the left grain boundary might be caused by alteration.
 505 Lithium, Rb, Cs and Ba (not shown) are positively correlated with K.

506 LB-A-CGM-3 (Fig. 9b) is in contact with muscovite LB-A-Ms-2 (high K) in the
 507 pegmatitic portion of the sample and is surrounded by secondary albite. The sequence of
 508 zones observed in the other CGM grains is less distinct in CGM-3. However, four zones were

509 defined on the basis of changing Ta/Nb ratios and trace element contents. The highest Sn
510 (>1600) and W (>900 ppm) were detected in irregular patches (zone 1) with moderate Ta/Nb
511 (1.23). This zone is also enriched in U (3145 ppm), which is additionally concentrated along
512 fractures, as are alkali metals. Zones 2 and 4 are richest in Ta with Ta/Nb of 2.06 and 2.13,
513 respectively. Zone 3 shows low trace element concentrations and the lowest Ta/Nb ratio
514 (0.98). Sn and W show minor variation between zones 2, 3 and 4 (660–800 ppm Sn, 470–
515 630 ppm W). Given the complex texture of CGM-3 as observed in the BSE image, the order
516 of the zones does not necessarily represent the order of crystallization. Petrographically, zone
517 4 seems to be associated with zone 5 in the adjacent muscovite.

518

519 **6. Crystallization history and rare-element evolution**

520

521 *6.1. Stages of pegmatite formation*

522

523 Three individual paragenetic *stages* (I, II, III) with consistent behavior among all
524 analyzed muscovite grains were defined. The geochemical evidence for the individual stages
525 is presented here and a paragenetic model for stage formation is presented in section 7. Each
526 muscovite grain shows petrographic discontinuity between these stages in the respective LA-
527 ICP-MS images and each stage can comprise multiple *zones* (e.g. I.1, I.2, I.3) in one grain.
528 Furthermore, the zones of all grains can be correlated based on fractionation patterns as
529 indicated by their K/Li, K/Rb and K/Cs ratios (Fig. 10a). Petrographic discontinuity was also
530 observed for individual CGM grains and CGM zones were assigned to the same three stages
531 as micas assuming contemporaneous crystallization, the evidence for which is presented in
532 subsection 6.1.3. In the following subsections, chemical variations within each stage are
533 described in more detail, first for muscovite and then for CGM.

534 The same numbering for two zones in different grains does not necessarily mean
535 contemporaneous crystallization. While this is likely the case for grains within one thin
536 section, onset of crystallization might vary along the length of the drill core or the pegmatite
537 dike system as a whole. The trace element data for each zone determined from the LA-ICP-
538 MS images and their correlation with paragenetic stages is summarized in supplementary
539 Tables ST1 (muscovite) and ST2 (CGM).

540

541 *6.1.1. Zoning in white mica*

542 Stage I is characterized by decreasing K/Rb, K/Cs (Fig. 10a) as well as an increase in
543 most other trace elements (e.g. Ti, Mn, Nb, Sn, Ta, Fig. 10b). In stage II, K/Rb varies only
544 slightly, but increases again in stage III. For K/Li, contrasting behavior is observed for the
545 central quartz–muscovite assemblages (Q-MA) compared to the border albitite (UB-A, LB-
546 A). In QM-A, K/Li exhibits a local minimum in zone II.2, while UB-A and LB-A show local
547 maxima. The K/Cs ratio additionally shows a strong local minimum in II.2 for most samples.
548 In stage III, alkali metal ratios strongly increase to values sometimes higher than the
549 corresponding ratios in stage I.

550 The intra-grain patterns for B, Ba and HFSE (Nb, Ti, Sn and Ta/Nb, Fig. 10b), are
551 more complex than for alkali metal ratios. Stage I is characterized by an initial decrease
552 followed by a strong increase for all of these elements except B and Nb. Boron decreases in
553 stage I, while Nb in the central sample (QM-A) initially increases before it decreases again.
554 This increase in Nb is also observed for the border albitite samples. Stage II is characterized
555 by even stronger variations. Boron shows an overall decrease but oscillates between
556 subsequent zones. Similar behavior, but with the opposite amplitude, is observed for Sn,
557 Ta/Nb and to a lesser degree Ti. Barium seems to correlate with B in LB-A-Ms-2, but shows
558 anti-correlation with B for the other grains. Niobium concentrations are high in stage II, but
559 they typically decrease towards stage III. In stage III, most elements decrease, except B. The
560 replacive BSE-bright mica (indicated by an asterisk in Fig. 10) is enriched in Nb and Ba and
561 depleted in Sn relative to stage III.

562 Individual error bars for element concentrations and element ratios were omitted in
563 Fig. 10 to ensure readability of the diagrams. However, abrupt concentration changes
564 between two zones as observed in K/Li, K/Rb, K/Cs, B, Ti, Sn and Ta/Nb significantly
565 exceed analytical uncertainty.

566 To investigate element variations within single zones, a concentration profile (Fig. 11)
567 for muscovite LB-A-Ms-2 (along the path A–B–C as shown in the last panel of Fig. 8) was
568 constructed using the average of three parallel lines of adjacent pixels to reduce scatter.
569 Small-scale variations aside, Cs appears to exhibit power-law behavior within zone I.3 and
570 within stage II. Lithium and Rb (not illustrated), show similar behavior to Cs. The behavior
571 of Ba is different: it shows an overall decrease from zones I.3 to II.3 and increases abruptly in
572 stage III. Boron shows anti-correlation with Ta, while Ti and Sn show good correlations with
573 Ta in most zones. Niobium and Ta show more complex behavior; they are positively
574 correlated in stages I and III, but some zones in stage II show anti-correlation.

575

576 *6.1.2. Zoning in columbite group minerals*

577 Zones in CGM of sample LB-A can easily be correlated using their intra-grain trace-
578 element patterns (Fig. 12). Three stages were defined based on petrography and geochemistry
579 and are consistent with the stages described for white mica. All grains show similar patterns
580 for Ti, Y, Sn and Ta/Nb, and correlate well in their overall W and U distribution. Based on
581 these element patterns, zones in CGM-3 could be correlated. The order of crystallization for
582 the zones in CGM-3, difficult to establish petrographically, is 1–3–2–4 as indicated in the
583 plot for Ta/Nb. In stage II, CGM-1 and CGM-3 show opposing patterns in Sn, W and U.
584 Most elements correlate well with Ta/Nb, but vary in detail. Titanium and Sn seem to
585 correlate with Ta/Nb of CGM-2 and in the older zones of the other grains, while Sn behaves
586 differently in CGM-3 after Zone II.1. Apart from Sc, all trace elements are enriched in stage I
587 of each grain. The grains show reverse zoning (decreasing Ta/Nb) in stage I, then normal
588 zoning from zone II.1 onwards. Stage III is characterized by the highest Ta/Nb as well as an
589 increase in Cs, which decreases in stage I and is very low in stage II.

590 The analytical uncertainties for CGM are large especially for LB-A-CGM-1 due to the
591 small grain size and consequently low number of pixels for each ROI. However, distinct
592 concentration changes between two zones significantly exceed analytical uncertainty.

593

594 *6.1.3. Contemporaneous crystallization of muscovite and CGM*

595 Concentration patterns observed for stages I to III for muscovite and CGM suggest
596 contemporaneous crystallization of these phases. Patterns for Sn and Ti for both minerals
597 correlate (Figs. 10b and 12), and patterns for Cs in CGM are similar to the pattern of K/Cs in
598 muscovite (Figs. 10a and 12), which suggests an anti-correlation for the alkali metals. The
599 pattern for Ta# in muscovite also closely resembles that of CGM. This becomes evident when
600 comparing Ta# profiles across LB-A-Ms-2 and LB-A-CGM-1 (Fig. 13a). The grains are
601 about 2 cm apart in the thin section and separated by fine-grained albite, and show almost
602 identical zoning, and similar absolute values of Ta#. Additionally, zone III.1 of LB-A-CGM-
603 3 is spatially closely associated with III.1 of LB-A-Ms-2 and both show high Ta# (0.68 and
604 0.46, respectively). This petrogenetic association is also evident in the composite BSE image
605 (Fig. 13b). Growth of Ms-2-III.1 was furthermore restricted by the contact with earlier (stage
606 I–II) zones of CGM-3.

607

608 6.2. Rare-element fractionation

609

610 6.2.1. Rayleigh fractional crystallization

611 Hulsbosch et al. (2014) demonstrated that, if a sequence of compositions of a mineral
 612 i is the product of Rayleigh fractional crystallization, which can be described by Eq. 1,
 613 $\log(K/Rb)$ and $\log(Cs)$ define a linear relationship (Eq. 3). The slope of this line (m) is
 614 defined by the bulk partition coefficients D_j for each element j (Eq. 4) and its intercept (b)
 615 depends on the starting composition of the melt as well as the partition coefficients $k_{j,i}$
 616 between mineral i and melt (Eq. 5).

617 Assuming closed system Rayleigh fractional crystallization for the studied pegmatite
 618 and applying the approach of Hulsbosch et al. (2014) to each zone identified in the
 619 concentration profile of muscovite LB-A-Ms-2 (Figs. 8 and 11), we can estimate the bulk
 620 partition coefficients D_j as well as the starting composition $C_{0,j}$ ($j = K, Rb$ and Cs) of the
 621 evolved melt by varying these until Eqs. 4 and 5 match m and b from linear regression of the
 622 empirical data. Furthermore, the distance z along the profile of the concentration
 623 measurements correlates to the amount of remaining melt F , assuming constant ratios
 624 between growth rates of the different minerals taking up the elements of interest.

625 Figure 14a shows $\log(K/Rb)$ and $\log(Cs)$ for zone I.3 in the direction B–A (Fig. 8).
 626 This direction was chosen, because it is parallel to the cleavage, the direction of fastest
 627 crystallization, and should therefore yield the highest resolution. The data define a linear
 628 trend with $m_{I.3} = -0.361$ and $b_{I.3} = 2.304$ (Fig. 14a). The following constraints were used to
 629 approximate the bulk partition coefficients: concentrations of Rb and Cs increase, which
 630 suggest that these elements behave incompatibly and therefore $D_{Rb} < 1$ and $D_{Cs} < 1$, while K
 631 shows a slight decrease, which is best approximated by $1.00 < D_K < 1.01$. Published data for
 632 muscovite/melt partition coefficients (Table 5) were used for calculating the intercept. An
 633 approximate starting composition for the evolved melt from which muscovite LB-A-Ms-2
 634 crystallized can be inferred by solving Eq. 2 for C_0 , and assuming that the average of the first
 635 few points of the profile represents the starting composition of the mineral at $F \approx 0.99$. It is
 636 then possible to model the concentration of Cs, K and Rb in the crystal for $1 > F > 0$ by using
 637 the approximated bulk partition coefficients and starting composition to solve Eq. 2. The
 638 linear relationship of distance z with $\log(Cs)$ (Fig. 14b, $R^2=0.814$) can then be used to fit the
 639 modeled concentrations to the observed profile. After fitting the modeled concentrations,
 640 partition coefficients for Nb and Ta were inferred from the trends observed in the respective

641 profile. The profiles for I.3 with the modeled concentrations for Cs, Rb and Nb obtained with
 642 three different D_j values each are shown in Fig. 14c.

643 The same approach was used to model zones II.1, II.2, II.3, III.1 and III.3. Melt
 644 compositions at the start of crystallization and at the end of each zone, m and b , as well as
 645 bulk partition coefficients for each zone are shown in Table 6. The bulk partition coefficients
 646 yielding best results for m and b do not always resemble the actual concentration trend for K
 647 and Rb observed in the profile and the values in parentheses in Table 6 are for bulk partition
 648 coefficients that best approximate K and Rb behavior. The melt compositions at the end of
 649 crystallization are more similar to the starting composition for the subsequent zone for these
 650 bulk partition coefficients, and m and b are more similar to the slope and intercept of zone I.3.
 651 The starting and end concentrations of each zone yield additional information: zone I.3 gets
 652 strongly enriched in Cs towards the end, while the initial melt concentration of zone II.1 is
 653 lower. As there is no mineral with Cs compatibility crystallizing, Cs must be removed from
 654 the crystallizing medium another way, or the crystallizing medium must have changed.
 655 Potassium behaves compatibly for all zones ($D_K > 1$) apart from II.2, but the starting
 656 concentrations of K in the melt only decrease from I.3 to II.2 and increase with II.3. Between
 657 stages II and III, another Cs-loss event accompanied by strong increase in K/Rb is observed.
 658 In zone III.2, Cs and Ta are highly compatible with bulk distribution coefficients of 5.25 and
 659 3.20, respectively.

660 Bulk partition coefficients are the sum of mineral/melt partition coefficients (Table 5)
 661 multiplied by the mineral fraction. This relationship allows constraint of the proportions of
 662 the crystallizing minerals, which was undertaken for the individual zones and is described in
 663 Supplementary Note C. Good results fitting bulk partition coefficients of D_j ($j = K, Rb, Cs$)
 664 were achieved for crystallization of muscovite (\pm albite, quartz) in the presence of an aqueous
 665 medium with oscillating proportions of the latter during stage II. Spreadsheets including the
 666 raw data and geochemical models for each zone can be found in supplementary file ST3.

667

$$668 \quad \frac{c_{liq,j}}{c_{o,j}} = F^{(D_j-1)} \quad (\text{Eq. 1})$$

$$669 \quad C_{i,j} = C_0 \times k_{d,i,j} \times F^{(D_j-1)} \quad (\text{Eq. 2})$$

$$670 \quad \log\left(\frac{C_{i,K}}{C_{i,Rb}}\right) = m \times \log(C_{i,Cs}) + b \quad (\text{after Hulsbosch et al., 2014}) \quad (\text{Eq. 3})$$

$$671 \quad m = \frac{D_K - D_{Rb}}{D_{Cs} - 1} \quad (\text{Eq. 4})$$

$$672 \quad b = \log \left(\frac{C_{0,K} \times K_{d,i,K}}{C_{0,Rb} \times K_{d,i,Rb}} \right) - m \times \log(C_{0,Cs} \times K_{d,i,Cs}) \quad (\text{Eq. 5})$$

673 With

674 F : mass fraction of residual melt;

675 $C_{0,j}$: initial melt concentration of element j at $F = 1$;

676 $C_{liq,j}$, $C_{i,j}$: concentrations of element j in residual melt and in mineral i at F ;

677 $k_{d,i,j}$: partition coefficient for element j between mineral i and liquid, $k_{d,i,j} = \frac{C_{i,j}}{C_{liq,j}}$

678 D_j : bulk partition coefficient for element j , $D_j = \sum_i X_i \times k_{d,i,j}$

679 X_i : mass fraction of mineral i , $\sum_i X_i = 1$.

680

681 6.2.2. Rare-element fractionation

682 To investigate the fractionation behavior and correlation of rare elements in all
 683 muscovite samples, the data was plotted on fractionation plots (Fig. 15). For stages I and II,
 684 concentrations of Li and Cs clearly increase with decreasing K/Rb and patterns similar to that
 685 of Cs (Fig. 15a), but with a greater scatter at lower K/Rb, are observed for Sn and Nb (not
 686 shown). The arrows in the K/Rb–Cs plot show the modeled concentration changes from start
 687 to end of the profiles across muscovite LB-A-Ms-2. The trends of stages I and II in LB-A-
 688 Ms-2 define a field which includes almost all measurements. The apparent Cs-loss after
 689 stages I and II (section 6.2.1) can be observed in this plot: Stage II starts at almost the same
 690 K/Rb as the end of stage I, but the Cs concentration is comparable to the starting
 691 concentration of zone I.3, while stage III starts at even lower Cs as well as higher K/Rb. The
 692 trend for zone III.1 can still satisfactorily be explained with fractional crystallization, but III.2
 693 shows a reversed trend.

694 For Ta/Nb, the behavior seems erratic, but the trends modeled for the zones in LB-A-
 695 Ms-2 (Fig. 15a, arrows) seem to explain well the behavior in the other grains at low K/Rb.
 696 Behavior at high Ta/Nb and high K/Rb, observed for stage III, seems more complex. Similar
 697 behavior is also observed for Ti in relation to K/Rb (not illustrated). However, compared to
 698 B, anti-correlation is visible for Ta/Nb (Fig. 15b) and Ti (not illustrated). A strong correlation
 699 of Mn and Li is observed, with two opposite trends for the two lithologies (Fig. 15b). The
 700 high-Li central samples (QM-A) increase in Li and Mn from stage I to stage II, while the
 701 low-Li, border samples decrease in both elements from stage I to stage II. Similarly, two
 702 trends with opposite slopes were observed for Li vs Ta/Nb (Fig. 15b, dashed lines).

703 The outermost muscovite zones, which crystallized during stage III, show high K/Rb
704 ratios combined with intermediate to low rare-element concentrations (Fig. 15).
705 Consequently, fractionation in terms of K/Rb (and K/Cs) is reversed towards the end, which
706 means that either less rare-elements are available in the crystallizing medium, or that the
707 system was flooded with K (or both). Apart from that, stage III muscovite still has high
708 Ta/Nb (Fig. 15b), with intermediate Ta and Nb of ~50–100 ppm and ~60–120 ppm,
709 respectively.

710 Barium (not illustrated) seems to slightly decrease with decreasing K/Rb for stages I
711 and II, as lowest Ba concentrations are found at low K/Rb, but the scatter is large and high Ba
712 concentrations at low K/Rb are particularly common in stage II. Behavior of Be, Ga, and
713 Zr/Hf is briefly described in Supplementary Note B.3.

714

715 **7. Discussion of zoning and rare-element fractionation**

716

717 Zoning (including oscillatory zoning) of white mica has been described in the Leinster
718 Batholith (Roycroft, 1991), S-type granites in northern Portugal (Gomes and Neiva, 2000)
719 and Nova Scotia, Canada (Clarke and Bogutyn, 2003), as well as granitic pegmatites in
720 Namibia (Roda-Robles et al., 2007). These studies document white micas which are zoned in
721 major elements; are macroscopically zoned, or show zoning by epitactic overgrowth of
722 different mica species. Only Clarke and Bogutyn (2003) provide *in-situ* trace element data,
723 but with low spatial resolution. While major-element zoning of white mica is common,
724 muscovite in our study is homogenous in its major-element composition within the analytical
725 precision of SEM-EDS. The homogeneity is evident from the lack of optical zoning (macro-
726 and microscopically), homogenous BSE intensities and low standard deviations for average
727 concentrations of K, Al and Si as determined by SEM-EDS. However, high-resolution LA-
728 ICP-MS imaging demonstrated that minor and trace element concentrations vary strongly
729 over several growth zones.

730 Studies on minor- and trace-element zoning in white mica from granites and
731 pegmatites are sparse. Viana et al. (2007) present chemical data for a single muscovite
732 megacryst (40x80 cm) from a rare-element pegmatite from the Eastern Pegmatite Province in
733 Minas Gerais, Brazil. Again, spatial resolution was low: samples were analyzed using X-ray
734 fluorescence spectrometry on subsamples with 30 mm diameter. The authors conclude that
735 the observed zoning is mainly caused by hydrothermal alteration because of depletion of
736 elements such as Rb, Ga, Y, Nb, Ta, and Sn towards a large fracture crosscutting the crystal

737 and the origin of the primary zoning is uncertain. Tantalum, Nb and Sn seem to correlate to
738 Rb in the study of Viana et al. (2007), but not in the present study.

739 Muscovite forming contemporaneously with, or after crystallization of, CGM and
740 after alkali feldspar in the Moose II LCT pegmatite was described by Anderson et al. (2013).
741 However, compared to the present study, concentrations of Li, Rb and Cs in muscovite were
742 an order of magnitude lower and no clear intra-grain zoning was observed. Nevertheless, the
743 authors describe strong enrichment of Cs and Rb at the margins of most grains, which are
744 attributed to late-stage reaction processes, rather than primary fractional crystallization.

745 Most trace element variations observed in the present study correspond well to
746 published bulk data for mica in spodumene pegmatites (e.g. Černý and Burt, 1984), except
747 for barium. In granitic melt systems, Ba is expected to decrease with increasing magmatic
748 fractionation (i.e. increasing K/Rb) due to fractional crystallization of alkali feldspar, which
749 was also observed for a large mica dataset for rare-element pegmatites (Černý and Burt,
750 1984). Nevertheless, in the present study, an increase in Ba towards the outer zones is
751 observed along with an increase in K/Rb and K/Cs and therefore magmatic fractionation
752 trends are reversed. A potential source for Ba and K in the border albitites is discussed below
753 (6.3.3).

754 Modeling of Rayleigh fractional crystallization showed that the strong Cs-enrichment
755 at the end of stage I observed in I.3 for muscovite LB-A-Ms-2 requires the Cs concentration
756 in the melt to reach weight-percent levels (Table 6). London et al. (1998) reported that
757 saturation for pollucite ($\text{CsAlSi}_2\text{O}_6$) in H_2O -saturated haplogranitic melts is reached at ~4.7
758 wt% Cs at 200 MPa and 680 °C. This is an extreme enrichment compared to the average
759 crustal abundance of 2 ppm Cs (Linnen et al., 2012), but not compared to ~1 wt% Cs
760 observed here. Furthermore, a review of the temperature dependence of pollucite solubility in
761 London (2005) proposes that Cs-saturation is reached at ~0.47 wt% Cs at 390 °C. However,
762 the effects of increasing peraluminosity and concentration of network modifiers (including
763 H_2O) were not addressed in these studies. In natural systems, pollucite precipitation might
764 also be influenced by these factors.

765 Pollucite has not been detected in the Leinster LCT pegmatites, probably because Cs-
766 concentrations were not high enough in earlier stages of pegmatite formation. For the Tanco
767 pegmatite, Manitoba, Canada, the starting concentration of Cs was high and Cs-saturation
768 might have already been reached after 40–50% solidification of the pegmatite-forming melt
769 (London, 2005). Published bulk compositions for rare-element pegmatites at Aclare

770 (O'Connor et al., 1991; Barros and Menuge, 2016) yield 63–77 ppm Cs. If this concentration
771 represents the actual starting concentration of rare-element pegmatite melt, this melt would
772 have to crystallize to more than 99% to produce the Cs enrichment observed in our samples.
773 Therefore, Cs saturation would only be attained at the very end of solidification if closed-
774 system fractional crystallization is the only process by which Cs is enriched. However,
775 fractional crystallization to such a high degree seems unlikely, as H₂O saturation in the
776 silicate melt was probably reached earlier. This saturation would cause the release of an
777 aqueous medium, influencing the distribution of Cs and other incompatible elements (see
778 below).

779 In the following subsections, we propose a crystallization model (6.3.1), which is then
780 discussed in the context of replacive albitite (6.3.2) and quartz–muscovite (6.3.3)
781 crystallization. Rare-element fractionation patterns, partition coefficients, element solubilities
782 and the observed differences between the individual stages, will be assessed to distinguish
783 between crystallization from *silicic melt*, from *aqueous melt* or from *hydrothermal fluid*. The
784 three terms will be used in accordance with recent literature (Thomas and Davidson, 2013,
785 2016) as follows: *silicic melt* for silicate-dominated volatile-bearing peraluminous melt;
786 *aqueous melt* for a H₂O-dominated alkaline and depolymerized fluid phase at magmatic
787 temperatures (which shares characteristics with a silicic melt and supercritical fluid); and
788 *hydrothermal fluid* for a supercritical saline (F-Cl-enriched) H₂O-dominated phase with low
789 silica content and abundant network modifiers like C, S, B and P. All three phases are
790 assumed to be immiscible with each other and may coexist. *Medium* is used as a generic term,
791 which can refer to any of the three phases.

792

793 7.1.1. Late crystallization from coexisting melts and saline fluid

794 Recent studies (Thomas and Davidson, 2016, and references therein) on fluid and
795 melt inclusions and melt–melt–fluid immiscibility show that parental pegmatite melts might
796 initially start as supercritical melts with complete miscibility of aqueous and silicic
797 endmembers. Full miscibility for these endmembers in Na-, B- and P-rich systems was also
798 experimentally demonstrated by Sowerby and Keppler (2002) and those authors concluded
799 that a combination of network modifiers could move the critical curve to moderate P–T
800 conditions plausible for pegmatite emplacement. After cooling below the critical temperature
801 of ~720 °C (Thomas and Davidson, 2016), two immiscible phases coexist, a volatile-rich
802 silicic melt (with up to 30 wt.% H₂O) and an aqueous depolymerized melt (referred to as

803 "fluid/melt" by Thomas and Davidson, 2016). Furthermore, hydrothermal fluid (or vapor) is
 804 released, while the system progresses from being melt-dominated to completely
 805 hydrothermal.

806 The apparent Cs-loss between stages I and II (Table 6; Fig. 15) can be explained by
 807 crystallization from Cs-poorer aqueous melt coexisting with silicic melt. Hydrothermal fluid,
 808 if released early, might also remove part of the Cs from both melts. The fluid/melt partition
 809 coefficient for Cs used for modeling in the present study (0.5, Jolliff et al., 1992) predicts
 810 compatibility of Cs in silicic melt, but fluid/melt partition coefficients for Cs as high as 7–23
 811 with decreasing pressure from 200–50 MPa in a Cl-F-rich system of hydrothermal fluid and
 812 high-silica melt were reported by Webster et al. (1989).

813 Zoning for the other elements observed in our muscovite samples can also be
 814 explained by a shift from – or by an oscillation between – crystallization from silicic melt to
 815 crystallization from H₂O-dominated media. We therefore propose that stage I zones
 816 crystallized from a silicic melt and that the transition to stage II marks the end of pure
 817 magmatic crystallization, with probable exsolution of a saline hydrothermal fluid besides
 818 coexisting aqueous and silicic melts. During stage II, crystal growth oscillates between
 819 crystallization from an aqueous melt (II.1 and II.3) and crystallization from a silicic melt
 820 (II.2). At the same time, both media become enriched in network modifiers such as B, F, P
 821 due to ongoing fractional crystallization. In stage III, crystallization from the last silicic melt
 822 is observed. After III.1, the saline hydrothermal fluid causes hydrothermal alteration,
 823 overprint and formation of zones III.2 and III*. This sequence is supported by the following
 824 observations:

825

- 826 - Stage I shows behavior of K, Rb, and Cs (Figs. 10a, 11 and 15) which is in good
 827 agreement with magmatic Rayleigh fractional crystallization, while in models for
 828 stage II, the bulk partition coefficients for K and Rb either do not match the
 829 observed concentration profile or they do not match slope and intercept for
 830 $\log(K/Rb)$ versus $\log(Cs)$ (Table 6). However, general trends for K/Rb and Cs
 831 (Fig. 15) in white mica can still be explained by fractional crystallization until
 832 zone III.2. Afterwards, the trends are reversed and precipitation happens by
 833 another process.
- 834 - Embayment textures often observed between zones of stages I and II (muscovite:
 835 Figs. 6–8; CGM: Fig. 4) suggest a petrogenetic gap and possible partial digestion
 836 of earlier zones. Additionally, the zones of stage II, which crystallized from

837 aqueous melt, show irregular (but not necessarily truncated) borders, while the
838 zones generated from silicic melt at the same stage show straighter, sub- to
839 euhedral borders.

- 840 - Boron is low in the silicic melt zones and high in zones potentially produced by
841 precipitation from aqueous melt (Fig. 10b). It is also high in fine-grained
842 hydrothermal epitactic mica (III.2). Boron typically partitions into aqueous media
843 in coexistence with a silicic melt (Thomas et al., 2003, and references therein).
- 844 - Most HFSE are enriched progressively towards the end of stage I (Fig. 10b),
845 which is in agreement with behavior of incompatible elements during magmatic
846 fractional crystallization. During stage II, behavior seems erratic with sudden
847 depletion or enrichment, requiring a change of the crystallization medium, which
848 is further investigated below.

849

850 Studies on natural fluid inclusions and experimental systems (e.g. Veksler, 2005;
851 Rickers et al., 2006; Hulsbosch et al., 2016; Thomas and Davidson, 2016) showed that Li, Be,
852 B, Na, P, Zr, Nb and W favor depolymerized alkaline aqueous melts, while Rb, Cs, Hf and Ta
853 partition into silicic melt. Both phases become enriched in F due to fractional crystallization
854 (Veksler, 2005). Most of this is in agreement with our observations for stage II: High-B, low-
855 Ta/Nb (i.e. Nb-enriched) muscovite crystallizes from aqueous melt, while low-B, high-
856 Ta/Nb, high-Cs muscovite crystallizes from silicic melt. High W in the magmatic zone of
857 stage II of muscovite LB-A-Ms-2 seems contrary to the aforementioned partition behavior.
858 However, absolute concentrations of W in the mica are low (< 8 ppm) and the behavior can
859 be explained by higher compatibility of W in muscovite compared to the silicic melt from
860 which it is crystallizing. This zone shows also high Sn concentrations. The behavior of Sn is
861 not well constrained in the literature: in an experimental F-rich H₂O–melt system, Sn favors
862 silicic melt, while in B- and P-rich H₂O–melt systems, Sn partitions into the aqueous medium
863 (Thomas et al., 2003; Veksler, 2005). Tin favoring the silicic melt over aqueous media is also
864 the conclusion of several experimental studies reviewed by Linnen and Cuney (2005).
865 However, these authors propose that Sn partitions into hydrothermal fluid at high Cl
866 concentrations, which might also happen at higher F concentrations. The effect of the
867 oxidation state of Sn was furthermore not investigated in these studies. In our samples, Sn
868 seems to favor silicic melt and strongly partitions into the growing muscovite (with up to
869 1000 ppm Sn). This compatibility suggests that tetravalent Sn is present, as it has a similar

870 ionic radius to other elements compatible with the octahedral site of white mica. Titanium
871 exhibits similar behavior to Sn and Ta and is probably controlled by similar processes.

872 Behavior of Nb and Ta in white mica seems to be in disagreement with Rayleigh
873 fractional crystallization even during stage I (arrow in Fig. 15). However, our geochemical
874 modeling did not consider fractional crystallization of CGM, which helps to explain the
875 distribution of these elements in muscovite. Zoning observed in CGM fits well into the
876 sequence of crystallization from coexisting silicic and aqueous melts towards hydrothermal
877 fluid described above as well as the bulk partition coefficients derived from geochemical
878 modeling.

879 Crystallization of CGM starts in stage I and continues until stage III, which is
880 recorded by CGM inclusions associated with zones I.3 and III.1 of muscovite in border
881 albitite samples, as well as the correlative Ta#-patterns of muscovite and CGM in the lower
882 border albitite sample (Fig. 13). CGM zones of stage I are rich in HFSE (Ti, Sn, W, U) and
883 exhibit increasing Mn# and decreasing Ta# from their centers to their rims. Increasing Mn# is
884 expected for magmatic fractional crystallization as observed in many other highly
885 fractionated pegmatites globally (e.g. Lahti, 1987; Mulja et al., 1996; Wise et al., 2012;
886 Badanina et al., 2015). High U-contents and uraninite inclusions are also consistent with
887 crystallization from silicic melt, where CGM can incorporate high amounts of U and
888 commonly show exsolution of uraninite after cooling (Romer and Wright, 1992). Decreasing
889 Ta#, referred to as reversed zoning by Lahti (1987), is inconsistent with the expected
890 magmatic trend of increasing Ta# predicted by columbite–tantanalite solubility experiments
891 (see Linnen and Cuney, 2005, and references therein). Reversed zoning of CGM in our
892 example is likely caused by contemporaneous crystallization of white mica and CGM, and
893 probably also by the presence of coexisting aqueous media. Muscovite/melt partition
894 coefficients for Nb and Ta of 3.5 and 0.42, respectively, for a Li-F-P-rich peraluminous
895 rhyolite presented by Raimbault and Burnol (1998), suggest strong compatibility of Nb, but
896 incompatibility of Ta, in muscovite. While Nb should still be more compatible in CGM
897 compared to muscovite, the volume of newly-formed mica is much larger than the volume of
898 crystallizing CGM. Additionally, Nb is more susceptible to partitioning into a coexisting fluid
899 while Ta remains in the melt as described above.

900 After stage I, CGM are partially resorbed as evident by truncation and crosscutting of
901 stage I zoning patterns (Figs. 4 and 5). This is followed by growth of Nb-rich (low-Ta#)
902 CGM from an aqueous melt phase, which is in good agreement with the high bulk partition
903 coefficients for Nb during growth of muscovite zones II.1 and II.3 (Table 6). The silicic melt-

904 related growth during muscovite zone II.2 is associated with high-Ta# CGM and strong
905 incompatibility of both Nb and Ta in the system. Tantalum has a very low bulk partition
906 coefficient in II.2 suggesting high compatibility in the crystallizing medium. Partial
907 resorption can be explained with increasing Li and F in the liquids. Both elements possibly
908 increase the solubility of CGM in silicate melts (Linnen and Cuney, 2005).

909 Decrease of Mn# during stages II to III, followed by an increase, is observed in the
910 EDS profile of CGM-1 (Fig. 5). The decrease might be linked to crystallization of Mn-rich F-
911 apatite and lithiophilite, which is in agreement with petrographic observations. The steep
912 increase in Mn# at the end might mark the termination of phosphate crystallization. Trace
913 elements (especially U) are also depleted at the beginning of stage II, but increase again
914 towards stage III. Texturally, each high-Ta# zone in CGM-1 shows subhedral boundaries, but
915 also common textures of partial digestion. For the other two CGM, textures are more
916 complex (Fig. 4b–c). Correlation of the zones showed that the high-Ta# part of stage II in
917 CGM-3 is not a Ta-rich overgrowth, as observed in the other grains, but replacement of the
918 Nb-rich zone II.1 by the high-Ta# zone II.3, which agrees with the texture observed on the
919 BSE image.

920 The crystallization history of CGM can be explained analogously to that of
921 muscovite. At stage I, CGM crystallize from a silicic melt; stage II is characterized by partial
922 digestion, replacement, and crystallization from two different melts (low-Ta/Nb aqueous melt
923 and high-Ta/Nb silicic melt); and in stage III high-Ta# CGM grow from the remaining melt.
924 Furthermore, geochemical modeling for muscovite showed that the vapor, which deposits the
925 epitactic mica (III.2) at the end of mica crystallization, is highly enriched in Ta compared to
926 Nb (180 ppm and 29 ppm, respectively). Bulk partition coefficients are large for both
927 elements (Table 6), but D_{Ta} is >2 times D_{Nb} . The reason for this fractionation could be strong
928 F-enrichment towards the end. Experimental work shows that F might increase the solubility
929 of both Nb and Ta in silicate melt (Keppler, 1993), but more recent experiments document no
930 significant influence of F (Fiege et al., 2011; Aseri et al., 2015). Either way, fluorine has little
931 effect on the Ta/Nb ratio of silicate melts (see also Linnen and Cuney, 2005). In contrast,
932 different stabilities of Ta- and Nb-F-complexes in Na-, Cs-, Rb-bearing aqueous solutions
933 have been exploited for hydrometallurgical separation of Ta and Nb for over 150 years (e.g.
934 Smith, 1905). In these processes, separation is possible because, compared to Nb, Ta forms
935 more stable (and more mobile [Parker and Fleischer, 1968]) fluoro-complexes in aqueous
936 solution.

937 A similar process of late-magmatic crystallization of mica was observed by Clarke
938 and Bogutyn (2003) for the South Mountain leucogranite in Nova Scotia. They infer the
939 origin of mica cores as precipitates from silicic melt, while mica rims are interpreted to have
940 formed late in the presence of a hydrothermal fluid. The epitactic rims also correlate locally
941 with hydrothermal alteration and aplite–pegmatite–greisen formation (Clarke and Bogutyn,
942 2003). The authors furthermore observed crystals where fluid-related growth was followed by
943 magmatic growth, followed by more fluid-related growth. These oscillations are interpreted
944 as crystallization during changing P – T – x caused by periodic build-up and release of an
945 aqueous phase. However, the published work on melt–melt–fluid immiscibility in granites
946 and pegmatites referenced above, suggests that silicic and aqueous media might actually
947 coexist without a need for periodical influxes.

948

949 *7.1.2. Formation of albitite*

950 Fine-grained albitites are widely regarded to appear late in the pegmatite-forming
951 process. They are generally considered as replacement units and are the main host for
952 economic Nb–Ta mineralization. Kontak (2006) proposes that secondary albite in the Brazil
953 Lake pegmatites of Nova Scotia formed by direct alkali-ion exchange between Na-rich *melt*
954 and alkali feldspar megacrysts. While the Brazil Lake pegmatites are compositionally and
955 geologically similar to the Leinster rare-element pegmatites, it is unlikely that this process
956 happened in the Leinster pegmatites. Albitite is abundant (up to 15%) in the studied drill core
957 and at other localities in the Leinster pegmatite belt. Furthermore, it is often not associated
958 with remnant alkali feldspar suggesting it either can form without any alkali feldspar present
959 or that the replacement of alkali feldspar was close to 100%. While formation of late-stage
960 (or secondary) muscovite is common (see 6.3.3.), it might not account for all released K if all
961 secondary albite replaced alkali feldspar. Furthermore, if albite formed by direct alkali-ion
962 exchange of alkali feldspar with a Na-rich medium, we would expect pseudomorphic
963 replacement of alkali feldspar by albite and diffuse grain boundaries or intimate intergrowth
964 between the reactant and product, which was not observed here. Moreover, experiments and
965 natural examples demonstrate that alkali feldspar replacement during such a reaction is
966 topotaxial and produces a common crystal orientation of secondary albite grains (e.g.
967 Holness, 2003; Norberg et al., 2011), again not observed here.

968 The small grain size and low size variation of albite crystals indicate a high nucleation
969 rate. Additionally, the common alignment of the lath-shaped and platy albite crystals parallel
970 to the pegmatite margin suggests crystallization from a flowing liquid. These observations

971 point towards sudden crystallization from a mobile medium, which was migrating through
972 the pegmatite body. Rapid nucleation of albite within a residual Na-rich magmatic liquid
973 might be explained by a sudden pressure drop after release of a vapor phase and transitioning
974 from lithostatic to hydrostatic pressure, or by an increasing solidus temperature due to
975 fractional crystallization of flux-bearing (Li, B, F, P) minerals (London, 2014). Neither
976 hypothesis explores the possibility of albite precipitation from a silica-bearing hydrothermal
977 fluid, which is an established mechanism for albite precipitation during albitization of
978 granitic rocks (e.g. Holness, 2003; Plümper and Putnis, 2009; Putnis and Austrheim, 2010).

979 The euhedral to subhedral shape of the outer zones of CGM within lower border
980 albitite suggest that albite crystallization did not commence before, or at least was still
981 ongoing, during stage III. This is also in agreement with petrographic observations as albite
982 laths truncate stage-II and -III trace-element zoning in muscovite LB-A-Ms-2 (Fig. 8). Direct
983 association of stage-III zones in LB-A-Ms-2 with remnant microcline suggests replacement
984 of microcline by muscovite via dissolution–precipitation along the grain boundary interface.
985 Microcline was dissolved and the stage-II muscovite provided a nucleation surface for
986 precipitation of stage-III muscovite. However, dissolution of microcline might have started
987 earlier causing flooding of the system with the network formers Al and Si, which could
988 explain alternation between crystallization from aqueous melt and crystallization from silicic
989 melt during stage II.

990 Embayment and truncation of the early muscovite and CGM zones, potentially caused
991 by an aggressive F-rich magmatic medium, makes contemporaneous dissolution of
992 microcline furthermore plausible. However, the K/Rb ratios of crystallizing liquid and
993 muscovite still decrease until the end of stage II. In stage III, a bulk K partition coefficient of
994 0.76–0.85 suggests K-enrichment of the liquid, which is caused by microcline breakdown. It
995 is also reasonable to consider fractional crystallization of albite as cause for a bulk K partition
996 coefficient <1 , but no feasible solution of the model for III.1 yields high proportions of albite.
997 If K is not partitioning into a vapor phase (which might not yet be involved in crystallization
998 during stage II), significant dissolution of microcline might not occur until very late, but still
999 before precipitation of albite. In our model, no melt is present after crystallization of zones
1000 III.3, but mica textures suggest that dissolution of silicates continues. This might alter the
1001 chemistry of the residual fluid by depleting the liquid in reactive species like F, and by
1002 increasing its pH through hydrolysis of silicates. Eventually, these chemical changes would
1003 shift the liquid into the stability field of albite, followed by sudden albite precipitation. This
1004 hypothesis is in agreement with studies on feldspar replacement reactions in granitic rocks

1005 (e.g. Wibberley and McCaig, 2000; Plümper and Putnis, 2009). These studies present
1006 thermodynamic models for albite–K-feldspar–white-mica phase equilibria as a function of
1007 Na^+ and K^+ activity over H^+ activity (Fig. 1 in Wibberley and McCaig, 2000). An increasing
1008 pH shifts the system into the feldspar stability fields and albite precipitates when $a_{\text{Na}} > a_{\text{K}}$.
1009 Furthermore, the resulting white mica instability is consistent with the breakdown of
1010 muscovite described above.

1011 Minute apatite inclusions in albite (Fig. 3f) indicate that albitization is accompanied
1012 by F-apatite precipitation, which is also in agreement with an increasing pH (e.g. Ayers and
1013 Watson, 1991). Phosphorous and Ca content of the liquid are probably high in the first place,
1014 due to absence of Ca- or P-bearing minerals during fractional crystallization. Additionally,
1015 breakdown of P-rich microcline released additional P and Ca, potentially contributing to
1016 apatite saturation.

1017 The porosity of albite crystals, the sharp grain boundaries between albite and remnant
1018 muscovite and microcline, as well as the co-precipitation of other phases (here F-apatite) are
1019 characteristics indicative of hydrothermal feldspar formation (Plümper and Putnis, 2009;
1020 Putnis and Austrheim, 2010). Furthermore, albite precipitation from a peralkaline, halogen-
1021 rich hydrothermal fluid is in agreement with fluid inclusion analyses of Barros (2017), who
1022 reports high salinity (>20 eq. wt.% NaCl) and homogenization temperatures of 250–300 °C
1023 for fluid inclusions associated with albitization at Aclare.

1024 After albite precipitation, Na^+ activity is strongly diminished, eventually leading to
1025 white mica stability. The residual liquid or vapor causes formation of fine-grained
1026 hydrothermal epitactic muscovite (III.2, Fig. 3g), formation of secondary minerals, as well as
1027 replacement of muscovite by BSE-bright Li-F-Mn-Cs-rich mica (III.*; Fig. 3d–e). The
1028 secondary fine-grained muscovite intergrown with quartz and replacing microcline along
1029 fractures (Fig. 3f) is probably also derived from this vapor. The fractures only rarely extend
1030 into albite and such alteration of albite is mainly observed along grain boundaries shared with
1031 microcline. This suggests that the release of the hydrothermal vapor is associated with a
1032 change of the stress field, which caused hydraulic fracturing while albite was still
1033 precipitating. In upper parts of the pegmatite, sub-vertical fractures and veins with mica and
1034 quartz crosscut the rock. This fracturing might have been caused by the fluid which migrated
1035 through the pegmatite towards the headwall.

1036

1037 *7.1.3. Formation of quartz–muscovite assemblages by hydrothermal replacement*

1038 White mica of the quartz–muscovite assemblage formed during stage II. The elongate
 1039 habit of core zones in QM-A-Ms-2 (Fig. 7) suggests that this mica might have initially
 1040 formed as a sericitic-like alteration of primary feldspar by an F- and rare-element-rich
 1041 aqueous medium. Further alteration led to near-total replacement of pegmatitic alkali feldspar
 1042 by muscovite and quartz. Pyrite and chalcopyrite are also common in the quartz–muscovite
 1043 assemblage, which is typical of phyllic alteration. The high Li-concentration in QM-A
 1044 (Fig. 10a), replacement of spodumene by white mica in other parts of the drill core, as well as
 1045 common Li-phosphates in adjacent albitite, all suggest that spodumene was also replaced.

1046 Beryl and garnet are probably remnants of the early pegmatite assemblage. Beryl is
 1047 strongly altered as evident by irregular grain boundaries and fractures often filled with Mn-
 1048 rich calcite or apatite. Garnet is associated with alteration to BSE-bright Li-Mn-Cs-rich mica
 1049 along fractures and grain boundaries. The only other remnants of stage I minerals are cores of
 1050 white mica between the quartz-muscovite assemblage and adjacent albitite (QM-A-Ms-3).

1051 Volumetrically, most of the mica crystallized late during stage II and mainly in stage
 1052 III, as indicated by the correlation of mica growth zones. This late formation helps to explain
 1053 the interfingering of albitite and QM-A: if albitite formed from hydrothermal fluid released
 1054 late in stage II, or at the beginning of stage III, this fluid must have been immiscible with the
 1055 medium producing QM-A. Direct exsolution of the albitite-forming fluid from QM-A
 1056 towards the end of quartz–muscovite crystallization also seems plausible.

1057

1058 **8. Implications for rare-element pegmatite crystallization**

1059

1060 *8.1. Stages of Leinster rare-element pegmatite formation*

1061

1062 The three stages of rare-element pegmatite formation from our model are summarized
 1063 in the following subsections and Fig. 16. The paragenetic sequence over these stages is
 1064 illustrated in Fig. 17.

1065

1066 *8.1.1. Stage I – Magmatic crystallization and exsolution of aqueous liquids*

1067 Stage I marks the end of pure magmatic crystallization and transition to a magmatic–
 1068 hydrothermal stage II (Fig. 16a). Stage I is characterized by progressive enrichment of the
 1069 melt in rare elements due to fractional crystallization of primary pegmatitic alkali feldspar,
 1070 plagioclase, muscovite, quartz, spodumene, accessory beryl and garnet, and later columbite–

1071 tantalite. An immiscible aqueous melt might already coexist at this stage, as suggested by
1072 fluid inclusion work for other localities, but no evidence was found in muscovite or CGM in
1073 the present study. During this stage Ta# is mainly increased by fractional crystallization of
1074 muscovite. At the end of stage I, the melt is also enriched in Ti, W, Sn, and U, as recorded by
1075 high concentrations of these in stage-I CGM.

1076

1077 *8.1.2. Stage II – Magmatic–metasomatic crystallization*

1078 Stage II is characterized by onset of crystallization from aqueous melt (Fig. 16b). The
1079 degree of fractionation (as expressed by decreasing K/Rb) increases only slightly, while
1080 highly incompatible Cs reaches its maximum concentration during the silicic melt-related
1081 growth of this stage. Muscovite crystallizing from aqueous melt is especially richer in B and
1082 Nb compared to muscovite crystallized from silicic melt, while the latter shows enrichment
1083 especially in Ta and Sn.

1084 Stage II also records the onset of metasomatic replacement of stage-I silicates by
1085 muscovite and quartz, as well as partial dissolution of primary pegmatite minerals including
1086 CGM. Resorption is likely caused by elevated reactivity of the liquids, especially due to F-
1087 enrichment (but also Li-B-P-enrichment) during fractional crystallization. Cesium
1088 concentrations of the crystallizing liquids are lower than expected after stage I as well as after
1089 the end of stage II. Besides Cs partitioning between the two melts, this could be explained by
1090 exsolution of a third liquid: an aqueous, halogen-rich, supercritical fluid, which removes part
1091 of the alkali metals from the other two liquids (Fig. 16c). Crystallization of muscovite further
1092 increases Ta# of remaining liquids. Partitioning of HFSE between melt, fluid, muscovite and
1093 CGM causes oscillating concentrations of these elements in stage II zones. The fluid pervades
1094 the almost solidified pegmatite body along grain boundaries and pathways created by partial
1095 resorption. Transition to a hydrostatic pressure regime causes hydraulic fracturing, creating
1096 additional pathways. Partial digestion also remobilizes elements such as Al and Si, which
1097 might generate polymerized media locally.

1098

1099 *8.1.3. Stage III – Last melt and hydrothermal precipitation*

1100 In stage III, final crystallization from melt is observed and is accompanied by further
1101 breakdown of microcline. The last melt is highly enriched in HFSE and has an extreme Ta#
1102 of ~0.8, while concentrations of Cs and Rb drop. The latter is probably caused by dilution
1103 with K released from microcline, as well as partitioning of rare alkali metals into aqueous,
1104 now highly B-F-P-enriched, fluid. During solidification of the last portions of melt, the

1105 remaining incompatible elements are increasingly absorbed by the saline hydrothermal fluid,
1106 leading to secondary overgrowth and formation of hydrothermal minerals. This highly
1107 reactive fluid causes (F-catalyzed) hydrolysis of earlier silicates, which eventually leads to
1108 precipitation of albite (and F-apatite) due to changing pH. During and after precipitation of
1109 albite the residual fluid migrates through the pegmatite body (Fig 16d) causing hydraulic
1110 fracturing and hydrothermal mineral precipitation including partial replacement of muscovite
1111 by Li-F-Mn-Fe-Cs-rich mica. Finally, the remaining vapor may leave the dike, as the
1112 volumetric proportion of hydrothermal rare-element-bearing minerals is low and prominent
1113 rare metal and B halos develop around these pegmatites (Barros, 2017).

1114

1115 *8.2. Consequences for Nb–Ta mineralization*

1116

1117 Crystallization of CGM started late in the primary magmatic evolution of the Leinster
1118 LCT pegmatites (Fig. 17). Perfectly euhedral crystals with normal zoning, and in sharp
1119 contact with other minerals, were not observed. High Ta# in CGM cores and reversed zoning
1120 suggest crystallization from a melt, whose Ta/Nb was already increased by fractional
1121 crystallization of muscovite. Columbite group minerals are mainly observed in the low-Li
1122 parts, which are associated with primary alkali feldspar, quartz and plagioclase. Higher CGM
1123 solubility at high Li concentrations of silicate melts (Linnen, 1998) impedes CGM
1124 crystallization before crystallization of spodumene. Nevertheless, even at the final stages, Nb
1125 and Ta concentrations of melt were far below their (F- and Li-dependent) experimental
1126 saturation thresholds of 70–490 ppm Nb and 510–6800 ppm Ta (Linnen and Cuney, 2005).
1127 Early CGM might form as inclusions in large silicate crystals, where they crystallize from an
1128 enriched boundary layer melt at the advancing crystallization front of the growing silicate
1129 (c.f. Fenn, 1986). In Leinster pegmatite samples, CGM inclusions can be found in alkali
1130 feldspar and muscovite. The cores of the analyzed CGM might be relics of microcline
1131 inclusions, which would add another constraint to the timing of onset of microcline
1132 dissolution (6.3.2). Relic grains inherited from replaced pegmatite units have been postulated
1133 for primitive CGM in albitites of rare-element pegmatites elsewhere (e.g. Novák et al., 2003;
1134 Wise and Brown, 2011). Stage I CGM zones were partly resorbed, overgrown or replaced
1135 during stage II. The rather low concentrations of Ta and Nb combined with high F
1136 concentration in the fluids make resorption likely. Crystallization might have been feasible
1137 nevertheless, because the earlier cores served as nucleation sites. Epitaxial crystal growth on
1138 an isomorphic substrate from undersaturated solutions was described by Murdaugh et al.

1139 (2007) who propose that the substrate (in this case, stage I CGM) interacts with the liquid by
1140 attracting the solubilized species (Nb, Ta complexes in the melt), which creates local
1141 supersaturation followed by crystallization (of stage-II CGM) on the surface of the substrate.
1142 Repetition of this process might also generate small-scale oscillatory zoning, as only thin
1143 crystal layers are produced during one iteration.

1144 The early magmatic CGM can show high Ta#, which would make them economically
1145 interesting. The main phases of Ta precipitation are melt-dominated phases of stages II and
1146 III as well as the late hydrothermal phase where the highest-Ta minerals are formed. Van
1147 Lichtervelde et al. (2009) interpret crystallization of late (or secondary) Ta phases such as
1148 late CGM and microlite as products of Ta remobilization during formation of secondary
1149 mica. This might only be partly true, as the late fluids appear already enriched in Ta
1150 compared to Nb due to muscovite crystallization. However, common embayment and
1151 truncation textures of CGM suggest Ta (and Nb) remobilization.

1152

1153 **9. Concluding remarks**

1154

1155 High-resolution chemical mapping of muscovite and columbite–tantalite allow
1156 reconstruction of complex crystallization processes. Melt–melt–fluid immiscibility during the
1157 magmatic–hydrothermal transition, which was previously proposed from experiments and
1158 fluid inclusion studies (Thomas et al., 2012; Thomas and Davidson, 2016), has been
1159 demonstrated by chemical mapping. The analytical approach allowed correlation not only of
1160 mineral zones between different grains, but also of two mineral species, resulting in our
1161 proposed three-stage model.

1162 The importance of aqueous media and at what point aqueous and silicic media coexist
1163 during pegmatite formation is still debated in the literature (e.g. Černý et al., 2005; Thomas et
1164 al., 2012; London, 2014; Thomas and Davidson, 2015). However, the authors agree that H₂O-
1165 dominated phases become more important as complete pegmatite solidification is
1166 approached. The transition from purely magmatic stage I to the magmatic-metasomatic stage
1167 II must be achieved by a change of the crystallizing medium. Furthermore, oscillations in
1168 mineral composition and habit clearly show that at least two different media were involved
1169 after stage I.

1170 Crystallization of columbite group minerals in Leinster rare-element pegmatites is
1171 both magmatic and hydrothermal. The increased abundance of CGM in replacive albitite
1172 units is likely caused by inheritance of early magmatic grains from resorbed magmatic units

1173 and additional growth within the albitite-forming medium. Furthermore, Nb and Ta can be
1174 remobilized by digestion of CGM during the magmatic–hydrothermal transition. Similar
1175 processes were observed for example by Dewaele et al. (2011) in Rwanda.

1176 The high-resolution chemical mapping approach used here allows deciphering of
1177 these complex rocks with small suite of samples. Analyzing two different mineral species,
1178 which co-crystallize and incorporate similar elements of interest, allows rigorous
1179 reconstruction of melt evolution. Columbite–tantalite and mica both incorporate HFSE and
1180 their crystallization is strongly influenced by network modifiers in the liquid. This makes
1181 combined analysis of CGM and mica a more suitable approach for understanding pegmatite-
1182 forming processes compared to studying Nb–Ta oxides alone. *In-situ* LA-ICP-MS chemical
1183 mapping of rock-forming minerals (muscovite) and associated accessory minerals (CGM)
1184 combined with geochemical modeling is therefore a powerful tool to reconstruct
1185 crystallization histories and to decipher the *mineralogical record* of igneous processes.

1186 Muscovite zones of stage III constitute up to 25% of individual grains and differ
1187 significantly from the rest of the grains. As a result of reversed fractionation trends in stage
1188 III, bulk data for muscovite cannot be used as an accurate indicator for magmatic
1189 fractionation at the magmatic–hydrothermal transition. Furthermore, even point analyses
1190 might yield ‘mixed’ signals or might over-represent late stages, if they are not carefully
1191 placed or the spot ablation diameters are large. However, whole-grain or bulk data with a
1192 large range from high to low K/Rb might still be adequate for regional geochemical
1193 estimations.

1194 Fractionation of Ta and Nb controlled by mica crystallization was demonstrated
1195 before for granitic melts by Stepanov et al. (2014). Our results show that crystallization of
1196 muscovite is also effective in changing Ta/Nb of pegmatite melts, but is furthermore
1197 controlled by the partitioning behavior of Nb and Ta in the presence of saline aqueous media.
1198 For mineral exploration for Ta and Cs, the discussed late stages are of highest interest. Both
1199 elements are remobilized, but do not necessarily precipitate again within the pegmatite body
1200 and may be lost to country rocks.

1201 Based on the microtextural and geochemical observations presented here, we
1202 moreover propose that pegmatite albitization during stage III is accomplished by a
1203 hydrothermal fluid rather than a highly-fluxed melt. We suggest that albite precipitation is
1204 caused by a chemical quench, not by sudden loss of network modifiers from a silicate melt,
1205 but by change of Na⁺ and K⁺ activities and pH of the albite-forming saline hydrothermal
1206 fluid. The system appears to remain close to the albite–microcline–white-mica stability triple

1207 point (Fig. 1 in Wibberley and McCaig, 2000), as all three phases are either precipitated,
1208 resorbed or both. After precipitation, the small grain size and microporosity of hydrothermal
1209 albite facilitate migration of the remaining fluid through the pegmatite body and into the host
1210 rock.

1211 The proposed three-step process during magmatic–hydrothermal transition in the
1212 Leinster rare-element pegmatites from a system dominated (I) by a single silicic melt, (II) by
1213 two melts (silicic and aqueous) in conjunction with a hydrothermal fluid and (III) by
1214 hydrothermal processes, might also happen at the transition from fertile granite magma to
1215 formation of other granite-related orebodies (c.f. Černý et al., 2005) such as Mo-Sn-W-rich
1216 greisens and veins, and disseminated magmatic–hydrothermal mineralization (Cu, Au, rare-
1217 earth elements, HFSE).

1218

1219 **Acknowledgements**

1220

1221 We would like to thank John Harrop and the team of Blackstairs Lithium Ltd for
1222 access to drill cores and exploration data, and their assistance; Koen Torremans (iCrag,
1223 University College Dublin [UCD]) for fruitful feedback about presenting the data and
1224 scientific discussions; Tom Culligan (UCD) for thin sectioning; and Daniel Kontak
1225 (Laurentian University) for stimulating discussions in the field. We further thank Rainer
1226 Thomas and two anonymous referees for their reviews and Edward M. Ripley for the
1227 editorial handling of the manuscript. This work was supported in part by Science Foundation
1228 Ireland [Grant Number 13/RC/2092] and is co-funded under the European Regional
1229 Development Fund and by iCrag industry partners.

1230

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1504 **Figures and Tables**

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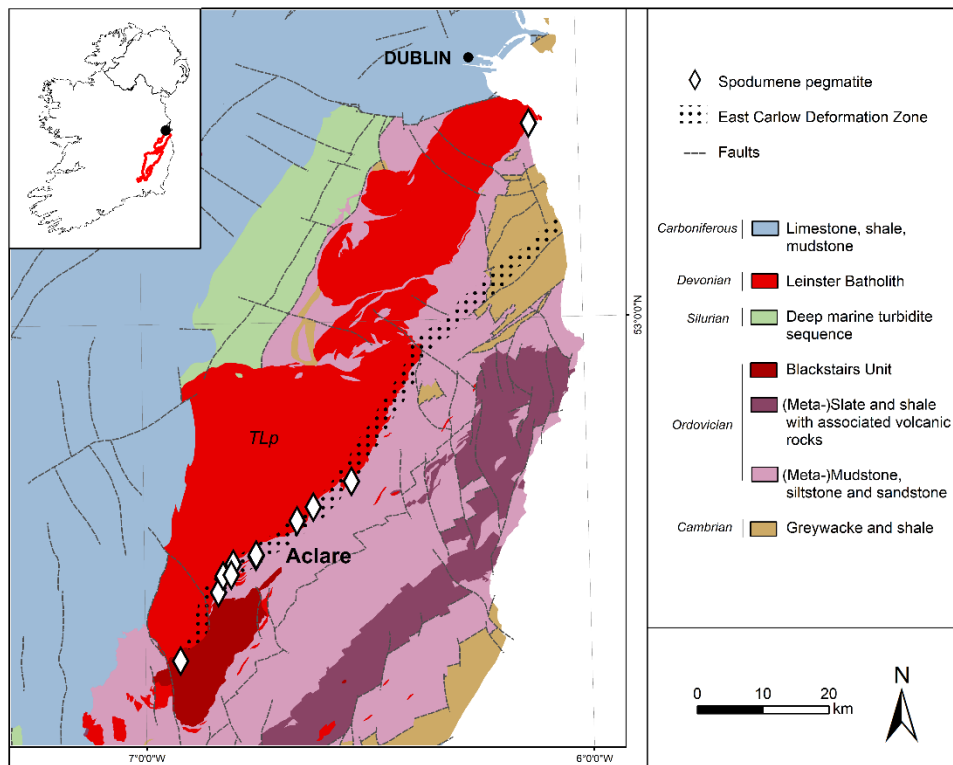


Fig. 1: Geological map of southeast Ireland. Spodumene pegmatite dikes (diamonds) are emplaced on the eastern margin of the Tullow Lowlands pluton (TLp) of the Leinster Batholith within the East Carlow Deformation Zone (McArdle and Kennedy, 1985). Map compiled with data from Geological Survey Ireland.

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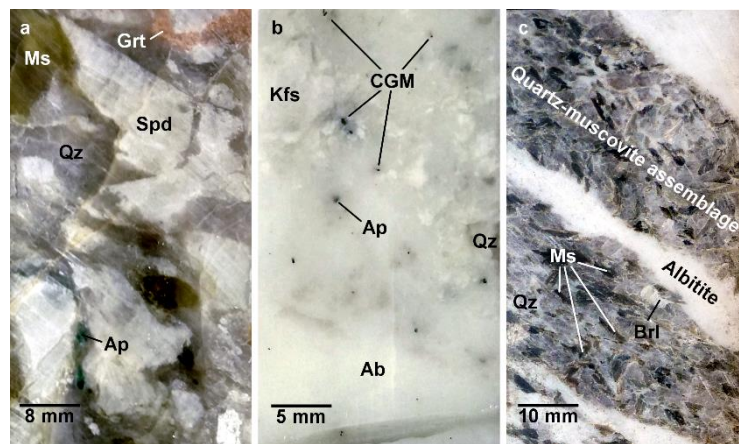


Fig. 2: Photographs of the different lithologies observed in drill core. **a:** Coarse-grained spodumene (Spd) pegmatite with abundant quartz (Qz) and muscovite (Ms), accessory garnet (Grt) and dark-green apatite (Ap). **b:** Albitite dominated by fine-grained granular albite (Ab) which is replacing coarse microcline (Kfs). Columbite-tantalite (CGM) is locally abundant. **c:** Bands of coarse-grained quartz-muscovite assemblage are common throughout the drill core. They are commonly intersected by albitite and bear beryl (Brl) and garnet.

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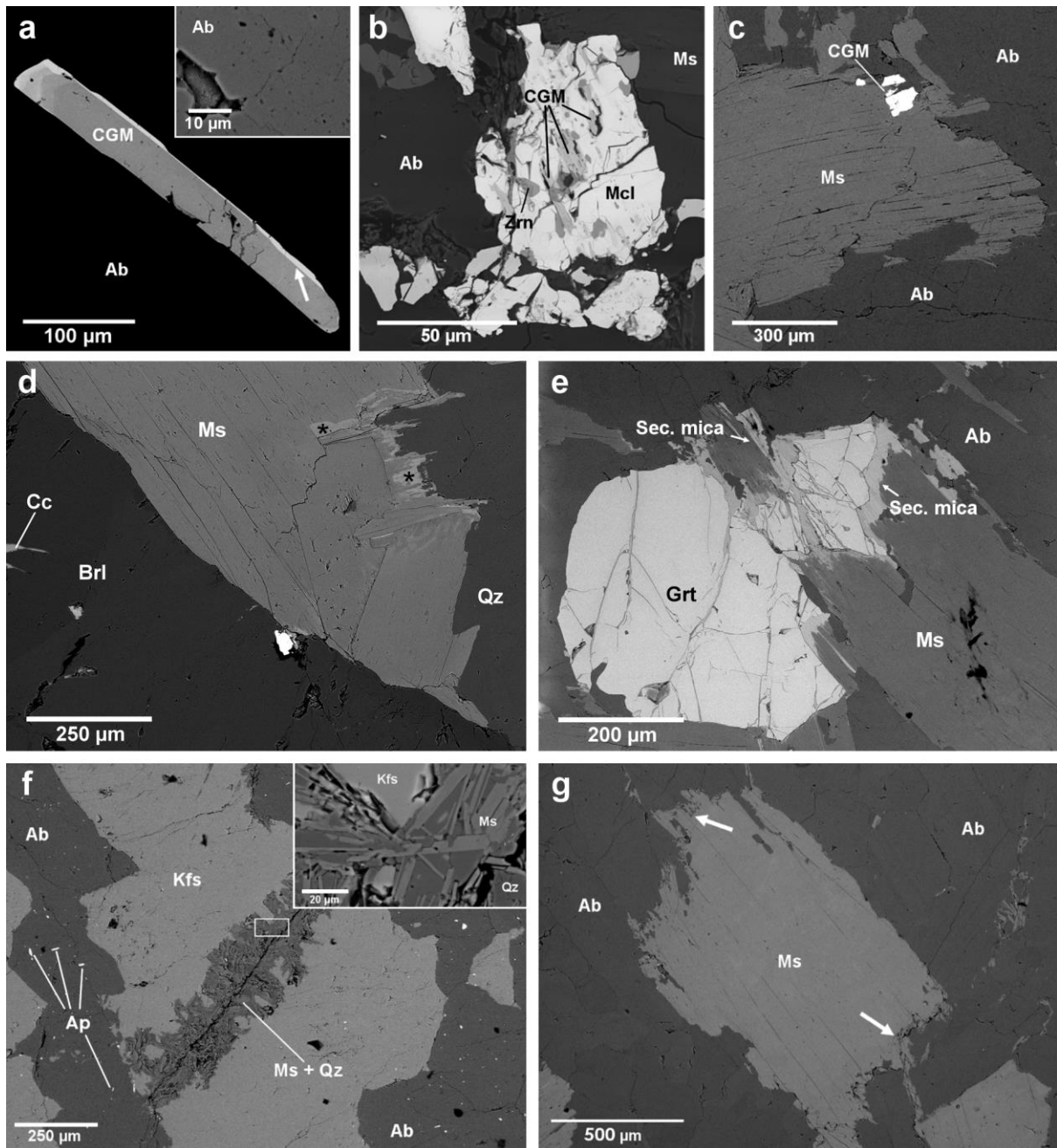


Fig. 3: Backscattered electron images of minerals in samples UB-A (a–c), QM-A (d–e) and LB-A (f–g). **a:** Elongate-prismatic columbite group mineral (CGM) with oscillatory zoning and Ta-rich overgrowth (arrow) between albite (Ab) laths. Inset: Microporosity in albite. **b:** Microlite (Mcl) overgrowing resorbed CGM and zircon (Zrn). **c:** Irregularly-shaped CGM associated with pegmatitic muscovite (Ms) in contact with albite. **d:** Muscovite and quartz (Qz) in contact with beryl (Brl). The primary Ms flakes are partly replaced and overgrown by BSE-bright mica indicated by an asterisk (*). Beryl is partly replaced by calcite (Cc). **e:** Spessartine garnet (Grt) and muscovite partly replaced and overgrown by BSE-bright mica. **f:** Remnant microcline (Kfs) replaced by lath-shaped albite with minute subhedral apatite inclusions (Ap). Microcline is commonly fractured and replaced by fine-grained rose-colored mica and quartz (inset). **g:** Coarse muscovite in albite matrix overgrown by fine-grained mica (arrows).

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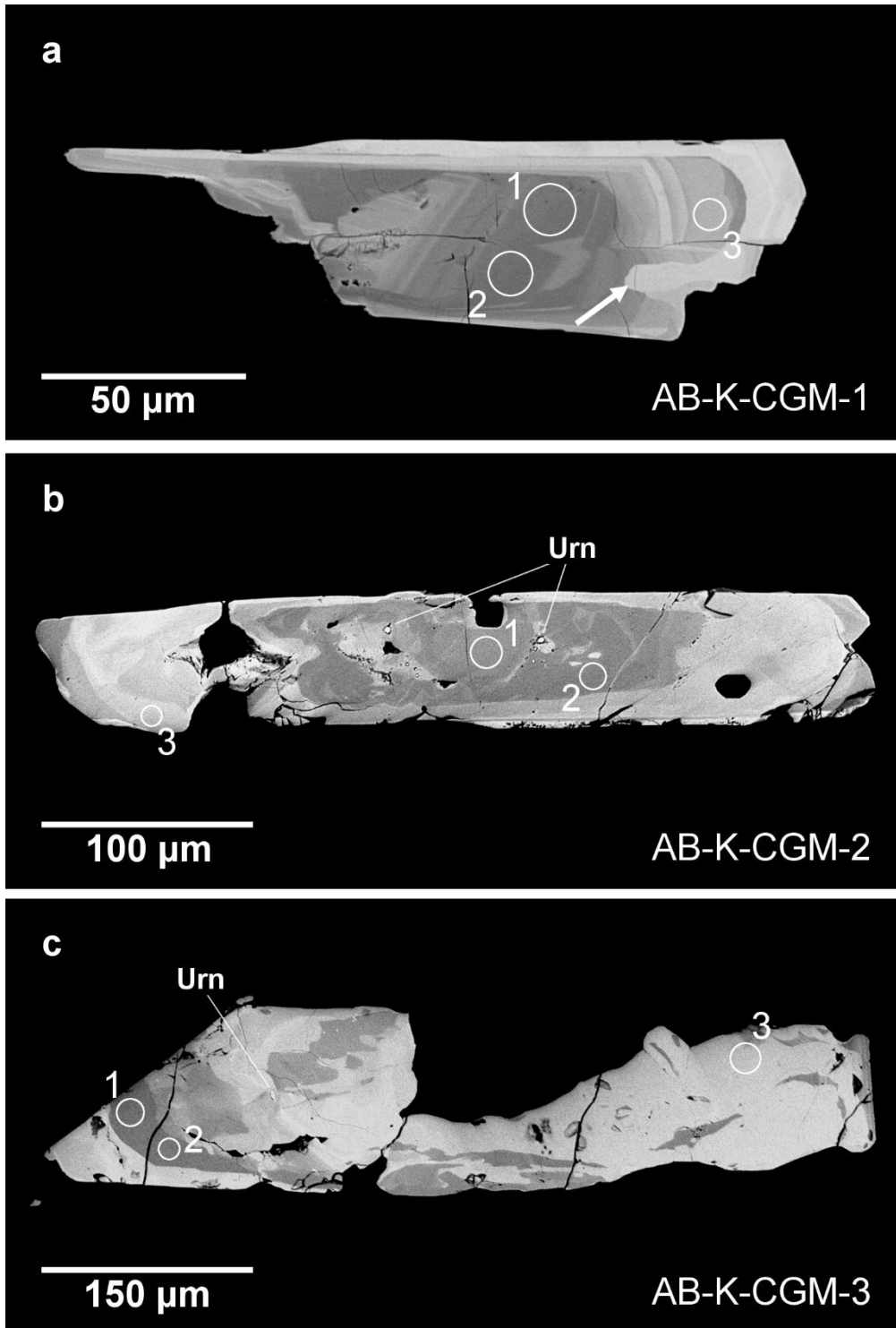


Fig. 4: Backscattered electron images of columbite group minerals (CGM) with uraninite (Urn) inclusions in sample LB-A. Major element analysis were analysed in the circled areas. **a:** Subhedral lath-shaped CGM with prominent oscillatory zoning within albitite. It shows signs of partial digestion and later overgrowth by Ta-enriched material (arrow). **b:** Anhedral elongate-prismatic CGM within albitite, close to former pegmatite. The zoning is less distinct and patchy in some areas. **c:** Subhedral to irregular elongate-prismatic CGM associated with pegmatitic muscovite and microcline. Zoning is patchy and irregular shape and truncation suggest partial digestion.

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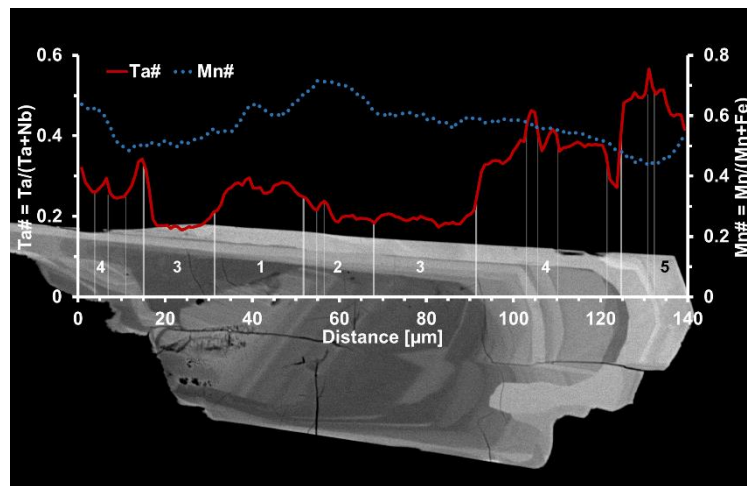


Fig. 5: SEM-EDS line-scan over LB-A-CGM-1 (Fig. 4a). Oscillatory zoning is mainly observed for strongly variable Ta# (solid red line) with overall increasing Ta# from core to rim. Mn# (dotted blue line) shows less variability: It decreases from core to rim initially, but increases in the Ta-enriched rims. The zones 1–5 refer to the zones defined based on the LA-ICP-MS images of this grain.

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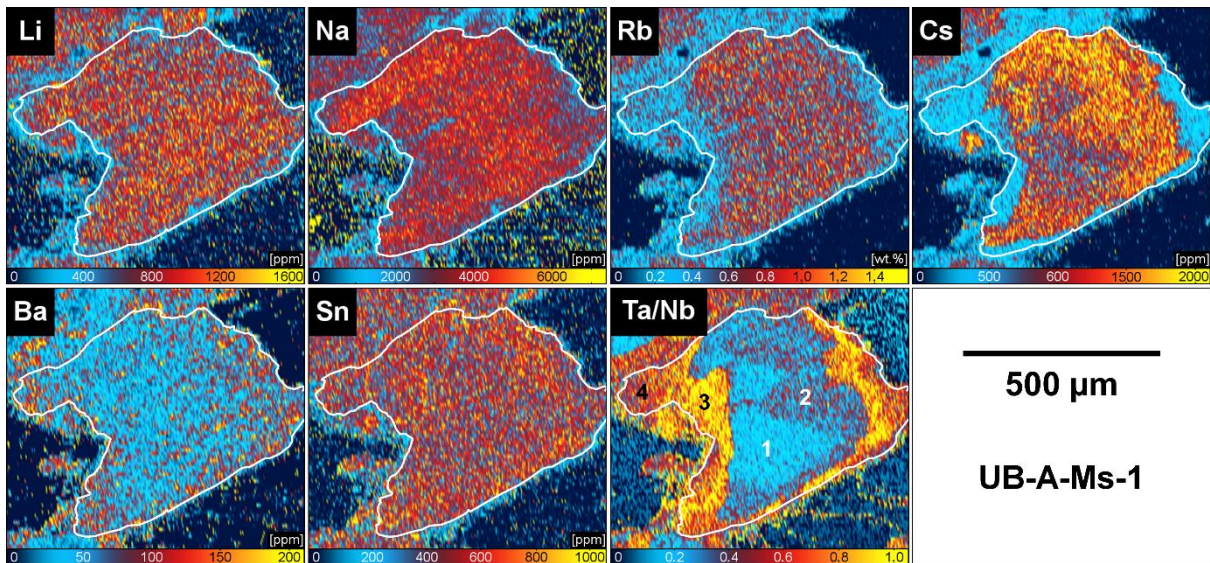


Fig. 6: LA-ICP-MS minor and trace element images of muscovite Ms-1 in albitite (sample UB-A). Four distinct growth zones were identified (numbers). The white line indicates the grain boundary as observed in reflected light.

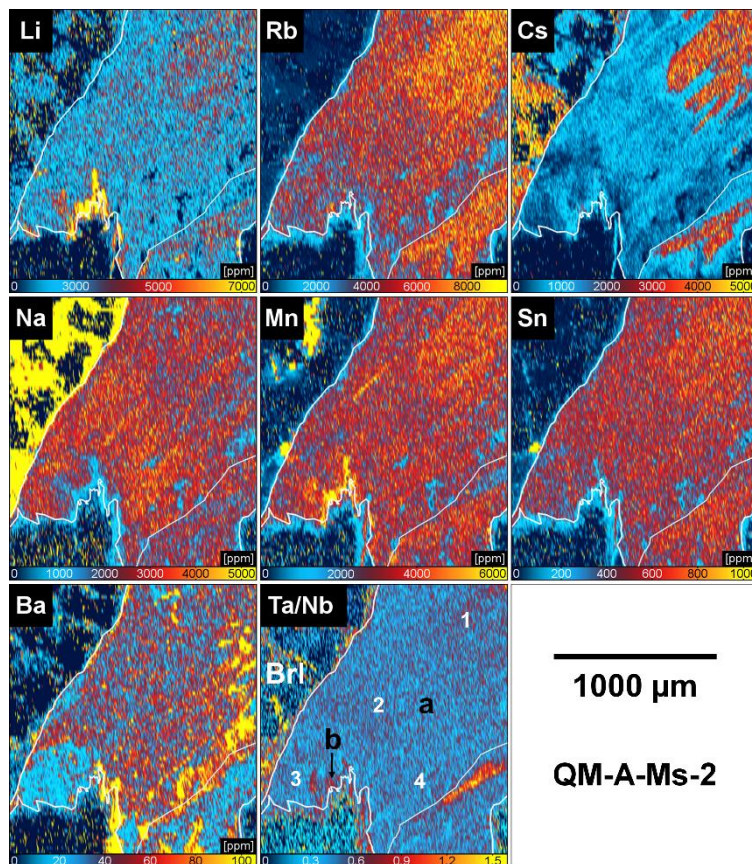


Fig. 7: LA-ICP-MS minor and trace element images of muscovite Ms-2 of the quartz–muscovite assemblage (sample QM-A). The mica is in contact with beryl (Brl) which is partly replaced by calcite. Four distinct growth zones were identified (numbers). The primary mica (a) is partly replaced by secondary mica (b). The white line indicates the grain boundary of muscovite as observed in reflected light.

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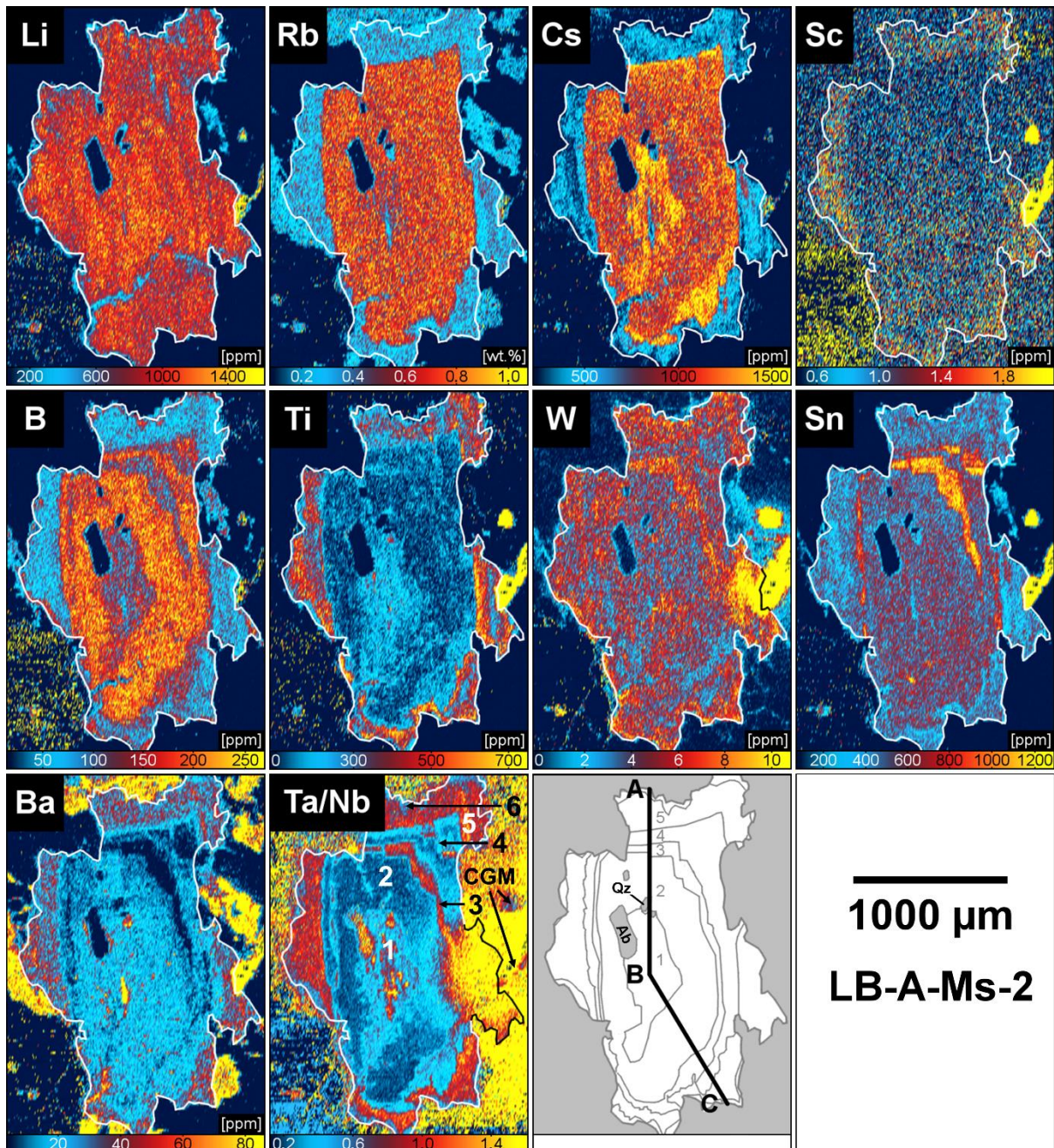


Fig. 8: LA-ICP-MS minor and trace element images of muscovite LB-A-Ms-2. The mica is in contact with microcline (high Ba), albite, and columbite (CGM). Six distinct growth zones were identified (numbers). The grain shows oscillatory zoning for most elements (B, Ba, Ti, Nb, Sn, Ta, W) and progressive zoning in Rb and Cs. This is followed by partial digestion and B-, Rb, and Cs-poor overgrowths (zones 5). The outline indicates the grain boundary as observed in reflected light. The last tile displays the location of the concentration profile, which is shown in Fig. 11.

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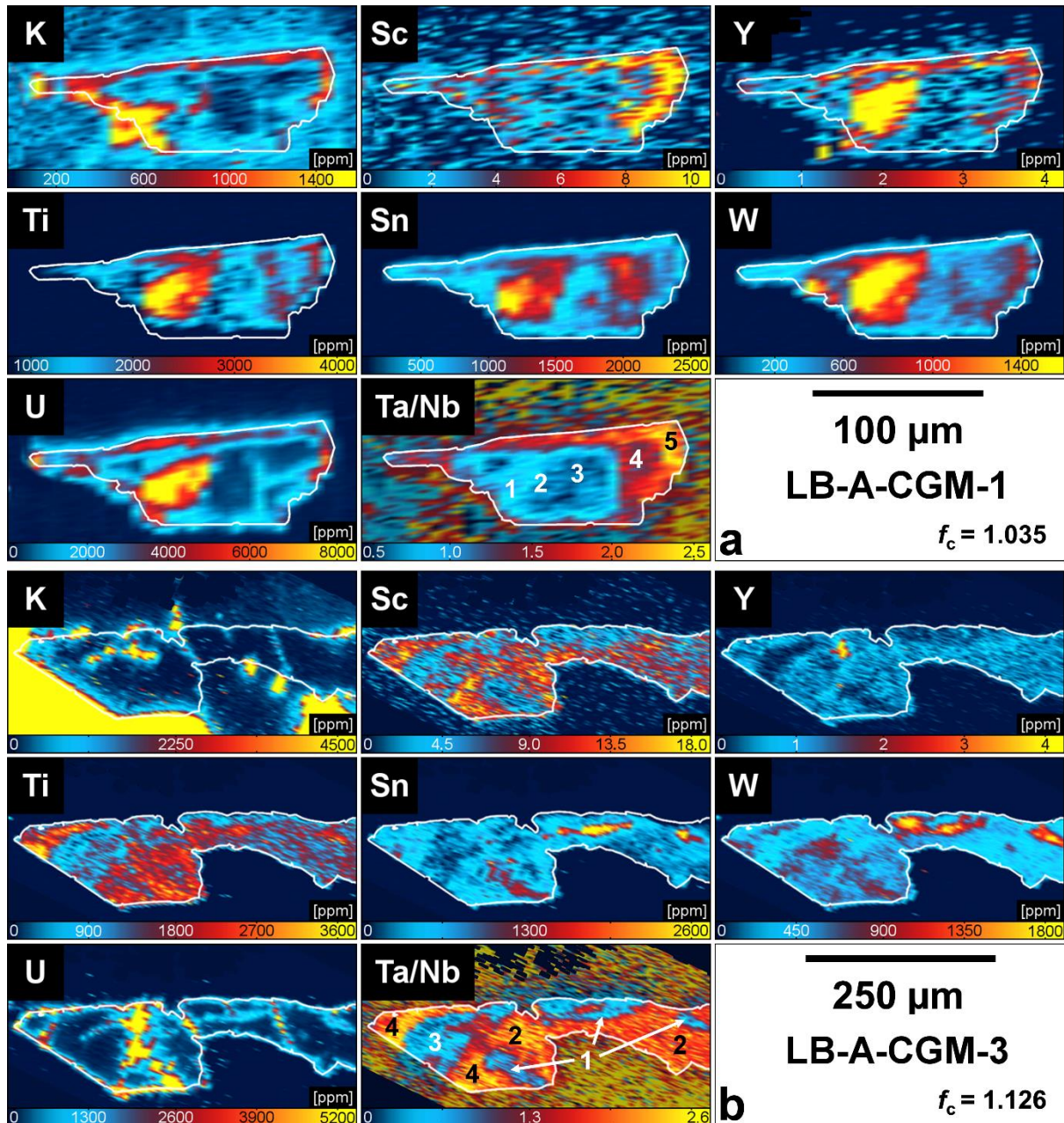


Fig. 9: Semi-quantitative LA-ICP-MS minor and trace elements images for columbite group minerals **a:** LB-A-CGM-1 within albitic portion of sample LB-A. From zone 1 to 3 in shows reverse zoning with decreasing Ta/Nb while the Ta-rich subhedral overgrowth (zones 4 and 5) shows normal zoning (increasing Ta/Nb). **b:** LB-A-CGM-3 is surrounded by albite and within the albitic portion of sample LB-A, but in contact to pegmatitic muscovite (high K). Only the boundary to muscovite is straight while the rest of the grain is strongly truncated. Four growth zones (numbers) were defined from the central parts to the upper left rim of the grain. The correction factors f_c ($=[\text{Ta}]_{\text{Iolite}}/[\text{Ta}]_{\text{SEM-EDS}}$) were used to correct the LA-ICP-MS data which was reduced without internal standard in a semi-quantitative mode of Iolite. Scales shown are corrected multiplication with f_c^{-1} .

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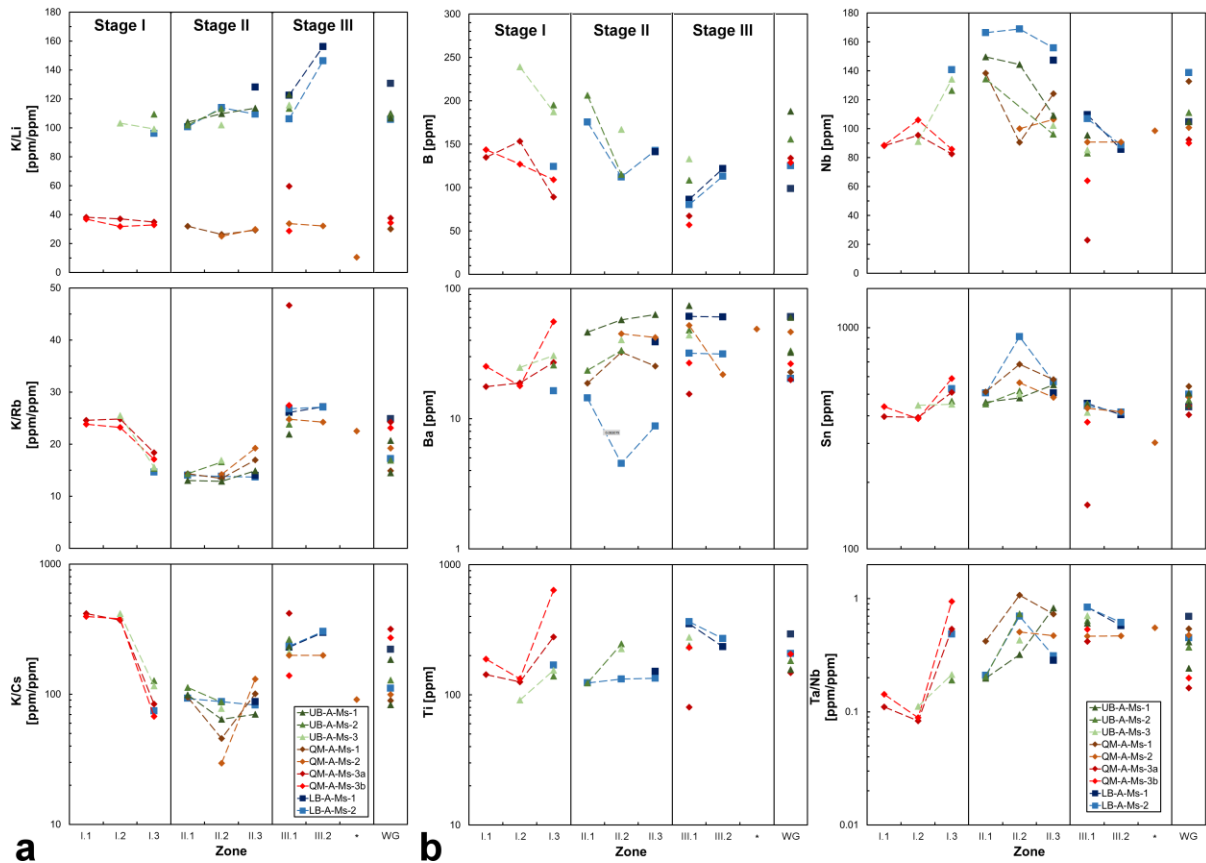


Fig. 10: Chemical variation in paragenetic stages and zones of all muscovite grains analyzed by LA-ICP-MS. Zones were correlated on basis of their K/Rb, K/Cs and K/Li patterns as shown in (a). Distribution of B, Ba and the high field strength elements Ti, Nb, Sn and Ta (expressed as Ta/Nb) in correlated mica growth zones is shown in (b). Samples from the upper border aplite (UB-A) are displayed in green (triangles), samples from the quartz muscovite assemblage are displayed in red (diamonds) and samples from the lower border aplite (LB-A) are displayed in blue (squares). Errors (2SE) for each element in the individual zones are generally <6% with most in the range of 1–3% (depending on the pixel area of individual zones). Absolute error values can be found in supplementary Table ST1. Three growth stages (I–III) were defined, based on resorption surfaces and trace element variations. Whole grain data (WG) is shown in the last column. The asterisk (*) on the x-axis marks replace BSE-bright mica in sample QM-A.

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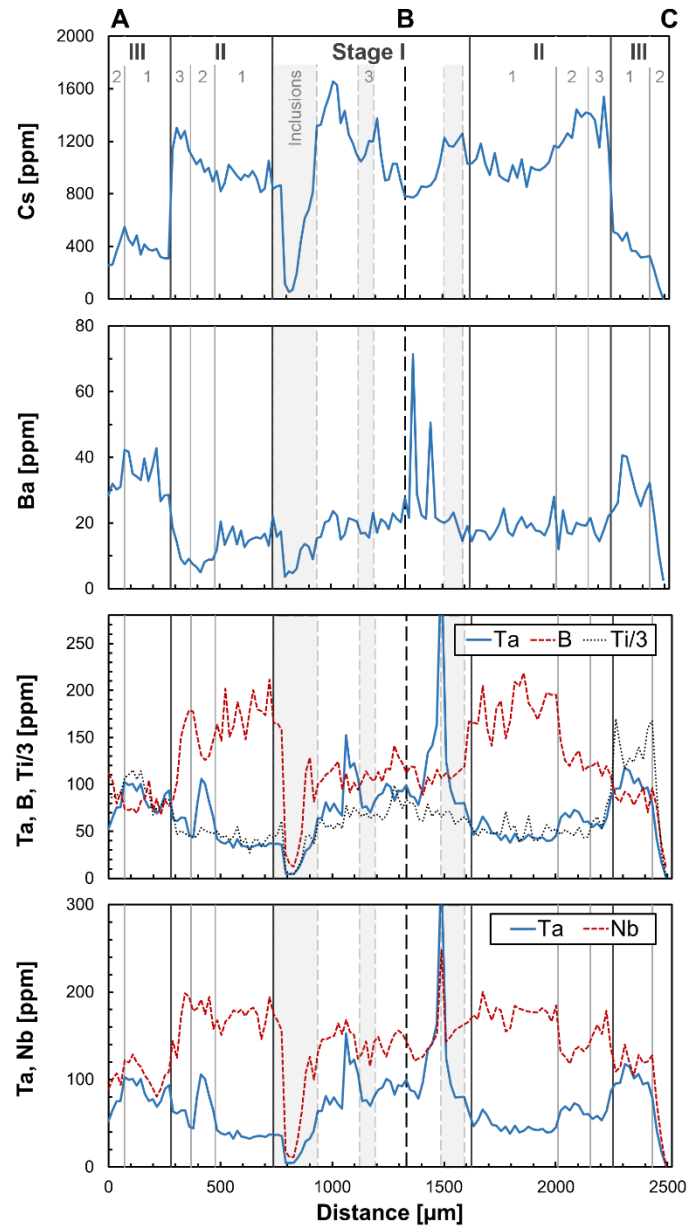


Fig. 11: Concentration profiles for Cs, Ba, B, Ti, Nb and Ta in muscovite LB-A-Ms-2 along the path shown in Fig. 10. Grey numbers refer to the individual zones of the crystal. Shaded areas mark inclusions. Stages I-III are the same as shown in Figs. 15 and 16. Cesium shows trends which would be expected for fractional crystallization of an incompatible element. Barium is depleted in stages I and II but enriched in stage III. Boron and Ta show anti-correlation, especially in the outer zones, while Ti and Ta seem correlated. Niobium and tantalum show clear anti-correlation for some zones, but correlation in others.

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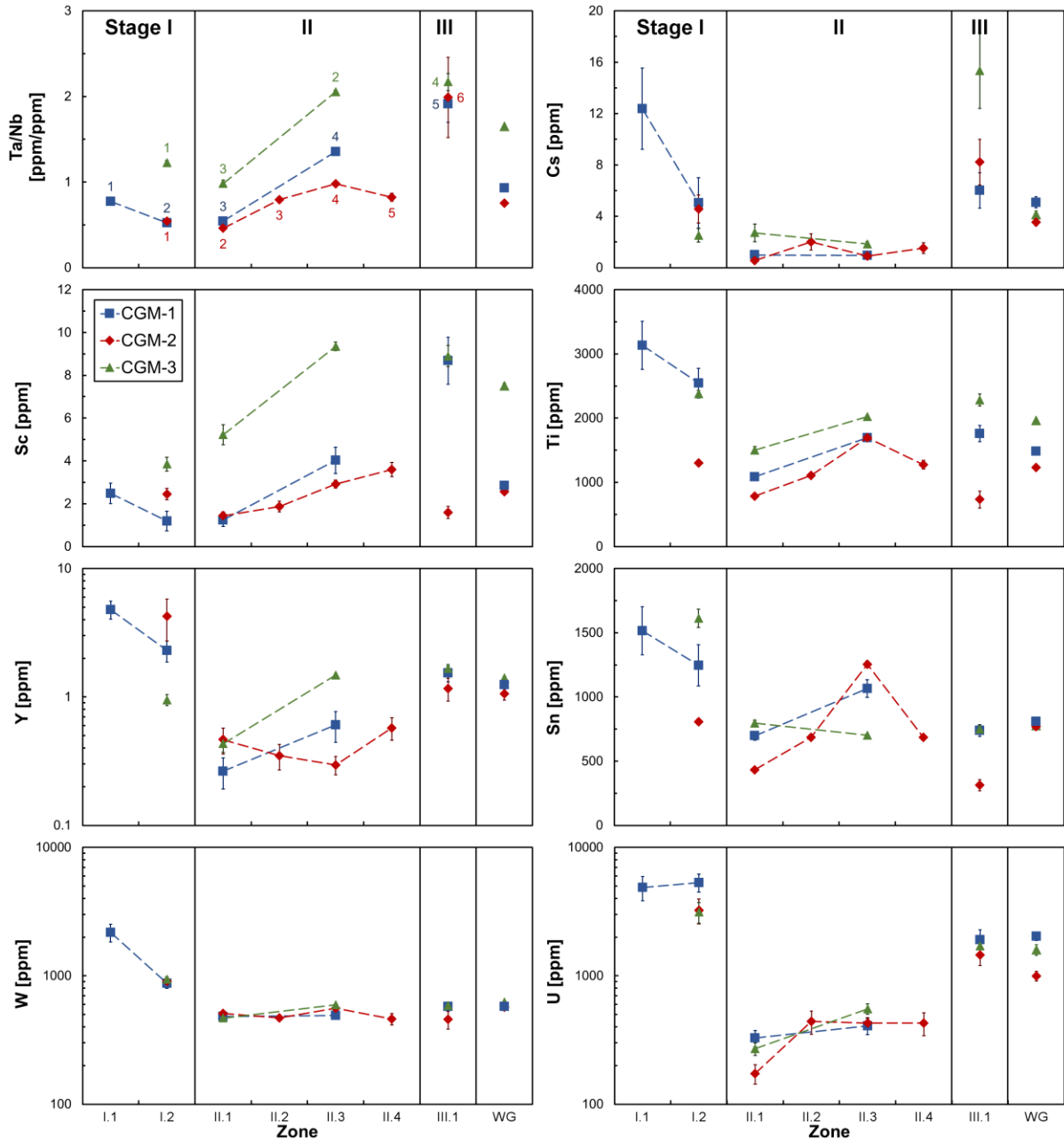


Fig 12: Correlated zones of columbite group minerals CGM-1 (squares), -2 (diamonds) and -3 (triangles) in the lower border aplite (sample LB-A) analyzed with LA-ICP-MS. Zones were correlated based on patterns of Ta/Nb, Ti, Y, Sn, W and U. The patterns can be subdivided into three stages (I–III) which are analogues to the stages observed in muscovite (Fig. 15). The error bars represent individual standard errors (2SE) for each zone (or whole grain) as exported from Iolite as well as propagated errors for Ta/Nb. WG: Whole grain.

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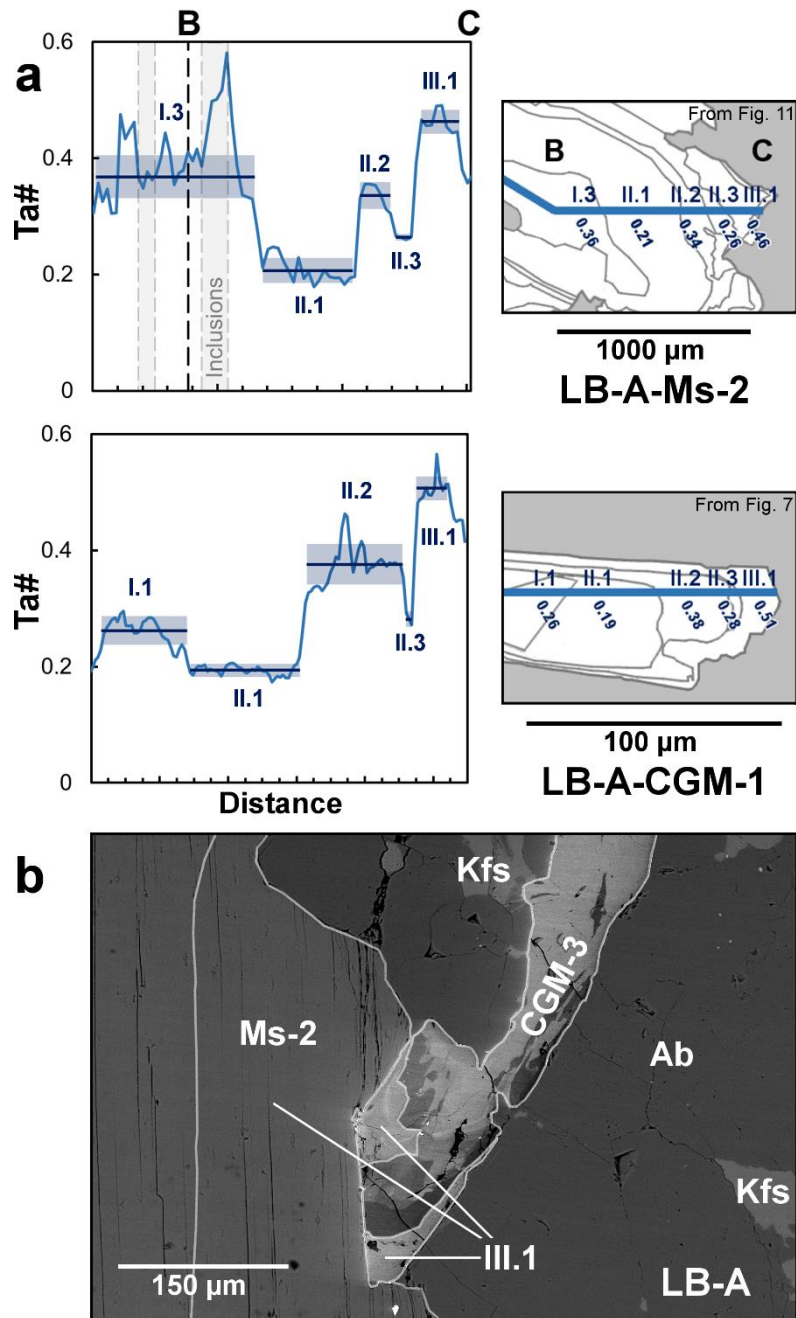


Fig. 13: Evidence for contemporaneous crystallization of columbite group minerals and white mica. **a:** Shown are profiles for $\text{Ta\#} = \text{Ta}/(\text{Ta}+\text{Nb})$ in muscovite LB-A-Ms-2 (Fig. 11) and columbite group mineral LB-A-CGM-1. Roman numerals (I–III) indicate the stages of pegmatite formation. Solid bars and shaded areas on the plots (left) show the average Ta# for each zone and the respective standard deviations. Absolute values for average Ta# are shown on the sketches (right). The patterns are the same in both types of minerals, suggesting contemporaneous crystallization. **b:** Composite BSE image of LB-A-CGM-1 in contact to LB-A-Ms-2, which illustrates the temporal association of zones III.1 of both muscovite and CGM.

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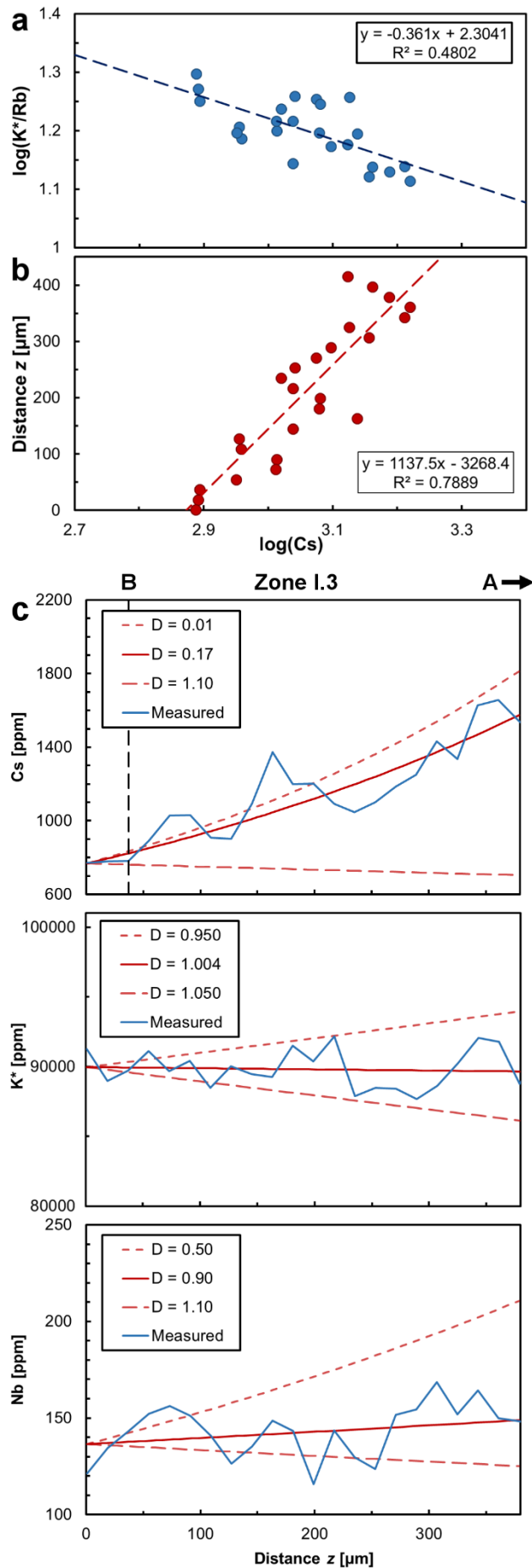


Fig. 14: Geochemical modeling of zone III.1 of muscovite LB-A-Ms-2. **a:** Slope and intercept of the linear relationship of $\log(K/Rb)$ vs $\log(Cs)$ depend on the bulk partition coefficients for each element as well as the starting composition of the crystallizing liquid. **b:** The distance z along the profile and $\log(Cs)$ show a linear relationship. This allows the melt fraction F to be inferred from the distance z . **c:** Modeled concentration for the concentration profiles of Cs, K and Nb in zone I.3 of muscovite LB-A-Ms-2 along the profile shown in Fig. 11 in direction B–A. Modeled concentrations are shown for different bulk partition coefficients D (red lines). Solid red lines represent D values which best fit the observed trends

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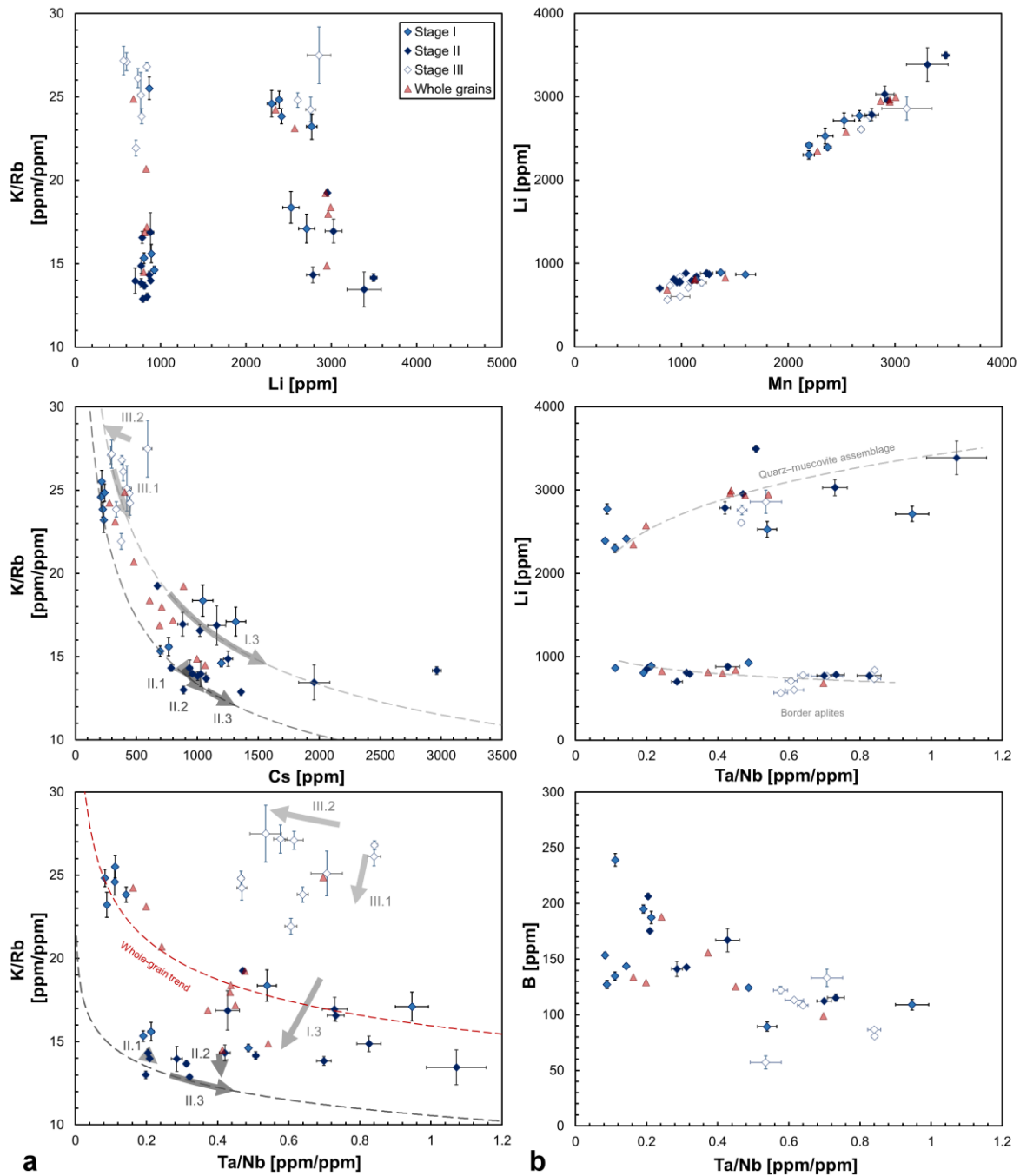


Fig. 15: Fractionation plots for rare elements in individual zones (diamonds) and whole grains (triangles) for all muscovite grains analyzed by LA-ICP-MS chemical mapping. The error bars represent individual standard errors (2SE) for each zone (or whole grain) as exported from Iolite as well as propagated errors for element ratios. **a:** K/Rb v. Li, Cs and Ta#. Arrows in the K/Rb v. Cs and K/Rb v. Ta/Nb plots are the modelled concentration ranges for the concentration profiles across the six individual zone (I.3–III.2) of muscovite LB-A-Ms-2. **b:** Li v. Mn, Li v. Ta/Nb and B v. Ta/Nb. Trends for Li v. Ta from regression for power-law behavior.

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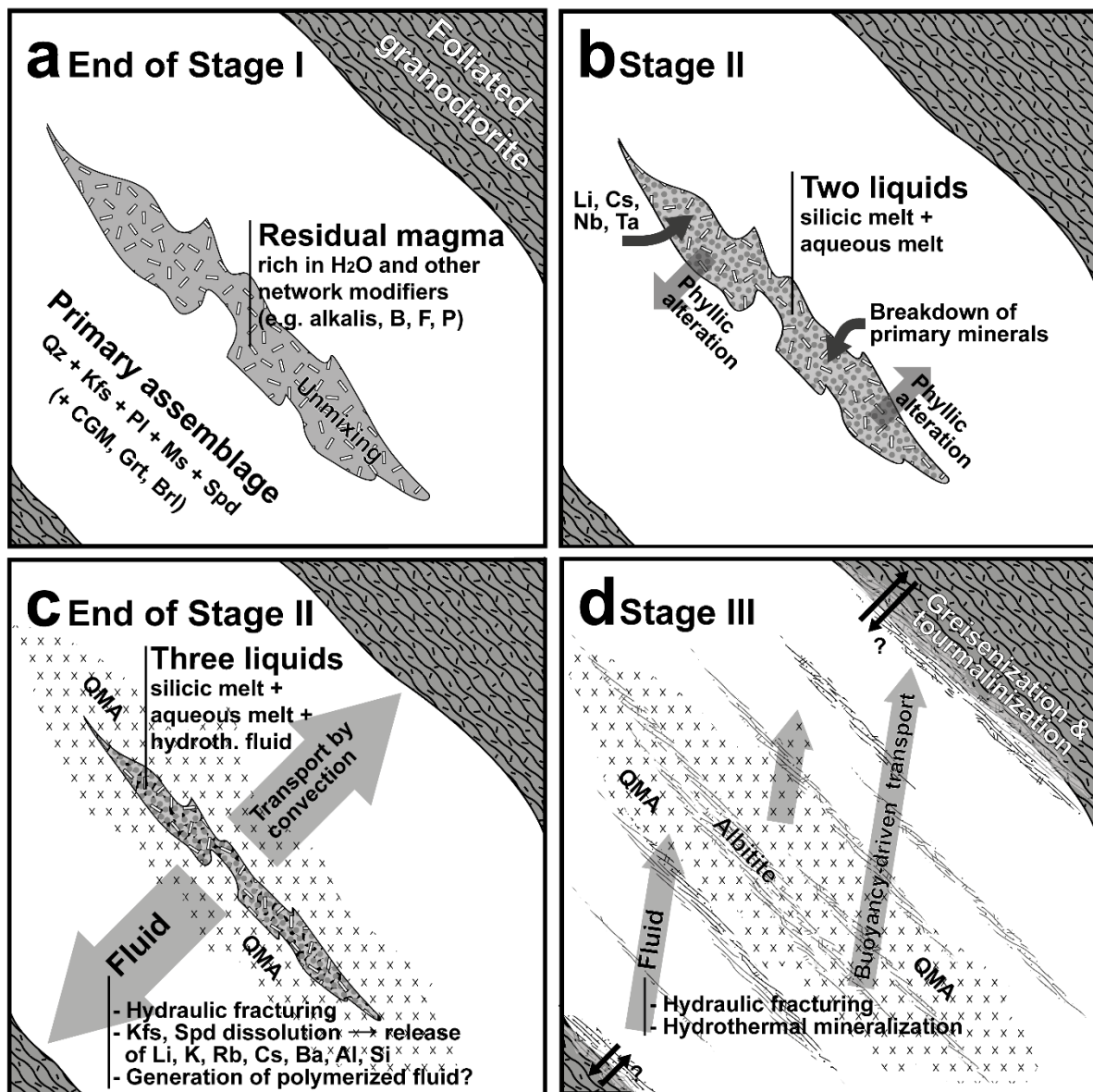


Fig. 16: Schematic illustration of our three-stage model of pegmatite crystallization summarizing the processes during magmatic–hydrothermal transition. **a:** Stage I marks the end of purely magmatic crystallization of the primary pegmatitic assemblage. The residual melt enriched in H₂O and network modifying elements starts to unmix an aqueous melt. **b:** In stage II, two liquids coexist. The aqueous melt alters parts of the primary assemblage to a phyllic quartz-muscovite assemblage (QM-A). Breakdown of primary minerals reincorporates rare elements into the residual melts. **c:** A hydrothermal fluid is released at some point. It causes further alteration and resorption of primary minerals. Local shift to hydrostatic pressure causes hydraulic fracturing. The temperature difference between core and margin facilitates fluid transport by convection. **d:** During stage III, albitite is precipitated from hydrothermal fluid. The fluid transports remobilized elements and causes greisenization and tourmalinization of the host rocks. Element transfer from the host rock might be possible, but was not assessed in this study. Cross sectional view. Based on the spodumene pegmatite solidification model for SE Ireland by Barros (2017).

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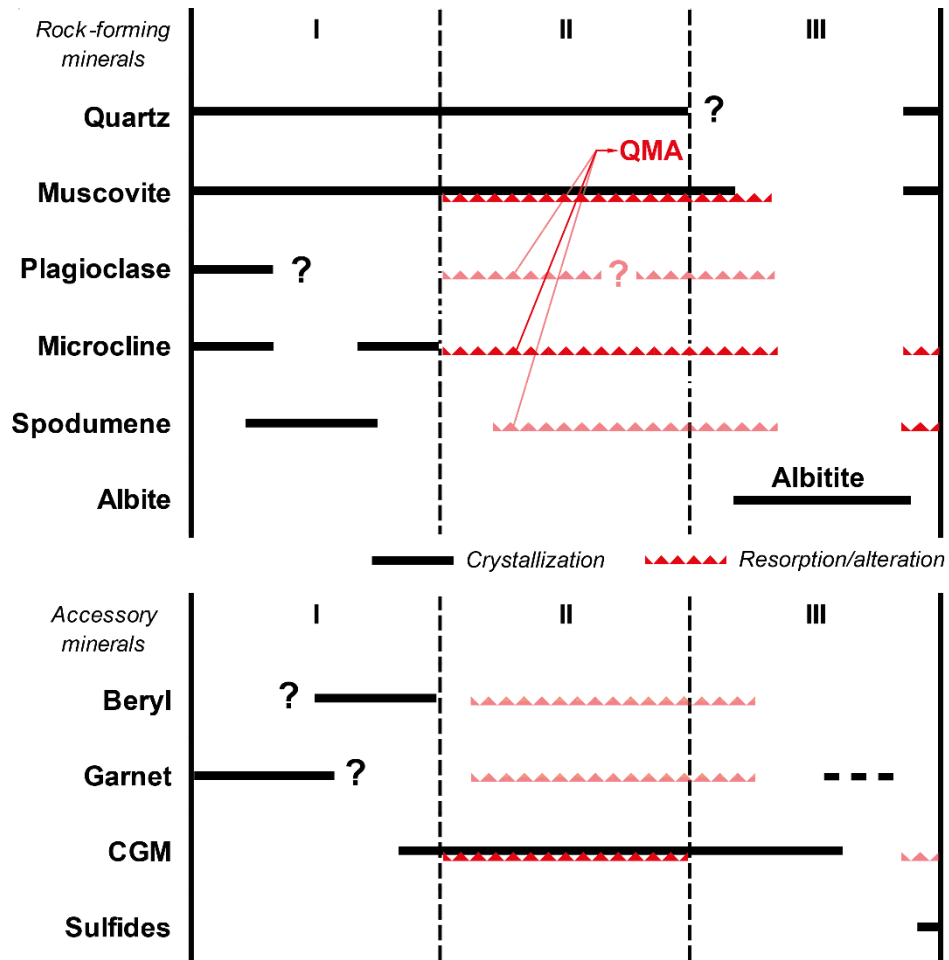


Fig. 17: Paragenetic sequence for rock-forming and accessory mineral crystallization and resorption/alteration during the three stages (I–III) of rare-element pegmatite formation. QMA: Onset of phyllic alteration and crystallization of quartz-muscovite assemblage.

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Table 1: Summary of all analyzed samples and minerals.

Sample	Lith.	Mineral	Comment
UB-A	b	<i>Muscovite</i>	
		Ms-1	Associated with several muscovite flakes in albitite.
		Ms-2	In paragenesis with CGM.
		Ms-3	CGM inclusion.
QM-A	c	<i>Muscovite</i>	
		Ms-1	In contact to multiple coarse muscovite flakes.
		Ms-2	Ms-2a in contact with beryl, replaced by Ms-2b.
		Ms-3	Located between albitite and quartz–muscovite assemblage.
LB-A	b	<i>Muscovite</i>	
		Ms-1	In contact with microcline, albite and CGM.
		Ms-2	In albite matrix; CGM inclusions.
		Ms-3	Fine-grained; filling feldspar fractures.
		<i>Albite</i>	
		Ab-1–3	Albitite-forming elongate-prismatic grains.
		<i>Microcline</i>	
		Kfs-1–3	Remnant perthitic microcline with diffuse crosshatch twinning.
		<i>CGM</i>	
		CGM-1	Oscillatory zoning; truncation.
CGM-2	Oscillatory and complex zoning; truncation.		
CGM-3	Complex zoning; truncation.		

Lithologies: b) albitite; c) quartz-muscovite assemblage.
 CGM: columbite group mineral (columbite–tantinite).

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Table 2: Major and minor element composition of muscovite in samples UB-A, QM-A and LB-A as determined by SEM-EDS. Concentrations are presented in wt.%. Cation calculation on basis of 20 oxygen atoms (excl. OH) using the following assumptions: $Al^{IV} = 8 - Si$; $Al^{VI} = Al_{total} - Al^{IV}$; $OH^* = 4 - F$; $Li_2O^* = 0.3935 F^{1.236}$ (Tischendorf et. al 1997).

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	Upper-border albitite (UB-A)						Quartz-muscovite assemblage (QM-A)						Lower-border albitite (LB-A)							
	Ms-1	1 σ	Ms-2	1 σ	Ms-3	1 σ	Ms-1	1 σ	Ms-2a	1 σ	Ms2-b	1 σ	Ms-3	1 σ	Ms-1	1 σ	Ms-2	1 σ	Ms-3	1 σ
	n=5		n=4		n=6		n=9		n=6		n=3		n=3	n=4		n=3		n=3		n=3
SiO ₂	45.51	0.09	45.25	0.23	45.59	0.39	45.45	0.13	45.45	0.08	48.22	2.06	45.52	0.18	45.49	0.10	45.39	0.10	47.55	0.96
Al ₂ O ₃	35.79	0.14	35.75	0.43	35.32	0.68	33.53	0.21	33.38	0.33	21.49	0.89	34.02	0.12	35.20	0.29	35.44	0.05	36.34	0.84
FeO	1.48	0.07	1.37	0.24	1.67	0.36	3.44	0.19	3.41	0.17	8.81	1.39	3.03	0.08	2.08	0.15	1.96	0.03	0.31	0.16
MnO	0.13	0.01	0.14	0.04	0.18	0.04	0.36	0.03	0.37	0.02	1.12	0.16	0.32	0.02	0.11	0.03	0.11	0.02	0.03	0.02
MgO	0.09	0.02	0.09	0.03	0.10		0.03	0.01	0.03	0.01	0.16	0.12	b.d.		0.11	0.01	b.d.		b.d.	
CaO	0.07	0.02	0.08	0.01	0.08	0.02	0.07	0.01	0.08	0.02	0.07	0.02	0.06	0.00	0.09	0.01	0.07	0.01	0.07	0.02
Na ₂ O	0.48	0.06	0.43	0.05	0.45	0.04	0.42	0.05	0.40	0.02	0.14	0.04	0.48	0.06	0.44	0.04	0.42	0.03	0.44	0.06
K ₂ O	10.55	0.18	10.65	0.12	10.63	0.09	10.63	0.11	10.63	0.06	10.44	0.16	10.69	0.07	10.80	0.05	10.79	0.03	10.57	0.27
Rb ₂ O	0.58	0.25	0.74	0.12	0.49	0.16	0.60	0.10	0.42	0.16	0.53	0.16	0.32	0.08	0.51	0.12	0.36	0.06	0.29	0.13
Cs ₂ O	0.09	0.08	0.10	0.07	0.03	0.03	0.05	0.02	0.06	0.04	0.19	0.05	0.03	0.03	0.03	0.03	0.04	0.02	b.d.	
F	0.49	0.08	0.52	0.06	0.56	0.05	1.00	0.09	1.01	0.06	4.37	0.83	0.85	0.03	0.45	0.05	0.39	0.03	b.d.	
Sum	95.26		95.12		95.10		95.60		95.21		95.53		95.32		95.30		94.98		95.60	
Li ₂ O*	0.15	0.03	0.17	0.03	0.18	0.02	0.39	0.05	0.40	0.03	2.78	0.70	0.32	0.01	0.14	0.02	0.11	0.01		
H ₂ O*	4.23	2.94	4.19	2.07	4.18	1.60	3.93	1.62	3.92	1.07	2.17	3.44	4.01	0.63	4.22	1.99	4.25	1.39	4.54	
O=F	0.21		0.22		0.24		0.42		0.43		1.84		0.36		0.19		0.16			
Sum*	99.43		99.26		99.22		99.50		99.10		98.64		99.30		99.47		99.18		100.14	
Si	6.121		6.107		6.147		6.184		6.198		6.815		6.179		6.137		6.130		6.206	
Al _{IV}	1.879		1.893		1.853		1.816		1.802		1.185		1.821		1.863		1.870		1.794	
Σ_T	8.000		8.000		8.000		8.000		8.000		8.000		8.000		8.000		8.000		8.000	
Al _{VI}	3.796		3.795		3.761		3.562		3.564		2.395		3.621		3.735		3.772		3.925	
Fe	0.166		0.155		0.188		0.392		0.389		1.041		0.344		0.235		0.222		0.030	
Mn	0.015		0.015		0.021		0.042		0.043		0.134		0.036		0.013		0.013		0.003	
Mg	0.018		0.019		0.020		0.007		0.006		0.033				0.022					
Li*	0.082		0.090		0.099		0.216		0.219		1.582		0.174		0.075		0.061			
Σ_Y	4.077		4.074		4.089		4.219		4.221		5.185		4.175		4.079		4.068		3.957	
Ca	0.010		0.012		0.011		0.011		0.011		0.011		0.009		0.012		0.010		0.010	
Na	0.124		0.113		0.118		0.111		0.106		0.037		0.126		0.116		0.111		0.113	
K	1.810		1.833		1.828		1.845		1.848		1.882		1.851		1.858		1.858		1.798	
Rb	0.050		0.064		0.042		0.052		0.036		0.048		0.028		0.044		0.031		0.023	
Cs	0.005		0.006		0.002		0.003		0.003		0.011		0.002		0.001		0.002			
Σ_X	1.999		2.028		2.001		2.022		2.004		1.989		2.016		2.031		2.012		1.944	
OH*	3.792		3.777		3.760		3.569		3.564		2.045		3.634		3.807		3.833		4.000	
F	0.208		0.223		0.240		0.431		0.436		1.955		0.366		0.193		0.167		0.000	
Σ_A	4.000		4.000		4.000		4.000		4.000		4.000		4.000		4.000		4.000		4.000	
$\Sigma_{X+Y+T+A}$	18.076		18.102		18.090		18.241		18.225		19.174		18.191		18.111		18.081		17.901	

b.d.: below detection limit

*calculated, 1 σ propagated from 1 σ for F

Table 3: Albite (Ab1–3) and microcline (Kfs1–3) composition in sample LB-A as determined by SEM-EDS. Element oxide concentrations in wt%; endmember concentrations in mol.%. Cation calculations on basis of 8 oxygen atoms.

	Albite						Microcline					
	LB-A		1σ		LB-A		1σ		LB-A		1σ	
	Ab-1	n=3	Ab-2	n=4	Ab-3	n=3	Kfs-1	n=5	Kfs-2	n=4	Kfs-3	n=6
SiO ₂	67.70	0.53	68.21	0.35	68.23	0.21	63.84	0.21	64.18	0.21	64.00	0.16
Al ₂ O ₃	19.91	0.27	19.82	0.05	19.94	0.08	18.84	0.11	19.10	0.06	19.00	0.07
P ₂ O ₅	b.d.		b.d.		b.d.		0.27	0.14	0.37	0.04	0.34	0.05
CaO	0.08	0.08	b.d.		0.04	0.04	0.08	0.02	0.08	0.02	0.06	0.05
Na ₂ O	11.27	0.09	11.29	0.11	11.39	0.09	0.62	0.06	0.95	0.10	0.86	0.15
K ₂ O	0.08	0.02	0.15	0.04	0.12	0.07	16.19	0.13	15.58	0.18	15.90	0.33
Sum	99.03		99.46		99.72		99.84		100.26		100.16	
Si	2.982		2.989		2.985		2.964		2.960		2.960	
Al	1.033		1.024		1.028		1.031		1.038		1.036	
P							0.005		0.007		0.007	
Σ _T	4.015		4.013		4.013		4.001		4.005		4.002	
Ca	0.004				0.002		0.004		0.004		0.003	
Na	0.962		0.959		0.966		0.056		0.085		0.077	
Ka	0.004		0.008		0.007		0.959		0.917		0.938	
Σ _X	0.970		0.970		0.974		1.019		1.005		1.018	
Σ _{T+X}	4.985		4.983		4.987		5.019		5.010		5.020	
An	0.37		0.00		0.19		0.39		0.38		0.29	
Ab	99.17		99.16		99.12		5.50		8.41		7.60	
Or	0.46		0.84		0.69		94.11		91.21		92.11	

n: measurements per grain.

b.d.: below detection limit.

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Table 4: Composition of columbite group minerals (CGM) in sample LB-A as determined by SEM-EDS. Element oxide concentrations in wt%. Cation calculations on basis of 6 oxygen atoms for the stoichiometric formula XY₂O₆.

	LB-A-CGM-1			LB-A-CGM-2			LB-A-CGM-3		
	1	2	3	1	2	3	1	2	3
Ta ₂ O ₅	21.17	20.18	40.60	22.36	19.12	36.99	28.45	28.18	47.79
Nb ₂ O ₅	58.87	60.21	40.40	58.65	60.90	43.09	51.20	53.17	31.20
FeO	7.23	9.08	8.32	8.27	8.09	8.53	10.02	9.38	9.62
MnO	12.10	10.34	9.57	11.04	11.30	9.54	8.75	9.08	8.25
Sum	99.37	99.82	98.89	100.32	99.41	98.14	98.43	99.81	96.87
Ta	0.36	0.34	0.75	0.37	0.32	0.68	0.50	0.49	0.94
Nb	1.64	1.66	1.24	1.63	1.68	1.31	1.49	1.52	1.02
Σ _Y	2.00	2.00	1.99	2.00	2.00	1.99	1.99	2.01	1.96
Fe	0.37	0.46	0.47	0.42	0.41	0.48	0.54	0.50	0.58
Mn	0.63	0.54	0.55	0.57	0.58	0.54	0.48	0.49	0.51
Σ _X	1.01	1.00	1.02	1.00	1.00	1.03	1.02	0.98	1.09
Σ _{X+Y}	3.00	3.00	3.01	3.00	3.00	3.02	3.01	2.99	3.05
Ta#	0.18	0.17	0.38	0.19	0.16	0.34	0.25	0.24	0.48
Mn#	0.63	0.54	0.54	0.57	0.59	0.53	0.47	0.50	0.46

Ta# = Ta/(Ta+Nb)

Mn# = Mn/(Mn+Fe)

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Table 5: Mineral/melt and fluid melt/partition coefficients k_d for K, Rb, Cs, Nb and Ta including references (a–h). Partition coefficients are for the respective mineral/fluid in peraluminous granitic, rhyolitic, or pegmatitic melt, unless stated otherwise.

Element	Muscovite	Alkali feldspar	Albite	Quartz	Fluid
K	2.52 a	3.13 b	0.10 d*	0.013 f	0.10 g
Rb	1.61 a	1.30 c	0.04 e	0.014 f	0.45 f
Cs	0.21 a	0.16 b	0.04 e	0.029 f	0.50 f
Nb	3.50 g		0.10 h'	0.010 ‡	0.08 i
Ta	0.42 g		0.13 h'	0.010 ‡	0.08 ‡
References	a: Icenhower & London (1996); b: Icenhower & London (1995); c: Walker et al. 1989; d: Philpotts & Schnetzler (1970); e: Joliff et al. (1992); f: Nash & Crecraft (1985); g: London(2005); h: Raimbault & Burnol 1998; h: Bea et al. (1994); i: Linnen & Cuney (2005).				

*Plagioclase in andesite.

'Plagioclase in peraluminous migmatite.

‡Assumed.

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Table 6: Results from geochemical modelling for the trace element distribution in profile B–A for each zone of muscovite LB-A-Ms-2. **a:** Slope (m) and (b) from linear regression of the data, as well as modeled values for m , b and residual melt at the end of each zone F_{end} . **b:** bulk partition coefficients for best solutions for modeled m and b or best fit of the observed concentration trend (parentheses) **c:** Initial melt/fluid composition. **d:** melt/fluid composition at F_{end} . Bulk partition coefficients and concentrations in brackets fit the actual observed profile best, while they yield poor solutions for m and b .

a Zone	From regression		Model		F_{end}
	m	b	m	b	
I.3	-0.361	2.30	-0.361	2.30	0.42
II.1	-0.652	3.09	0.652 (-0.068)	3.09 (1.36)	0.93
II.2	-0.612	2.98	0.612 (-0.303)	2.98 (2.06)	0.82
II.3	-0.566	2.84	-0.566 (-0.327)	2.83 (2.10)	0.77
III.1	-0.165	1.82	-0.165 (-0.280)	1.73 (2.06)	0.63
III.2	-0.048	1.57	-0.045	1.39	0.85
b Bulk partition coefficients					
Zone	D_K	D_{Rb}	D_{Cs}	D_{Nb}	D_{Ta}
I.3	1.004	0.710	0.173	0.90	1.10
II.1	1.68 (1.05)	1.205 (1.001)	0.279	1.80	0.10
II.2	1.48 (0.70)	0.93 (0.43)	0.109	0.10	0.01
II.3	1.38 (1.16)	0.870	0.103	2.00	0.001
III.1	0.76 (0.85)	0.640	0.250	0.20	0.28
III.2	0.90	1.120	5.250	1.30	3.20
c Initial melt/fluid composition ($F = 1$)					
Zone	K [wt%]	Rb [ppm]	Cs [ppm]	Nb [ppm]	Ta [ppm]
I.3	3.57	3100	4800	39	224
II.1	3.52	3900	5635	50	85
II.2	3.50	3830	5550	47	158
II.3	3.68	4430	6720	52	115
III.1	3.50	2100	1980	52	170
III.2	3.51	1960	2850	29	180
d Melt/fluid composition at F_{end}					
Zone	K [wt%]	Rb [ppm]	Cs [ppm]	Nb [ppm]	Ta [ppm]
I.3	3.56	4002	9835	43	205
II.1	3.35 (3.50)	3840 (3900)	5940	47	91
II.2	3.18 (3.71)	3880 (4290)	6620	56	192
II.3	3.34 (3.53)	4590	8495	40	149
III.1	3.90 (3.75)	2480	2800	36	237
III.2	3.55	1920	430	28	126

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