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Michel Pichavant

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**Experimental crystallization of the Beauvoir granite as a model for the evolution of Variscan rare metal magmas**

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1 **Experimental crystallization of the Beauvoir granite as a model for**  
2 **the evolution of Variscan rare metal magmas**

3  
4 **Michel Pichavant\***

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6 Université d'Orléans, Institut des Sciences de la Terre d'Orléans (ISTO), UMR 7327, 1A rue  
7 de la Férollerie, CS 20066, 45071, Orléans Cedex 02, France

8  
9 \*Corresponding author. E-mail: michel.pichavant@cnrs-orleans.fr

10  
11 **ABSTRACT**

12 New experiments on the strongly peraluminous, Li-, P- and F-rich Beauvoir granite (Massif  
13 Central, France) provide a basis for understanding crystallization and chemical fractionation  
14 in Variscan rare metal magmas. Crystallization experiments were performed on two natural  
15 granite compositions under H<sub>2</sub>O-saturated conditions at 100, 200 and 300 MPa, from 540°C  
16 to 700°C and between ~NNO+3 and NNO-1.4. Experimental charges were examined by SEM  
17 and their products (glasses and crystals) analyzed for major elements by EMPA. Trace  
18 element concentrations in selected glasses were also determined by LA ICP-MS. Despite  
19 experimental durations commonly exceeding 1000 h and some up to 4000 h, kinetic problems  
20 were encountered in particular in the 100 MPa charges whereas, at 200 and 300 MPa, results  
21 consistent with previous melting experiments were obtained. Beauvoir melts crystallize  
22 quartz, plagioclase, K-feldspar and mica as major phases. At NNO-1.4, mica is a biotite  
23 whereas it is a Li-mica between ~NNO+3 and NNO-1. Apatite, Fe-Ti oxides, either hematite  
24 or magnetite, topaz, amblygonite, cassiterite and columbite-tantalite appear as accessory  
25 phases between ~NNO+3 and NNO+1. Experimental plagioclases are albitic (An < 4.5 mol%)  
26 and more Ca and K-rich than natural albites in the granite whereas experimental K-feldspars  
27 are more sodic (Ab < 45 mol%) than the natural crystals. The less evolved starting melt  
28 crystallized Li phengites whereas the most evolved yielded Li-, F-rich micas near the  
29 polyolithionite-zinnwaldite series, similar to natural micas in the granite. Equilibrium  
30 crystallization increases A/CNK, F and P and concentrates Li, Be, B, Rb, Cs, W, U in the  
31 melt. Nb and Ta are also enriched, their behavior being controlled by the solubility of  
32 columbite-tantalite in the melt. Other elements are either unchanged (Mn, Zn, Ti) or depleted  
33 (Sr, Pb) during magmatic fractionation. Sn is concentrated in Li-mica and hematite and it  
34 behaves compatibly at high fO<sub>2</sub>. Beauvoir melts crystallize at very low temperatures, below  
35 670°C for the two compositions studied and solidus temperatures, determined from previous  
36 melting experiments and confirmed by the new crystallization experiments, are near 550°C.  
37 The experiments demonstrate that most of the mineralogical and geochemical characteristics

38 that make the Beauvoir granite distinctive result from magmatic rather than hydrothermal  
39 post-magmatic processes. Albitic plagioclase, Li-mica, topaz and amblygonite are of  
40 magmatic origin. Glass major element compositions suggest that the two granite samples  
41 represent crystallized liquids. Trace element fractionations for most elements at Beauvoir can  
42 be accounted for by magmatic crystallization-differentiation processes. Implications for the  
43 mineralogy,  $fO_2$ , volatile concentrations, crystallization and conditions of emplacement,  
44 fractionation mechanisms and origin of the Beauvoir granite are discussed.

45

46 **Key words:** rare metal granite, crystallization experiments, mica compositions, magmatic  
47 fractionation

48

## 49 INTRODUCTION

50 The Beauvoir granite (northwest French Massif Central, FMC) is a composite granitic  
51 intrusion with mineralogical and geochemical characteristics emblematic of Variscan rare  
52 metal granites (Linnen and Cuney, 2005; Breiter, 2012; Romer and Pichavant, 2021). Since  
53 Aubert (1969), the Beauvoir granite has been extensively studied. Scientific results obtained  
54 from the ~900 m long continuous core drilling Géologie Profonde de la France (GPF)  
55 program have led to an integrated petrological, geochemical, geophysical, structural and  
56 geochronological description of the Beauvoir granite and its country rocks (Cuney and  
57 Autran, 1987). This has formed the basis for metallogenic models of mineralizations  
58 associated with peraluminous granites (Cuney et al., 1992; Raimbault et al., 1995). Recently,  
59 the Beauvoir granite has attracted a renewed interest, mainly centered on the magmatic-  
60 hydrothermal evolution and on W deposition processes. Harlaux et al. (2018) have re-  
61 investigated the primary fluid inclusions hosted in quartz and topaz from the granite and the  
62 associated La Bosse W-bearing stockwork. Several episodes of wolframite generation and W  
63 deposition have been recognized in the Echassières district around the Beauvoir granite  
64 (Monnier et al., 2019; 2020).

65 Although the Beauvoir granite can be locally extensively transformed as a result of  
66 greisenisation and kaolinization, results from the GPF program have emphasized the  
67 magmatic evolution of the granite (Cuney and Autran, 1987). Raimbault et al. (1995) showed  
68 that the Beauvoir granite was built as several independent magma batches. Its P- and Ta-rich  
69 nature was recognized and also the geochemical similarity between the Beauvoir granite and  
70 other enriched crustal magmas such as rare element pegmatites (Raimbault et al., 1995; Cerny  
71 et al., 2005a). Subsequently, the Beauvoir granite has served as a reference for the

72 mineralogical and geochemical characteristics of other rare metal granites such as Montebbras  
73 (Marcoux et al., 2021), Argemela (Michaud and Pichavant, 2020) and Podlesi (Breiter et al.,  
74 1997) in the Variscan belt and also Pitinga (Costi et al., 2009) and Yichun (Pollard, 2021)  
75 outside the Variscan belt.

76 The Beauvoir granite is specific in many aspects, one of the most unusual being the  
77 very low solidus temperatures, < 600°C for H<sub>2</sub>O-saturated conditions between 100 and 300  
78 MPa (Pichavant et al., 1987a), i.e. more than 100°C lower than the solidus of the haplogranite  
79 Qz-Ab-Or system (Tuttle and Bowen, 1958). These low solidus temperatures have been an  
80 important anchoring point in models proposed for the origin, magmatic evolution and  
81 magmatic-hydrothermal transition of the Beauvoir granite (Aïssa et al., 1987; Cuney and  
82 Autran, 1987; Cuney et al., 1992; Fouillac and Rossi, 1991; Raimbault et al., 1995). The  
83 solidus temperature determinations were based on melting experiments and only a few  
84 crystallization experiments were performed (Pichavant et al., 1987a). Since 1987, additional  
85 experimental investigations have been carried out on the Beauvoir granite (Lahlafi, 1997;  
86 Pichavant et al., 2016; unpublished) and new constraints have become available on the  
87 magmatic evolution. The aim of this paper is to present a synthesis of experiments available  
88 on the Beauvoir granite.

89 Pichavant et al. (1987a) pointed out the restricted number of experimental phase  
90 equilibria available on natural rare metal granites in comparison with data on equivalent  
91 synthetic compositions. Since that time and the works of Kovalenko (1979) on ongonites and  
92 of Weidner and Martin (1987) on the Slip leucogranite from the St Austell pluton, several  
93 experimental studies have come out on highly evolved granites. Solidus and liquidus  
94 temperatures, crystallization sequences and melt fractionation trends have been determined on  
95 one sample from the vertically zoned, F-bearing Xianghualing pluton in south China (Xiong  
96 et al., 2002). Lukkari and Holtz (2007) worked out the phase relations and mutual stabilities  
97 of F-bearing phases for the Kymi topaz granite in south Finland. Aksyuk et al. (2016)  
98 presented solidus data for a biotite and a Li-F granite from the Voznesenka area, far-east  
99 Russia. More recently, phase equilibria have been determined for the different facies of the  
100 Qitianling pluton, south China (Huang et al., 2021). All these experimentally investigated  
101 granites have in common to be F-bearing or F-rich and metaluminous to slightly  
102 peraluminous and to present A-type affinities. In contrast, rare metal granites in the Variscan  
103 belt are mostly strongly peraluminous and P-rich, besides being also high in F and Li  
104 (Raimbault et al., 1995; Linnen and Cuney, 2005). This underlines the importance of phase  
105 equilibrium data on the Beauvoir granite which, together with the Slip leucogranite (Weidner

106 and Martin, 1987), represents the only experimentally investigated example of peraluminous,  
107 P-rich natural rare metal granite composition (PHP type of Linnen and Cuney, 2005). Below,  
108 the experimental phase relations for two facies of the Beauvoir granite are presented, focusing  
109 on liquidus and solidus temperatures, crystallization sequence, melt and mineral composition  
110 trends and rare element enrichment mechanisms. The experimental results constrain the  
111 conditions of crystallization of PHP rare metal magmas in the Variscan belt (Linnen and  
112 Cuney, 2005; Roda Robles et al., 2018; Michaud and Pichavant, 2020) and provide insight on  
113 the behavior of rare metals at the magmatic stage.

114

### 115 **THE BEAUVOIR GRANITE**

116 The Beauvoir granite is located within the Echassières granitic complex in the northwest part  
117 of the FMC which belongs to the northern margin of Gondwana, the southern continent  
118 involved in the Variscan collision (Faure et al., 2009). The Echassières granitic complex  
119 outcrops in a tectonic window that exposes the Para-Autochthonous and Lower Gneiss Units,  
120 structurally the deepest formations of the stack of metamorphic nappes in the FMC (Faure et  
121 al., 2009). Granitic rocks from the Echassières complex, including the Colettes and the  
122 Beauvoir granite, intrude biotite-muscovite micaschists from the Para-Autochthonous Unit  
123 (Cuney and Autran, 1987; see map in Harlaux et al., 2017).

124 The main granite unit in the Echassières complex is the Colettes granite (surface  
125 extension 40 km<sup>2</sup>), which is a biotite-muscovite granite. The Beauvoir granite forms a small  
126 (surface extension 0.1 km<sup>2</sup>) satellite intrusion south of the Colettes. Field relations and  
127 previous works demonstrate that the Beauvoir is intrusive into the Colettes granite. However,  
128 radiometric ages for the two granites overlap, from 312 +/- 8 Ma (Colettes) to between 308  
129 and 317 Ma (Beauvoir, see details in Cuney and Marignac, 2015 and Monnier et al., 2019).  
130 Both granites crosscut the quartz-wolframite veins of the La Bosse stockwork hosted in  
131 country rock micaschists south of the granitic complex. This early mineralizing episode (335  
132 Ma, Harlaux et al., 2018; Monnier et al., 2019) has been interpreted to be genetically related  
133 to the La Bosse granite whose existence is postulated at depth (Aubert, 1969; Cuney et al.,  
134 1992; Harlaux et al., 2017).

135 The Beauvoir granite is mineralogically and geochemically highly specific. The GPF  
136 drill hole intersected both the upper and lower contacts of the granite with metamorphic  
137 country rocks at depths of 100 and 880 m respectively below the surface. Petrographic and  
138 structural studies show that the granite was emplaced as an inclined sheet-like body in country  
139 rock micaschists, remnants of which occur as roof pendants of several m in the upper part and

140 as sheets at the base of the granite. Analysis of the drill core revealed that the granite is  
141 composite and consists of 3 main units (Cuney and Autran, 1987; Cuney et al., 1992),  
142 including from top to bottom the B1 (from 100 to 450 m depth), B2 (from 450 to 750 m  
143 depth) and B3 (from 750 to 880 m depth) units. Several porphyritic microgranites are  
144 encountered near the bottom of the drill hole.

145 Mineralogically, the Beauvoir is an albite-lepidolite granite. There are minor but  
146 systematic variations in textures and proportions of the main mineral phases (albite, lepidolite,  
147 quartz, K-feldspar) between the different facies (Rossi et al., 1987; Cuney et al., 1992;  
148 Harlaux et al., 2017). The B1 facies is hololeucocratic, rich in albite and lepidolite and  
149 relatively poor in K-feldspar and it contains globular quartz with a snowball texture. The B2  
150 facies, slightly darker than the B1, is enriched in K-feldspar and depleted in albite and  
151 lepidolite. The B3 facies is characterized by pink perthitic K-feldspars which are more  
152 abundant than micas. The granite hosts accessory phases such as topaz, apatite, amblygonite  
153 and zircon and a rare element mineral assemblage including cassiterite, columbite-tantalite  
154 (C-T), microlite and uraninite (Rossi et al., 1987; Cuney et al., 1992).

155 Geochemically, the Beauvoir granite is moderately silicic (68-72 wt% SiO<sub>2</sub>), strongly  
156 peraluminous (A/CNK = 1.25-1.45), enriched in Na (up to ~5 wt% Na<sub>2</sub>O), P (from 1 to > 2  
157 wt% P<sub>2</sub>O<sub>5</sub>) and F (from 1.5 to > 2.5 wt%) and depleted in Fe (< 0.5 wt% Fe<sub>2</sub>O<sub>3</sub>), Ca (< 1 wt%  
158 CaO), Ti (< 100 ppm) and Mg (< 300 ppm, Raimbault et al., 1995). Li (from ~2000 to > 5000  
159 ppm), Sn (up to ~1500 ppm), Nb (up to ~150 ppm), Ta (up to ~450 ppm) are strongly  
160 enriched as well as W, Cs, Rb and Be whereas Ba, Pb, La, Zr, REE and Th are depleted  
161 (Raimbault et al., 1995). Fe/Mn, Nb/Ta and Zr/Hf are particularly low whereas Fe/Mg is  
162 particularly high. These enrichment and depletion patterns become progressively more  
163 marked from base to top, i.e., from the B3, B2 to the B1 unit. However, some levels within  
164 the B2 and B3 (the B' facies) preserve whole-rock compositions outside the main trends and  
165 which have been interpreted as witnesses of a magma batch less evolved than the one at the  
166 origin of the B1, B2 and B3 units (Raimbault et al., 1995).

167 The top part of the Beauvoir granite has been hydrothermally altered. Greisenisation  
168 develops along fissures and fractures and the granite transforms into a quartz-muscovite  
169 assemblage which can cover an important surface in outcrop (15 vol% in the kaolin open pit,  
170 Cuney et al., 1992). Both the Beauvoir and the Colettes granites experienced extensive  
171 kaolinization. However, hydrothermal alteration is generally inconspicuous in core samples  
172 (Cuney et al., 1992) and of negligible importance from a geochemical point of view, except  
173 for Sr and Be concentrated in late phosphate minerals (Raimbault et al., 1995; Charoy et al.,

174 2003). Yet, this does not necessarily ensure that granite whole-rocks are equivalent to magma  
175 compositions since some elements (in particular F and Li) are enriched in micaschists around  
176 the granite. These elements were probably extracted by late-magmatic fluids coming from the  
177 Beauvoir magma (Cuney et al., 1992).

178

## 179 **EXPERIMENTAL METHODS**

### 180 **Starting materials**

181 Two Beauvoir granite samples were selected from the GPF drill core, one from the B1  
182 (depth: 278.20-279.95 m) and the other from the B2 (depth: 606.05-606.95 m) unit. Both  
183 samples were crushed and sieved to grain sizes of ~50  $\mu\text{m}$ . The resulting rock powders were  
184 analysed for major elements plus FeO, F, CO<sub>2</sub>, total H<sub>2</sub>O and Li at CRPG, Vandoeuvre les  
185 Nancy (Pichavant et al., 1987a). Systematic differences consistent with those noted at the  
186 scale of the entire GPF core appear between the two samples. The B1 is more sodic and  
187 peraluminous, less potassic and so more evolved than the B2. Total Fe concentrations  
188 decrease from the B2 to the B1 sample which is also the most P-, F- and Li-rich (Table 1).  
189 Pichavant et al. (1987a) noted that the modal proportions of major phases in the two facies are  
190 in the ranges expected; both quartz and K-feldspar increase and albite and lepidolite decrease  
191 from the B1 to the B2 sample. No marked change in the major element composition of major  
192 phases was found except for lepidolite, higher in Si and F and lower in Fe in the B1 than in  
193 the B2 (Pichavant et al., 1987a).

194 The two rock powders were used directly in the melting experiments (Pichavant et al.,  
195 1987a). For the crystallization experiments detailed in this study, two types of starting glasses  
196 were prepared. First, hydrous glasses were synthesized by melting the two rock powders plus  
197 5 wt% H<sub>2</sub>O at 800°C, 100 MPa for 4 to 5 days. Second, dry glasses were prepared by melting  
198 the rock powders at 1400°C, 0.1 MPa for ~3h. In both cases, two cycles of melting, with  
199 grinding in between, were performed to improve the chemical homogeneity of the glasses  
200 (Table 1). Both types of glasses, hydrous and dry, were crushed to grain sizes of ~50  $\mu\text{m}$  and  
201 used in the crystallization experiments.

202 Compositions of granite whole rocks and starting glasses are compared on Table 1.  
203 The correspondence is generally good although some differences are apparent for elements  
204 present in low concentrations (e.g., 0.22 vs. 0.40 wt% CaO in B1, Table 1). Minor variability  
205 is also noted between glass batches (0.62 vs. 0.40 wt% FeO<sub>t</sub> for B2, Table 1). These  
206 discrepancies are analytical. They reflect the different methods and uncertainties associated

207 with the analysis of whole rocks and glasses (see below) and are not due to systematic  
208 deviations between glass and whole rock compositions.

209

## 210 **Experiments**

211 Crystallization experiments on the Beauvoir granite were performed over a period of more  
212 than 30 years and successively in two laboratories (Nancy and Orléans).

213

### 214 *Unbuffered (type 1) experiments*

215 These were carried out between 1986 and 1988 in Nancy in Tuttle-type cold-seal pressure  
216 vessels working horizontally and pressurized with Ar. Temperature was measured by external  
217 type K thermocouples and permanently recorded. Each thermocouple and bomb-furnace  
218 assembly were calibrated under pressure using an internal dual thermocouple which served to  
219 precisely locate the hot spot zone and to determine the corrections to be applied to the  
220 external temperature readings. In these experiments, temperature is known to better than +/-  
221 10°C. Pressure, measured with a Heise manometer, is known to better than +/- 2 MPa. Run  
222 durations lasted from a minimum of 672 h (28 days) around the liquidus to a maximum of  
223 2184 h (91 days) at subliquidus temperatures.

224 Experimental charges consisted of 95 % (~47 mg) of hydrous glass (containing  
225 approximately 5% H<sub>2</sub>O) plus 5 % doubly distilled demineralized water so that the total  
226 amount of H<sub>2</sub>O present was ~10 wt%. H<sub>2</sub>O solubilities in F-, Li-, B- and P-rich silicic melts  
227 such as the Macusani obsidians are ~8.5 wt% at 300 MPa (Holtz et al., 1993). Therefore,  
228 Beauvoir experimental charges with 10 wt% H<sub>2</sub>O in total are considered H<sub>2</sub>O-saturated.  
229 Charges were loaded in Au capsules (25 mm length, 2.5 mm internal diameter, thickness 0.2  
230 mm) subsequently sealed by arc-welding. B1 and B2 capsules were placed side by side in the  
231 same bomb to allow direct comparison of the results. A total of 24 charges were produced (12  
232 for the B1, Table 2 and 12 for the B2, Table 3) of which 14 have been reported but only  
233 partially described (Pichavant et al., 1987a). Although the  $fO_2$  was not controlled in these  
234 experiments, the redox conditions were highly oxidizing because of an Ar pressurizing  
235 medium very poor in hydrogen. Thus, H<sub>2</sub> generated by H<sub>2</sub>O dissociation inside experimental  
236 capsules became lost to the pressurizing medium, hence lowering  $fH_2$  and increasing  $fO_2$ . In  
237 practice, this highly oxidizing environment is marked by the common presence of thin red-  
238 brick platelets of a hematite solid solution which is particularly abundant in B2 charges (see  
239 below).

240

241 *Redox-buffered (type 2) experiments*

242 These experiments were performed to investigate the influence of  $fO_2$  on mica crystallization  
243 in evolved silicic melts (Lahlafi, 1997; Pichavant et al., 2016; Pichavant, unpublished). Most  
244 were carried out between 1994 and 1996 in Orléans in horizontal externally heated rapid-  
245 quench cold-seal hydrothermal pressure vessels (Pichavant 1987; Schmidt et al. 1995) and at  
246 300 MPa. Total pressure was read with a Bourdon-tube manometer with an uncertainty  
247 estimated to  $\pm 20$  bar. Temperatures were measured permanently with a type-K  
248 thermocouple located in a well drilled at the bottom of the vessel. Temperature readings,  
249 calibrated against measurements using an internal thermocouple working under pressure, are  
250 accurate to better than  $\pm 10^\circ\text{C}$ . At the end of the experiments, the vessel was tilted vertically  
251 and capsules slid from the hot spot to the cold bottom part of the vessel in a few seconds.  
252 Different techniques were employed to control and vary the redox conditions (see Pichavant  
253 et al., 2016 for details). The *oxidizing experiments* were all performed using Ar as  
254 pressurizing gas yielding a moderately oxidizing  $fO_2$  around  $\text{NNO} + 1$  ( $\Delta\text{NNO} = +1$ , Lahlafi,  
255 1997; Pichavant et al., 2016). They include one experiment on the B1 (Table 2) and six on the  
256 B2 (four at  $620^\circ\text{C}$  and two at  $700^\circ\text{C}$ , both regrouped in Table 3) which have been previously  
257 partially described (Lahlafi, 1997; Pichavant et al., 2016). They lasted from 1008 h (42 days)  
258 to 4032 h (168 days). The *reducing experiments*, all on the B2 (three at  $620^\circ\text{C}$  regrouped in  
259 Table 3, one at  $630^\circ\text{C}$  and one at  $700^\circ\text{C}$ ) have been previously partially described (Lahlafi,  
260 1997; Pichavant et al., 2016) except the one at  $630^\circ\text{C}$ . Most employed the double capsule  
261 method of Eugster (1957). A Co-CoO buffer assemblage was used, yielding a  $\Delta\text{NNO}$  of  
262 around  $-1.4$  (Table 3). The buffer was loaded into a 0.4 mm wall thickness external Au  
263 capsule to minimize  $\text{H}_2$  loss toward the Ar gas and experimental durations were limited to 360  
264 h (15 days). The  $630^\circ\text{C}$  experiment was performed in 2017 in an internally-heated pressure  
265 vessel (Scaillet et al., 1995) pressurized with an Ar- $\text{H}_2$  gas mixture to control the  $fO_2$  (Table  
266 3). Total pressure was permanently recorded and is known to better than  $\pm 20$  bar.  
267 Temperature was continuously measured by three thermocouples with an uncertainty of  $\pm$   
268  $5^\circ\text{C}$ . The experiment lasted for 1123 h (48 days) under an experimental  $fO_2$  of  $\text{NNO}-1$   
269 ( $\Delta\text{NNO} = -1$ ) as determined from CoPd solid sensors (Michaud et al., 2021). At the end of the  
270 experiment, the power to the furnace was switched off and temperature dropped by about  
271  $300^\circ\text{C}$  during the first 4 mn. Last, one *two-stage reducing – oxidizing experiment* was  
272 performed on the B2 (Pichavant et al., 2016).

273 All these experiments used Au capsules as containers (inner diameter: 2.5 mm, length:  
274 20 mm, wall thickness: 0.2 mm). Charges consisted of about 50 mg of the dry glass plus about

275 5 mg of doubly distilled demineralized water so that the proportion of H<sub>2</sub>O was kept at ~10  
276 wt.% of the total charge which, from above, corresponds to H<sub>2</sub>O-saturated conditions.

277 Following quench, pressure vessels were opened. Experimental capsules were  
278 weighted to check for leaks, then opened and charges recovered to be analysed.

279

## 280 **Analytical methods**

281 Analysis of experimental charges focused on solid phases, glasses and crystals. No attempt  
282 was made to recover and analyze the fluid phase. Initially, Pichavant et al. (1987a) used  
283 optical microscopy and X-ray diffraction for charge characterization. Later, scanning electron  
284 microscopy (SEM) became the main phase identification tool (Lahlafi, 1997; Pichavant et al.,  
285 2016). In this study, experimental phase assemblages have been determined by SEM and  
286 optical microscopy, and confirmed from electron microprobe data and mass balance  
287 calculations. Several charges previously analysed by X-ray diffraction were examined by  
288 SEM to check the consistency of phase identification between the two methods. Most type 2  
289 experimental charges were examined with a JEOL 6100 scanning electron microscope  
290 (BRGM, Orléans) under conditions summarized in Lahlafi (1997) and Pichavant et al. (2016).  
291 More recently, a Zeiss Merlin Compact (ISTO, Orléans) instrument operating under either  
292 secondary or back-scattered electron (BSE) mode and fitted with a Bruker energy dispersive  
293 system (EDS) was used for the type 1 and some type 2 experimental charges.

294 Building on the rare analyses of feldspars from crystallization experiments in  
295 Pichavant et al. (1987a), experimental charges were analysed by electron microprobe (EMPA)  
296 and the major element compositions of experimental glasses and crystals systematically  
297 determined. Most type 2 experimental charges were analysed using a CAMECA SX 50  
298 instrument (BRGM-CNRS) working under 15 kV acceleration voltage, 12 nA sample current  
299 and 10 and 5 s counting time on peak and background respectively (Lahlafi, 1997; Pichavant  
300 et al., 2016). For the analysis of glasses, the beam was defocussed to 10 µm (vs. 1-2 µm for  
301 crystals) and the raw Na<sub>2</sub>O and K<sub>2</sub>O concentrations were corrected using a Macusani glass  
302 (Pichavant et al., 1987b) secondary standard following procedures detailed in Pichavant  
303 (1987). More recently, type 1 and some type 2 experimental charges were analysed using a  
304 CAMECA SX Five instrument (ISTO-BRGM) working under 15 kV acceleration voltage, 6  
305 nA sample current and 10 and 5 s counting time on peak and background respectively. For the  
306 analysis of glasses, the beam was defocused to 10 µm and focused to 1-2 µm for crystals.  
307 Silicate analytical programs (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K with P and F) were used. In  
308 some sessions, Rb and Sn were added to the list of elements analysed but the Rb data were

309 discarded because of an interference with Si. Sn was also analysed separately under higher  
310 sample current (20 nA) and counting times (60 and 30 s on peak and background). Attempts  
311 were made to circumvent the problem of Na<sub>2</sub>O and K<sub>2</sub>O migration in glass. Time series data  
312 established that alkali concentrations in experimental Beauvoir glasses strongly decrease with  
313 counting time and, for a given counting time, with the sample current. “Zero time”  
314 calculations (using number of counts calculated at  $t = 0$  s rather than number of counts  
315 measured after  $t = 10$  s) were tested but this resulted in small insufficient corrections.  
316 Combining results from time series measurements with analysis of secondary standards  
317 (Pichavant, 1987), correction factors from 15 to 25% and 5 to 7.5% respectively for Na<sub>2</sub>O  
318 and K<sub>2</sub>O were applied to the raw glass data. For glasses, relative analytical errors, determined  
319 as standard deviations on multiple analyses on Macusani glass JV2, are: SiO<sub>2</sub> (0.5–1%), TiO<sub>2</sub>  
320 (80%), Al<sub>2</sub>O<sub>3</sub> (1–1.5%), FeO (25%), MnO (100%), MgO (100%), CaO (15%), P<sub>2</sub>O<sub>5</sub> (20%), F  
321 (5–10%). For Na<sub>2</sub>O and K<sub>2</sub>O, the relative analytical errors are estimated to 5–10%.

322 Micas were too small to be analysed in all charges with the electron microprobe. This  
323 difficulty was circumvented by using the EDS coupled with the Zeiss Merlin Compact SEM  
324 to estimate mica compositions. The analyses were performed with an acquisition time of 30 s  
325 and a sample current of 600 pA. The internal calibration of the instrument was used  
326 unmodified and the data were processed with the ESPRIT2.3 software from Bruker. The SEM  
327 data were compared with EMPA compositions of experimental micas analyzed in the same  
328 charge. For most elements (Si, Al, Fe, Mg, Na, K, P), relative differences between SEM and  
329 EMPA results were lower than the analytical errors of the electron microprobe. F was the only  
330 element significantly underestimated by SEM (by an average factor of 2.3) and F  
331 concentrations were corrected accordingly.

332 Proportions of glass and major mineral phases present in experimental charges were  
333 determined by mass balance, knowing the composition of the bulk charge (Table 1) and of  
334 each phase present from electron microprobe data. The calculations were performed on eight  
335 major oxides (SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O) simultaneously (i.e., using  
336 input matrices with eight rows) and with a variable number of phases (depending on the  
337 assemblage present in the charge) using linear least square procedures detailed in Albarède  
338 (1995).

339 Experimental glasses and quartz crystals were analysed for trace elements by LA ICP-  
340 MS. A RESOLUTION -SE 193 nm excimer laser coupled to an Agilent 8900 QQQ ICP-MS was  
341 used (ISTO-IRAMAT). Ablation was performed at 10 Hz (glass) and 7 Hz (Qz) and a fluence  
342 of 4 J.cm<sup>-2</sup>. The spot diameter was set at 10 μm. SiO<sub>2</sub> from electron microprobe analysis was

343 used as an internal standard, NIST610 as an external standard (Pearce et al. 1997) and  
344 Macusani glass JV2 (Pichavant et al. 1987b) as control. Reference glasses (NIST610 and  
345 Macusani) were analyzed three times at the beginning and at the end of each run of ten  
346 analyses. A total of 28 isotopes (Li7, Be9, B11, Na23, Al27, Si29, P31, K39, Ti49, Mn55,  
347 Zn66, Ge72, Rb85, Sr88, Zr90, Nb93, Sn118, Cs133, Ba137, La139, Sm147, Eu153, Gd157,  
348 Yb172, Ta181, W182, Pb208, U238) were measured. The raw data were processed off-line  
349 using the Glitter software where time-resolved signals were examined one by one. Element  
350 concentrations were calculated for the initial ~ 30 s of all ablation signals relative to the gas  
351 blank (~ 20 s), with a linear interpolation across standard analyses.

352

## 353 RESULTS

### 354 Experimental products and textures

355 Phase assemblages and proportions determined by mass balance (major phases only) are  
356 detailed in Table 2 and 3 for the B1 and B2 experiments respectively. Glass is the most  
357 abundant phase in the charges, being readily identified by optical methods and SEM. It  
358 frequently contains fluid inclusions of small to medium size (10-30  $\mu\text{m}$ ) homogeneously  
359 distributed in the charge. All glass-containing charges appeared as solid consolidated beads  
360 upon opening the capsule. In contrast, the B1N-16 charge (the only one without glass present,  
361 Table 2) was recovered as a soft loose powder.

362 Phases crystallizing from Beauvoir granitic melts include quartz (Qz), an albitic  
363 plagioclase (Pl) and K-feldspar (Af). SEM observations show that Qz forms euhedral, faceted,  
364 mostly equant and sometimes globular crystals up to 20-30  $\mu\text{m}$  large (Fig. 1a) which can  
365 contain inclusions of micrometric micas. In charges close to the liquidus, Pl crystallizes as  
366 euhedral elongated laths isolated in glass, typically 10-15  $\mu\text{m}$  long but which can reach ~100  
367  $\mu\text{m}$  in some B1 experiments (Fig. 1b). They appear uniformly grey and so chemically  
368 homogeneous in BSE mode (Fig. 1b). In contrast, in sub-liquidus charges, feldspars grow to  
369 sizes generally larger than under near-liquidus conditions, up to ~100  $\mu\text{m}$ . Small euhedral Qz  
370 crystallize at their extremities (Fig. 1c). These large feldspars are chemically heterogeneous.  
371 They are made up of white to dark grey domains in BSE mode corresponding to K- and Na-  
372 rich zones (Fig. 1c). In some crystals, the transition from one zone to the other is progressive  
373 and geometrically complex (Fig. 1c). In others, the two zones are well separated, both  
374 geometrically and compositionally, and two chemically homogeneous feldspar phases, Pl and  
375 Af can be individualized (Fig. 1d). Af most commonly appears as small (maximum 15  $\mu\text{m}$ )

376 euhedral homogeneous K-rich phases coexisting with Pl in composite crystals (Fig. 1d) and  
377 was unfrequently found as isolated crystals isolated in glass.

378 Beauvoir melts have been shown previously to crystallize a mica phase (Pichavant et  
379 al., 1987a; Lahlafi, 1997; Pichavant et al., 2016). Under the most reducing conditions  
380 corresponding to the CCO buffer (NNO-1.4), biotite (Bt) is the liquidus phase at 300 MPa in  
381 B2 (experiments B2O-38/40, Table 3; Lahlafi, 1997; Pichavant et al., 2016). This Bt is a  
382 moderately F-rich siderophyllite (Pichavant et al., 2016). It amounts to several wt.% of the  
383 charge and reaches a maximum size of 30–40  $\mu\text{m}$  (see Fig. 1b in Pichavant et al., 2016). For  
384 strongly oxidizing (NNO+3) to moderately reducing conditions (NNO-1) in B2 (Table 3) as  
385 well as between NNO+3 and NNO+1 in B1 (Table 2), Beauvoir melts crystallize a Li-, F-  
386 bearing mica. This mica (designated below as Li-mica, Li-Mi) has compositions ranging from  
387 relatively Li-, F-poor and mainly dioctahedral to Li-, F-rich and markedly trioctahedral. SEM  
388 observations show that Li-Mi appears mostly as platelets, either elongated as in B2 (Fig. 1e)  
389 or more rectangular and equant as in B1 charges, sometimes forming aggregates and  
390 inclusions in quartz and feldspars. Li-Mi is generally very flat and thin, typically 10-15  $\mu\text{m}$   
391 long and 2-3  $\mu\text{m}$  large in B2 (Fig. 1e) and  $\sim$ 2  $\mu\text{m}$  long and 1-2  $\mu\text{m}$  large in B1 charges (Fig.  
392 1f; g). Exceptionally, Li-Mi can be up to several tens  $\mu\text{m}$  long in some B2 charges  
393 (experiments B2O-2/5, Table 3, see Fig. 1a in Pichavant et al., 2016).

394 Several accessory phases were encountered although the accessory assemblage was  
395 not systematically determined in all charges. The most systematic include apatite (Ap) in both  
396 B1 and B2 charges and Fe-Ti oxides in B2 charges only, either hematite (Hm) or magnetite  
397 (Mt, Table 2; 3). Ap forms small subhedral crystals up to 5-10  $\mu\text{m}$  (Fig. 1e), sometimes but  
398 rarely larger and often grouped in aggregates. In the type 1 experiments which are the most  
399 oxidized (NNO+3), Hm forms thin red-brown losange-shaped platelets up to several tens  $\mu\text{m}$   
400 long (Fig. 1h), readily detected by optical microscopic examination and locally abundant in  
401 B2 charges (B2N-19, B2N-20, Table 3). In the less oxidized type 2 experiments (NNO+1) on  
402 B2, a small (a few  $\mu\text{m}$ ) sub-hexagonal oxide phase identified as magnetite (Lahlafi, 1997) is  
403 present. No Fe-Ti oxide crystallized in B2 experiments performed at NNO-1 and NNO-1.4,  
404 (Table 3). Topaz was extensively looked for but only found in one charge, B1N-21, where it  
405 appears as small ( $< 5 \mu\text{m}$ ) homogeneously distributed euhedral prisms slightly brighter than  
406 quartz and feldspar in BSE mode (Fig. 1f, g). This B1N-21 charge contains an Al-, F-rich  
407 phosphate phase of the amblygonite-montebbrasite series present together with apatite. It forms  
408 relatively abundant, subhedral 10  $\mu\text{m}$  large crystals darker than the other phases in BSE mode  
409 (Fig. 1g). Cassiterite and C-T are conspicuous in B1 as well as in B2 charges.

410

**411 Experimental phase relations**

412 Results of the crystallization experiments are reported in Table 2 and 3 for the B1 and B2  
413 starting compositions respectively. Below, we focus on results in the strongly oxidizing to  
414 moderately reducing  $fO_2$  range (from NNO+3 to NNO-1, Table 2; 3), i.e., the most reducing  
415 (NNO-1.4) B2O-38/40 and B2O-41 charges are excluded. Therefore, only conditions of  
416 crystallization of Qz, Af, Pl and Li-Mi are discussed and those for Bt are not considered  
417 further.

418 Some inconsistencies were found between experiments in the sense that the same P-T  
419 conditions did not always yield the same phase assemblages. For example, at fixed T and P  
420 (620°C and 300 MPa) for the B1 composition, Li-Mi is present in B1N-22 (type 1  
421 experiment) whereas it is absent in B1O-1 (type 2 experiment) which also lacks Af and Qz  
422 (Table 2). For the B2 composition, both Pl and trace Af crystallized in B2O-2/5 (type 2  
423 experiment) at 620°C and 300 MPa whereas these two phases are absent in B2N-25 (type 1  
424 experiment, Table 3) performed under the same P-T conditions. These inconsistencies are  
425 attributed to several experimental factors such as use of different equipment and contrasted  
426 experimental durations. By opposite, phase identification issues are not considered  
427 responsible for these inconsistencies. Phase assemblages are identical, whether determined  
428 from SEM (this study) or X-ray diffraction (Pichavant et al., 1987a). Starting compositions  
429 were successfully mass balanced from linear combinations of phases present in the charges  
430 (low  $\Sigma r^2$  in Table 2 and 3), implying that our phase identification methods are reliable. In only  
431 one case (B1N-1), 2 wt% Qz (undetected by X-ray and SEM) had to be added to the phase  
432 assemblage for the charge to be successfully mass balanced. In the same way, the presence of  
433 fluid inclusions in most charges confirms that  $H_2O$ -saturated conditions (i.e.,  $a_{H_2O} = 1$ ) were  
434 effectively imposed. Thus, differences in phase assemblages for fixed composition and P, T  
435 conditions cannot be due to  $a_{H_2O}$  being variable between charges although, in this study, melt  
436  $H_2O$  concentrations have not been determined. Beauvoir melt inclusions contain between 3.6  
437 and 6.2 wt%  $H_2O$  (Kovalenko et al., 1998).

438 These inconsistencies have been considered in the construction of the P-T diagrams  
439 (Fig. 2; 3). For the B1, saturation curves at 300 MPa exclude two experimental charges, B1O-  
440 1 and B1N-15 (Table 2). SEM observations and mass balance calculations show that these  
441 charges are much less crystallized than the others at the same pressure (B1N-21 and B1N-22,  
442 Table 2). Moreover, Qz, Af and Li-Mi are absent in B1O-1 and B1N-15 whereas all are  
443 present in B1N-22 (Table 2). These inconsistencies are attributed to differences in

444 experimental durations, much shorter for B1O-1 (1008 h) and B1N-15 (1104 h) than for B1N-  
445 21 and B1N-22 (2184 h, Table 2). For the B2, the Pl and Af saturation curves pass at  
446 temperatures slightly lower (-10 and -20°C respectively) than the 300 MPa B2O-2/5 type 2  
447 charges which contain Pl and trace Af. In other words, results from the B2N-25 and B2N-24  
448 type 1 charges (Table 3) were preferred.

449 For the B1 composition, the 100 MPa solidus is bracketed by the 540°C glass absent  
450 (B1N-16) and the 560°C trace glass present (B1N-11) charges. The 300 MPa solidus is half-  
451 bracketed by the 580°C glass bearing (B1N-21) charge (Table 2). Although solidus  
452 temperatures determined from melting experiments are preferred because of the possibility of  
453 supercooling problems in crystallization experiments (Pichavant et al., 1987a and see below),  
454 the latter are only ~20°C lower than the former at 100 MPa (Fig. 2). At this pressure, Qz, Pl,  
455 Af and Li-Mi all saturate from 590°C to > 600°C. Remarkably, temperatures of Qz, Pl and Af  
456 saturation are higher at 300 MPa (from 625°C to > 640°C) than at 100 MPa (Fig. 2). This is  
457 symptomatic of kinetic difficulties (melt supercooling) at 100 MPa since, under water-  
458 saturated conditions, anhydrous phases such as Qz and feldspars must saturate at  
459 progressively lower temperatures upon increasing pressure (Tuttle and Bowen, 1958; Luth,  
460 1976). Consequently, the Qz, Pl and Af saturation curves are drawn separated in two parts,  
461 one appropriate for 100 MPa and the other for 300 MPa. By opposite, kinetic problems are  
462 negligible for Li-Mi (see below) and Li-Mi saturation is represented by a single continuous  
463 curve with a positive slope between 100 and 300 MPa (Fig. 2). Qz, Pl and Li-Mi appear all  
464 together on the B1 liquidus (at 600°C, 100 MPa and at 640°C, 300 MPa) and so their relative  
465 crystallization order cannot be specified. They are followed by Af which is the fourth and last  
466 major phase in the sequence.

467 For the B2 composition, the solidus is only approached (and half-bracketed) at 100  
468 MPa by the 560°C (B2N-12) charge which contains a trace of glass and it is < 580°C at 300  
469 MPa (Fig. 3). The 100 MPa solidus temperature is lower by 20-30°C than the one determined  
470 from the melting experiments (Pichavant et al., 1987a). Qz and Pl crystallize at progressively  
471 lower temperatures at 300 (615-625°C) than at 200 MPa (> 640°C), as expected under water-  
472 saturated conditions (Tuttle and Bowen, 1958; Luth, 1976). In comparison, these two phases  
473 saturate below 640°C at 100 MPa which indicates supercooling problems at this pressure.  
474 Therefore, the Qz and Pl saturation curves are drawn in two parts, one appropriate for 100  
475 MPa and the other for 200 to 300 MPa (Fig. 3). As supercooling problems are less important  
476 to negligible for Af and Li-Mi (see below), saturation conditions are represented by single  
477 continuous curves between 100 and 300 MPa. One notes the contrast in slope between the Li-

478 Mi (positive) and the Qz, Pl and Af saturation curves (all negative, Fig. 3). Li-mica is the  
479 liquidus phase at 300 MPa being joined by Qz and Pl on the liquidus at 200 MPa. At 100  
480 MPa, the four major phases crystallize all together on the liquidus (B2N-20 charge, Table 3).  
481 The 300 MPa experiments imply that Qz crystallizes before Pl and the 300 and 200 MPa data  
482 that Af is the fourth and last major phase in the sequence (Fig. 3).

483

## 484 **Major element compositions**

### 485 *Glasses*

486 Major element compositions of experimental glasses corrected for alkali migration are  
487 reported in Table 4. Except the few data from Lahlafi (1997) which are normalized to 100  
488 wt%, other glass analyses are shown unnormalized. Average standard deviations for SiO<sub>2</sub> and  
489 Al<sub>2</sub>O<sub>3</sub> are no higher than analytical errors, thus indicating that the experimental glasses are  
490 homogeneous. We note that the MnO, MgO, CaO and SnO<sub>2</sub> concentrations are in the same  
491 range as standard deviations and in fact often lower than detection limits. They are reported  
492 only for indicative purposes in Table 4. Experimental Beauvoir glasses are extremely felsic,  
493 being composed of essentially four oxides (Si, Al, Na, K) plus P<sub>2</sub>O<sub>5</sub>, F and H<sub>2</sub>O. This is  
494 reflected in the calculated normative Qz, Ab and Or concentrations which sum to more than  
495 90-95%. Normative An contents are between 0.2 and 0.7% for the B1 and between 0.2 and  
496 1.4% for the B2 glasses. Normative Corundum (from 4.9 to 7% for the B1 and from 2.5 to  
497 5.5% for the B2) and A/CNK (1.37-1.60 for the B1 and 1.20-1.44 for the B2) demonstrate  
498 that all glasses are strongly peraluminous. Near-liquidus experimental glasses (e.g., B1N-15  
499 for B1 and B2N-26 for B2, Table 4) are not markedly more peraluminous than their  
500 corresponding starting glasses (Table 1), suggesting that the influence of alkali migration on  
501 glass analyses has been satisfactorily counteracted.

502 Both B1 and B2 glasses display the same compositional trends with progressive  
503 crystallization and decreasing melt fraction (*f*, Fig. 4). Normative Corundum and A/CNK both  
504 increase and residual melts become progressively more peraluminous. P<sub>2</sub>O<sub>5</sub> and F  
505 concentrations (n.b., not normalized to 100% anhydrous) also increase, indicating their  
506 progressive accumulation in residual melts. The most evolved B1 melts reach ~1.70 wt%  
507 P<sub>2</sub>O<sub>5</sub> and ~3.3 wt% F (for ~1.50 and ~2.3 wt% in starting materials) and the most evolved B2  
508 melts ~1.30 wt% P<sub>2</sub>O<sub>5</sub> and ~2.6 wt% F (for ~1 and ~1.7 wt% in starting materials). By  
509 opposite, normative Anorthite are much lower in experimental glasses than in starting  
510 materials but the trends (Fig. 4d) are blurred by the large uncertainty on CaO in glasses by  
511 electron microprobe because of the low concentrations involved.

512 The major element compositions of starting materials and experimental glasses are  
513 plotted in the Qz-Ab-Or diagram (Fig. 5). Globally, the B1 are more Ab-rich and Qz-poor  
514 than the B2 compositions. The former plot left to the H<sub>2</sub>O-saturated haplogranite minimum  
515 liquidus temperature trend (Tuttle and Bowen, 1958) whereas the latter plot mostly on the 300  
516 MPa minimum point (Fig. 5). Both glass groups have Qz higher than H<sub>2</sub>O-saturated minimum  
517 liquidus temperature points at 100 MPa with added F (Manning, 1981). Compositions of  
518 several glasses (see captions to Fig. 5) and starting materials overlap as expected for charges  
519 above or near the liquidus and in fact demonstrates the internal consistency of experiments  
520 and analyses. Glasses from sub-liquidus charges do not systematically vary with the phase  
521 assemblage, being tightly grouped and little dispersed around their respective starting  
522 compositions. The 300 MPa B1 glasses (B1N-23, -22, -21) show slight variations in Ab/Or at  
523 constant Qz contents whereas the 100 MPa glasses (B1N-1, B1N-17) evolve toward distinctly  
524 higher Qz contents (Fig. 5). In the same way, the sub-liquidus B2 glass compositions have  
525 constant Qz, plotting close to the starting composition (Fig. 5). Two glasses have very high  
526 Qz contents in comparison with the other B2 compositions, B2N-3 (which come from a 100  
527 MPa experiment) and B2O-38/40 (analysis from Lahlafi, 1997). The B2N-18 glass has Qz  
528 and Or respectively lower and higher than the other B2 compositions.

529

### 530 *Quartz*

531 Representative major element compositions of experimental quartz are reported in Table 5.  
532 The complete database can be found in the Supplementary Material (Table S1). In most  
533 charges, quartz is very close to pure SiO<sub>2</sub>. The only element systematically detected with the  
534 electron microprobe is Al with Al<sub>2</sub>O<sub>3</sub> concentrations between 0.07 to 0.64 wt%, on average  
535 0.23 wt%. Phases with concentrations much richer in Al<sub>2</sub>O<sub>3</sub> (2.83-3.01 wt%, Table 5) were  
536 found in one low temperature 100 MPa B1 charge (B1N-17, Table 2). SEM examinations  
537 show that these Al-rich phases are morphologically and texturally identical to Qz. They  
538 coexist with Qz having “normal” Al<sub>2</sub>O<sub>3</sub> concentrations in the same charge. The high Al<sub>2</sub>O<sub>3</sub>  
539 analyses do not show elevated alkali contents but are systematically associated with totals in  
540 the 97.5-98 wt% range, lower than for the other Qz (Table 5). Since Li is present at elevated  
541 concentrations in the B1 starting material (1.28 wt% Li<sub>2</sub>O, Table 1), Li incorporation in the  
542 quartz lattice according to the coupled Si = Al + Li substitution (Breiter et al., 2014) might  
543 account for the analytical results. These peculiar compositions would thus correspond to  
544 virgilite solid solutions between quartz and spodumene of stoichiometry Li<sub>x</sub>Al<sub>x</sub>Si<sub>3-x</sub>O<sub>6</sub>  
545 (French et al., 1978; Sirbescu et al., 2017), with x ~0.10 from our data (Table 5; S1).

546

547 *Feldspars*

548 Representative compositions of experimental feldspars are reported in Table 6 and the entire  
549 database is available in the Supplementary Material (Table S2). Feldspar compositions were  
550 determined in all feldspar-bearing charges including in some previously analysed by  
551 Pichavant et al. (1987a). Despite their small size (5  $\mu\text{m}$ ) in some charges, overall feldspars  
552 were correctly analysed and satisfactory structural formulae ( $\text{Si}+\text{Al}+\text{P} = 4.01$ ;  $\text{K}+\text{Na}+\text{Ca} =$   
553  $0.97$  apfu on average) were obtained. Three groups of compositions are distinguished  
554 corresponding to Pl, Af and heterogeneous feldspars (Fig. 1c). All three groups contain  
555 significant  $\text{P}_2\text{O}_5$  concentrations, higher in plagioclase (from  $\sim 0.6$  to  $\sim 1.4$  wt%  $\text{P}_2\text{O}_5$ ) than in  
556 K-feldspar (from  $\sim 0.4$  to  $\sim 1$  wt%  $\text{P}_2\text{O}_5$ , Table 6). The incorporation of phosphorus in  
557 experimental feldspars from this study is consistent with the peraluminous composition and  
558 elevated  $\text{P}_2\text{O}_5$  contents of Beauvoir melts (Simpson, 1977; London, 1992; London et al.,  
559 1999).

560 The three groups of compositions are plotted on the An vs. Or diagram of Fig. 6. Use  
561 of a binary instead of the more familiar ternary An-Or-Ab representation is warranted since  
562 feldspars in this study have very low An ( $< 5\%$ , Table 6; S2). A minor dispersion is apparent  
563 and feldspars in the same charge can have An, Or or Ab contents that differ by 1-2 % from  
564 each other. Pl are albitic with on average  $\sim 10\%$  Or and An from  $\sim 0.5$  to  $\sim 4.5\%$  (Fig. 6). There  
565 are slight tendencies for An to increase with temperature and Or to decrease with pressure. Pl  
566 compositions from B1 and B2 charges overlap but the least An-rich ( $< 1.5\%$  An) mostly  
567 correspond to B1 and the most An-rich (An  $> 2.5\%$ ) to B2 charges. For comparison, natural  
568 albite from starting rocks ( $\text{Or}_{0.8}\text{Ab}_{98.8}\text{An}_{0.4}$ , Pichavant et al., 1987a) has An at the low end of  
569 the experimental range and Or much lower than Pl from this study (Fig. 6). Af compositions  
570 are very close to binary, most being grouped between  $\text{Or}_{67}$  and  $\text{Or}_{73}$  with An contents  $\sim 0$   
571 although some compositions extend to lower Or and An  $> 0$ . No difference appears between  
572 B1 and B2 charges (Fig. 6) but Af from 100 MPa charges have lower Or than those from 300  
573 MPa charges. Natural K-feldspar from starting rocks ( $\text{Or}_{89}\text{Ab}_{11}$ , Pichavant et al., 1987a) plots  
574 outside the experimental range, being much more potassic and less sodic than Af from this  
575 study. Analyses of heterogeneous feldspars yield a group of compositions intermediate  
576 between Pl and Af.

577 Equilibrium between feldspar pairs coexisting in the same charge was tested by using  
578 the SOLV CALC software of Wen and Nekvasil (1994) with the feldspar solution model of  
579 Nekvasil and Burnham (1987). 14 pairs from 3 B1 and 3 B2 charges were tested. 10 returned

580 equilibration temperatures within 2-32°C of experimental values as illustrated (Fig. 6). 4 pairs  
581 were out-of-equilibrium because of Pl compositions slightly outside the solvus. Thus, a  
582 majority of feldspar pairs in our experimental charges represent compositions equilibrated on  
583 the ternary solvus. The intermediate compositions of heterogeneous feldspars are interpreted  
584 as out-of-equilibrium compositions from inside the solvus rather than as mixtures of  
585 compositions at equilibrium on the solvus (Fig. 1c; 6).

586

587 *Li-micas*

588 Li-mica compositions were determined by EMPA in B2 charges only. In B1 charges where  
589 micas are very small, compositions were estimated by SEM. Li-Mi in charge B2N-25 were  
590 analysed both by EMPA and SEM to calibrate the SEM analyses. Li<sub>2</sub>O contents in Li-Mi  
591 were estimated from F concentrations, using the equation [di 1] of Tischendorf et al. (1997).  
592 Results were checked against mineral separate data on Beauvoir micas (Monier et al., 1987).  
593 Equation [di 1] performs very well (relative differences between measured and expected  
594 concentrations < 5%) for very Li-rich micas (from 5 to > 7 wt% Li<sub>2</sub>O). For less Li-rich micas,  
595 [di 1] underestimates Li<sub>2</sub>O concentrations by 15-30%. Representative EMPA and SEM  
596 compositions of experimental Li-Mi are reported in Table 7 and the entire database can be  
597 found in Table S3. The data demonstrate a marked contrast in Li-Mi compositions between  
598 the B1 and B2 charges. In B2, Li-Mi are grouped around the Li phengite end-member (n.b.,  
599 the nomenclature of Tischendorf et al., 1997 is used for consistency with the representation of  
600 mica compositions) whereas, in B1, they plot around the cryophyllite end-member and so  
601 possess a marked trioctahedral character (Fig. 7a). Combining EMPA and SEM data (Table  
602 S3), Li-Mi in B2 charges have 43.6-48.3 wt% SiO<sub>2</sub>, 29.6-34.9 wt% Al<sub>2</sub>O<sub>3</sub>, 1.62-7.43 wt%  
603 FeO<sub>t</sub>, 0.07-0.60 wt% MgO, 0-0.44 wt% MnO, 0.69-2.23 wt% Na<sub>2</sub>O and 8.9-10.2 wt% K<sub>2</sub>O. F  
604 ranges from 1.37 to 4.91 wt% and Li<sub>2</sub>O from 0.60 to 3.25 wt%. SnO<sub>2</sub> concentrations exceed  
605 the detection limit (~400 ppm Sn under our electron microprobe operating conditions),  
606 reaching values up to ~0.3 wt% SnO<sub>2</sub> in the more oxidized type 1 charges. For example, in  
607 charge B2N-25, SnO<sub>2</sub> concentrations range from 0.14 to 0.32 wt% (Table 7; S3) and nine  
608 separate analyses (not detailed in Table S3, detection limit ~200 ppm Sn) yielded an average  
609 concentration of 0.27 +/- 0.05 wt% SnO<sub>2</sub>. Compositions of B2 Li-Mi do not systematically  
610 change with experimental P-T conditions. Yet, FeO<sub>t</sub> broadly decreases with decreasing melt  
611 fraction and we note that Li-Mi in the reduced type 2 B2O-50 charge have lower FeO<sub>t</sub> (2.28-  
612 2.55 wt%) than in oxidized near-liquidus charges (4.77-5.68 wt% FeO<sub>t</sub> in B2N-25) and Sn  
613 concentrations below detection (Table 7; S3).

614 In the three B1 charges analyzed, Li-Mi have 50.9-56.9 wt% SiO<sub>2</sub>, 18.2-22.0 wt%  
615 Al<sub>2</sub>O<sub>3</sub>, 1.24-5.40 wt% FeO<sub>t</sub>, 0.09-2.31 wt% MgO, 1.07-3.00 wt% Na<sub>2</sub>O and 5.29-7.42 wt%  
616 K<sub>2</sub>O. F ranges from 7.13 to 8.79 wt% (applying the constant x 2.3 correction factor  
617 determined on B2N-25) and Li<sub>2</sub>O from 5.32 to 7.02 wt% with [di 1] (Table 7; S3). SiO<sub>2</sub>,  
618 Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Na<sub>2</sub>O, F and Li<sub>2</sub>O do not significantly vary between the three charges. However,  
619 MgO progressively decreases from B1N-23, -22 to -21 (i.e., with decreasing *f*) and Li-Mi in  
620 B1N-21 has FeO<sub>t</sub> (1.24-2.70 wt%) lower than in B1N-22 and B1N-23 (3.41-5.40 wt%, Table  
621 7; S3) so that the former and the two latter charges plot in separate fields (Fig. 7a). Apart from  
622 the first-order differences in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, F and Li<sub>2</sub>O between B1 and B2 micas, MgO and  
623 Na<sub>2</sub>O are enriched and K<sub>2</sub>O depleted in B1 compared to B2 whereas FeO<sub>t</sub> are similar in the  
624 two mica groups (Table 7).

625

### 626 *Accessory phases*

627 Representative major element compositions of accessory phases are given in Table 8.  
628 Although few analyses are available and their quality is relatively poor because of the small  
629 size of the crystals, topaz, amblygonite and apatite are all very F-rich. Atomic F/(F+OH) in  
630 topaz ranges from 0.89 to 0.99 and in amblygonite from 0.94 to 0.95. Apatite are fluor-  
631 apatites with atomic F concentrations commonly exceeding 1 atom per formula unit (Table 8).  
632 F concentrations in topaz and glass from charge B1N-21 (Table 4; 8) are consistent with the  
633 proposed distribution of F between topaz and silicic melts (Soufi, 2021). In this same charge,  
634 the distribution of F between amblygonite and melt broadly follows the experimental  
635 calibration of London et al. (2001).

636 Experimental hematites are very Fe-rich and Ti-poor. They have a minimum of 95%  
637 Hm (Fe<sub>2</sub>O<sub>3</sub>, Table 8), consistent with the high *f*O<sub>2</sub> of type 1 experiments (Table 3). Hematites  
638 contain very little MnO and MgO but significant Al<sub>2</sub>O<sub>3</sub> (0.79-2.71 wt%) and SnO<sub>2</sub> (1.39-1.57  
639 wt%). Separate analyses (not detailed in Table 8) yielded an average of 1.81 (+/- 0.22) wt%  
640 SnO<sub>2</sub> for Hm in charge B2N-25. Such high Sn concentrations in Hm are consistent with those  
641 detected in coexisting Li-Mi (see above).

642

### 643 **Trace element compositions**

644 Trace elements were analyzed in several highly oxidizing (~NNO+3) B2 charges and in Qz  
645 crystals from one charge and concentrations of selected elements are reported in Table 9. The  
646 charges analyzed are crystallized except one which is essentially crystal-free. Yet,  
647 examination of time-resolved ablation spectra allowed glass signals to be unambiguously

648 identified in all charges. Multiple analyses (from 2 to 6) are available on each glass. Chemical  
649 dispersions (defined as standard deviation/mean of analyses) are mostly  $< 10\%$  (Table 9),  
650 globally demonstrating homogeneous trace element distributions in the experimental glasses  
651 analyzed. In some charges and for some elements, chemical dispersions are higher ( $> 20\%$ ).  
652 This is the case in particular for Ba and La which have low concentrations in the analyzed  
653 glasses ( $\sim 1$  ppm for Ba and  $\sim 0.1$  ppm for La, Table 9), not much above instrumental  
654 uncertainties. For Zr and Sn which have glass concentrations respectively of 3-4 ppm and  
655 between  $\sim 15$  and  $\sim 35$  ppm (Table 9), the relatively high dispersions (20-30%) in some  
656 charges could reflect glass contamination by zircon and Sn-bearing phases (cassiterite, micas  
657 and hematite). Dispersions  $> 10\%$  for Ta in two charges might also be due to contamination  
658 with C-T and it is possible that hematite contamination explains some Ti dispersions  $> 10\%$ .  
659 Almost all Sm, Eu, Gd and Yb concentrations were below detection and these elements are  
660 not reported in Table 9.

661 The evolution of trace element concentrations with progressive crystallization is  
662 illustrated on Fig. 9. Experimental melt (i.e., glass) concentrations ( $C$ ) referenced to those in  
663 the initial melt ( $C_0$ , represented by the essentially crystal-free charge B2N-26) are plotted as a  
664 function of the melt fraction. For most elements, concentrations increase with decreasing  $f$ . Li,  
665 Be, B, Cs, U are the most strongly enriched,  $C/C_0$  reaching averages of  $\sim 1.4$  ( $f \sim 75\%$ ) and  
666  $\sim 1.7$  ( $f \sim 50\%$ , Fig. 9). Below 25% crystallization, Li, Be, B, Cs, U concentrations follow  
667 Rayleigh fractionation for a bulk mineral/melt partition coefficient ( $D$ ) of 0.01 (Fig. 9),  
668 indicating a strongly incompatible behavior. Upon further lowering  $f$ , rates of enrichment  
669 decrease and concentrations plot on a Rayleigh fractionation trend for a higher  $D$  (0.5),  
670 suggesting that these elements become less incompatible as  $f$  drops. Rb and W are also  
671 concentrated in the melt although less markedly ( $C/C_0 \sim 1.2$  for  $f \sim 50\%$ ), most probably  
672 because both are more compatible in Li-Mi than Li, B, Cs according to the muscovite/melt  
673 partition coefficients summarized by Michaud and Pichavant (2020). We conclude that the  
674 behavior of Li, Be, B, Rb, Cs, W, U reflects their globally incompatible character during  
675 crystallization of Beauvoir melts. The  $D$  values, their variability from one element to the other  
676 and their evolution with varying  $f$  control the observed levels of enrichment.

677 Nb and Ta are also concentrated in the melt during crystallization.  $C/C_0$  are quite high,  
678  $\sim 1.3$  for Nb and  $\sim 1.5$  for Ta for  $f \sim 50\%$  (Fig. 9), indicating preferential concentration of Ta  
679 rather than Nb. However, at the difference of the group of elements above, Nb and Ta are  
680 essential structural components of C-T [(Fe,Mn)(Nb,Ta)<sub>2</sub>O<sub>6</sub>], an accessory phase present in  
681 experimental charges. Therefore, the measured glass Nb and Ta concentrations should

682 represent C-T solubilities provided that chemical equilibrium is established between melt and  
683 accessory phases in the experiments. C-T solubilities in silicic melts are complex functions of  
684 temperature and compositions of the melt and of the C-T phase (Linnen and Keppler, 1997;  
685 Linnen, 1998; Van Lichtervelde et al., 2018). At a temperature of 600°C appropriate for  
686 Beauvoir melts, the calculated Nb concentration of a 500 ppm Mn melt at equilibrium with  
687  $\text{MnNb}_2\text{O}_6$  is 52 ppm (Linnen and Keppler, 1997). At the same temperature, the empirical  
688 saturation model of Michaud and Pichavant (2020) yields 55 ppm Nb and 43 ppm Ta for a  
689 500 ppm Mn and 2000 ppm Fe melt saturated with C-T with at.  $\text{Mn}/(\text{Mn}+\text{Fe}) = \text{Ta}/(\text{Ta}+\text{Nb}) =$   
690 0.5. For Beauvoir temperature and melt compositions, Linnen (1998) estimated a  
691 concentration of 50 ppm Ta at saturation with  $\text{MnTa}_2\text{O}_6$ , increasing to 1200-3000 ppm Ta and  
692 40-100 ppm Nb at saturation with  $\text{MnNb}_2\text{O}_6$  if the influence of Li and F melt concentrations  
693 on C-T solubility is accounted for. Although the calculations above do not all agree with  
694 concentrations measured in experimental Beauvoir glasses (38-49 ppm Nb, 20-34 ppm Ta,  
695 Table 9), most, in particular for Nb, are in the same range. Considering the uncertainties in the  
696 calculations and simplifying assumptions involved, this is taken as permissive evidence that  
697 our Nb and Ta glass concentrations represent C-T solubilities. The observed Nb and Ta  
698 enrichments with decreasing  $f$  (Fig. 9) would thus reflect a C-T solubility increase resulting  
699 from progressive melt fractionation during crystallization (higher F, P, Li, Fig. 4; 9).

700 Sn is an essential structural component in cassiterite ( $\text{SnO}_2$ ), another accessory phase  
701 present in the charges and, so, Sn melt concentrations should reflect cassiterite solubilities  
702 (Linnen et al., 1995; 1996; Bhalla et al., 2005). Extrapolating to lower temperatures the data  
703 of Bhalla et al. (2005) at NNO+2.3 (vs.  $\sim$ NNO+3 in our experiments), the solubility of  
704 cassiterite at 600°C is 120 ppm Sn, i.e.  $\sim$ 4 times higher than the measured Sn glass  
705 concentrations (between  $\sim$ 15 and  $\sim$ 35 ppm, Table 9). We also note the marked Sn depletions  
706 in B2N-25 and B2N-18 glasses and the global absence of Sn enrichment in the melt (Fig. 9).  
707 Sn alloying with the Au capsule (Linnen et al., 1995; Michaud et al., 2021) is probably  
708 responsible for Sn glass concentrations at cassiterite saturation being lower than calculated  
709 solubilities. Additionally, the high Li-mica and hematite Sn concentrations indicate that Sn is  
710 compatible at  $\sim$ NNO+3 (see also below).

711 Several elements have concentrations that do not increase in the melt when decreasing  
712  $f$ . This is the case for Mn which, following initial enrichment, returns to melt concentrations  
713 not much different from the initial  $C_0$  for  $f \sim 50\%$  (Fig. 9). Such a behavior could reflect  
714 increased Mn sequestration by Li-Mi at low  $f$  (see partition coefficient in Michaud and  
715 Pichavant, 2020) although Mn melt concentrations also depend on accessory phase

716 solubilities, as it is an essential structural component in CT. Zn is neither significantly  
717 enriched nor depleted and Ti shows a similar although more irregular behavior (Table 9). The  
718 only element regularly depleted in the melt upon decreasing  $f$  is Sr.  $C/C_0$  is 0.37 ( $f \sim 75\%$ ) and  
719 0.27 ( $f \sim 50\%$ ) and the Sr data can be approximately fitted by Rayleigh fractionation for  $D = 3$   
720 (Fig. 9) thus indicating a marked compatible character during crystallization of Beauvoir  
721 melts. In comparison, Pb is more irregular than Sr although a depletion trend appears if the  
722 anomalous concentration in charge B2N-18 (Table 9) is discarded. The Ba and La systematics  
723 are unclear because of their very low melt concentrations, as discussed above.

724 Experimental Qz crystals were analyzed only in B2N-25 because of size limitations  
725 (Fig. 1a). Five analytical spots were performed. Only one yielded a stable signal during  
726 almost the entire ablation time interval before finally the underlying glass was hit. This Qz  
727 has 81.34 ppm Li, 367.92 ppm Al and 152.94 ppm P (not corrected for possible interferences,  
728 Audétat et al., 2014) and it contains Ti, Zn, Sn and Cs concentrations in the few ppm range  
729 (Table 9).

730

### 731 **Mineral/melt partitioning**

732 The distribution of F between mica and melt is strongly concentration dependent (Fig. 10).  
733 Below  $\sim 3$  wt% F in melt, an approximately linear dependence is observed between F in mica  
734 vs. F in melt with a slope of  $\sim 1.4$  (30 data points). F is therefore preferentially partitioned in  
735 Li-Mi than in silicic melt, consistent with previous results ( $K_d \text{ Mu/L} = 1.8$ , Icenhower and  
736 London, 1995; 0.94-1.56, Pichavant et al., 2016). Above  $\sim 3$  wt% F in melt, F concentrations  
737 in mica increase drastically. This goes along with important changes in mica crystal chemistry  
738 toward a more marked trioctahedral character. The F  $K_d \text{ Li-Mi/L}$  reaches values between 2  
739 and 3, in the range of biotite-liquid F partitioning data ( $K_d \text{ Bt/L} = 2.3$ , Icenhower and  
740 London, 1997; average of 2.3, Pichavant et al., 2016). Therefore, F partitioning closely  
741 follows the major element composition and structure of the mica. No attempt was made to  
742 constrain the distribution of Li between mica and melt since in this study Li concentrations in  
743 micas are calculated (see above).

744 The trace element data in charge B2N-25 allow the Qz/L partition coefficients for Li,  
745 Al, P, Ti, Zn, Sn, Cs, W to be estimated (Table 9). For Li, the experimentally determined  
746 partition coefficient (0.027) is significantly lower than calculated from the Yellowstone tuffs  
747 ( $\sim 0.073$ , Neukampf et al., 2019) and the Macusani volcanics (0.17, Michaud and Pichavant  
748 (2020).

749 Sn concentrations in charge B2N-25 yield very high partition coefficients for Li-mica  
750 and hematite ( $K_d \text{ Li-Mi/L} \sim 170$  and  $K_d \text{ Hm/L} \sim 890$  respectively) using the separate Sn  
751 analyses of Li-mica and hematite reported above and the glass analysis from Table 9. These  
752 partition coefficients represent maximum values because Sn was progressively lost from the  
753 melt to the capsule. However,  $K_d \text{ Li-Mi/L}$  from this study is markedly higher than previous  
754 muscovite/L partitioning data (0.38-0.49, Raimbault and Burnol, 1998; 0.48-0.49, Michaud  
755 and Pichavant, 2020) implying that Sn is compatible in micas under our experimental  
756 conditions. Given the high  $fO_2$  of the B2N-25 experiment ( $\sim \text{NNO}+3$ ), tin should be present as  
757  $\text{Sn}^{4+}$  (Linnen et al., 1995; 1996) and the very elevated  $K_d \text{ Li-Mi/L}$  from this study suggests  
758 that  $\text{Sn}^{4+}$  preferentially partitions in mica rather than in melt.

759

## 760 **DISCUSSION**

### 761 **Evaluation of kinetic issues**

762 In this study, crystallization experiments have been conducted at temperatures uncommonly  
763 low (down to  $\sim 550^\circ\text{C}$ , Table 2; 3) for silica-rich melt compositions and, so, an evaluation of  
764 kinetic issues is particularly necessary. Silicic crystal-melt systems have been known for long  
765 to be difficult to equilibrate. In crystallization experiments, supercooling is of general concern  
766 and, in melting experiments, superheating can be necessary to overcome the sluggish  
767 dissolution kinetics of some phases, in particular quartz (Piwinskii and Martin, 1970;  
768 Pichavant et al., 1987a and references therein).

769 Several observations indicate kinetic difficulties in our experiments despite the long  
770 experimental durations. The most critical concerns saturation temperatures for major phases at  
771 100 MPa which are lower than at higher pressures under water-saturated conditions (see  
772 above), a behavior symptomatic of supercooled melts. The effect of melt supercooling is to  
773 delay phase appearance for a given temperature and/or shift phase appearance to a lower  
774 temperature for a given experimental duration. In supercooled charges which contain  
775 proportions of crystals lower than equilibrium, melts compositions can be metastable. Results  
776 of melting experiments (Pichavant et al., 1987a; Table S4) confirm the very low saturation  
777 temperatures in the 100 MPa crystallization experiments. Qz saturation temperatures are  
778 lower by  $<115^\circ\text{C}$  in crystallization than in melting experiments on B1, and by  $85^\circ\text{C}$  on B2  
779 (Fig. 2; 3). For Pl, differences between melting and crystallization saturation temperatures are  
780  $<80^\circ\text{C}$  for B1 and  $55^\circ\text{C}$  for B2 (Fig. 2; 3). Af in crystallization experiments saturate at  
781 temperatures  $20^\circ\text{C}$  lower than in melting experiments and, for Mu, the two saturation  
782 temperatures are within  $\pm 5^\circ\text{C}$  of each other (Fig. 2; 3). Therefore, the 100 MPa

783 crystallization experiments underestimate the Qz and Pl saturation temperatures and also  
784 slightly the Af. We stress that this does not necessarily imply that saturation temperatures  
785 from melting experiments approach equilibrium more closely because melting kinetics of  
786 major phases can be sluggish, particularly for Qz as noted above.

787 In contrast, at 300 MPa for B2, Pl, Af and Li-Mi saturation curves in crystallization  
788 and melting experiments are within 5°C of each other (Fig. 3). Qz is the only major phase  
789 whose saturation temperature could be slightly underestimated since it persists up to 40°C  
790 higher in melting than in crystallization experiments (Fig. 3). In the 200 MPa B2 experiments,  
791 all major phases saturate at temperatures consistent with those at 300 MPa (Fig. 3). For B1,  
792 saturation temperatures are all higher in crystallization than in melting experiments, most  
793 probably because of the low sensitivity of the X-ray phase identification method used in the  
794 melting experiments (Pichavant et al., 1987a). Therefore, there is no indication that  
795 equilibrium is not approached in the 300 MPa B1 crystallization charges. We conclude that  
796 melt supercooling issues in this study mainly concern the 100 MPa and are minor or absent in  
797 the 200 and 300 MPa charges. Such a marked influence of pressure is most probably due to  
798 the significantly higher melt H<sub>2</sub>O concentrations at 300 and 200 than at 100 MPa which  
799 would speed up crystallization kinetics at high pressures.

800 Major element compositions of major phases provide additional insights on  
801 equilibrium states. Although the glasses are chemically homogeneous, some specific  
802 compositions might correspond to metastable melts. This includes the 100 MPa glasses which  
803 have normative Qz higher than the other glasses (Fig. 5) and could be too SiO<sub>2</sub>-rich because  
804 of Qz proportions less than equilibrium. Similarly, the distinctive normative Or-rich  
805 composition of B2N-18 glass (Fig. 5) could indicate delayed Af appearance. The observation  
806 that feldspar pairs mostly correspond to compositions at equilibrium on the ternary solvus  
807 (Fig. 6) does not necessarily imply that all phases in our experiments reached equilibrium  
808 compositions. The heterogeneous feldspars (and their compositions inside the solvus) and the  
809 Al-rich quartz solid solutions are interpreted as remnants of non-equilibrium compositions  
810 still present in some charges despite long experimental durations.

811

### 812 **Natural feldspar and mica compositions**

813 At the difference of the melting experiments where mineral assemblages and compositions are  
814 inherited from the starting granites (Pichavant et al., 1987a), experiments from this study  
815 provide information on compositions of phases crystallizing from B1 and B2 melts. This  
816 allows crystallization of the Beauvoir granite to be reconstructed and compositions of major

817 mineral phases, mainly feldspars and micas, in the granite to be interpreted in the light of  
818 experimental results.

819 Averages of natural feldspar compositions along the GPF drill core ( $\text{Or}_1\text{Ab}_{98.5}\text{An}_{0.5}$  for  
820 plagioclase,  $n = 69$  and  $\text{Or}_{90}\text{Ab}_{10}$  for K-feldspar,  $n = 42$ , Johan et al., 1988) are very close to  
821 compositions in our starting rocks (Fig. 6). Only 5 plagioclases have  $> 1\%$  An (maximum 2.5)  
822 and 3 have  $> 1.5\%$  Or (maximum 7.4, Johan et al., 1988). In comparison, experimental Pl  
823 have An mostly  $> 1\%$  and are much more K-rich ( $\sim 10\%$  Or) than the natural compositions  
824 (Fig. 6). Natural K-feldspars range from  $\text{Or}_{87}$  up to  $\text{Or}_{100}$  and only one composition ( $\text{Or}_{78}$ ,  
825 Johan et al., 1988) approaches the Af experimental range ( $\text{Or}_{67-73}$ , Fig. 6). The natural feldspar  
826 pair in the starting rocks yields equilibration temperatures of 391 and 407°C for pressures of  
827 100 and 300 MPa respectively (Wen and Nekvasil, 1994) and, therefore, their compositions  
828 were frozen  $\sim 150^\circ\text{C}$  colder than the Beauvoir solidi (Fig. 2; 3). Clearly, most feldspars do not  
829 preserve magmatic compositions. However, a few rare analyses (the most An- and Or-rich Pl  
830 and the most Na-rich Af) suggest that primary compositions were close to the experimental  
831 ranges. We conclude that feldspars in the Beauvoir granite have been extensively re-  
832 equilibrated during the post-magmatic evolution.

833 Several mica crystallization stages have been recognized in the Beauvoir granite. The  
834 earliest corresponds to relatively Li-poor Fe-bearing Li-Mi (Li-, Fe-muscovites of  
835 Kosakevitch, 1976) subsequently interpreted as near-liquidus phases from relatively  
836 unfractionated melts (Monier and Tegye, 1985; Monier et al., 1987). These compositions are  
837 quite rare and represented in our dataset by only one EMPA analysis (the right most in Fig.  
838 7b). They have not been exactly reproduced in the experiments, and the B2 Li-Mi  
839 compositions have Mg-Li slightly higher than early stage micas (Fig. 7a; b). The main stage is  
840 characterized by the crystallization of Li-, F-rich zinnwaldites to polyolithionites which  
841 postdate the early stage compositions and have been previously interpreted as crystallized  
842 from fractionated sub-liquidus melts (Monier et al., 1987). This mica crystallization stage has  
843 been adequately simulated by the B1 experiments where Li-Mi compositions are closely  
844 similar to the natural Beauvoir micas (Fig. 7).

845 The evolution of Beauvoir micas from early Li-poor Fe-bearing Li-Mi to zinnwaldites  
846 and polyolithionites (increasing  $\text{Fe}_t + \text{Mn} + \text{Ti} - \text{Al}^{\text{VI}}$  with decreasing Mg – Li) parallels the  
847 compositional shift of experimental micas from the B2 to the B1 charges. This trend ((1) in  
848 Fig. 7a) is positively correlated with the melt F content (Fig. 8). It describes the compositional  
849 evolution of Li-Mi crystallizing from a progressively more F-rich peraluminous granitic melt.  
850 The mica becomes more silicic, less aluminous and its trioctahedral character increases, a

851 general evolution which can be understood from the structural role of F in aluminosilicate  
852 melts (increase of  $a_{\text{SiO}_2}$ , complexing between F and Al, Manning, 1981; Xiong et al., 1998;  
853 1999). The F control of experimental mica compositions along trend (1) is also marked in  
854 PHP rare metal granites. In the Argemela intrusion which contains significantly less F than  
855 Beauvoir (0.5-1.0 wt% F, Michaud and Pichavant, 2020), most micas plot at the high Mg-Li  
856 end of trend (1), in the same domain as experimental B2 micas (Fig. 7a; b). Thus, Beauvoir  
857 melts with F contents intermediate between our two starting compositions would be expected  
858 to crystallize Li-Mi filling the gap between the B1 and B2 experimental compositions, in the  
859 range inferred for the early stage micas. Another evolutionary trend ((2) in Fig. 7a and 8) is  
860 apparent both in natural and experimental micas.  $\text{Fe}_t + \text{Mn} + \text{Ti} - \text{Al}^{\text{VI}}$  decreases with  
861 decreasing Mg – Li as illustrated by the Beauvoir mica separate data (Fig. 7b) and by the  
862 experimental compositions from B1N-23, -22 to -21 (i.e., upon decreasing temperature and  
863 melt fraction, Fig. 4; 7a; 8). This trend is a mica fractionation trend, i.e., it reflects the  
864 removal and progressive exhaustion of mafic components from the F-rich peraluminous  
865 granitic melt as mica crystallizes. The observed zonation of mica compositions across the  
866 GPF drill core (zinnwaldites at the base and polyolithionites at the top, Monier et al., 1987) is  
867 consistent with crystallization from a more fractionated melt in the latter than in the former  
868 case. We conclude that the composition of Beauvoir micas preserves two distinct magmatic  
869 evolutionary trends (Fig. 7a).

870 However, several mica chemical features do not fit in an entirely magmatic  
871 interpretation. Micas from the B1 unit have  $\text{FeO}_t$  and MgO concentrations (respectively < 1  
872 and < 0.1 wt%, Monier et al., 1987) much lower than in B1 charges (~1-5.5 and ~0-2 wt%  
873 respectively, Table 7; S3). Conversely, MnO concentrations in natural micas are higher (on  
874 average ~0.8 wt% and up to ~1.5 wt% MnO in the B2 unit, Monier et al., 1987) than in  
875 experimental micas (0-0.4 wt%, Table 7; S3). This suggests that  $\text{FeO}_t$ , MgO and MnO in  
876 micas do not represent magmatic concentrations and have been modified by post-magmatic  
877 fluid circulations.

878

### 879 **Redox conditions and magmatic F, Li concentrations**

880 The presence of hematite and magnetite in our experiments constitutes the main point of  
881 divergence between the experimental and natural phase assemblages since the Beauvoir  
882 granite contains no Fe-Ti oxide except secondary rutile (e.g., Monier et al., 1987; Cuney et  
883 al., 1992). Below, we exclude the possibility that Fe-Ti oxides were once present but all  
884 completely destroyed during late-stage crystallization processes, either magmatic or post-

885 magmatic. Therefore, the lack of Fe-Ti oxides in the granite can be used to constrain the  
886 redox conditions. In our experiments, hematite was found in the most oxidizing ( $\sim$ NNO+3)  
887 and magnetite in less oxidizing (NNO+1) charges (Lahlafi, 1997). It is recalled that no Fe-Ti  
888 oxide crystallized in the NNO-1 and NNO-1.4 experiments. This constrains the  $fO_2$  of the  
889 Beauvoir granite to a range more reducing than NNO+1 and more oxidizing than NNO-1.4  
890 since Bt would be present under such highly reducing conditions (Table 3), which is not  
891 observed (Cuney et al., 1992). Previously, an oxidizing magmatic evolution has been  
892 recognized at Beauvoir (Cuney et al., 1992 and see the Ta, Nb, Sn mineralization section  
893 below). A progressive oxidizing trend is developed at the scale of the GPF drill core,  
894 superimposed on more reducing conditions as demonstrated by lepidolites with low  $Fe^{3+}/Fe^{2+}$   
895 at the base, presence of uraninite in B3 and B2 (Cuney et al., 1992) and absence of Fe-Ti  
896 oxides in the lower granite units. Therefore, the  $< NNO+1$  to  $> NNO-1.4$  range inferred from  
897 our experiments is interpreted as representative of early magmatic conditions. This implies  
898 that most of our crystallization experiments have been performed at an inappropriately  
899 oxidizing  $fO_2$ . This has minor consequences for the stability of major phases since varying  
900  $fO_2$  from  $\sim$ NNO+3 to NNO-1 has no systematic influence on the location of saturation curves  
901 (Fig. 2; 3). However,  $fO_2$  has definitely an influence on phase compositions (see above the Fe  
902 and Sn contents of experimental micas). The specific behavior of some trace elements  
903 (compatible for Sn and strongly incompatible for U, Fig. 9) also reflect the oxidizing  
904 conditions of most of our experiments.

905 Crystallization of topaz and amblygonite in experiments from this study provides  
906 unambiguous confirmation that both can be magmatic phases in the Beauvoir granite (Monier  
907 and Tegye, 1985; Rossi et al., 1987; Cuney et al., 1992). Previously, topaz has been reported  
908 to be present in early crystallization experiments. However, topaz identification was uncertain  
909 (see Pichavant et al., 1987a). In this study, topaz was identified by SEM and analyzed by  
910 electron microprobe. It appears only in charge B1N-21 at 580°C, 300 MPa which is one of the  
911 two most evolved B1 charges. Melt in B1N-21 has the highest F concentration (3.31 wt% if  
912 unnormalized) and one of the two highest normative Corundum (6.5%, Fig. 4; Table 4). The  
913 rarity of topaz in our experimental charges contrasts with its ubiquitous presence in the  
914 Beauvoir granite. Previous work has emphasized F and Li loss from the crystallizing magma  
915 and F concentrations as high as 4 wt% have been considered possible for Beauvoir melts  
916 (Cuney et al., 1992). An average F concentration of 4.9 wt% has been found in re-  
917 homogenized melt inclusions from the B1 unit (Kovalenko et al., 1998). Such F concentration  
918 levels are on average above our experimental melt concentrations although the most F-

919 enriched B1 glasses approach the 4 wt% range, if normalized to 100% anhydrous (i.e., 3.70  
920 wt% F for B1N-21). However, experimental topazes have elevated F concentrations (at  
921  $F/(F+OH) = 0.89-0.99$ , Table 8). This is higher than the old values from the GPF drill core (at  
922  $F/(F+OH) = 0.78-0.92$ , Monier and Tegye, 1985) but in the range of recent data for topaz in  
923 the B1 unit (0.96-1.04) and in a dike associated with the B2 unit (0.93-0.94, L. Monnier, pers.  
924 comm. 2022). In other words, there is no indication that the F concentration in the B1N-21  
925 experimental melt was much lower than in natural Beauvoir melts. In comparison,  
926 experimental F concentrations in B2 charges were probably insufficiently high given the  
927 relatively Li-, F-poor Li-Mi compositions crystallized in B2 (Fig. 7 and see above).

928 Topaz is a rather low temperature and late crystallizing phase in our experiments,  
929 appearing later than mica in the B1 300 MPa crystallization sequence. The data suggest that a  
930 minimum F content of 3-3.5 wt% in the melt is necessary for topaz to be stable (see also  
931 Soufi, 2021). In our experiments, such elevated F contents are reached in the sub-liquidus  
932 domain where quartz and feldspar crystallization enrich the residual melt in F (Fig. 4). The  
933 low topaz crystallization temperature observed in this study is consistent with at.  $F/(F+OH)$   
934  $\sim 1$  in experimental topaz since at higher temperatures F partitions less favorably in topaz than  
935 in other phases (Soufi, 2021). In melts with  $F \gg 3-3.5$  wt%, topaz with at.  $F/(F+OH) < 1$  is a  
936 high temperature near-liquidus phase (Xiong et al., 1999; Lukkari and Holtz, 2007). This is  
937 not what is observed at Beauvoir where topaz is a sub-liquidus low temperature phase and has  
938 at.  $F/(F+OH) \sim 1$ . We conclude that the rarity of topaz in our experiments is simply a  
939 reflection of the small number of low melt fraction charges available for the B1 composition  
940 (Fig. 4). At 580°C and 300 MPa, melt fractions are still high ( $f=67$  wt% in the topaz-bearing  
941 charge B1N-21, Table 3) so that, during the crystallization of the last (>50 wt%) B1 melt  
942 fraction, topaz should be present. Under these conditions, the melt F content should also reach  
943 the 4 wt% level typical of the B1 unit (Cuney et al., 1992; Kovalenko et al., 1998).

944 Experimental amblygonites from this study are richer in F ( $\sim 13$  wt% F, Table 8) than  
945 their natural counterparts in the Beauvoir granite ( $\sim 10.5-11.5$  wt% F, London et al., 2001).  
946 Yet, it is possible that amblygonites from the more evolved B1 and B2 units have higher F  
947 contents since the data above (from Ph. Rossi) are for the B3. Apatites in experiments and in  
948 the GPF drill core (Johan et al., 1988; Cuney et al., 1992) are both F-rich, the natural having  
949 generally higher MnO concentrations ( $\sim 3$  to  $\sim 6$  wt%) than the experimental compositions  
950 (Table 8). In conclusion, the range of F melt concentrations generated in our B1 charges is in  
951 the range or slightly lower than in the natural magma. However, the B2 experiments probably  
952 underestimate the F concentrations in the natural magma. In fact, our starting B2 sample,

953 although stratigraphically from the B2 unit, has geochemical characteristics typical of B'2  
954 compositions (high SiO<sub>2</sub> and low Al<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub> and F, Raimbault et al., 1995). This explains  
955 our experimental results in particular the relatively Li-, F-poor compositions of Li-Mi  
956 crystallized in B2 (see above).

957

### 958 **Crystallization and conditions of emplacement of the Beauvoir granite**

959 Results from this study confirm the very low magmatic temperatures of the Beauvoir granite.  
960 Further to the solidi previously discussed (Fig. 2; 3; Pichavant et al., 1987a), the 100 MPa  
961 liquidus temperatures are 715°C for B1 and 720°C for B2 (from the melting experiments  
962 because of melt supercooling in the 100 MPa crystallization experiments) and the 300 MPa >  
963 640°C for B1 (620°C from the melting experiments) and 640°C for B2 (670°C from the  
964 melting experiments). Thus, in the 100-300 MPa range, the two Beauvoir compositions  
965 studied begin to crystallize at temperatures lower than the H<sub>2</sub>O-saturated haplogranite solidus  
966 (Tuttle and Bowen, 1958; Fig. 2; 3). Such magmatic conditions are exceptional and only  
967 approached by flux-rich granitic compositions (Xiong et al., 2002; Lukkari and Holtz, 2007;  
968 Aksyuk et al., 2016), granitic pegmatites (Burnham and Nekvasil, 1986) and by the Macusani  
969 glass (Pichavant et al., 1987b; London et al., 1989).

970 Two types of experimental results suggest that the B1 and B2 granite units have the  
971 significance of crystallized liquids. First, the four major phases (Qz, Pl, Af, Li-Mi) saturate in  
972 very narrow temperature intervals, both in B1 and B2 (Fig. 2; 3). Saturation temperature  
973 intervals are of 20-30°C at 100 MPa, probably a consequence of melt supercooling, and of 30-  
974 40°C at 300 MPa. Thus, liquidus temperatures are only a little higher than temperatures of  
975 multiple saturation of the melt with the four major phases. This requires that the B1 and B2  
976 starting granites are compositionally close to their respective multiply saturated melts.  
977 Second, residual melts in both the B1 and B2 charges little depart from their respective  
978 starting compositions (Fig. 5). Deviations are within 2-3% normative, at the exception of a  
979 few charges (the 100 MPa, B2O-38/40, B2N-18, Fig. 5) discussed previously. Such a  
980 behavior again requires that compositions of liquidus and multiple saturation melts are close  
981 to each other and, so, the two starting compositions must represent essentially frozen liquids.

982 This result opens perspectives for constraining the crystallization pressure of Beauvoir  
983 melts. Experimental data are available on the influence of pressure (under water-saturated  
984 conditions, Tuttle and Bowen, 1958) and of additional components at constant pressure (F, Li,  
985 P, A/CNK, (F: Manning, 1981; Li: Martin, 1983; A/CNK: Holtz et al., 1992a; b; P: London et  
986 al., 1993) on the location of minima and eutectics in the haplogranite system (Fig. 5).

987 However, the combined effect of these different variables is as yet undetermined. As an  
988 illustration, the F-rich B1 and B2 compositions plot at normative Quartz contents significantly  
989 above the minimum liquidus points with added F at 100 MPa (Manning, 1981; Fig. 5). This is  
990 attributed to the influence of very high A/CNK and normative Corundum in Beauvoir melts  
991 (Holtz et al., 1992a; b). Therefore, pressures of Beauvoir melt crystallization cannot be  
992 constrained directly from the reference liquidus points presently available. Melts multiply  
993 saturated with the four major phases at 300 MPa plot closer than at 100 MPa to their  
994 respective starting compositions which would tend to suggest that 100 MPa is too low a  
995 pressure for early crystallization. However, the 100 MPa melts probably represent metastable  
996 compositions (see above). We must conclude that no reliable barometric information can be  
997 presently extracted from the major element compositions of Beauvoir granites.

998 Petrographic observations and textural evidence have shown that albite and lepidolite  
999 are the two earliest major phases to crystallize in Beauvoir magmas (Kosakevitch, 1976).  
1000 Mica is earlier than albite in some samples but the reverse is observed in others and, so, the  
1001 two phases can be considered to appear almost together on the liquidus. Quartz, frequently  
1002 euhedral and with albite inclusions present in external growth zones (M. Cuney, personal  
1003 communication, 2022), is also an early phase, being followed by K-feldspar. By reference to  
1004 the P-T diagrams, these textural relations require that crystallization started at pressures > 300  
1005 MPa for B1 and at ~200-250 MPa for B2 (Fig. 2; 3). Final solidification of the pluton took  
1006 place at its emplacement level (~ 80 MPa from the P-T conditions of exsolution of the  
1007 magmatic fluids, Cuney et al., 1992). Therefore, pressures of early (> 200-250 MPa) and final  
1008 crystallization (80 MPa) are significantly different and Beauvoir melts started to crystallize at  
1009 depths higher than their emplacement level. Since they represent crystallized liquids, this  
1010 implies that little melt-crystals segregation took place during final ascent.

1011

### 1012 **Fractionation in the Beauvoir granite**

1013 The major and trace element zonation observed among the different Beauvoir granite units  
1014 has been used as a reference example of chemical fractionation in rare metal granites (Zhu et  
1015 al., 2001; Costi et al., 2009; Cuney and Marignac, 2015; Pollard, 2021). Although  
1016 mechanisms of fractionation in rare metal granites and pegmatites are still debated, this study  
1017 demonstrates that most of the distinctive mineralogical and geochemical characteristics of the  
1018 Beauvoir granite result from magmatic rather than hydrothermal post-magmatic processes.  
1019 Albitic plagioclase, Li-, F-rich mica, topaz and amblygonite are of magmatic origin. A/CNK,

1020 F and P<sub>2</sub>O<sub>5</sub> concentrations increase and trace elements fractionate as a result of progressive  
1021 crystallization (Fig. 4; 9).

1022         The major element signature of fractionation at Beauvoir is examined by comparing  
1023 granite whole rock and experimental glass compositions (Fig. 11). The granite units globally  
1024 define a progressive fractionation trend marked by increasing A (= 1000 (Al – (Na + K +  
1025 2Ca) at.) at decreasing B (=1000 (Fe+Mg+Ti) at., Fig. 11a). This natural trend, classical for  
1026 rare metal granites (Linnen and Cuney, 2005; Cuney and Marignac, 2015), is well reproduced  
1027 by the experimental data (Fig. 11b) and this confirms that Beauvoir granites are reliable  
1028 proxies for magmatic liquid compositions. In the Q\*<sup>3</sup>-B\*<sup>3</sup>-F\*<sup>3</sup>-M\*<sup>3</sup> representation, all  
1029 granite compositions plot close to each other but the two groups of experimental glasses  
1030 define fractionation trends marked by increasing M\*<sup>3</sup>/F\*<sup>3</sup> at constant Q\*<sup>3</sup> (Fig. 11c; d).  
1031 These trends match with the evolutions at constant normative Quartz contents in the Qz-Ab-  
1032 Or diagram (Fig. 5) and with the increase in normative Corundum with decreasing melt  
1033 fraction and progressive fractionation (Fig. 4). The 100 MPa glasses again deviate from the  
1034 trends, being distinctly shifted toward Q\*<sup>3</sup>-rich compositions (Fig. 11d). We note that the two  
1035 B1 and B2 glass fractionation trends do not coincide (Fig. 11b; d) as observed in the Qz-Ab-  
1036 Or diagram where the B1 and B2 data points plot in different fields (Fig. 5). The two B1 and  
1037 B2 trends also remain separate from each other when plotted as a function of melt fraction  
1038 (Fig. 4). Therefore, the B1 and the B2 samples do not belong to the same evolutionary trend  
1039 and this demonstrates that our two Beauvoir starting compositions are not comagmatic.  
1040 Reminding that our B2 starting rock has geochemical attributes of B'2 compositions, the  
1041 experimental glasses thus confirm previous conclusions from whole rock data that the B and  
1042 B' represent two distinct magmatic series (Raimbault et al., 1995). Experimental data are  
1043 lacking to discuss the mutual relationships within the B series, i.e., between the B1, B2, B3  
1044 compositions which are geochemically close to each other (Raimbault et al., 1995; Fig. 11c).  
1045 A progressive decrease in normative Quartz is observed at the scale of the GPF drill core from  
1046 the B3, B2 to the B1 units, positively correlated with an increase of the F content (Cuney et  
1047 al., 1992). This evolution has been attributed to the role of F on granite phase equilibria  
1048 (Manning, 1981; Cuney et al., 1992) although other components (Li, P, A/CNK) must also be  
1049 involved (see above, Fig. 5). However, the important point to be emphasized is that this  
1050 geochemical variability among the B units is not generated at the emplacement level of the  
1051 intrusion because differentiation of Beauvoir melts yields derivative products with almost  
1052 constant normative Quartz (Fig. 5; 11). Therefore, our results suggest that the B1, B2 and B3  
1053 granite units represent three independent magma batches generated at depth.

1054 Trace element fractionation generated in experiments from this study are compared  
1055 with those observed in Beauvoir granites (Fig. 12). For most elements, the data points plot in  
1056 the upper right and lower left quadrants and so most elements fractionate (become either  
1057 enriched or depleted) similarly in experiments and from B2 to B1. This strongly suggests that  
1058 magmatic crystallization is at the origin of the trace element fractionations observed at  
1059 Beauvoir. Elements enriched include Li, Be, U, F, P, Rb, W while Sr, Pb are depleted. The  
1060 former group plots close to the 1:1 line (except Be, Fig. 12) and so, for these elements, the  
1061 experimentally generated enrichments are similar in magnitude to those observed from B2 to  
1062 B1. Cs is an exception (enriched in the experiments but depleted from B2 to B1) explained by  
1063 the high Cs concentration in our B2 starting sample (Raimbault et al., 1995). For Sr and Pb,  
1064 the experimental depletions are respectively higher and lower than from B2 to B1. Ti is  
1065 significantly fractionated neither in the experiments nor in the granites (Raimbault et al.,  
1066 1995). Zn and Mn plot close to the vertical axis (Fig. 12) and so they do not fractionate in the  
1067 experiments (Fig. 9), although both are depleted from B2 to B1 (Raimbault et al., 1995).  
1068 However, the significant variations of whole rock Mn concentrations in the top part of B1  
1069 (where a 20 m Mn-enriched “fringe zone” overlies a Mn-depleted level of about the same  
1070 thickness, Raimbault et al., 1995) and the observation that the natural lepidolites and apatites  
1071 are generally richer in Mn than their experimental counterparts (see above) suggests Mn re-  
1072 distribution during cooling of the intrusion.

1073

#### 1074 **Origin of the Beauvoir granite**

1075 The constraints placed on the evolution of the Beauvoir granite raise the question of its origin.  
1076 There is agreement that it is ultimately related to the tectonic evolution, thermal maturation  
1077 and partial melting of the continental crust during late Variscan times (e.g., Gebelin et al.,  
1078 2009; Lardeaux, 2014; Augier et al., 2015; Barbey et al., 2015). In this framework, the  
1079 genesis of highly fractionated granitic melts such as Beauvoir can be accounted for by two  
1080 possible models (1) extreme differentiation from less evolved crustal parental magmas (e.g.,  
1081 Raimbault et al., 1995; Cerny et al., 2005b; London, 2008; Hulsbosch, 2019) or (2) direct  
1082 anatectic origin (e.g., Stewart, 1978; Christiansen et al., 1986; Cuney and Autran, 1987;  
1083 Nabelek et al., 1992a; b; Muller et al., 2017). In fact, results of this study do not favor any of  
1084 these two models. The thermal characteristics of Beauvoir melts (liquidus temperatures of  
1085 670°C maximum at 300 MPa) make it possible that they represent near-solidus residual melts  
1086 from the crystallization of parental peraluminous leucogranitic magmas (e.g., Scaillet et al.,  
1087 1995). Alternatively, these liquidus temperatures are within the P-T evolution of metamorphic

1088 units during late Variscan times and appropriate for crustal melting either under fluid-absent  
1089 (muscovite-dehydration melting) or fluid-present (Cuney and Autran, 1987; Gardien et al.,  
1090 1997; Lardeaux, 2014; Augier et al., 2015; Barbey et al., 2015; Michaud et al., 2021).  
1091 Although an origin of rare metal granites by fluid-absent melting of residual lithologies  
1092 previously enriched by the removal of a low-temperature melt fraction has been commonly  
1093 proposed (see Michaud et al., 2021), this model can be discarded for Beauvoir since it would  
1094 imply melt generation at temperatures much higher (at least 100°C higher for biotite-  
1095 dehydration melting) than the B1 and B2 liquids.

1096 Geological evidence in support of any of the two models is ambiguous. At Beauvoir,  
1097 there is no candidate parental magma exposed (it would likely be represented by granitic units  
1098 intermediate between the Beauvoir and Colettes) but other granites are probably present at  
1099 depth (Aubert, 1969; Cuney and Marignac, 2015). The anatectic model (Cuney and Autran,  
1100 1987) has been ruled out on a geochemical basis (Raimbault et al., 1995). However, updated  
1101 versions of the model have been recently elaborated (Cuney and Barbey, 2014). We also note  
1102 that the differentiation model called for initial melts slightly enriched in rare metals (Sn and  
1103 W) originated from geochemically specialized lower crustal sources (Raimbault et al., 1995).  
1104 Differentiation, postulated to start at the anatexis level, generated strongly peraluminous, F-  
1105 and P-bearing and rare metal enriched melts (Raimbault et al., 1995). Further differentiation  
1106 during ascent led to the individualization of the B and B' magma series, the B1 and B2 units  
1107 representing two variably differentiated liquids from the same B magma and the B3 possibly a  
1108 slightly cumulative part of the B2 (Raimbault et al., 1995).

1109 Our experimental results confirm that the Beauvoir intrusion was built from at least  
1110 two distinct magmatic batches (see above, Fig. 11), all strongly peraluminous, P- and F-rich  
1111 and with elevated rare metal contents. They stress the importance of deep-seated fractionation  
1112 processes rather than those occurring in situ at the emplacement level. We note that the  
1113 fractionation mechanisms supporting the differentiation model are still poorly defined. For  
1114 example, amplification of melt structure and viscosity fluctuations during ascent has been  
1115 proposed to promote dynamic separation between more evolved less polymerized and less  
1116 evolved more polymerized melts (Raimbault et al., 1995). A combination of Bagnold effect  
1117 and filter-press processes has been suggested to control fractionation during ascent of rare  
1118 metal granitic melts in dykes (Marignac et al., 2009; Cuney and Marignac, 2015). These  
1119 mechanisms need further testing and validation and we conclude that the origin of the  
1120 Beauvoir melts still requires more work.

1121

**1122 Ta, Nb, Sn mineralization**

1123 Ta and Nb are both enriched although much more in granites than in experiments as indicated  
1124 by their position well above the 1:1 line (Fig. 12). The experimental Ta and Nb contents  
1125 (maximum 34 ppm Ta and 49 ppm Nb, Table 9) stay globally in the range of B2  
1126 concentrations (~45 ppm Ta and ~50 ppm Nb, Raimbault et al., 1995). They do not reach the  
1127 high to very high values observed in B1, ~150 ppm Nb and up to ~450 ppm Ta in the upper  
1128 “fringe zone” (Raimbault et al., 1995). C-T solubility data (Linnen and Keppler, 1997;  
1129 Linnen, 1998; Van Lichtervelde et al., 2018) have demonstrated higher solubility limits for  
1130 the Ta than for the Nb C-T end-members which provides an explanation for the fractionation  
1131 of Ta over Nb and the preferential Ta enrichment observed in B1. They also stress the  
1132 importance of the melt Li and F concentrations in controlling C-T saturation in rare metal  
1133 magmas. In this respect, it is worth emphasizing that our trace element data concern the B2  
1134 magma only. Fractionation in B2 charges increases F, P, Li (Fig. 4; 9) which leads to a C-T  
1135 solubility increase responsible for the Ta and Nb enrichments observed in residual melts (Fig.  
1136 9). Fractionation in B1 generates melts more F-, P- and presumably more Li-rich than in B2  
1137 (Fig. 4). Thus, Ta and Nb melt concentrations at C-T saturation higher than in B2 charges can  
1138 be expected and it is possible that residual B1 melts would have Ta and Nb approaching the  
1139 concentration levels observed in the B1 unit. This interpretation is consistent with a magmatic  
1140 control of the Ta and Nb mineralization at Beauvoir (Raimbault et al., 1995).

1141 For Sn, the strong enrichment observed in granites (B2: 300-800 ppm; B1: 800-1600  
1142 ppm, Raimbault et al., 1995) has no counterpart in experimental melts (Fig. 9; 11). In the  
1143 ~NNO+3 charges, Sn melt concentrations are controlled by cassiterite crystallization, Sn  
1144 partitioning toward Li-Mi and Hm and Sn loss to the capsule. In Beauvoir granites, Sn is  
1145 carried mainly by magmatic cassiterite implying that Beauvoir melts became cassiterite-  
1146 saturated at some point during their evolution. Sn whole rock concentrations and their  
1147 variations within and between units mainly reflect the proportion of cassiterite crystals which,  
1148 at cassiterite saturation, is controlled by the Sn content of the initial melt (a high Sn melt will  
1149 produce a higher amount of cassiterite than a low Sn melt when brought at cassiterite  
1150 saturation). Experimental data have shown that cassiterite solubility mainly depends on  $fO_2$  at  
1151 a given temperature and melt A/CNK, the influence of F being negligible (Bhalla et al., 2005  
1152 and references therein). Cassiterite solubilities are of the order of 100 ppm at NNO+2-3 but  
1153 increase rapidly to the several 1000 ppm range or more under reducing conditions (Bhalla et  
1154 al., 2004 and references therein). Therefore, magmatic oxidation is a very efficient  
1155 mechanism to promote cassiterite saturation (Linnen et al., 1995; 1996; Pichavant et al.,

1156 2016). At Beauvoir, several lines of evidence for a late progressive oxidation of the intrusion  
1157 have been presented (Cuney et al., 1992 and see the redox section above). This promoted  
1158 cassiterite saturation in melts enriched in Sn by crystallization-differentiation at the intrusion  
1159 level (Michaud and Pichavant, 2020). Sn contents of initial melts are unknown but can be  
1160 estimated to be of a few hundred ppm for B2 or more for B1, considering the respective  
1161 whole rock concentrations. Some Sn was extracted and transported by postmagmatic  
1162 hydrothermal fluids as suggested by the Sn depletion in the upper part of the cupola (Cuney et  
1163 al., 1992; Raimbault et al., 1995). The final Sn distribution in the intrusion was probably  
1164 controlled by the re-mobilization by late postmagmatic fluids of Sn from cassiterite and Sn-  
1165 bearing micas.

1166

### 1167 **Broader implications for granitic magmatism**

1168 One important result from this study is the confirmation of the very low magmatic  
1169 temperatures of the Beauvoir granites (see above). This demonstrates that natural granites  
1170 solidi are in fact quite variable. Many (Burnham and Nekvasil, 1986; London et al., 1989;  
1171 Xiong et al., 2002; Lukkari and Holtz, 2007; Aksyuk et al., 2016; this study) are much colder  
1172 than the H<sub>2</sub>O-saturated haplogranite solidus (Tuttle and Bowen, 1958). It is important to  
1173 consider the latter as a theoretical reference rather than as a universal benchmark for the  
1174 solidus of granitic rocks (see Ackerson et al., 2018).

1175 Two-feldspar thermometry and more recent geothermobarometric methods such as Ti-  
1176 in-quartz generally have yielded temperatures between 400 and 600°C for the crystallization  
1177 of granitic rocks (Moazzen and Droop, 2005; Glazner and Johnson, 2013; Ackerson et al.,  
1178 2018; London et al., 2020). Despite the particularly low solidus temperatures for Beauvoir,  
1179 albite and K-feldspar record equilibration temperatures that are still ~150°C colder (see  
1180 above). These subsolidus equilibration temperatures have led to speculations on mechanisms  
1181 of final consolidation of granitic bodies (Ackerson et al., 2018). By far the most likely  
1182 explanation is that such low crystallization temperatures indicate fluid-assisted mineral re-  
1183 equilibration during the post-magmatic evolution, the interpretation proposed above for  
1184 Beauvoir and other granites (Moazzen and Droop, 2005; Lukkari and Holtz, 2007). For  
1185 example, feldspars experience major chemical, textural and structural transformations during  
1186 the cooling of granitic bodies (Parsons, 1978; Smith and Brown, 1988). These reactions are  
1187 triggered by fluid percolation and fluid-rock interaction as demonstrated by fluid inclusions  
1188 (Kontak et al., 1984) and stable isotope studies (Taylor and Forester, 1971; Fouillac and  
1189 Rossi, 1991). Both quartz and feldspars in the GPF drill core show a systematic decrease in

1190  $\delta^{18}\text{O}$  from base to top, interpreted to indicate interaction with meteoric fluids at high  
1191 temperature (Fouillac and Rossi, 1991; Cuney et al., 1992). Thus, despite its exceptionally  
1192 low solidus temperature which makes the post-magmatic “window” narrower, the Beauvoir  
1193 granite reminds us of the importance of re-equilibration processes involving hydrothermal  
1194 fluids in the final solidification of granitic plutons.

1195

## 1196 CONCLUSIONS

1197 Crystallization experiments performed on two Beauvoir granite samples (B1 and B2) simulate  
1198 the magmatic evolution and chemical fractionation in strongly peraluminous, F- and P-rich  
1199 rare metal magmas. The main conclusions of the study are the following:

1200 - Beauvoir melts crystallize a magmatic assemblage which includes quartz, albitic  
1201 plagioclase, K-feldspar, Li-mica, apatite, cassiterite and columbo-tantalite. This assemblage,  
1202 joined by topaz and amblygonite in the B1 experiments, closely reproduces the granite  
1203 mineralogy. Fe-Ti oxides are present for  $f\text{O}_2$  between  $\sim\text{NNO}+3$  and  $\text{NNO}+1$ .

1204 - The crystallization experiments confirm the very low solidus temperatures of the  
1205 granites. In the 100-300 MPa range, B1 and B2 have liquidus temperatures lower than the  
1206  $\text{H}_2\text{O}$ -saturated haplogranite solidus, an exceptional behavior characteristic of flux-rich  
1207 granitic melts.

1208 - Upon progressive crystallization, residual melts become more F- and P-rich. Melt  
1209 major element compositions evolve at constant Qz contents and become more peraluminous.  
1210 F-rich topaz and amblygonite crystallize as sub-liquidus phases from these evolved melts.

1211 - Comparison between natural and experimental mineral compositions suggest that  
1212 feldspars in the granite have been re-equilibrated during the post-magmatic evolution. Both  
1213 natural and experimental micas follow similar trends from Li phengites to zinnwaldites and  
1214 polyolithionites. Compositions closely similar to the natural Beauvoir micas crystallize in the  
1215 B1 experiments.

1216 - The  $f\text{O}_2$  ranged from  $< \text{NNO}+1$  to  $> \text{NNO}-1.4$  during the early magmatic stage, later  
1217 evolving to highly oxidizing conditions at the magmatic-hydrothermal transition. F, Li melt  
1218 concentrations in B1 experiments reproduce or are slightly lower than the concentrations in  
1219 the natural magma. Those in B2 underestimate most natural B2 concentrations since the  
1220 starting sample has geochemical attributes of B'2 compositions. Glass major elements suggest  
1221 that our two starting compositions are not comagmatic. The major distinction between the B  
1222 and B' geochemical series at Beauvoir is confirmed. The intrusion was made from at least two  
1223 independent magma batches.

1224 - The low liquidus temperatures, narrow saturation temperature intervals and grouped  
1225 residual melts imply that the Beauvoir granites represent crystallized liquids. Beauvoir melts  
1226 started to crystallize at depths ( $\geq 200$  MPa) significantly higher than their emplacement level  
1227 (80 MPa). Our results stress the importance of deep-seated processes (either partial melting or  
1228 differentiation) as a way to generate the specific major element compositions of Beauvoir  
1229 melts.

1230 - Upon magmatic crystallization, the melt becomes enriched in Li, Be, B, Rb, Cs, W,  
1231 U, Nb, Ta and depleted in Sr and Pb. Fractionation trends observed in Beauvoir granites are  
1232 similar to those in experiments suggesting that crystallization at the emplacement level  
1233 controls chemical fractionation for most elements.

1234 - Sn is compatible in micas and hematite under highly oxidizing conditions. This,  
1235 together with cassiterite crystallization and Sn loss, prevents Sn enrichment in residual melts.  
1236 Cassiterite saturation in Beauvoir magmas was promoted by late magmatic oxidation of the  
1237 intrusion.

1238 - Most of the mineralogical and geochemical characteristics that make the Beauvoir  
1239 granite distinctive result from magmatic rather than hydrothermal processes. However,  
1240 feldspar and mica compositions and fractionation patterns for some elements (Mn) confirm  
1241 that post-magmatic fluids were involved in the final stages of crystallization of the intrusion.

1242

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1579

## 1580 **FIGURE CAPTIONS**

1581 **Fig. 1.** SEM images of major phases and textures in crystallization experiments. (a) euhedral  
 1582 quartz (Qz) and plagioclase (Pl) in glass (Gl), charge B2N-18. (b) large homogenous  
 1583 plagioclase crystals (Pl) in glass (Gl), charge B1N-1. (c) large heterogeneous feldspar crystals  
 1584 in glass (Gl), charge B2N-3. The potassic and sodic zones are denoted by K and Na  
 1585 respectively. Notice the progressive and geometrically complex transitions between the two  
 1586 zones and the small quartz (Qz) crystals at the extremities of the feldspars. (d) euhedral  
 1587 homogeneous K-feldspar crystals (Af) coexisting with homogeneous plagioclase (Pl) in

1588 composite crystals embedded in glass (Gl), charge B1N-22. (e) Li-mica crystals (Li-Mi) in  
1589 glass (Gl), charge B2N-25. Apatite (Ap) appears in white at the bottom of the image. (f)  
1590 Euhedral topaz crystals (Tpz) coexisting with quartz (Qz), K-feldspar (Af), plagioclase (Pl),  
1591 Li-mica (small white grey interstitial phases and aggregates) and glass (Gl) in charge B1-21.  
1592 (g) Several crystals of Li-Al phosphates (LiP) of the amblygonite-montebrasite series  
1593 dispersed in charge B1-21. Notice also the presence of topaz (Tpz). (h) Crystal of hematite  
1594 (Hm) in glass (Gl), charge B2N-19. See Tables 2 and 3 for experimental conditions.

1595

1596 **Fig. 2.** Summary P-T phase diagram for the B1 Beauvoir composition under H<sub>2</sub>O-saturated  
1597 conditions and for a  $fO_2$  between NNO+3 and NNO+1. The solid symbols are experimental  
1598 data points from Table 2. Solid curves represent phase equilibria constrained from  
1599 crystallization experiments (this study) and dashed curves from melting experiments  
1600 (Pichavant et al., 1987a). Solidus curves appear in black and Qz, Pl, Af and Li-Mi saturation  
1601 curves in red, blue, green and yellow respectively. Phases are stable on the left of their  
1602 respective saturation curve. The P-T location of minimum liquidus temperature points in the  
1603 H<sub>2</sub>O-saturated haplogranite system (“haplogranite minimum”, Tuttle and Bowen, 1958) is  
1604 shown for comparison (grey solid curve). See text for the construction of the diagram and for  
1605 interpretations.

1606

1607 **Fig. 3.** Summary P-T phase diagram for the B2 Beauvoir composition under H<sub>2</sub>O-saturated  
1608 conditions and for a  $fO_2$  between NNO+3 and NNO-1. The solid symbols are experimental  
1609 data points from Table 3. Solid curves represent phase equilibria constrained from  
1610 crystallization experiments (this study) and dashed curves from melting experiments  
1611 (Pichavant et al., 1987a). Solidus curves appear in black and Qz, Pl, Af and Li-Mi saturation  
1612 curves in red, blue, green and yellow respectively. Phases are stable on the left of their  
1613 respective saturation curve. The P-T location of minimum liquidus temperature points in the  
1614 H<sub>2</sub>O-saturated haplogranite system (“haplogranite minimum”, Tuttle and Bowen, 1958) is  
1615 shown for comparison (grey solid curve). See text for the construction of the diagram and for  
1616 interpretations.

1617

1618 **Fig. 4.** Changes in Beauvoir experimental melt compositions during progressive  
1619 crystallization and decreasing melt fraction (expressed in wt%). Symbols are in red for B1  
1620 and in blue for B2. Melt fractions are melt (L) proportions in experimental charges (solid  
1621 symbols) calculated by mass balance (Table 2 and 3). For starting melts (open symbols), melt

1622 fractions are 100%. (a) F concentrations (wt%) vs. melt fraction; (b) P<sub>2</sub>O<sub>5</sub> concentrations  
1623 (wt%) vs. melt fraction; (c) normative Corundum (%) vs. melt fraction; (d) normative  
1624 Anorthite (%) vs. melt fraction. In (a), numbers in grey refer to the charge numbering in  
1625 Tables 2 and 3. Data for experimental melts are from Table 4 and for starting melts from  
1626 Table 1. Note that the F and P<sub>2</sub>O<sub>5</sub> concentrations are not normalized to 100% anhydrous.  
1627 Error bars are shown.

1628  
1629 **Fig. 5.** Qz, Ab, Or compositions of Beauvoir starting materials (stars) and experimental  
1630 glasses (open circles). Symbols are in red for the B1 and in blue for the B2 composition.  
1631 Normative compositions (data in Tables 1 and 4) are projected on the Qz-Ab-Or space.  
1632 Numbers in grey refer to the charge numbering in Tables 2 and 3. Note that, in panel B1,  
1633 compositions of glass B1O-1 and of starting materials overlap and, in panel B2, compositions  
1634 of glasses B2N-19, B2N-20, B2N-25, B2N-26 and of starting materials overlap. For  
1635 reference, the positions of H<sub>2</sub>O-saturated minimum liquidus temperature points in the  
1636 haplogranite system at 100, 200 and 300 MPa (Tuttle and Bowen, 1958) are shown as black  
1637 squares. The positions of H<sub>2</sub>O-saturated minimum liquidus temperature points in the  
1638 haplogranite system at 100 MPa with 1 and 2 wt% added F (Manning, 1981) are shown as  
1639 black circles.

1640  
1641 **Fig. 6.** Compositions of feldspars in the crystallization experiments. All data from Table S2  
1642 are plotted. The B1 symbols and tie-lines are in red and the B2 in blue. Pl: plagioclase; Af: K-  
1643 feldspar; I: heterogeneous feldspar. Notice the heterogeneous feldspars plotting intermediate  
1644 between Pl and Af. Two-feldspar equilibration temperatures calculated using the  
1645 SOLVCALC software of Wen and Nekvasil (1994) for 4 representative Pl and Af pairs are  
1646 shown together with experimental pressures on their respective tie-lines. For charge B2N-24,  
1647 the calculated temperature is 578°C (vs. 580°C, Table 3) and, for charge B1N-21, 567°C (vs.  
1648 580°C, Table 2). For charge B2N-20, two plagioclase compositions have been selected for the  
1649 calculations, the < 2 mol% An difference between the two being representative of the  
1650 chemical dispersion within charges. The two Pl-Af pairs yield temperatures of 608 and 588°C  
1651 (vs. 620°C, Table 3). Results of other two-feldspar calculations are summarized in text.  
1652 Average compositions of feldspars in B1 and B2 starting rocks (data from Pichavant et al.,  
1653 1987a) are shown for comparison.

1654

1655 **Fig. 7.** Compositions of (a) experimental and (b) natural micas plotted in the  $\text{Fe}_t + \text{Mn} + \text{Ti} -$   
1656  $\text{Al}^{\text{VI}}$  (apfu) vs.  $\text{Mg} - \text{Li}$  (apfu) diagram of Tischendorf et al. (1997). Abbreviated names of  
1657 end-member compositions appear in grey (nomenclature after Tischendorf et al., 1997). Data  
1658 for experimental micas include electron microprobe (EMPA) and SEM analyses (Table 7 and  
1659 S3). For the SEM analyses, F concentrations are corrected by a constant factor ( $\times 2.3$ ). The  
1660 data for the natural Beauvoir micas (Monier et al., 1987) include electron microprobe  
1661 (EMPA) and wet chemical analyses (CHEM). The data for the natural Argemela micas are  
1662 averages of EMPA analyses from Michaud and Pichavant (2020). Except for the wet chemical  
1663 analyses of Beauvoir micas, the  $\text{Li}_2\text{O}$  contents of micas analyzed by EMPA and SEM are all  
1664 calculated from their F concentrations, using the [di 1] equation of Tischendorf et al. (1997).  
1665 In (a), 21, 22, 23 refer to the charge number in Table 2. The two arrows represent the  
1666 evolutionary trends (1) and (2) discussed in text.

1667  
1668 **Fig. 8.** (a)  $\text{Mg} - \text{Li}$  (apfu) and (b)  $\text{Fe}_t + \text{Mn} + \text{Ti} - \text{Al}^{\text{VI}}$  (apfu) of experimental micas as a  
1669 function of the F content of the coexisting melt. Data for experimental micas include electron  
1670 microprobe (EMPA) and SEM analyses (Table 7 and S3). For the SEM analyses, F  
1671 concentrations are corrected by a constant factor ( $\times 2.3$ ).  $\text{Li}_2\text{O}$  concentrations of micas  
1672 analyzed by EMPA and SEM are all calculated from their F contents, using the [di 1]  
1673 equation of Tischendorf et al. (1997). F concentrations in experimental melts are raw data  
1674 from Table 4 (i.e., not normalized to 100%) with error bar shown. 21, 22, 23, 25 refer to the  
1675 charge number in Table 2 (i.e., 21-23 refers to the B1N-21 to -23 and 25 to the B2N-25  
1676 charge). The two arrows represent the evolutionary trends (1) and (2) discussed in text.

1677  
1678 **Fig. 9.** Evolution of trace element concentrations during progressive crystallization of the B2  
1679 Beauvoir melt. Concentrations of trace elements (Li, Be, B, Mn, Rb, Cs, W, U, Nb, Ta, Sn,  
1680 Sr) in selected B2 glasses (C), referenced to those in the initial melt ( $C_0$ , represented by the  
1681 crystal-free charge B2N-26), are plotted as  $\log(C/C_0)$  vs. the melt fraction ( $f$ ). Glass  
1682 concentrations are from Table 9 and melt fractions from Table 3. Dashed curves are Rayleigh  
1683 fractionation trends calculated (see Hanson, 1978) for bulk mineral/melt partition coefficients  
1684 (D) of 0.01, 0.5 and 3. The horizontal dotted line corresponds to  $C = C_0$ . See text.

1685  
1686 **Fig. 10.** F concentration in experimental micas as a function of the F content of the coexisting  
1687 melt. Data for experimental micas include electron microprobe (EMPA) and SEM analyses  
1688 (Table 7 and S3). F concentrations from SEM data are corrected by a constant factor ( $\times 2.3$ ). F

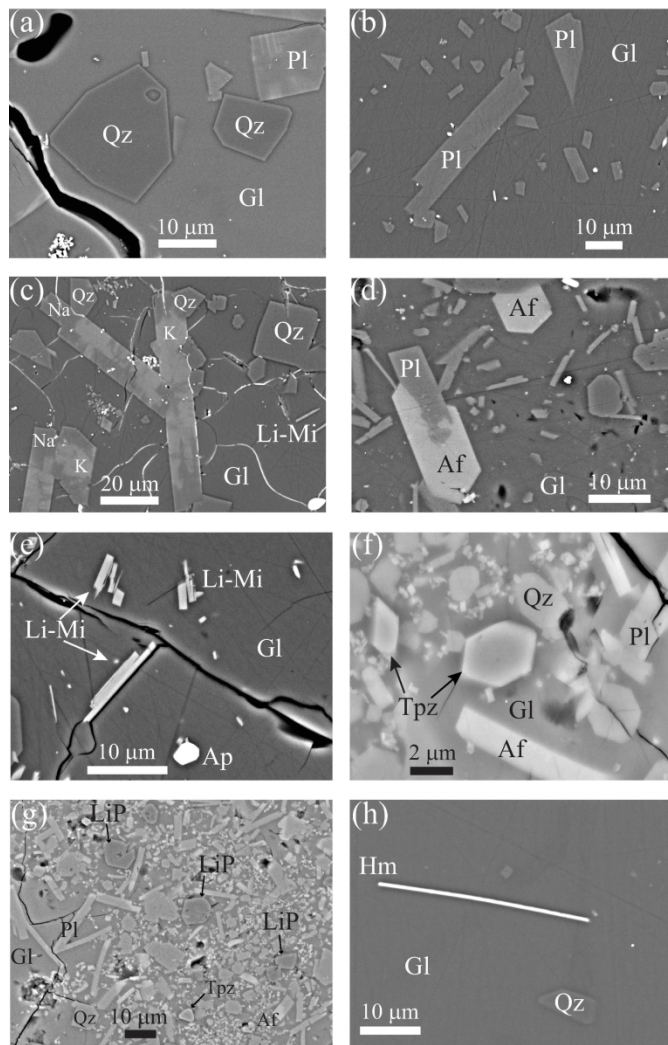
1689 concentrations in experimental melts are raw data from Table 4 (i.e., not normalized to 100%)  
 1690 with error bar shown. 21, 22, 23, 25 refer to the charge number in Table 2 (i.e., 21-23 refers to  
 1691 the B1N-21 to -23 and 25 to the B2N-25 charge).

1692

1693 **Fig. 11.** Comparison between major element fractionation in Beauvoir granites (left column)  
 1694 and in experimental glasses from this study (right column). Top panels (a) and (b): major  
 1695 element compositions plotted in the A-B diagram of Debon and Le Fort (1983). Bottom  
 1696 panels (c) and (d): major element compositions plotted in the Q\*3-B\*3-F\*3-M\*3  
 1697 representation of La Roche et al. (1980), see also Cuney and Marignac (2015) and inset for  
 1698 the significance of the Q\*3, B\*3, F\*3, M\*3 apexes. Concentrations are expressed in  
 1699 millications, i.e., as 1000 x atomic concentrations (at.). Abbreviations: Qz: quartz, Ann:  
 1700 annite, Phl: phlogopite, Pl: plagioclase, Af: K-feldspar, Mu: muscovite. In (d), experimental  
 1701 mica compositions from charges B1N23 and B2N-25 are also plotted (respectively Li-Mi B1  
 1702 and Li-Mi B2). The Beauvoir whole rock data are exclusively from Raimbault et al. (1995)  
 1703 and the experimental data are from this paper (averages of starting compositions in Table 1  
 1704 and selected glass compositions from Table 4). Notice the specific Q\*3-rich compositions of  
 1705 glasses B1N-17 and B2N-3 (respectively labelled 17 and 3) from 100 MPa crystallization  
 1706 charges.

1707

1708 **Fig. 12.** Comparison between trace element (Sn, Ta, Be, Nb, Li, P, U, F, Rb, W, Ti, Mn, Zn,  
 1709 Pb, Sr, Cs) fractionation in experiments from this study and in Beauvoir granites. Horizontal  
 1710 axis:  $\log(C/C_0)$  where C is the trace element concentration in the most fractionated glass B2-  
 1711 24 and  $C_0$  the trace element concentration in the parental glass B2-26 (Table 9). Vertical axis:  
 1712  $\log(C/C_0)$  where C is the trace element concentration in B1 granite (ESP 270, Raimbault et  
 1713 al., 1995) and  $C_0$  the trace element concentration in glass B2-26 (Table 9) assumed  
 1714 representative of the B2 granite. Experimental and natural enrichment and depletion  
 1715 directions are indicated. The location of data points relative to the 1:1 dotted line indicates  
 1716 how close elements are from an evolution identical in experiments and granites, whether an  
 1717 enrichment or a depletion. Color coding reflects the four groups of elements distinguished,  
 1718 those enriched both in the experiments and in the granites (red circles), those depleted both in  
 1719 the experiments and in the granites (black circles), those whose behavior should be controlled  
 1720 by accessory phase solubilities (blue squares) and those very much fractionated neither in the  
 1721 experiments nor in the granite (grey diamonds).

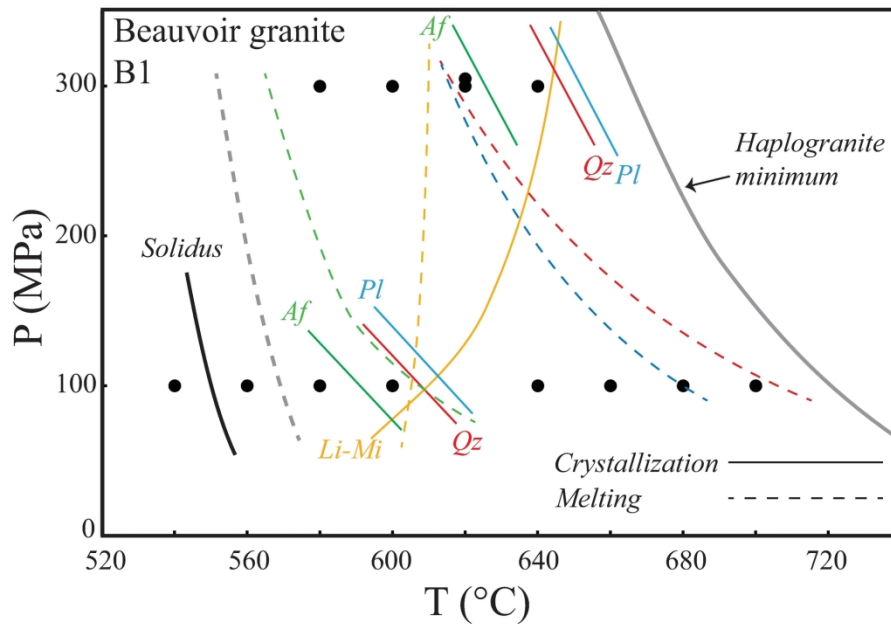


Pichavant, Fig.1

Fig. 1. SEM images of major phases and textures in crystallization experiments. (a) euhedral quartz (Qz) and plagioclase (Pl) in glass (Gl), charge B2N-18. (b) large homogeneous plagioclase crystals (Pl) in glass (Gl), charge B1N-1. (c) large heterogeneous feldspar crystals in glass (Gl), charge B2N-3. The potassic and sodic zones are denoted by K and Na respectively. Notice the progressive and geometrically complex transitions between the two zones and the small quartz (Qz) crystals at the extremities of the feldspars. (d) euhedral homogeneous K-feldspar crystals (Af) coexisting with homogeneous plagioclase (Pl) in composite crystals embedded in glass (Gl), charge B1N-22. (e) Li-mica crystals (Li-Mi) in glass (Gl), charge B2N-25. Apatite (Ap) appears in white at the bottom of the image. (f) Euhedral topaz crystals (Tpz) coexisting with quartz (Qz), K-feldspar (Af), plagioclase (Pl), Li-mica (small white grey interstitial phases and aggregates) and glass (Gl) in charge B1-21. (g) Several crystals of Li-Al phosphates (LiP) of the amblygonite-montebbrasite series dispersed in charge B1-21. Notice also the presence of topaz (Tpz). (h) Crystal of hematite (Hm) in glass (Gl), charge B2N-19. See Tables 2 and 3 for experimental conditions.

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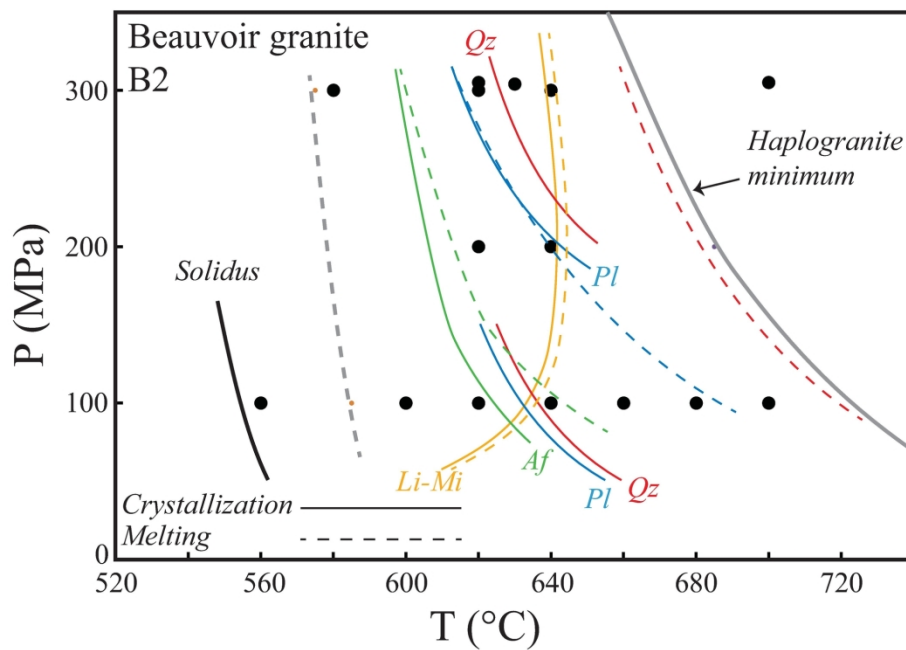




## Pichavant, Fig.2

Fig. 2. Summary P-T phase diagram for the B1 Beauvoir composition under H<sub>2</sub>O-saturated conditions and for a  $f_{O_2}$  between NNO+3 and NNO+1. The solid symbols are experimental data points from Table 2. Solid curves represent phase equilibria constrained from crystallization experiments (this study) and dashed curves from melting experiments (Pichavant et al., 1987a). Solidus curves appear in black and Qz, Pl, Af and Li-Mi saturation curves in red, blue, green and yellow respectively. Phases are stable on the left of their respective saturation curve. The P-T location of minimum liquidus temperature points in the H<sub>2</sub>O-saturated haplogranite system ("haplogranite minimum", Tuttle and Bowen, 1958) is shown for comparison (grey solid curve). See text for the construction of the diagram and for interpretations.

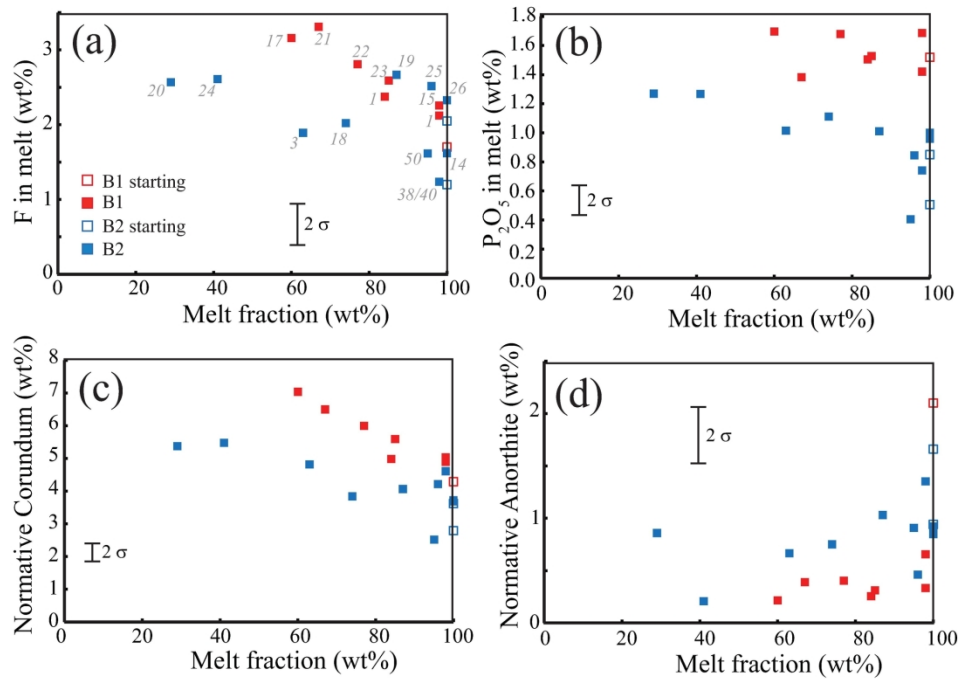
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### Pichavant, Fig.3

Fig. 3. Summary P-T phase diagram for the B2 Beauvoir composition under H<sub>2</sub>O-saturated conditions and for a fO<sub>2</sub> between NNO+3 and NNO-1. The solid symbols are experimental data points from Table 3. Solid curves represent phase equilibria constrained from crystallization experiments (this study) and dashed curves from melting experiments (Pichavant et al., 1987a). Solidus curves appear in black and Qz, Pl, Af and Li-Mi saturation curves in red, blue, green and yellow respectively. Phases are stable on the left of their respective saturation curve. The P-T location of minimum liquidus temperature points in the H<sub>2</sub>O-saturated haplogranite system ("haplogranite minimum", Tuttle and Bowen, 1958) is shown for comparison (grey solid curve). See text for the construction of the diagram and for interpretations.

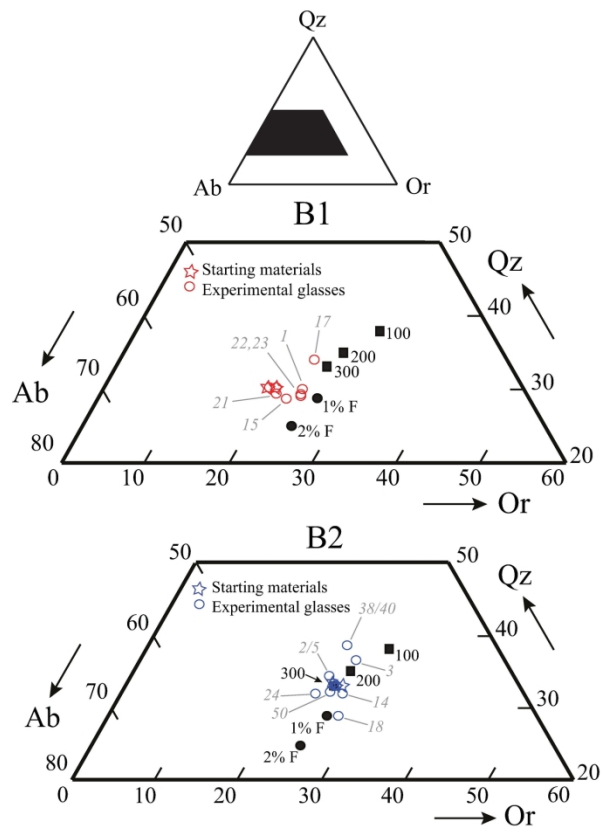
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Pichavant, Fig.4

Fig. 4. Changes in Beauvoir experimental melt compositions during progressive crystallization and decreasing melt fraction (expressed in wt%). Symbols are in red for B1 and in blue for B2. Melt fractions are melt (L) proportions in experimental charges (solid symbols) calculated by mass balance (Table 2 and 3). For starting melts (open symbols), melt fractions are 100%. (a) F concentrations (wt%) vs. melt fraction; (b) P<sub>2</sub>O<sub>5</sub> concentrations (wt%) vs. melt fraction; (c) normative Corundum (%) vs. melt fraction; (d) normative Anorthite (%) vs. melt fraction. In (a), numbers in grey refer to the charge numbering in Tables 2 and 3. Data for experimental melts are from Table 4 and for starting melts from Table 1. Note that the F and P<sub>2</sub>O<sub>5</sub> concentrations are not normalized to 100% anhydrous. Error bars are shown.

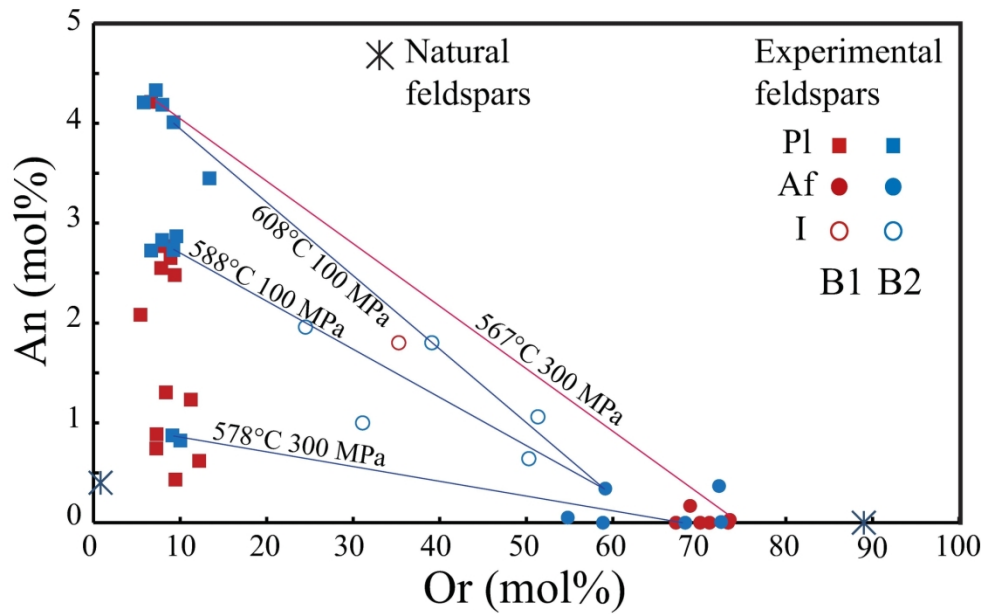
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Pichavant, Fig. 5

Fig. 5. Qz, Ab, Or compositions of Beauvoir starting materials (stars) and experimental glasses (open circles). Symbols are in red for the B1 and in blue for the B2 composition. Normative compositions (data in Tables 1 and 4) are projected on the Qz-Ab-Or space. Numbers in grey refer to the charge numbering in Tables 2 and 3. Note that, in panel B1, compositions of glass B1O-1 and of starting materials overlap and, in panel B2, compositions of glasses B2N-19, B2N-20, B2N-25, B2N-26 and of starting materials overlap. For reference, the positions of H<sub>2</sub>O-saturated minimum liquidus temperature points in the haplogranite system at 100, 200 and 300 MPa (Tuttle and Bowen, 1958) are shown as black squares. The positions of H<sub>2</sub>O-saturated minimum liquidus temperature points in the haplogranite system at 100 MPa with 1 and 2 wt% added F (Manning, 1981) are shown as black circles.

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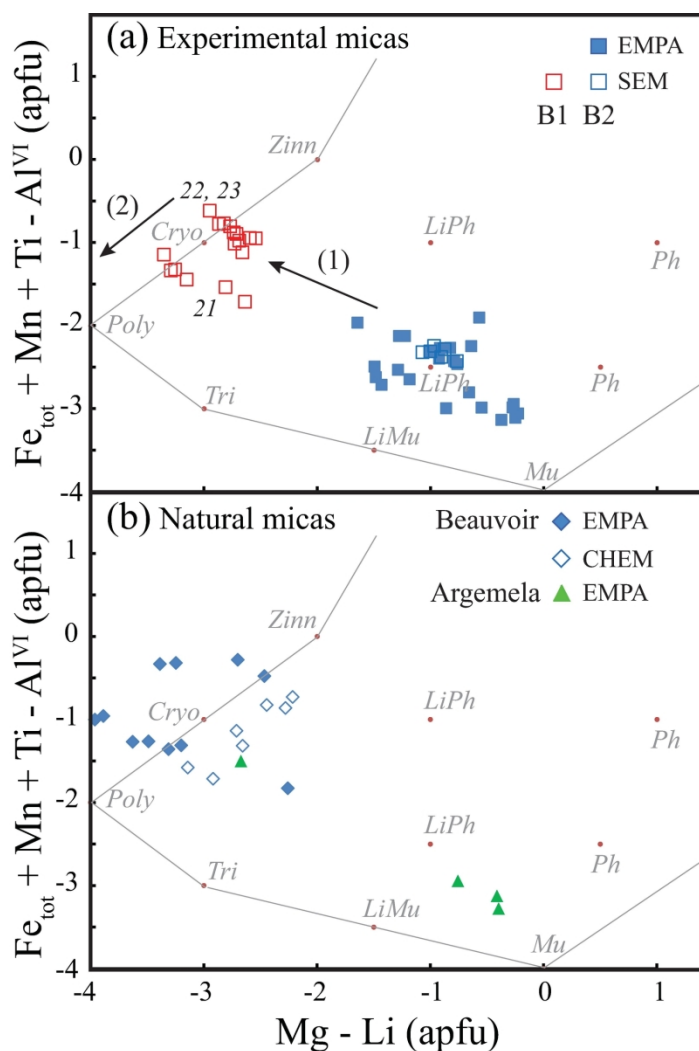


Pichavant, Fig. 6

Fig. 6. Compositions of feldspars in the crystallization experiments. All data from Table S2 are plotted. The B1 symbols and tie-lines are in red and the B2 in blue. Pl: plagioclase; Af: K-feldspar; I: heterogeneous feldspar. Notice the heterogeneous feldspars plotting intermediate between Pl and Af. Two-feldspar equilibration temperatures calculated using the SOLVCALC software of Wen and Nekvasil (1994) for 4 representative Pl and Af pairs are shown together with experimental pressures on their respective tie-lines. For charge B2N-24, the calculated temperature is 578°C (vs. 580°C, Table 3) and, for charge B1N-21, 567°C (vs. 580°C, Table 2). For charge B2N-20, two plagioclase compositions have been selected for the calculations, the < 2 mol% An difference between the two being representative of the chemical dispersion within charges. The two Pl-Af pairs yield temperatures of 608 and 588°C (vs. 620°C, Table 3). Results of other two-feldspar calculations are summarized in text. Average compositions of feldspars in B1 and B2 starting rocks (data from Pichavant et al., 1987a) are shown for comparison.

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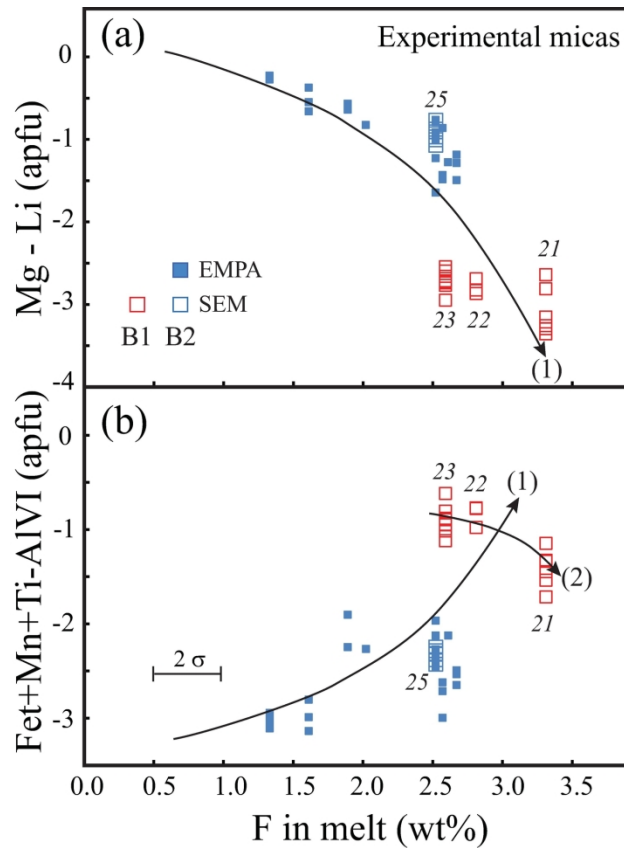




Pichavant, Fig.7

Fig. 7. Compositions of (a) experimental and (b) natural micas plotted in the  $Fe_{tot} + Mn + Ti - Al^{VI}$  (apfu) vs.  $Mg - Li$  (apfu) diagram of Tischendorf et al. (1997). Abbreviated names of end-member compositions appear in grey (nomenclature after Tischendorf et al., 1997). Data for experimental micas include electron microprobe (EMPA) and SEM analyses (Table 7 and S3). For the SEM analyses, F concentrations are corrected by a constant factor ( $\times 2.3$ ). The data for the natural Beauvoir micas (Monier et al., 1987) include electron microprobe (EMPA) and wet chemical analyses (CHEM). The data for the natural Argemela micas are averages of EMPA analyses from Michaud and Pichavant (2020). Except for the wet chemical analyses of Beauvoir micas, the Li<sub>2</sub>O contents of micas analyzed by EMPA and SEM are all calculated from their F concentrations, using the [di 1] equation of Tischendorf et al. (1997). In (a), 21, 22, 23 refer to the charge number in Table 2. The two arrows represent the evolutionary trends (1) and (2) discussed in text.

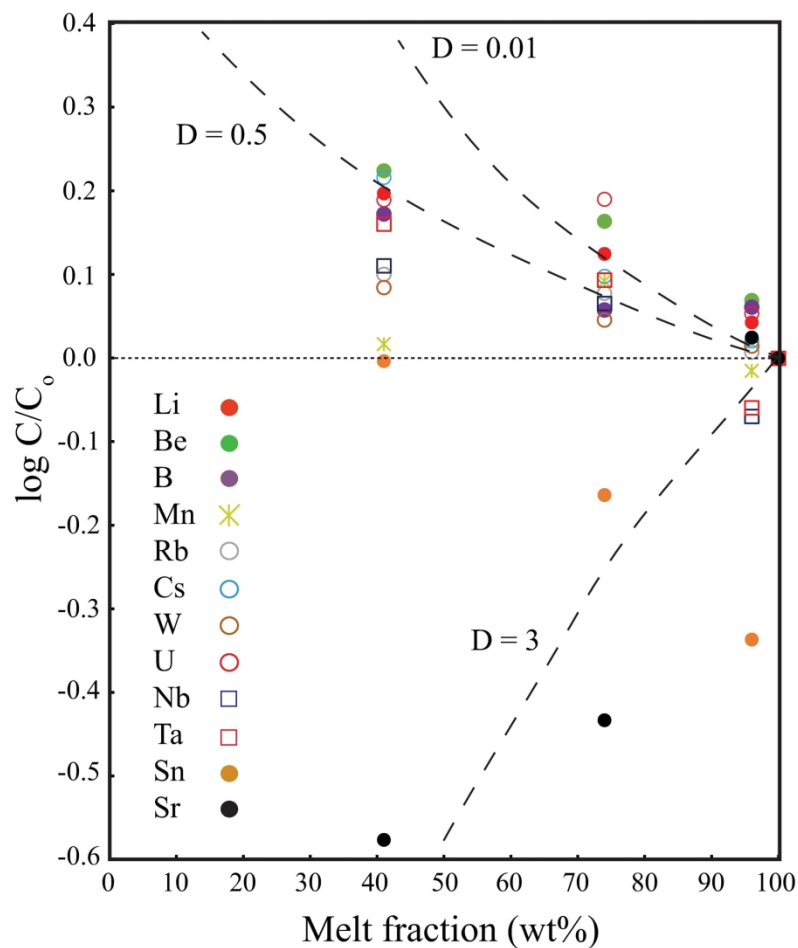
165x240mm (300 x 300 DPI)



Pichavant, Fig.8

Fig. 8. (a) Mg - Li (apfu) and (b) Fet + Mn + Ti - AlVI (apfu) of experimental micas as a function of the F content of the coexisting melt. Data for experimental micas include electron microprobe (EMPA) and SEM analyses (Table 7 and S3). For the SEM analyses, F concentrations are corrected by a constant factor ( $\times 2.3$ ). Li<sub>2</sub>O concentrations of micas analyzed by EMPA and SEM are all calculated from their F contents, using the [di 1] equation of Tischendorf et al. (1997). F concentrations in experimental melts are raw data from Table 4 (i.e., not normalized to 100%) with error bar shown. 21, 22, 23, 25 refer to the charge number in Table 2 (i.e., 21-23 refers to the B1N-21 to -23 and 25 to the B2N-25 charge). The two arrows represent the evolutionary trends (1) and (2) discussed in text.

154x249mm (300 x 300 DPI)

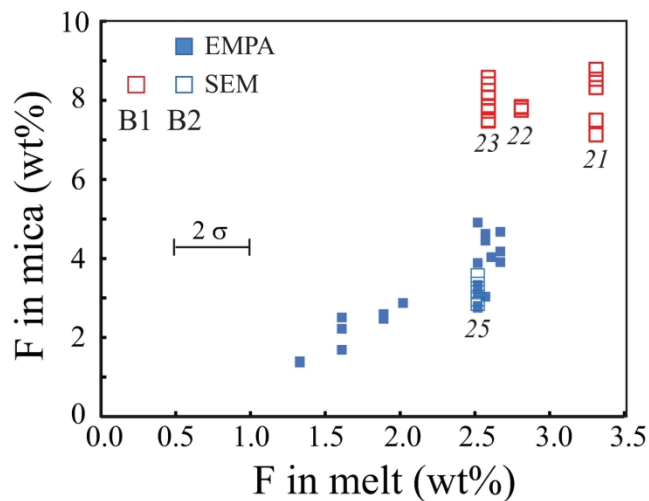


Pichavant, Fig.9

Fig. 9. Evolution of trace element concentrations during progressive crystallization of the B2 Beauvoir melt. Concentrations of trace elements (Li, Be, B, Mn, Rb, Cs, W, U, Nb, Ta, Sn, Sr) in selected B2 glasses (C), referenced to those in the initial melt ( $C_0$ , represented by the crystal-free charge B2N-26), are plotted as  $\log (C/C_0)$  vs. the melt fraction (f). Glass concentrations are from Table 9 and melt fractions from Table 3.

Dashed curves are Rayleigh fractionation trends calculated (see Hanson, 1978) for bulk mineral/melt partition coefficients ( $D$ ) of 0.01, 0.5 and 3. The horizontal dotted line corresponds to  $C = C_0$ . See text.

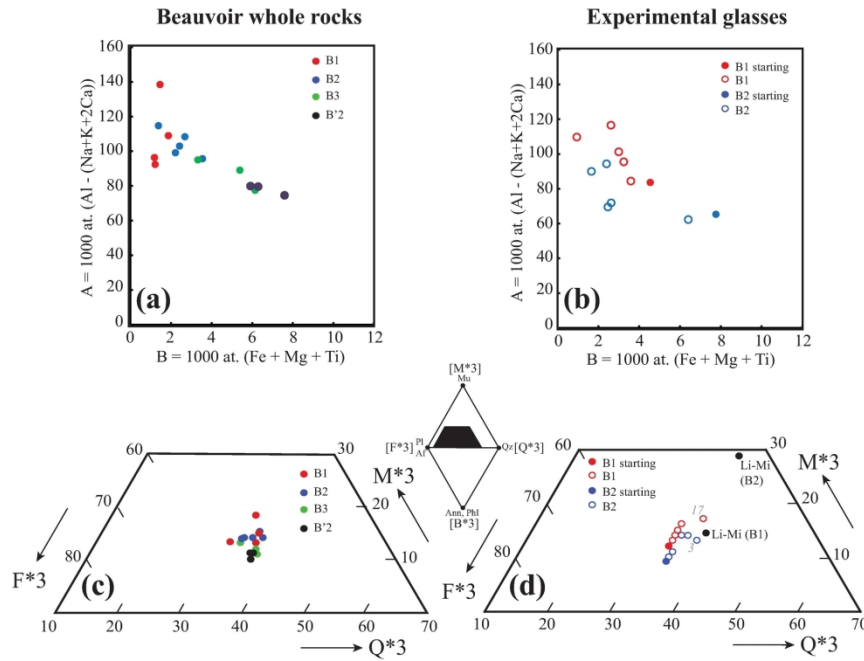
175x249mm (300 x 300 DPI)



Pichavant, Fig.10

Fig. 10. F concentration in experimental micas as a function of the F content of the coexisting melt. Data for experimental micas include electron microprobe (EMPA) and SEM analyses (Table 7 and S3). F concentrations from SEM data are corrected by a constant factor ( $\times 2.3$ ). F concentrations in experimental melts are raw data from Table 4 (i.e., not normalized to 100%) with error bar shown. 21, 22, 23, 25 refer to the charge number in Table 2 (i.e., 21-23 refers to the B1N-21 to -23 and 25 to the B2N-25 charge).

149x224mm (300 x 300 DPI)

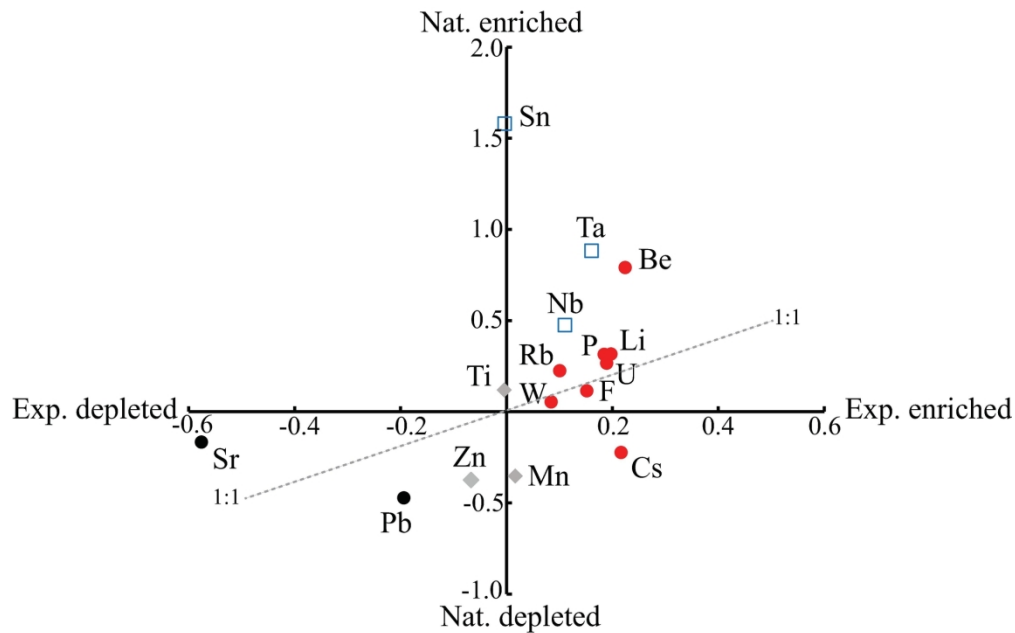


Pichavant, Fig. 11

Fig. 11. Comparison between major element fractionation in Beauvoir granites (left column) and in experimental glasses from this study (right column). Top panels (a) and (b): major element compositions plotted in the A-B diagram of Debon and Le Fort (1983). Bottom panels (c) and (d): major element compositions plotted in the Q\*3-B\*3-F\*3-M\*3 representation of La Roche et al. (1980), see also Cuney and Maignac (2015) and inset for the significance of the Q\*3, B\*3, F\*3, M\*3 apices. Concentrations are expressed in millications, i.e., as 1000 x atomic concentrations (at.). Abbreviations: Qz: quartz, Ann: annite, Phl: phlogopite, Pl: plagioclase, Af: K-feldspar, Mu: muscovite. In (d), experimental mica compositions from charges B1N23 and B2N-25 are also plotted (respectively Li-Mi B1 and Li-Mi B2). The Beauvoir whole rock data are exclusively from Raimbault et al. (1995) and the experimental data are from this paper (averages of starting compositions in Table 1 and selected glass compositions from Table 4). Notice the specific Q\*3-rich compositions of glasses B1N-17 and B2N-3 (respectively labelled 17 and 3) from 100 MPa crystallization charges.

171x221mm (300 x 300 DPI)





Pichavant, Fig.12

Fig. 12. Comparison between trace element (Sn, Ta, Be, Nb, Li, P, U, F, Rb, W, Ti, Mn, Zn, Pb, Sr, Cs) fractionation in experiments from this study and in Beauvoir granites. Horizontal axis:  $\log(C/C_0)$  where C is the trace element concentration in the most fractionated glass B2-24 and  $C_0$  the trace element concentration in the parental glass B2-26 (Table 9). Vertical axis:  $\log(C/C_0)$  where C is the trace element concentration in B1 granite (ESP 270, Raimbault et al., 1995) and  $C_0$  the trace element concentration in glass B2-26 (Table 9) assumed representative of the B2 granite. Experimental and natural enrichment and depletion directions are indicated. The location of data points relative to the 1:1 dotted line indicates how close elements are from an evolution identical in experiments and granites, whether an enrichment or a depletion. Color coding reflects the four groups of elements distinguished, those enriched both in the experiments and in the granites (red circles), those depleted both in the experiments and in the granites (black circles), those whose behavior should be controlled by accessory phase solubilities (blue squares) and those very much fractionated neither in the experiments nor in the granite (grey diamonds).

187x223mm (300 x 300 DPI)



**Table 1.** Compositions of starting materials

sample #	B1 WR	B1 glass 1997	B2 WR	B2 glass 1997	B2 glass 2017	
n		6		6	10	
		av*		av*	av	sd
SiO <sub>2</sub>	69.04	69.36	71.62	71.18	72.47	0.88
TiO <sub>2</sub>	0.03	0.03	0.02	0.01	0.02	0.03
Al <sub>2</sub> O <sub>3</sub>	16.72	16.48	15.79	15.66	14.78	0.87
Fe <sub>2</sub> O <sub>3</sub>	0.05	nd	0.04	nd	nd	nd
FeO	0.12	0.33	0.47	0.62	0.40	0.06
MnO	0.03	0.02	0.10	0.09	0.07	0.06
MgO	0.02	0.04	0.01	0.04	0.01	0.01
CaO	0.22	0.40	0.19	0.32	0.18	0.05
Na <sub>2</sub> O	5.11	5.16	4.52	4.50	4.48	0.23
K <sub>2</sub> O	3.17	2.97	3.84	3.89	4.07	0.16
P <sub>2</sub> O <sub>5</sub>	1.50	1.52	0.95	0.85	0.51	0.15
SnO <sub>2</sub>	nd	nd	nd	nd	0.00	0.01
F	2.39	1.70	1.77	1.20	2.05	0.30
Li <sub>2</sub> O	1.28	nd	0.71	nd	nd	nd
CO <sub>2</sub>	0.03	nd	0.03	nd	nd	nd
H <sub>2</sub> O	0.40	nd	0.23	nd	nd	nd
Total	98.83	98.01	99.58	98.36	99.04	
O=F	1.01	0.72	0.75	0.51	0.86	
Total	97.82	97.29	98.83	97.86	98.18	
Qz	28.34	28.73	31.50	30.78	31.72	
Ab	45.87	46.29	39.86	39.88	39.51	
Or	19.87	18.59	23.65	24.06	25.04	
An	1.16	2.10	0.98	1.66	0.94	
Co	4.76	4.29	4.02	3.62	2.79	
Total	100.00	100.00	100.00	100.00	100.00	
A/CNK	1.37	1.33	1.32	1.28	1.22	

Granite whole-rock (WR) samples analyzed by wet chemistry (Pichavant et al., 1987a)

Glasses analyzed by electron microprobe. n: number of electron microprobe spots; av: average; sd: standard deviation

\*data from Lahlafi (1997)

FeO = FeO total except for the WR data (FeO = FeO)

nd: not determined

Qz, Ab, Or, An, Co: normative quartz, albite, orthoclase, anorthite and corundum concentrations

A/CNK = Al<sub>2</sub>O<sub>3</sub>/(Na<sub>2</sub>O+K<sub>2</sub>O+CaO) molar

**Table 2.** Conditions and results of the B1 crystallization experiments.

Charge #	T °C	P MPa	duration h	phase assemblage	$\Sigma r^2$ control	fO <sub>2</sub>	$\Delta$ NNO	Reference
<i>Nancy</i>								
B1N-16	540	100	2064	Qz, Pl, Af, Mu	nd	unbuffered	~+3	
B1N-11	560	100	1800	(L), Qz, Pl, Af, Mu	nd	unbuffered	~+3	(1)
B1N-17	580	100	2064	L(60), Qz(8), Pl(24), Af(6), Mu(1), Ap	0.03	unbuffered	~+3	
B1N-1	600	100	1800	L(84), Qz (2), Pl(13), Mu(1)	0.09	unbuffered	~+3	(1)
B1N-13	640	100	1104	L(100)	nd	unbuffered	~+3	(1)
B1N-9	660	100	1560	L(100)	nd	unbuffered	~+3	(1)
B1N-7	680	100	1560	L(100)	nd	unbuffered	~+3	(1)
B1N-2	700	100	672	L(100)	nd	unbuffered	~+3	(1)
B1N-21	580	300	2184	L(67), Qz(9), Pl(16), Af(6), Mu(1) Tpz, Li-P, Ap	0.00	unbuffered	~+3	
B1N-15	600	300	1104	L(98), Pl(2), Ap	0.11	unbuffered	~+3	(1)
B1N-22	620	300	2184	L(77), Qz(7), Pl(14), Af(2), (Mu), Ap	0.01	unbuffered	~+3	
B1N-23	640	300	2184	L(85), Qz(2), Pl(12), (Mu), Ap	0.06	unbuffered	~+3	
<i>Orléans</i>								
B1O-1	620	300	1008	L(98), Pl(2), Ap	0.02	intrinsic	+1	

L: silicate glass, Qz: quartz, Pl: plagioclase, Af: K-feldspar, Mu: muscovite, Tpz: topaz, Li-P: amblygonite, Ap: apatite.

$\Delta$ NNO: deviation in log fO<sub>2</sub> from the NNO oxygen buffer (Chou, 1987) calculated at the same P and T than the experiment.

Numbers in brackets are proportions of major phases (wt%) calculated by mass balance.  $\Sigma r^2$  = sum of residuals. (phase A): < 1 wt% phase A present.

(1) experiments partially described in Pichavant et al. (1987a).

**Table 3.** Conditions and results of the B2 crystallization experiments.

Charge #	T °C	P MPa	duration h	phase assemblage	$\Sigma r^2$	fO <sub>2</sub> control	$\Delta$ NNO	Reference
<i>Nancy</i>								
B2N-12	560	100	1800	(L), Qz, Pl, Af, Mu	nd	unbuffered	~+3	(1)
B2N-3	600	100	1080	L(63), Qz(9), Pl(15), Af(9), Mu(4)	0.00	unbuffered	~+3	(1)
B2N-20	620	100	2064	L(29), Qz(20), Pl(28), Af(20), Mu(4), Hm	0.14	unbuffered	~+3	
B2N-14	640	100	1104	L(100)	nd	unbuffered	~+3	(1)
B2N-10	660	100	1560	L, Hm	nd	unbuffered	~+3	(1)
B2N-8	680	100	1560	L, Hm	nd	unbuffered	~+3	(1)
B2N-4	700	100	672	L(100)	nd	unbuffered	~+3	(1)
B2N-18	620	200	2064	L(74), Qz(10), Pl(11), Mu(5)	0.00	unbuffered	~+3	
B2N-19	640	200	2064	L(87), Qz(5), Pl(5), Mu(3), Hm	0.08	unbuffered	~+3	
B2N-24	580	300	2184	L(41), Qz(19), Pl(21), Af(10), Mu(9)	0.02	unbuffered	~+3	
B2N-25	620	300	2184	L(96), Qz(2), Mu(2), Hm, Ap	0.07	unbuffered	~+3	
B2N-26	640	300	2184	L(100)	nd	unbuffered	~+3	
<i>Orléans</i>								
B2O-2/5*	620	300	1008-4032	L, Qz, Pl, (Af), Mu, Mt, Ap	nd	intrinsic	+1	(2)
B2O-6/7*	700	300	168-1008	L, Ap, Mt	nd	intrinsic	+1	(2)
B2O-38/40*	620	300	240-360	L(98), Bt(2), Ap	0.49	CCO buffer	-1.4	(2)
B2O-41	700	300	168	L, Ap	nd	CCO buffer	-1.4	(2)
B2O-50	630	304	1123	L(95), Mu(5), Ap	0.15	Ar-H <sub>2</sub>	-1	

L: silicate glass, Qz: quartz, Pl: plagioclase, Af: K-feldspar, Mu: muscovite, Bt: biotite, Ap: apatite, Hm, hematite, Mt: magnetite.

$\Delta$ NNO: deviation in log fO<sub>2</sub> from the NNO oxygen buffer (Chou, 1987) calculated at the same P and T than the experiment.

Numbers in brackets are proportions of major phases (wt%) calculated by mass balance.  $\Sigma r^2$  = sum of residuals. nd: not determined (mass balance calculation not performed). (phase A): < 1 wt% of phase A present.

\*Multiple experiments were performed for different durations under identical P-T conditions and results are grouped (see text).

- (1) experiments partially described in Pichavant et al. (1987a).
- (2) experiments partially described in Lahlafi (1997) and Pichavant et al. (2016).

**Table 4.** Major element compositions of experimental glasses

sample #	B1		B1		B1		B1	
charge #	B1N-1		B1N-15		B1N-17		B1N-21	
n	5		5		6		6	
	av	sd	av	sd	av	sd	av	sd
SiO <sub>2</sub>	63.37	0.22	62.70	0.63	61.56	0.55	61.90	0.98
TiO <sub>2</sub>	0.01	0.01	0.00	0.01	0.02	0.02	0.01	0.01
Al <sub>2</sub> O <sub>3</sub>	15.23	0.23	15.42	0.26	15.85	0.27	16.54	0.62
FeO	0.19	0.11	0.13	0.09	0.15	0.08	0.05	0.05
MnO	0.03	0.04	0.04	0.04	0.04	0.05	0.04	0.05
MgO	0.04	0.05	0.03	0.02	0.01	0.02	0.01	0.01
CaO	0.04	0.02	0.06	0.03	0.04	0.02	0.07	0.02
Na <sub>2</sub> O	4.40	0.11	4.73	0.11	3.95	0.20	4.67	0.19
K <sub>2</sub> O	3.34	0.03	3.07	0.09	3.08	0.15	2.91	0.19
P <sub>2</sub> O <sub>5</sub>	1.51	0.16	1.42	0.14	1.70	0.18	1.38	0.09
SnO <sub>2</sub>	nd		nd		nd		nd	
F	2.37	0.10	2.26	0.05	3.16	0.09	3.31	0.32
Total	90.52		89.87		89.55		90.88	
O=F	1.00		0.95		1.33		1.39	
Total	89.52		88.91		88.22		89.49	
Qz	28.86		27.07		31.61		27.26	
Ab	43.07		46.58		39.59		45.89	
Or	22.84		21.13		21.54		19.96	
An	0.26		0.33		0.22		0.39	
Co	4.99		4.89		7.04		6.50	
Total	100.00		100.00		100.00		100.00	
A/CNK	1.39		1.37		1.60		1.51	

Glasses analyzed by electron microprobe. n: number of electron microprobe spots; av: average; sd: standard deviation. For B1, glasses from charges B1N-11, -13, -9, -7, -2 (Table 2) have not been analyzed and for B2, glasses from charges B2N-10, -8, -4 and B2O-6/7, -41 (Table 3)

\*data from Lahfafi (1997) normalized to 100%

FeO = FeO total

nd: not determined

Qz, Ab, Or, An, Co: normative quartz, albite, orthoclase, anorthite and corundum concentrations

A/CNK = Al<sub>2</sub>O<sub>3</sub>/(Na<sub>2</sub>O+K<sub>2</sub>O+CaO) molar

B1		B1		B1		B2		B2	
B1N-22		B1N-23		B1O-1		B2N-3		B2N-14	
5		6		6		5		5	
av	sd	av	sd	av*	av	sd	av		
62.22	0.54	63.20	0.44	71.19	65.93	0.66	65.48	1.13	
0.01	0.02	0.01	0.01	0.02	0.02	0.02	0.01	0.02	
16.10	0.24	16.00	0.18	17.22	14.43	0.16	14.38	0.57	
0.15	0.04	0.19	0.12	0.03	0.16	0.08	0.19	0.06	
0.05	0.07	0.06	0.08	0.00	0.14	0.05	0.08	0.06	
0.03	0.04	0.02	0.02	0.01	0.01	0.01	0.01	0.01	
0.07	0.03	0.05	0.01	0.13	0.12	0.03	0.16	0.02	
4.43	0.12	4.52	0.11	5.20	3.72	0.20	4.10	0.18	
3.25	0.10	3.31	0.04	3.28	3.58	0.07	3.75	0.14	
1.68	0.28	1.53	0.08	1.69	1.02	0.13	0.96	0.07	
nd		nd		nd	nd		nd		
2.81	0.10	2.59	0.08	2.12	1.89	0.22	1.62	0.13	
90.81		91.48		100.90	90.99		90.75		
1.18		1.09		0.89	0.80		0.68		
89.63		90.39		100.00	90.20		90.07		
27.70		27.66		28.96	34.59		30.61		
43.58		43.95		45.38	35.83		39.50		
22.32		22.48		19.97	24.09		25.25		
0.40		0.31		0.66	0.67		0.92		
6.00		5.59		5.03	4.82		3.72		
100.00		100.00		100.00	100.00		100.00		
1.47		1.44		1.40	1.41		1.29		

B2 B2N-18		B2 B2N-19		B2 B2N-20		B2 B2N-24	
7		10		6		2	
av	sd	av	sd	av	sd	av	sd
65.02	0.23	65.09	0.38	62.90	0.56	64.50	0.46
0.02	0.02	0.03	0.05	0.03	0.02	0.02	0.02
15.05	0.09	14.41	0.13	15.01	0.13	15.63	0.24
0.30	0.13	0.12	0.03	0.08	0.05	0.14	0.13
0.07	0.03	0.07	0.07	0.12	0.07	0.07	0.08
0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01
0.13	0.03	0.18	0.02	0.15	0.03	0.04	0.02
4.31	0.11	4.03	0.17	3.96	0.20	4.38	0.25
3.99	0.04	3.61	0.14	3.36	0.23	3.27	0.12
1.11	0.10	1.01	0.17	1.27	0.14	1.27	0.13
nd		0.00		nd			
2.02	0.15	2.67	0.33	2.57	0.07	2.61	0.09
92.04		91.24		89.45		91.94	
0.85		1.12		1.08		1.10	
91.19		90.11		88.37		90.84	
27.55		31.45		31.25		30.07	
41.19		39.03		39.24		42.25	
26.66		24.43		23.28		22.00	
0.75		1.03		0.86		0.21	
3.84		4.06		5.38		5.48	
100.00		100.00		100.00		100.00	
1.29		1.33		1.44		1.44	

B2		B2		B2		B2		B2	
B2N-25		B2N-26		B2O-2/5		B2O-38/40		B2O-50	
2		10		8		12		6	
av	sd	av	sd	av*	av*	av	sd	av	sd
64.80	0.56	64.52	0.39	73.48	73.97	67.79	0.66	67.79	0.66
0.01	0.02	0.03	0.05	0.02	0.04	0.02	0.03	0.02	0.03
14.46	0.23	13.94	0.21	15.76	15.79	13.72	0.21	13.72	0.21
0.16	0.03	0.42	0.05	0.16	0.51	0.36	0.05	0.36	0.05
0.08	0.06	0.09	0.07	0.11	0.09	0.07	0.07	0.07	0.07
0.01	0.01	0.01	0.01	0.07	0.03	0.01	0.01	0.01	0.01
0.08	0.05	0.15	0.02	0.11	0.27	0.16	0.04	0.16	0.04
4.13	0.14	3.99	0.15	4.57	4.07	4.38	0.20	4.38	0.20
3.55	0.10	3.63	0.17	3.77	3.78	3.66	0.12	3.66	0.12
0.85	0.39	1.00	0.12	1.19	0.74	0.41	0.10	0.41	0.10
0.01	0.01	0.01	0.01	nd	nd	0.00	0.01	0.00	0.01
2.52	0.31	2.33	0.32	1.33	1.24	1.61	0.32	1.61	0.32
90.65		90.11		100.57	100.53	92.19		92.19	
1.06		0.98		0.56	0.52	0.68		0.68	
89.59		89.12		100.01	100.01	91.51		91.51	
31.02		31.43		32.96	36.01	31.15		31.15	
40.20		39.17		39.61	35.18	41.35		41.35	
24.10		24.87		22.82	22.85	24.07		24.07	
0.46		0.85		0.55	1.35	0.91		0.91	
4.22		3.68		4.05	4.61	2.52		2.52	
100.00		100.00		100.00	100.00	100.00		100.00	
1.34		1.30		1.34	1.40	1.20		1.20	

**Table 5.** Representative compositions of experimental quartz

sample #	B1		B1		B1		B2		B2	
charge #	B1N-17		B1N-21		B1N-22		B1N-23		B2N-3	
SiO <sub>2</sub>	94.59	94.12	98.67	98.49	99.78	98.52	99.15	99.89	99.25	
TiO <sub>2</sub>	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.03	
Al <sub>2</sub> O <sub>3</sub>	2.88	3.01	0.43	0.08	0.18	0.20	0.08	0.23	0.33	
FeO	0.00	0.00	0.01	0.07	0.00	0.00	0.00	0.01	0.13	
MnO	0.07	0.06	0.08	0.06	0.00	0.00	0.13	0.00	0.00	
MgO	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	
CaO	0.00	0.00	0.00	0.00	0.02	0.01	0.03	0.01	0.00	
Na <sub>2</sub> O	0.02	0.11	0.05	0.00	0.02	0.01	0.01	0.03	0.00	
K <sub>2</sub> O	0.00	0.09	0.01	0.01	0.02	0.00	0.00	0.00	0.06	
P <sub>2</sub> O <sub>5</sub>	0.09	0.14	0.03	0.00	0.00	0.00	0.05	0.09	0.05	
SnO <sub>2</sub>	nd	nd	nd	nd	nd	nd	nd	nd	nd	
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Total	97.66	97.53	99.31	98.71	100.01	98.74	99.44	100.25	99.87	
O=F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Total	97.66	97.53	99.31	98.71	100.01	98.74	99.44	100.25	99.87	

FeO = FeO total

nd: not determined

**Table 6.** Representative compositions of experimental feldspars

sample #	B1		B1		B1		B1		B1	
charge #	B1N-1		B1N-15		B1N-17		B1N-21		B1N-22	
feldspar	Pl	Pl*	Pl*	Pl	I	Af	Pl	Af	Pl	Af
SiO <sub>2</sub>	65.12	67.87	67.41	67.15	65.09	64.22	67.43	63.93	66.90	63.31
TiO <sub>2</sub>	0.02	nd	nd	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	19.75	20.31	20.13	19.47	19.34	19.78	20.46	19.06	20.43	19.09
FeO	0.00	nd	nd	0.00	0.12	0.00	0.00	0.00	0.07	0.19
MnO	0.22	nd	nd	0.00	0.00	0.07	0.06	0.00	0.00	0.00
MgO	0.00	nd	nd	0.00	0.00	0.00	0.00	0.00	0.01	0.00
CaO	0.57	0.18	0.15	0.12	0.35	0.03	0.51	0.01	0.53	0.00
Na <sub>2</sub> O	10.06	10.30	10.27	9.39	6.81	3.41	9.99	2.91	9.83	3.26
K <sub>2</sub> O	1.40	1.24	1.23	2.00	5.80	11.55	1.62	12.28	1.50	11.62
P <sub>2</sub> O <sub>5</sub>	1.36	nd	nd	1.24	1.25	0.96	0.66	1.02	1.15	0.82
F	0.00	nd	nd	0.00	0.25	0.01	0.04	0.10	0.09	0.00
Total	98.48	99.90	99.19	99.39	99.00	100.02	100.77	99.30	100.51	98.29
O=F	0.00	0.00	0.00	0.00	0.10	0.00	0.02	0.04	0.04	0.00
Total	98.48	99.90	99.19	99.39	98.89	100.02	100.75	99.26	100.47	98.29
Or	8.1	7.3	7.3	12.2	35.3	68.9	9.4	73.5	8.9	70.1
Ab	89.1	91.8	92.0	87.2	62.9	30.9	88.1	26.5	88.5	29.9
An	2.8	0.9	0.7	0.6	1.8	0.2	2.5	0.0	2.7	0.0

Pl: plagioclase; Af: K-feldspar, I: heterogeneous feldspar

\*data from Pichavant et al. (1987a)

\*\*data from Lahlahi (1997)

FeO = FeO total

nd: not determined

Ab, Or, An: molar proportions of albite, orthoclase, anorthite end-members

B1 B1N-23 PI	B1 B1O-1 PI**	B2 B2N-3 PI	PI*	Af	I	Af*	B2 B2N-18 PI	B2 B2N-19 PI	B2 B2N-20 PI	I
66.90	65.75	66.23	66.50	64.47	63.36	65.29	66.20	66.06	65.82	64.55
0.00	nd	0.00	nd	0.00	0.00	nd	0.00	0.03	0.00	0.01
20.43	20.04	20.72	20.48	19.05	19.49	19.48	20.31	20.57	20.94	20.15
0.07	nd	0.17	nd	0.28	0.00	nd	0.06	0.11	0.14	0.00
0.00	nd	0.13	nd	0.00	0.00	nd	0.00	0.15	0.00	0.03
0.01	nd	0.00	nd	0.01	0.03	nd	0.01	0.01	0.00	0.00
0.53	0.43	0.57	0.69	0.00	0.13	0.01	0.60	0.88	0.80	0.41
9.83	10.55	10.45	9.19	4.54	5.61	4.90	10.08	10.44	9.60	8.57
1.50	0.94	1.17	2.25	9.88	8.74	9.04	1.67	1.02	1.55	4.34
1.15	0.90	1.04	nd	1.01	0.67	nd	0.84	0.91	0.88	1.08
0.09	nd	0.00	nd	0.00	0.00	nd	0.00	0.00	0.05	0.00
100.51	98.61	100.48	99.11	99.23	98.03	98.72	99.77	100.18	99.78	99.14
0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
100.47	98.61	100.48	99.11	99.23	98.03	98.72	99.77	100.18	99.76	99.14
8.9	5.4	6.7	13.4	58.9	50.3	54.8	9.6	5.8	9.2	24.5
88.5	92.5	90.6	83.2	41.1	49.1	45.1	87.6	90.0	86.8	73.5
2.7	2.1	2.7	3.5	0.0	0.6	0.1	2.9	4.2	4.0	2.0

	B2 B2N-24		B2 B2O-2/5
Af	Pl	Af	I**
63.78	66.77	66.28	63.45
0.00	0.01	nd	nd
19.04	20.16	19.91	18.49
0.00	0.00	nd	nd
0.00	0.00	nd	nd
0.00	0.01	nd	nd
0.07	0.17	0.2	0.07
4.52	10.25	7.52	2.89
10.03	1.75	5.23	11.60
0.92	0.75	0.9	0.44
0.06	0.00	nd	nd
98.43	99.88	100.04	96.94
0.02	0.00	0.00	0.00
98.40	99.88	100.04	96.94
59.1	10.0	31.1	72.3
40.5	89.2	67.9	27.4
0.3	0.8	1.0	0.4

**Table 7.** Representative compositions of experimental micas

sample # charge #	B1 B1N-21	B1 B1N-22	B1 B1N-23	B2 B2N-3	B2 B2N-18	B2 B2N-19	B2 B2N-20	B2 B2N-24	B2 B2N-25	B2 B2O-2/5*	B2 B2O-50
SiO <sub>2</sub>	53.61	51.19	51.04	47.36	45.92	45.00	45.62	47.07	43.70	45.00	45.74
TiO <sub>2</sub>	nd	nd	nd	0.21	0.20	0.05	0.00	0.00	0.00	0.04	0.06
Al <sub>2</sub> O <sub>3</sub>	21.50	19.74	20.01	29.56	31.88	34.25	34.90	30.25	32.82	33.25	33.66
FeO	2.18	5.34	5.40	7.43	5.12	2.87	1.81	4.57	4.92	3.49	2.28
MnO	nd	nd	nd	0.17	0.17	0.07	0.22	0.44	0.00	0.04	0.00
MgO	0.16	1.17	2.26	0.60	0.47	0.27	0.11	0.10	0.16	0.29	0.26
CaO	nd	nd	nd	0.02	0.04	0.02	0.00	0.03	0.05	0.00	0.00
Li <sub>2</sub> O	6.75	6.04	6.80	1.31	1.75	2.62	3.00	2.50	1.79	0.61	1.13
Na <sub>2</sub> O	2.03	1.30	1.43	0.83	0.70	1.02	1.26	0.87	0.85	0.85	0.95
K <sub>2</sub> O	6.24	7.26	7.12	9.17	10.15	8.96	9.56	9.13	9.65	9.59	10.12
P <sub>2</sub> O <sub>5</sub>	0.78	0.78	0.23	0.17	0.10	0.39	0.30	0.23	0.06	0.00	0.24
SnO <sub>2</sub>	nd	nd	nd	nd	nd	0.17	0.11	0.10	0.14	nd	0.03
F	8.53	7.84	8.58	2.47	2.87	4.18	4.62	4.03	3.14	1.40	2.22
Total	101.79	100.66	102.87	99.31	99.37	99.89	101.51	99.33	97.27	94.56	96.69
O=F	3.59	3.30	3.61	1.04	1.21	1.76	1.95	1.70	1.32	0.59	0.94
Total	98.19	97.36	99.26	98.27	98.16	98.13	99.57	97.63	95.95	93.98	95.76
Mg-Li	-3.2555	-2.8253	-2.9487	-0.5697	-0.8262	-1.2878	-1.4836	-1.2776	-0.9247	-0.2760	-0.5502
Fe <sub>t</sub> +Mn+Ti-Al <sup>VI</sup>	-1.3250	-0.7700	-0.6168	-1.9034	-2.2680	-2.5341	-2.6212	-2.1248	-2.3983	-2.9863	-2.9897

Analyses by SEM for the B1 and by EMPA for the B2 charges

Li<sub>2</sub>O estimated from the F concentration (Tischendorf et al., 1997)

\*data from Lahlafi (1997)

FeO = FeO total

**Table 8.** Representative compositions of accessory phases

sample # charge #	B1			B2				
	B1N-21			B2N-25	B2N-19		B2N-25	
phase	topaz	topaz	amblygonite	amblygonite	apatite	hematite	hematite	hematite
SiO <sub>2</sub>	32.07	37.01	4.56	2.05	0.07	1.26	0.95	0.13
TiO <sub>2</sub>	0.03	0.00	0.19	0.11	0.08	0.14	0.33	2.42
Al <sub>2</sub> O <sub>3</sub>	57.60	50.47	35.34	35.39	0.01	2.71	2.22	0.79
FeO	0.04	0.04	0.11	0.03	0.32	83.14	85.19	83.53
MnO	0.15	0.07	0.14	0.00	3.63	0.13	0.23	0.00
MgO	0.04	0.01	0.02	0.04	0.03	0.00	0.04	0.02
CaO	0.02	0.05	0.00	0.03	51.84	0.00	0.05	0.02
Na <sub>2</sub> O	0.06	0.49	0.24	0.23	0.00	0.13	0.11	0.00
K <sub>2</sub> O	0.08	0.30	0.39	0.05	0.00	0.12	0.09	0.00
P <sub>2</sub> O <sub>5</sub>	0.98	0.78	49.57	51.69	38.15	0.11	0.00	0.00
SnO <sub>2</sub>	0.00	0.00	0.00	0.00	0.02	1.39	1.40	1.57
F	20.93	18.33	13.25	13.07	5.63	0.22	0.13	0.00
Total	112.00	107.55	103.81	102.70	99.76	89.35	90.74	88.48
O=F	8.81	7.72	5.58	5.50	2.37	0.09	0.06	0.00
Total	103.18	99.83	98.23	97.19	97.39	89.26	90.69	88.48
XF	0.99	0.89	0.95	0.94	1.55	Hm=0.997	0.993	0.950
XOH	0.01	0.11	0.05	0.06	-0.55	Ilm=0.003	0.007	0.050

Total Fe as FeO

XF = at. F/(F+OH) with F+OH = 2 for topaz and apatite and F+OH = 1 for amblygonite

XOH = 1-XF

Hm=hematite, Ilm=ilmenite

**Table 9.** Selected trace element concentrations

sample #	B2								B2	B2
charge #	B2N-26		B2N-25		B2N-18		B2N-24		B2N-25	B2N-25
phase	Glass		Glass		Glass		Glass		Quartz	Kd Qz/L
	av (ppm)	sd/av(%)	av (ppm)	sd/av(%)	av (ppm)	sd/av(%)	av (ppm)	sd/av(%)	ppm	
Li	2737.6	1.1	3021.1	3.8	3648.6	5.2	4310.3	10.8	81.3	0.027
Be	32.0	3.3	37.5	7.8	46.6	8.6	53.6	15.8	<0.8	
B	10.0	4.9	11.6	9.3	11.5	10.6	14.9	19.2	<1.9	
Na	26154.3	1.5	27739.9	1.7	27848.6	3.9	29257.3	6.9	<22.6	
Al	66231.2	2.0	70296.0	4.8	78139.7	7.4	74862.6	5.0	367.9	0.005
P	3057.8	2.9	3110.0	3.7	3547.7	4.7	3621.3	10.3	152.8	0.049
Ti	41.8	7.5	19.4	10.5	66.9	14.5	41.4	2.2	2.4	0.123
Mn	483.0	2.0	466.4	1.4	598.8	4.4	501.8	5.0	<3.9	
Zn	114.6	6.8	108.1	4.4	110.9	9.1	98.2	8.4	2.8	0.026
Rb	2024.2	0.6	2057.8	2.9	2420.9	4.5	2550.3	7.1	<1.0	
Sr	9.0	4.7	9.5	3.5	3.3	17.9	2.4	2.7	<0.1	
Zr	3.3	6.9	2.8	26.7	4.0	12.8	4.3	7.6	<0.0	
Nb	38.1	4.0	32.5	2.3	44.3	7.0	49.2	3.6	<0.0	
Sn	35.4	3.6	16.3	26.6	24.3	16.8	35.1	22.3	3.0	0.185
Cs	624.6	1.3	655.1	2.7	782.7	4.3	1027.6	10.1	2.0	0.003
Ba	0.8	14.9	0.7	32.7	0.4	60.7	1.3	70.7	0.2	
La	0.1	13.9	0.1	72.8	0.3	21.1	0.0	6.1	<0.0	
Ta	23.2	5.7	20.2	12.2	28.7	17.6	33.5	9.3	<0.0	
W	36.2	3.6	37.4	3.6	40.2	6.2	44.0	13.5	0.1	0.002
Pb	78.1	1.6	94.8	3.4	240.5	3.5	50.0	7.8	<0.3	
U	8.6	4.5	9.7	4.2	13.3	8.6	13.3	11.4	<0.0	
Nb/Ta	1.64		1.61		1.54		1.47			

sd : standard deviation ; av : average