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# **A felsic meta-igneous source for Li-F-rich peraluminous granites: insights from the Variscan Velay dome (French Massif Central) and implications for rare-metal magmatism**

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Julien Mercadier, Jean-Marc Montel

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# Contributions to Mineralogy and Petrology

## A felsic meta-igneous source for Li-F-rich peraluminous granites: insights from the Variscan Velay dome (French Massif Central) and implications for rare-metal magmatism

--Manuscript Draft--

<b>Manuscript Number:</b>	CTMP-D-23-00068R2	
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	CNRS/INSU (TelluS-2022)	Dr Pierre Bouilhol
<b>Abstract:</b>	<p>The Velay anatectic dome in the Variscan French Massif Central exposes a low pressure-high temperature metamorphic sequence, which represents an ideal natural laboratory for documenting the behavior of rare-metals and fluxing elements during crustal melting. We investigated the silicate and bulk-rock geochemistry of sub- to supra-solidus metapelites and orthogneisses, as well as related granites, and performed forward thermodynamically constrained geochemical modelling to quantify the respective effects of melting pressure, temperature, H<sub>2</sub>O activity, and protolith composition on the Li and F contents of granitic melts. We find that biotite compositions are good proxies of melt compositional evolutions during prograde melting. The crystallization of peritectic cordierite at low-pressure (&lt; 5 kbar) and "water-fluxed" melting both inhibit the Li enrichment of anatectic melts. Metapelite-derived melts consistently show modest Li-F contents, and a decoupling is observed as melts with the highest Li concentrations (~200-400 ppm) are produced below 750°C, whereas F-richest melts (~0.2-0.4 wt%) are produced above 750°C near the biotite-out isograd. Peraluminous orthogneiss anatexis can generate a melt that is concomitantly enriched</p>	

	<p>in both F (~0.3-1 wt%) and Li (~600-1350 ppm) at relatively low temperature (&lt; 750°C), which can evolve towards rare-metal granite compositions (~10,000 ppm Li; ~2 wt% F) after 80–90 wt% of fractional crystallization. Melting of felsic meta-igneous rocks followed by magmatic differentiation is thus a viable mechanism to form Li-F-rich rare-metal granites and pegmatites, providing a direct link between protracted crust recycling and rare-metal magmatism in late-orogenic settings.</p>
<b>Response to Reviewers:</b>	<p>Dear Prof. Müntener – Executive editor, Our answers to your comments are provided in a specific file attached to our submission (Rebuttal letter-R2) and we also provide a specific version of the revised manuscript with changes highlighted in red and yellow (Manuscript with marked changes). Best regards, Christophe Ballouard, Simon Couzinié, Pierre Bouilhol, Matthieu Harlaux, Julien Mercadier, Jean-Marc Montel</p>

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1 **Title:** A felsic meta-igneous source for Li-F-rich peraluminous granites: insights from the  
2 Variscan Velay dome (French Massif Central) and implications for rare-metal magmatism

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## 10 **Abstract**

11 The Velay anatectic dome in the Variscan French Massif Central exposes a low pressure-high  
12 temperature metamorphic sequence, which represents an ideal natural laboratory for  
13 documenting the behavior of rare-metals and fluxing elements during crustal melting. We  
14 investigated the silicate and bulk-rock geochemistry of sub- to supra-solidus metapelites and  
15 orthogneisses, as well as related granites, and performed forward thermodynamically  
16 constrained geochemical modelling to quantify the respective effects of melting pressure,  
17 temperature, H<sub>2</sub>O activity, and protolith composition on the Li and F contents of granitic melts.  
18 We find that biotite compositions are good proxies of melt compositional evolutions during  
19 prograde melting. The crystallization of peritectic cordierite at low-pressure (< 5 kbar) and  
20 “water-fluxed” melting both inhibit the Li enrichment of anatectic melts. Metapelite-derived  
21 melts consistently show modest Li–F contents, and a decoupling is observed as melts with the  
22 highest Li concentrations (~200-400 ppm) are produced below 750°C, whereas F-richest melts  
23 (~0.2-0.4 wt%) are produced above 750°C near the biotite-out isograd. Peraluminous



24 orthogneiss anatexis can generate a melt that is concomitantly enriched in both F (~0.3-1 wt%)  
25 and Li (~600-1350 ppm) at relatively low temperature (< 750°C), which can evolve towards  
26 rare-metal granite compositions (~10,000 ppm Li; ~2 wt% F) after 80–90 wt% of fractional  
27 crystallization. Melting of felsic meta-igneous rocks followed by magmatic differentiation is  
28 thus a viable mechanism to form Li-F-rich rare-metal granites and pegmatites, providing a  
29 direct link between protracted crust recycling and rare-metal magmatism in late-orogenic  
30 settings.

### 31 **Key words**

32 Rare-metal granites; Crustal melting; Mineral/mineral element partitioning; Trace element  
33 geochemistry; Lithium-fluorine; Variscan orogeny

### 34 **Introduction**

35 Major hard-rock deposits of Li and other rare-metals (Sn, Ta, Nb, Cs and Be) strategic for the  
36 high-technology industry and the energy transition are associated with low-volume (typically <  
37 1 km<sup>3</sup>) highly peraluminous leucogranite and pegmatite intrusions, which formed in relation  
38 with crustal magmatism in late-orogenic setting since the Mesoarchean (Linnen et al. 2012;  
39 Gourcerol et al. 2019). Peraluminous high phosphorous rare-metal granites and LCT (Li-Cs-  
40 Ta-rich) pegmatites (RMGP) typically host a disseminated mineralization of Li (e.g., lepidolite-  
41 zinnwaldite, spodumene, petalite, Li-phosphates), Nb-Ta (columbite- or pyrochlore-group  
42 minerals), Sn (cassiterite), Be (beryl), and F (topaz). They may exhibit incompatible and fluxing  
43 (F-Li) element concentrations up to three orders of magnitude higher than other types of  
44 peraluminous granites (Černý and Ercit 2005; Linnen and Cuney 2005; Romer and Pichavant  
45 2021).

46 Magmatic-hydrothermal processes including fluid-melt immiscibility and alkali  
47 metasomatism may lead to significant enrichments and redistributions of rare-metals at the end

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48 of the crystallization of granitic and pegmatitic intrusions (Harlaux et al. 2017; Kaeter et al.  
49 2018; Ballouard et al. 2020; Pfister et al. 2023). However, the occurrence of hypabyssal to  
50 volcanic analogues of RMGPs (Pichavant et al. 1987, 1988; Raimbault and Burnol 1998) as  
51 well as experimental studies (Linnen and Cuney 2005; Pichavant 2022) indicate that their rare-  
52 metal enrichment is dominantly a primary magmatic feature. The geological processes leading  
53 to the formation of such rare-metal and flux-rich granitic melts remain controversial. The  
54 RMGPs are generally interpreted as residual silicate melts produced by extreme fractionation  
55 ( $\geq \sim 99$  wt%) of less evolved peraluminous felsic magmas ("residual model": Černý et al. 2005;  
56 Hulsbosch et al. 2014; London 2018; Roda-Robles et al. 2018). The latter model is hampered  
57 by the common lack of spatial and/or temporal relations between RMGPs and their parental  
58 granitic sources, and alternative models involve low-degree of crustal partial melting and/or  
59 suitable pre-enriched protoliths ("anatectic model": Stewart 1978; Müller et al. 2017; Knoll et  
60 al. 2018, 2023; Konzett et al. 2018; Gourcerol et al. 2019).

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61 Those two models are not mutually exclusive and the formation of RMGPs could result  
62 from the local superimposition of geologic processes occurring at different spatial-temporal  
63 scales and in distinct tectonic settings (Romer and Pichavant 2021). Of peculiar importance is  
64 the weathering-related enrichment of rare-metals such as Sn, W or Li in siliciclastic sedimentary  
65 protoliths (i.e., sedimentary recycling) before tectonic stacking and partial melting in collisional  
66 orogens (Romer and Kroner 2015, 2016). Additionally, polycyclic crustal evolution involving  
67 re-melting of granites combined with magmatic differentiation could ultimately lead to the  
68 generation of fertile meta-igneous protoliths for RMGPs (Černý 1989), as proposed for U-rich  
69 leucogranites (Turpin et al. 1990; Ballouard et al. 2018).

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70 Micas represent major hosts for rare-metals and halogen elements in aluminous  
71 metamorphic rocks and mica-breakdown melting reactions are thus key to control rare-metal  
72 and fluxing element partitioning in granitic melts (Bea et al. 1994; Icenhower and London 1995;

73 [Michaud et al. 2021](#)). Lithium, Cs, Ta, and F are preferentially incorporated in biotite relative  
74 to muscovite, whereas the opposite is true for Be, Sn, and W ([Kunz et al. 2022](#)). As the  
75 dehydration-melting reaction of biotite occurs at higher temperature than that of muscovite  
76 ([Vielzeuf and Holloway 1988](#); [Patiño-Douce 1999](#); [Weinberg and Hasalová 2015](#)), the rare-  
77 metal budget of anatectic melts is controlled by: (i) the pressure-temperature conditions of  
78 partial melting and H<sub>2</sub>O activity; (ii) the bulk metal concentration of the protolith; and (iii) its  
79 mineralogical composition, notably the amount of micas and the relative proportions of  
80 muscovite vs. biotite, impacting melting degree and residue-melt element partitioning at given  
81 P-T conditions. The dynamic of melt extraction from migmatitic sources can also affect the  
82 rare-metal concentrations of anatectic magmas. For example, low-temperature melts can be  
83 either enriched or depleted in certain elements, and the preservation of their rare-metal  
84 signatures will depend on their capacity to be extracted before dilution by higher temperature  
85 melts having different compositions ([Wolf et al. 2018](#); [Romer and Pichavant 2021](#)).

86 Several studies argued that biotite-breakdown at T > 800°C is decisive for the generation of  
87 rare-metal-rich granitic melts ([Simons et al. 2016](#); [Wolf et al. 2018](#); [Michaud et al. 2021](#); [Kunz  
88 et al. 2022](#)). However, the partitioning of rare-metals and halogens during crustal melting  
89 remains poorly understood, as some elements might be liberated in the melt at low or high  
90 temperature, as for example documented for W and Sn, respectively ([Zhao et al. 2022](#)). Besides,  
91 the influence of peritectic garnet and cordierite produced upon biotite breakdown on controlling  
92 the melt rare-metal endowment has yet to be fully investigated. Indeed, discrepancies exist  
93 between experimental and natural partitioning data for cordierite, Li being suggested either as  
94 compatible ([Bea et al. 1994](#)) or incompatible ([Evensen and London 2003](#)) in this mineral.

95 Furthermore, the dehydration of the lower crust induced by granulite-facies metamorphism  
96 could liberate metamorphic fluids enriched in F and mica-hosted metals, thus enhancing fluxed  
97 melting of the overlying crust and the formation of RMGP melts ([Cuney and Barbey 2014](#)).

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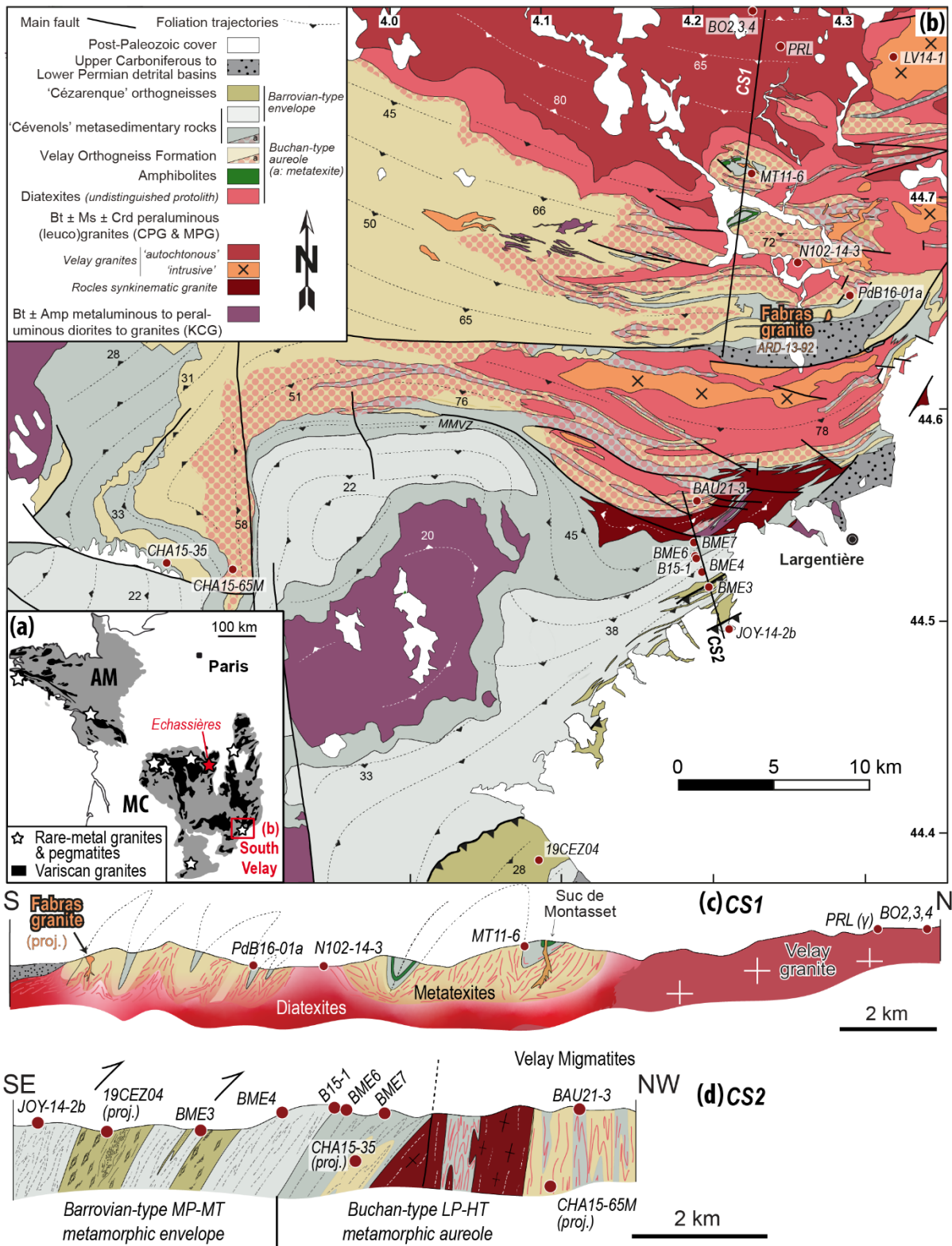
98 However, there is scarce evidence for the circulation of such enriched fluids in the deep  
99 Variscan crust, and the impact of flux-melting on the rare-metal enrichment of silicate melts  
100 remains ill-defined.

101 To constrain the rare-metal and fluxing element partitioning during crustal anatexis, we  
102 undertook a silicate and bulk-rock geochemical study of the rocks composing the Velay  
103 anatectic dome (Variscan French Massif Central). This well-studied area exposes a low  
104 pressure-high temperature (LP-HT) prograde metamorphic sequence ranging from greenschists  
105 to migmatites and granites, and represents an ideal natural laboratory to document the behavior  
106 of rare-metals and fluxing elements upon crustal partial melting. We primarily focused on the  
107 partitioning of Li and F, two fluxing elements with different geochemical properties that would  
108 allow an appraisal of the behavior of other elements with economic interest (e.g., Nb, Ta, Sn,  
109 W, Be, Cs). By coupling our results with thermodynamically-constrained geochemical  
110 modeling, we quantify the respective effects of melting pressure, temperature, H<sub>2</sub>O activity,  
111 and protolith composition on the Li and F contents of granitic melts. We conclude that  
112 peraluminous orthogneiss melting at relatively low temperature (< 750°C) and fluid-absent  
113 conditions plays a key role for the generation of Li-F-rich granites and probably peraluminous  
114 RMGPs in general.

### 115 **Geological setting**

116 The French Massif Central (FMC) exposes a fragment of the inner zone of the European  
117 Variscan belt resulting from the continental collision between Laurussia and Gondwana ([Faure  
118 et al. 2009](#); [Vanderhaeghe et al. 2020](#)). The Variscan evolution in this area features three main  
119 stages: (i) early subduction of narrow oceanic basins at 400–360 Ma ([Lotout et al. 2020](#)); (ii)  
120 crustal thickening and nappe stacking, and (iii) extensional tectonics coeval with a HT regime  
121 from ca. 320 to 300 Ma that led to the development of granite–migmatite domes such as the  
122 Velay complex in the eastern FMC ([Ledru et al. 2001](#); [Bouilhol et al. 2006](#); [Barbey et al. 2015](#))

123 (Fig. 1a). Late-orogenic extensional and transcurrent tectonics in the FMC was  
1  
2 124 contemporaneous with peraluminous rare-metal magmatism marked by the emplacement of  
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5 125 numerous stocks and dykes of Li-F-rich granites, rhyolites and pegmatites at ca. 310 Ma  
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7 126 (Marignac and Cuney 1999; Cuney et al. 2002; Gourcerol et al. 2019) (Fig. 1a). Such  
8  
9 127 occurrences include notably the Beauvoir lepidolite leucogranite, hosted by the zinnwaldite-  
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12 128 muscovite granite of Colettes within the Echassières district of the northern FMC, that  
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14 129 represents one of the best studied peraluminous rare-metal granites in the world (Cuney et al.  
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16 130 1992; Raimbault et al. 1995; Harlaux et al. 2017; Monnier et al. 2022) (Fig. 1a). A potential  
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19 131 ‘primitive’ or ‘less evolved’ analogue of Variscan RMGPs is represented by the Li-rich (> 300  
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22 132 ppm) two-mica and topaz-bearing Fabras leucogranite in the southern border of the Velay  
23  
24 133 anatectic dome (Bambier et al. 1985; Montel and Abdelghaffar 1993) (Fig. 1b). The Fabras  
25  
26 134 leucogranite is a small stock (600 x 300m), intruding metatexitic gneisses, that is located close  
27  
28  
29 135 to the border of a Upper Carboniferous to Lower Permian intramontane detrital basin (Montel  
30  
31 136 and Abdelghaffar 1993; Barbey et al. 2015). This leucogranite was possibly sourced from the  
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34 137 anatectic rocks occurring in the core of the Velay dome, which exposes deeper structural levels  
35  
36 138 of the Late Carboniferous Variscan crust (Montel et al. 1992; Ledru et al. 2001).



**Fig. 1** Geological features of the south Velay area within the French part of the European Variscan belt. **a** Distribution of Variscan granites as well as peraluminous rare-metal granites and pegmatites (Gourcerol et al. 2019) within the Armorican Massif (AM) and the Massif Central (MC). **b-c-d** Simplified geological map and cross sections of the southern part of the Velay dome showing the sample locations. Map redrawn from the regional

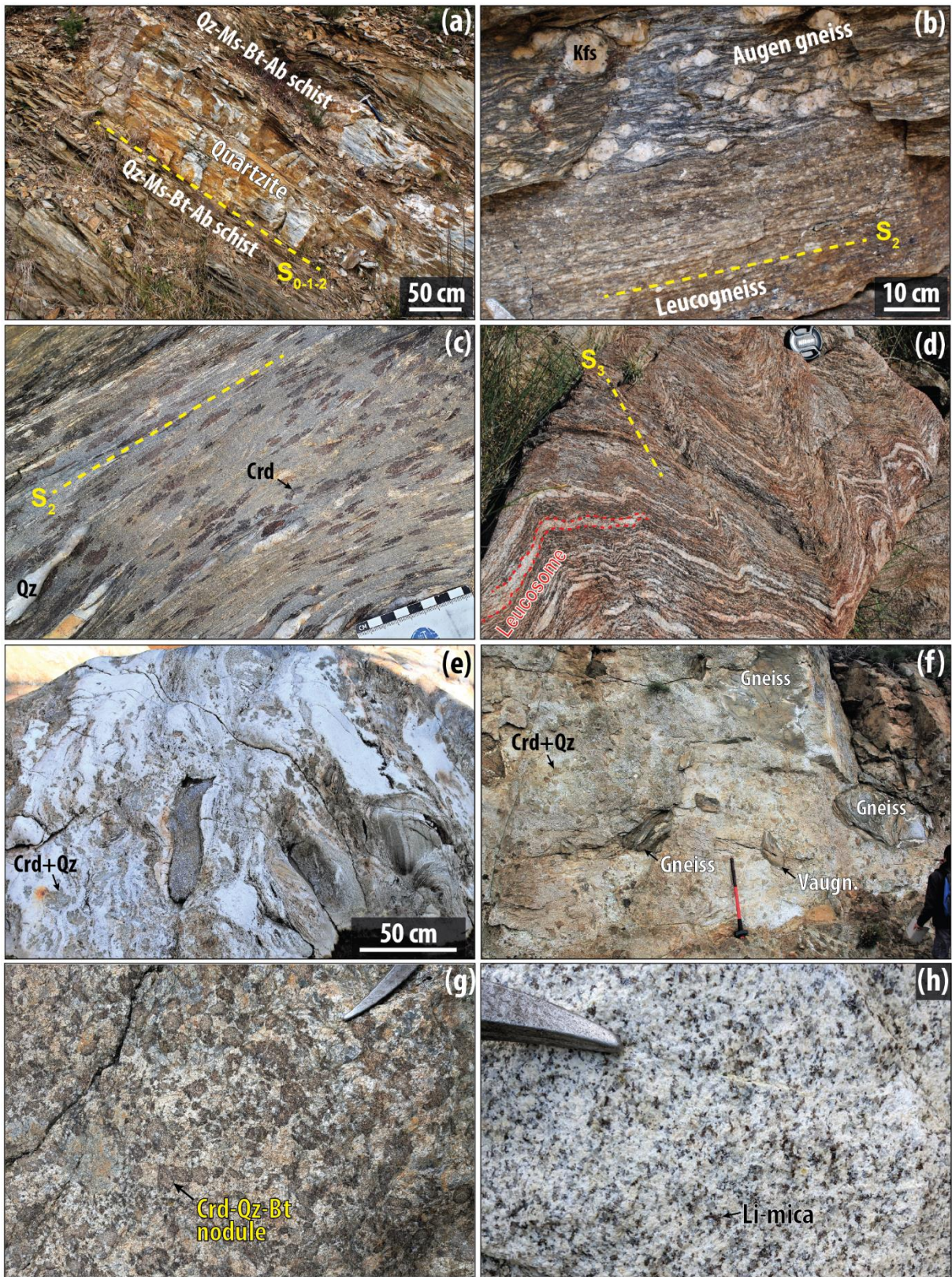


144 geological maps at the 1:50,000 scale. MMVZ: Mylonitic Metamorphic Vellave Zone (from Bouilhol et al. 2006).  
145 CPG: cordierite-bearing peraluminous granite. MPG: muscovite-bearing peraluminous granite. KCG: K-feldspar  
146 porphyritic calc-alkaline granite. Proj: projected.

147 Basement rocks within the Southern Velay region consist of: (i) detrital metasedimentary  
148 rocks (former pelites, greywackes, sandstones) with Ediacaran maximum depositional ages  
149 (590–555 Ma, Couzinié et al. 2019) (Fig. 2a); (ii) Cadomian augen gneisses and leucogneisses,  
150 representing former S-type (leuco)granites emplaced at ca. 540 Ma (Couzinié et al. 2017) (Fig.  
151 2b); (iii) Early Ordovician (ca. 490 Ma) felsic metavolcanic rocks (“Cézarenque”  
152 orthogneisses) interlayered with post-Ediacaran detrital metasedimentary sequences (Couzinié  
153 et al. 2022); and (iv) scarce amphibolites (Ledru et al. 2001). The felsic meta-igneous rocks are  
154 peraluminous, and even ferrosilicic for the Early Ordovician ones (Fig. 3a) (Couzinié et al.  
155 2022). Cadomian and Ordovician orthogneisses testify to early partial melting events in the  
156 continental crust before the onset of the Variscan orogeny.

157 Several tectonic-metamorphic events have shaped the terrains exposed in the southern part  
158 of the Velay dome. A first event produced a regional schistosity under Barrovian greenschist-  
159 to lower amphibolite-facies MP-MT conditions (Toteu and Macaudiere 1984; Arnaud et al.  
160 2004), presumably related to the main crustal thickening stage at ca. 360–340 Ma (Chelle-  
161 Michou et al. 2017). The Barrovian metamorphic rocks were reworked by a protracted  
162 metamorphic LP–HT event between 320 and 300 Ma (Ledru et al. 2001; Bouilhol et al. 2006;  
163 Barbey et al. 2015; Laurent et al. 2017) as evidenced by a typical Buchan-type prograde  
164 sequence, which is composed from south to north of biotite–cordierite–andalusite micaschists  
165 (Fig. 2c) progressing to biotite-sillimanite ± cordierite gneisses/migmatites (Fig. 2d,e)  
166 (Weisbrod 1968; Montel et al. 1992; Bouilhol et al. 2006).





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168 **Fig. 2** Field relations of the metamorphic and granitic rocks observed in and near the Velay anatectic dome: **a**

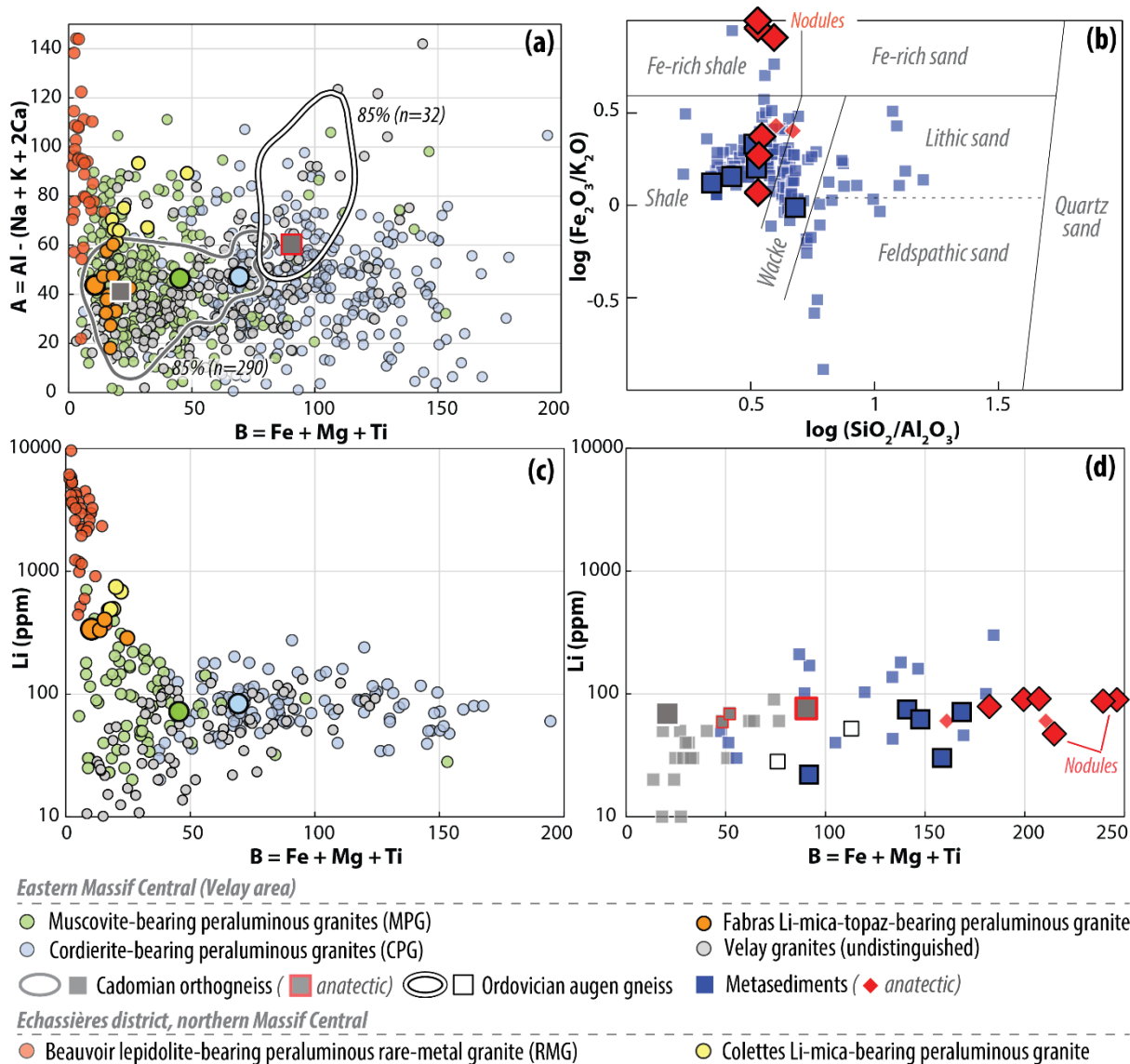
169 Quartz-muscovite-biotite-albite schists with interlayered quartzite (44.5018, 4.1222); **b** Concordant contact

170 between a ca. 540 Ma-old augen gneiss and leucogneiss (44.5630, 3.7602); **c** Cordierite-bearing micaschist



171 exhibiting regional foliation S2 and cordierite porphyroblasts (44.5369, 4.1969); **d** Metatexitic paragneiss showing  
172 S3 folds affecting the metamorphic foliation S2 (44.6254, 4.0157); **e** Diatexite hosting quartz-cordierite aggregates  
173 and various metamorphic enclaves (44.7122, 4.2703); **f-g** Heterogeneous Velay granite cluttered with various  
174 enclaves (**f**: 44.7475, 4.2371) including gneisses and cordierite-quartz-biotite restitic nodules (**g**: 44.79133;  
175 4.25904); **h** Li-mica-topaz-bearing Fabras leucogranite (4.286; 44.645). Abbreviations: Vaugn – vaugnerite; S -  
176 foliation. Longitude and latitude coordinates are reported as decimal degrees.

177 In the migmatitic zone, metatexites (Fig. 2d) are Bt-rich, Ms-free and locally Crd-bearing  
178 (mineral abbreviations after Whitney and Evans 2010) indicating fluid-present melting  
179 conditions at 650-720°C and 3-5 kbar (Montel et al. 1992; Barbey et al. 2015; Couzinié et al.  
180 2021). Towards the north, the progressive development of Crd and/or Grt-bearing diatexites  
181 (Fig. 2e) is attributed to a major crustal melting event under static conditions (Ledru et al. 2001)  
182 by massive Bt breakdown around 800°C at 3–4 kbar (Montel et al. 1992; Barbey et al. 2015).  
183 Diatexites grade more or less progressively to the heterogeneous “autochthonous”  
184 peraluminous Velay granite that is Bt- and/or Crd-bearing, and contains numerous and various  
185 enclaves (Fig. 2f,g) (Williamson et al. 1997; Ledru et al. 2001; Villaros et al. 2018). In addition  
186 to the main Velay granite, other smaller granitic intrusions were emplaced at different crustal  
187 levels throughout the tectonic-metamorphic evolution of the dome, crosscutting the pre-existing  
188 metamorphic rocks, the migmatites, and locally the Velay granite. They belong to two main  
189 groups: (i) older Kfs porphyritic, locally amphibole-bearing, metaluminous to slightly  
190 peraluminous calc-alkaline granitoids (KCG of Barbarin 1999) associated to mantle-derived  
191 potassic diorites (“vaugnerites”); and (ii) late Crd- or Ms-bearing peraluminous granites and  
192 porphyries (CPG and MPG) (Fig. 3a) (Montel and Abdelghaffar 1993; Barbey et al. 2015;  
193 Laurent et al. 2017; Moyen et al. 2017; Villaros et al. 2018). The Fabras topaz and Li-mica-  
194 bearing leucogranite belongs to this second group (Figs. 2h and 3a).



**Fig. 3** Whole-rock compositions of peraluminous granites, metasedimentary rocks and orthogneisses from the Velay area and comparison with literature data for granites from the French Massif Central (see [Online Resource 2](#) as well as [Moyen et al. 2017](#), [Couzinié et al. 2017, 2022](#), [Raimbault et al. 1995](#) and [Harlaux 2016](#) for the full dataset). **a** Peraluminous index ( $A = Al - [Na + K + 2Ca]$ ) versus differentiation index ( $B = Fe + Mg + Ti$ ) diagram (Debon and Le Fort 1988) for orthogneisses (shown as fields representing 85% of the samples) and granites. **b** Classification diagram of Herron (1988) for metasedimentary rock samples. **c** and **d** Li concentrations versus B parameter diagram for granites in **c** as well as for potential source rocks including orthogneisses and metasedimentary rocks in **d**. Symbols with larger sizes represent the samples investigated in this study for silicate mineral compositions. Restitic nodules compositions were calculated based on point counting and mineral compositions.

## 206 **Methods**

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3 207 Whole-rock geochemical analyses were performed at the SARM (CRPG-CNRS, Vandoeuvre-  
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5 208 lès-Nancy, France). Mineral backscattered electron (BSE) imaging and micro-XRF chemical  
6  
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8 209 mapping as well as *in situ* geochemical analyses were performed on thick and thin sections at  
9  
10 210 the GeoRessources laboratory of the University of Lorraine (Nancy, France). Mineral  
11  
12 211 compositions were determined using electron microprobe analyses (EMPA) and laser ablation-  
13  
14 212 inductively coupled plasma-mass spectrometry (LA-ICP-MS). Additional analytical details,  
15  
16 213 along with data, are provided in [Online Resources 1 and 2](#).

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21 214 Phase equilibrium modeling was undertaken using the software Perple\_X (version 6.9.1,  
22  
23 215 [Connolly 2009](#)) in the system (Na<sub>2</sub>O–CaO–)K<sub>2</sub>O–FeO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O–TiO<sub>2</sub>, i.e.,  
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25 216 (NC)KFMASHT. We selected the thermodynamic data file hp62 and the a–x models of [White](#)  
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27 217 [et al. \(2014\)](#) for garnet, orthopyroxene, cordierite, ilmenite, biotite, staurolite, white mica and  
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29 218 melt, and [Fuhrman and Lindsley \(1988\)](#) for feldspar. Bulk compositions used in the modeling  
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31 219 are provided in [Online resource 3 \(Table S1\)](#).  
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## 36 220 **Sample petrology and P–T conditions of equilibration**

### 39 221 *Subsolidus metasedimentary rocks*

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42 222 We investigated a total of nineteen rock samples collected across the study area ([Fig. 1b](#))  
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44 223 for which GPS coordinates and hand sample photographs are provided in [Online resources 2](#)  
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46 224 [and 3 \(Fig. S1\)](#), respectively. Five samples correspond to pre-Silurian subsolidus  
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48 225 metasedimentary rocks from the metamorphic envelope of the Velay dome (BME4; BME6;  
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50 226 BME7; JOY14-2b; B15-1) ([Fig. 2a,c](#)). Those rocks have mineral assemblages of Qz–Ms ± Bt ±  
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52 227 Grt ± Chl ± Ab with Crd–And poikiloblasts developed in the deepest parts of the section (BME6  
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54 228 and BME7). Most samples show typical shale/pelite compositions, except for sample B15-1  
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56 229 that is akin to graywackes ([Fig. 3b](#)). Subsolidus metasedimentary rocks have bulk Li and F  
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230 concentrations of 20-75 ppm and 0.07-0.09 wt%, respectively (Fig. 3d). Available P-T  
231 estimates point to equilibration temperatures in the range 500–550°C for pressures of 3-5 kbar  
232 (Bouilhol et al. 2006 and references therein). Consistently, Ti-in-biotite geothermometry (using  
233 the calibrations of Henry et al. 2005 and Wu and Chen 2015) applied to our samples yields  
234 temperatures between 500 and 650°C (Online Resource 2).

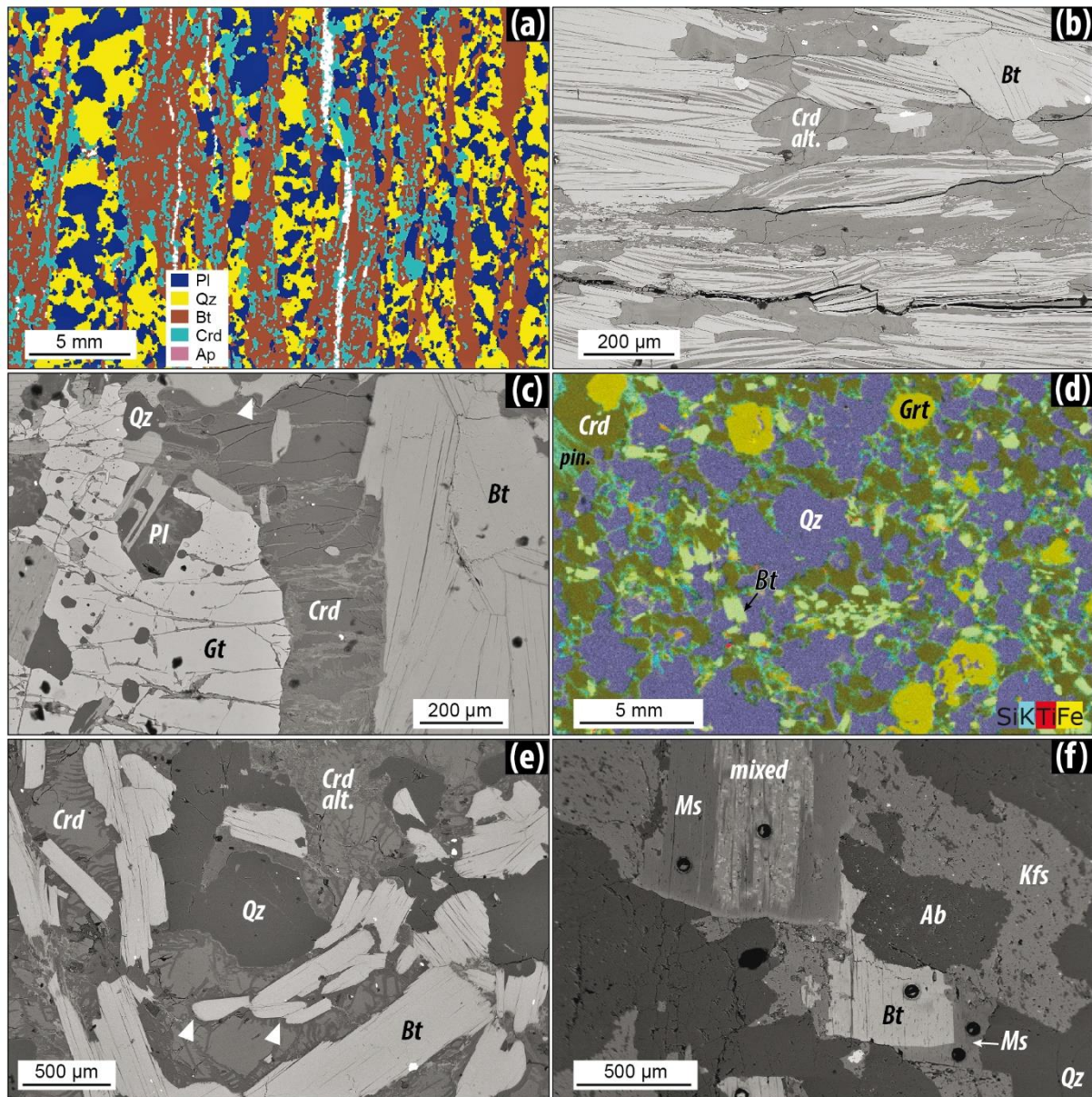
### 235 *Suprasolidus metasedimentary rocks*

236 Eight suprasolidus metasedimentary rock samples were collected from the migmatitic domain  
237 of the Velay dome: three metatexitic paragneisses (MT11-6; BAU21-3a; BAU21-3b), a fine-  
238 grained gneiss resister (PdB16-01a), a diatexite (N102-14-3), and three, about 3 cm large,  
239 restitic nodules (B02; B03; B04) collected from a very heterogeneous portion of the Velay  
240 granite scattered with up to ~2 m large migmatitic enclaves (Fig. 2d,e,f,g). Anatectic  
241 metasedimentary rocks, except restitic nodules, show a shale composition similar to most  
242 subsolidus metasedimentary rock samples (Fig. 3b) with comparable whole-rock Li contents  
243 (60-120 ppm) but higher F (0.15-0.18 wt%) concentrations (Fig. 3d). Based on point counting  
244 and mineral composition analyses, the restitic nodules (enriched in Fe) have similar bulk Li  
245 concentrations (50-90 ppm) and relatively low bulk F contents (0.04-0.05 wt%) (Fig. 3d).

246 The metatexitic paragneisses contain tonalitic leucosomes along with Bt-Crd ± Sil ± Grt ±  
247 Ap ± Fe-Ti oxides melanosomes (Fig. 4a), and K-feldspar is additionally present in BAU21-3a  
248 melanosome. Metatexitic paragneisses show conspicuous biotite-breakdown textures (Fig 4b,c)  
249 which are lacking in the Bt-Pl-Qz gneiss PdB16-01a. Muscovite is present in the subsolidus  
250 metasedimentary rock samples but absent in the metatexitic, suggesting it was fully consumed  
251 at lower temperature ( $\leq \sim 675^\circ\text{C}$ ,  $\leq 5.5$  kbar) during subsolidus or suprasolidus prograde  
252 reactions ( $\text{Ms} + \text{Qz} \pm \text{Pl} = \text{Sil} \pm \text{melt} \pm \text{H}_2\text{O} \pm \text{Kfs}$ ), depending on pressure and protolith  
253 compositions (Online resource 3, Fig. S2). The extensive preservation of biotite and sillimanite  
254 together with the general lack of K-feldspar as a reaction product suggest that melting was fluid-



255 assisted (Weber and Barbey 1986; Montel et al. 1992) and that cordierite formed through the  
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 256 reaction  $Bt + Sil + Qz + H_2O = Crd \pm Grt + melt$  (Yardley and Barber 1991). Sample N102-14-  
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 257 3 is a diatexite with a melanosome comprising biotite with corroded edges, quartz and poikilitic  
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 258 cordierite as well as accessory apatite and Fe-Ti oxides. The leucosome is primarily composed  
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 259 of quartz, plagioclase, subordinate K-feldspar, biotite and apatite.



260  
 261 **Fig. 4** Petrological features of the studied samples from the Velay anatectic dome. **a** Mineral distribution map of  
 262 metatextitic paragneiss sample MT11-6, determined by micro-XRF imaging, showing biotite-bearing tonalitic  
 263 leucosome and intricate biotite-cordierite association in the melanosome; **b** Cordierite (altered to pinite) replacing

264 biotite in the melanosome of metatexite MT11-6; **c** Suprasolidus fabric of metatexite BAU21-3b with cordierite  
1 rimming garnet in contact with corroded biotite (triangle tip) and lobate quartz; **d** Micro-XRF map of restitic  
2 265  
3 nodule sample BO3 showing the intricate cordierite-quartz-biotite association; **e** Suprasolidus fabric in nodule  
4 266  
5 sample BO2 with corroded biotite (triangle tips) replaced by cordierite and lobate quartz; **f** Li-rich biotite (Li-  
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7 siderophyllite) and Fe-rich muscovite in the Fabras topaz-bearing leucogranite ARD13-92. Mixed zone  
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9 corresponds to fine-grained assemblage of co-crystallized dioctahedral and trioctahedral micas.  
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12 The restitic metasedimentary nodules are embedded in a granitic matrix with sharp contacts  
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14 ([Fig. 2g](#)). They are equivalent to sample B8-A described by [Montel et al. \(1992\)](#). The nodules  
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16 are primarily composed of roughly 50 vol% Crd, 35 vol% Qz, 10 vol% Bt and 5 vol% Grt ([Fig.](#)  
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18 [4d](#)), along with accessory ilmenite. Garnet is lacking in sample BO4 which contains sillimanite  
19 273  
20 included in biotite. Lobate shapes of Crd-Bt and Crd-Qz contacts, the presence of films of Crd  
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22 wetting quartz junctions ([Fig. 4d,e](#)) collectively support equilibrium with a melt. According to  
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24 [Barbey et al. \(1999\)](#), the Crd-Qz assemblages were produced upon peritectic reactions of the  
25 276  
26 form  $Bt + \text{melt} = \text{Crd} + \text{melt}$  in a magma experiencing decompression. The reaction involved  
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28 feldspar and sillimanite consumption, when present, and the formation of excess quartz. The  
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30 nodules are thus interpreted as clusters of restitic minerals (Bt, Grt and Sil) having reacted with  
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32 their host liquid upon ascent ([Montel et al. 1992](#)).  
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40 281 The results of conventional thermobarometry and pseudosection calculations ([Online](#)  
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42 [Resource 3, Figs. S2 and S3](#)) performed on the investigated anatectic samples are summarized  
43 282  
44 in [Table 1](#) and are consistent with those obtained by [Montel et al. \(1992\)](#). Migmatites and restitic  
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46 nodules were equilibrated at mid-crustal pressures of 4–5 kbar and temperatures of 700–830°C  
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48 with a progressive increase of peak temperatures from metatexites through diatexites to restitic  
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50 nodules as also recorded by Ti-in-biotite thermometry ([Table 1](#)).  
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289 **Table 1** Summary of P–T estimates obtained for the migmatites investigated in this study.

Sample	Ti-in-Bt (H05)	Ti-in-Bt ; $4.5 \pm 1.0$ kbar (W15)	Na-in-Crd (T18); GASP (H01)	Grt-Bt (H00); GASP (H01)	Grt-Crd (B93); GASP (H01)	Pseudosection analysis
PdB16-01a	699±22°C; n=16	647±53°C; n=16	-	-	-	-
MT11-6	704±29°C; n=37	669±58°C; n=37	-	-	-	700-770°C < 4.6 kbar
BAU21-3a	695±25°C; n=40	647±51°C; n=40	-	-	-	-
BAU21-3b	711±50°C; n=27	689±61°C; N=27	-	736°C 5.4 kbar	-	700-780°C > 5 kbar
N102-14-3	717±7°C; n=15	711±22°C; n=15	-	-	-	690-780°C < 4.5 kbar
BO2	732±23°C; n=30	747±66°C; n=30	760±20°C; n=12 > 4.4 kbar	739°C > 4.2 kbar	753°C > 4.3	790-835°C 4-5 kbar
BO3	736±20°C; n=18	744±42°C; n=18	761±19; n=17 > 4.7 kbar	723°C > 4 kbar	755°C > 4.5 kbar	790-835°C 4-5 kbar
BO4	733±26°C; n=19	727±51°C; n=18	758±28°C; n=15	-	-	750-820°C 4-5 kbar

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291 H05 and W15 refer to the Ti-in-biotite thermometers of Henry et al. (2005) and Wu and Chen (2015), respectively. The italic values represent

292 pressures calculated via the GASP barometer (Holdaway 2001) at temperatures obtained by Na-in-cordierite (Tropper et al. 2018), Grt-Bt

293 (Holdaway 2000) and Grt-Crd (Bhattacharya 1993) thermometers. Uncertainties are two standard deviations. GASP barometry along with Grt-

294 Bt and Grt-Crd thermometry relied on average mineral compositions calculated for each sample, as all minerals were chemically unzoned.

295 When sillimanite is absent from the mineral assemblage, the calculated value represents a minimal pressure.

## 296 ***Orthogneisses***

297 Three samples of peraluminous Qz-Pl-Kfs-Ms-Bt meta-igneous rocks collected within the

298 Velay dome (CHA15-65M) and its immediate metamorphic envelope (CHA15-35 and

299 19CEZ04) were investigated. These samples consist of two Cadomian orthogneisses, including

300 one augen gneiss (CHA15-65M;  $549 \pm 5$  Ma, Couzinié et al. 2021) and one equigranular

301 leucocratic gneiss (leucogneiss CHA15-35, Fig. 2b;  $544 \pm 5$  Ma, Couzinié et al. 2021), as well

302 as one Ordovician augen gneiss (19CEZ04, ca. 490-480 Ma, Couzinié et al. 2022). The

303 leucogneiss sample shows a particularly evolved geochemical signature with a marked

304 depletion in Fe, Mg and Ti (Fig. 3a) and high F concentrations of 0.15 wt% compared to other  
305 orthogneisses (F ~0.08 wt%). The orthogneisses have bulk Li contents of 30-80 ppm similar to  
306 those of metasedimentary rocks (Fig. 3d).

307 The Cadomian augen gneiss is metatextitic and consists of Bt-Ms melanosomes interlayered  
308 with quartzofeldspathic leucosomes. According to Couzinié et al. (2021), melting would have  
309 proceeded via the eutectic melting reaction again under water-fluxed conditions, with  
310 preservation of muscovite due to the low melting temperature of 660-730 °C at 3-7 kbar. The  
311 two other orthogneiss samples do not show mineralogical and textural evidence of partial  
312 melting.

### 313 *Variscan granites*

314 Three samples representative of the peraluminous Variscan igneous suites were collected: PRL  
315 is a typical biotite-cordierite Velay granite (CPG) with Crd-Qz nodular aggregates; LV14-1 is  
316 a biotite-muscovite leucogranite (MPG) from the Quatre-Vios massif (“*microgranite de*  
317 *Laviolle*” in Montel and Abdelghaffar 1993; Thierry et al. 2014); and ARD13-92 is a Li-rich  
318 two-mica-topaz granite from the Fabras stock (Fig. 2h). The Fabras granite is characterized by  
319 low concentrations in Fe, Mg and Ti along with high Li (280-400 ppm) and F (0.4-0.5 wt%)  
320 contents compared to most granites from the eastern FMC (avg. Li  $\leq$  200 ppm; F  $\leq$  0.2 wt%),  
321 including the Velay (PRL) and Quatre-Vios granite samples (Fig. 3a,c). The composition of the  
322 Fabras granite is roughly similar to that of the Li-mica-bearing Colettes granite, hosting the  
323 Beauvoir peraluminous rare-metal leucogranite in the Echassières district, northern FMC (Figs.  
324 1a and 3a,c). The Fabras and Quatre-Vios granites contain di- and tri-octahedral micas showing  
325 intergrowth textures suggesting co-crystallization (Fig. 4f).

### 326 **Compositions of micas, cordierite and garnet**

### 327 *Major element composition and classification*



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328 Micas (muscovite and biotite), garnet and cordierite from ortho- and para-derived metamorphic  
329 rocks along with granites from the Velay dome were analyzed to determine their major and  
330 trace element compositions, with a focus on F and Li contents. Cordierite has similar Mg#  
331  $[Mg/(Mg+Fe) - \text{apfu}]$  values between 0.5 and 0.6 in suprasolidus metasedimentary rocks and  
332 the cordierite-bearing granite. Cordierite is completely altered to pinitite (i.e., a fine-grained  
333 assemblage of chlorite and white micas) in subsolidus metasedimentary rocks. Garnet from  
334 metasedimentary rocks is chemically homogeneous and has a dominant almandine component  
335 ( $0.72 \leq X_{\text{Alm}} \leq 0.78$ ).

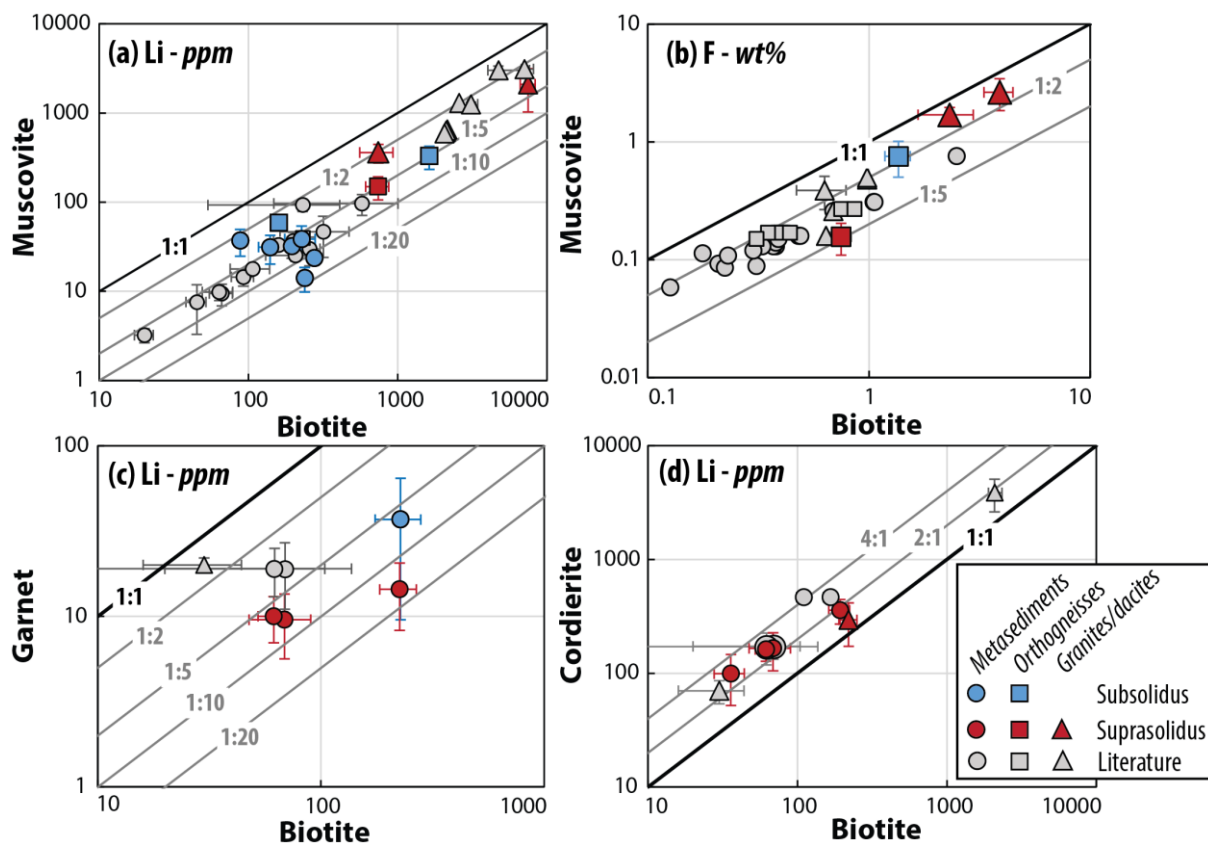
336 Tri- and di-octahedral micas from most samples globally show Fe-biotite ( $0.30 \leq \text{Mg\#}$   
337  $\leq 0.45$ ) and muscovite compositions (see classification diagrams in [Online Resource 3, Fig.](#)  
338 [S4](#)). Exceptions comprise the Fabras leucogranite which contains Fe-rich muscovite along with  
339 Li-rich trioctahedral micas ( $0.10 \leq \text{Mg\#} \leq 0.20$ ), having intermediate compositions between Fe-  
340 biotite and zinnwaldite (Li-siderophyllite according to [Tischendorf et al. 1997](#)). Moreover,  
341 biotite in the Cadomian leucogneiss is characterized by low Mg# of ~0.1 (siderophyllite of  
342 [Tischendorf et al. 1997](#)) whereas biotite from the Ordovician orthogneiss is slightly more  
343 magnesian compared to other samples (Mg# ~0.50). Dioctahedral micas in B15-1  
344 metagraywacke are more heterogeneous in terms of composition than that from metapelites and  
345 reach higher Fe concentrations.

#### 346 ***Mineral/mineral element partitioning***

347 Partitioning data of Li and F between coexisting micas, garnet and cordierite for rocks from the  
348 Velay dome are shown in [Figure 5](#) and [Table 2](#). No significant compositional differences are  
349 observed within migmatites between micas from melanosomes and that from respective  
350 leucosomes, indicating that leucosome micas could be restitic. This is true for Li and F, and  
351 also for other elements, thus leucosomes and melanosomes are not distinguished in the  
352 following. In all rock types, biotite is systematically enriched in Li and F compared to

353 muscovite, by factors of ~2 to 10 and ~2 to 5, respectively (Fig. 5a,b). A similar behavior is  
 354 observed for Cs, Nb and Ta, whereas the opposite is true for Be, Sn and W that preferentially  
 355 partition in muscovite relatively to biotite (Online Resource 3, Fig. S5, Table S2).

356 Biotite has 6 to 15 times more Li than garnet in metasedimentary rocks (Fig. 5c). In  
 357 contrast, the Li concentration of cordierite is about 2 to 3 times higher than that of coexisting  
 358 biotite (Fig. 5d). We note that Be is strongly enriched in cordierite compared to biotite (factor  
 359 of ~100 to 400) and Cs shows biotite over cordierite content ratios ( $Kd^{Bt/Crd}$ ) between ~1 and 5  
 360 (Online Resource 3, Fig. S6, Table S2). Cordierite and garnet do not incorporate significant  
 361 amounts of other rare-metals and halogens. Mineral/mineral element partitioning data obtained  
 362 for rocks from the Velay dome are consistent with those calculated using published data for  
 363 igneous and metamorphic rocks from other areas (Fig. 5).



364  
 365 **Fig. 5** Mean Li and F concentrations of coexisting biotite, muscovite **a-b**, garnet **c** and cordierite **d** for para- and  
 366 ortho-derived metamorphic rocks, migmatites and granites from the Velay dome. Literature data for granites,

367 dacites, gneisses and metasedimentary rocks (Bea et al. 1994; Neves 1997; Acosta-Vigil et al. 2010; Simons et al.  
 1 368 2017; Zhou et al. 2021; Kunz et al. 2022; Sallet et al. 2023) are shown for comparison. Error bars show two  
 2 369 standard deviations.

370 The affinity of Be for cordierite results from its structure, since cordierite is isostructural  
 371 with beryl. Beryllium is incorporated in tetrahedra, replacing Al through the coupled exchange  
 372  $Be^{2+} + Si^{4+} \rightarrow 2 Al^{3+}$ , or alternatively by adding a monovalent cation in the central channel,  
 373 such as  $K^+$  or  $Na^+$  (Franz and Morteani 2002; Bertoldi et al. 2004). Lithium is accommodated  
 374 in the octahedral site, replacing Fe and Mg, again with some charge compensation in other sites  
 375 (Gordillo et al. 1985; Bertoldi et al. 2004).

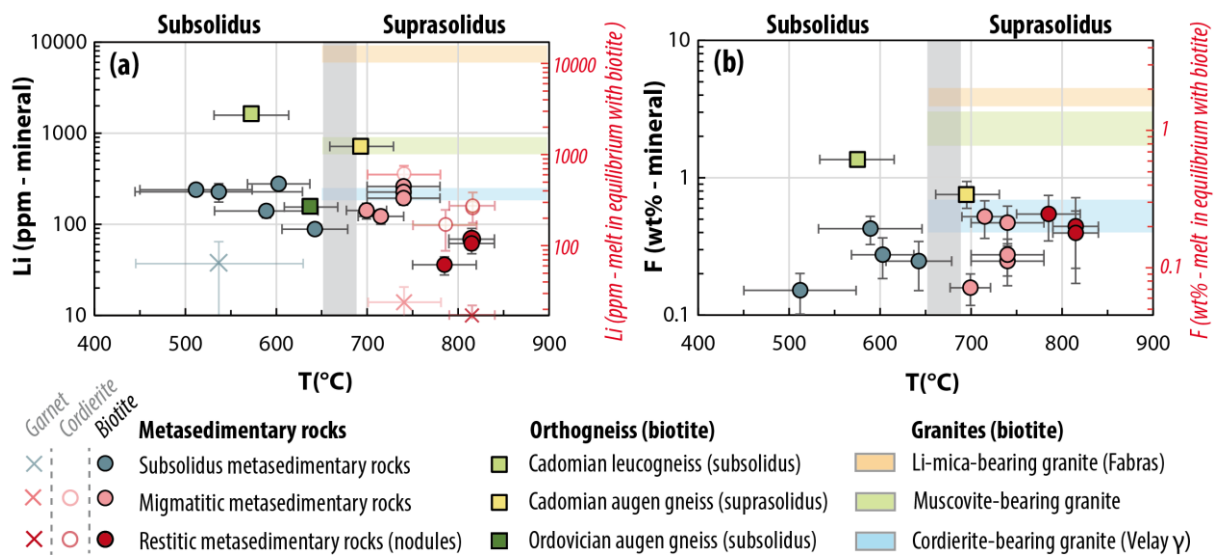
376 **Table 2** Mineral-mineral partitioning data of Li and F for Velay samples.

Sample	Li						F					
	$Kd^{Bt/Ms}$	$2\sigma$ (+)	$2\sigma$ (-)	$Kd^{Crd/Bt}$	$2\sigma$ (+)	$2\sigma$ (-)	$Kd^{Bt/Grt}$	$2\sigma$ (+)	$2\sigma$ (-)	$Kd^{Bt/Ms}$	$2\sigma$ (+)	$2\sigma$ (-)
<i>Subsolidus metasedimentary rock</i>												
BME4	4.5	3.6	1.7	-	-	-	-	-	-	-	-	-
JOY14-2b	5.9	6.2	2.7	-	-	-	6.2	23.2	3.4	-	-	-
B15-1	2.4	1.5	0.8	-	-	-	-	-	-	-	-	-
BME6	16.9	9.3	5.0	-	-	-	-	-	-	-	-	-
BME7	11.7	3.7	2.6	-	-	-	-	-	-	-	-	-
<i>Subsolidus Ordovician orthogneiss</i>												
19CEZ04	2.7	0.9	0.6	-	-	-	-	-	-	-	-	-
<i>Subsolidus Cadomian orthogneiss</i>												
CHA15-35	5.0	2.8	1.5	-	-	-	-	-	-	1.8	1.3	0.6
<i>Suprasolidus metasedimentary rock</i>												
BAU21-3b	-	-	-	-	-	-	15.7	16.7	6.7	-	-	-
N102-14-3	-	-	-	1.8	0.9	0.6	-	-	-	-	-	-
B02	-	-	-	2.4	2.4	1.2	7.2	8.8	3.7	-	-	-
B04	-	-	-	2.8	2.5	1.6	-	-	-	-	-	-
B03	-	-	-	2.6	1.1	0.8	6.1	4.0	2.1	-	-	-
<i>Suprasolidus Cadomian orthogneiss</i>												
CHA15-65M	5.0	3.3	1.8	-	-	-	-	-	-	4.8	2.8	1.5
<i>Cordierite-bearing granite</i>												
PRL	-	-	-	1.3	0.9	0.6	-	-	-	-	-	-
<i>Muscovite-bearing granite</i>												
LV14-01	2.1	1.3	0.8	-	-	-	-	-	-	1.4	0.7	0.5
<i>Li-mica-bearing granite</i>												
ARD13-92a	3.6	4.5	1.5	-	-	-	-	-	-	1.5	1.0	0.5

### 377 ***Lithium and halogen compositional evolutions as a function of temperature and protolith***

378 We here document the behavior of Li and F during prograde regional metamorphism and crustal  
 379 melting using minerals that are stable both at sub- and supra-solidus conditions namely biotite,  
 380 cordierite and garnet (Fig. 6). The composition of muscovite is not described in the following  
 381 as it does not occur in the investigated anatectic metamorphic rock samples, except for one

382 augen gneiss. The Li concentrations of biotite from subsolidus metasedimentary rocks are  
 383 similar to those from migmatitic paragneisses ranging from ~90 to 280 ppm (Fig. 6a). However,  
 384 a significant drop of biotite Li concentrations down to 35-70 ppm is observed above ~750°C  
 385 for high-temperature restitic nodules. The Li content of cordierite mimics that of biotite and  
 386 decreases with temperature from migmatites (~360 ppm) to restitic nodules (~100-160 ppm).  
 387 Garnet has a higher Li content (~40 ppm) in subsolidus metasedimentary rocks compared to  
 388 suprasolidus equivalents (~10-15 ppm). Fluorine shows a distinct behavior than Li as the  
 389 concentration in biotite, ranging from 0.15 to 0.55 wt%, is roughly constant or tends to increase  
 390 with temperature (Fig. 6b). Beryllium (~0.01-0.70 ppm), W (~2-9 ppm) and Cs (~20-50 ppm)  
 391 show a behavior comparable to Li as their concentrations decrease above ~750°C in biotite  
 392 from anatectic metasedimentary rocks (Online Resource 3, Fig. S7). However, Sn (~9-20 ppm),  
 393 Nb (~30-120 ppm) and Ta (~2-8 ppm) behave like F as their concentrations in biotite slightly  
 394 increase or remain constant with increasing temperature.



396 **Fig. 6** Evolution of the average **a** Li and **b** F compositions of biotite, cordierite and garnet, with errors at 2 sigma  
 397 deviation (SD), as a function of peak temperatures for para- and ortho-derived metamorphic rocks from the Velay  
 398 dome. The range of Li-F contents in igneous biotite from Variscan granites is shown for comparison (colored  
 399 fields). Temperatures were calculated based on the Ti-in-biotite geothermometer (Henry et al. 2005) for subsolidus  
 400 metamorphic rocks and errors bars show 2SD. Mean temperatures and associated uncertainties for suprasolidus

401 metamorphic rocks were estimated based on pseudosection analyses (Table 1), except for one sample (PdB16-01),  
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2 402 for which temperature was determined by Ti-in-biotite thermometry. The grey field corresponds to the temperature  
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4 403 range of muscovite dehydration for metasedimentary rocks. The red axes on the right side of each diagram  
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6 404 correspond to the composition of the melt in equilibrium with biotite for suprasolidus rocks calculated using  
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8 405 preferred  $K_d^{\text{biotite/melt}}$  values of 0.55 (Li) and 2.25 (F) of Villaros and Pichavant (2019).  
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11 406 The Li-F compositions of biotite in para-derived migmatites are similar to that of biotite  
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13 407 from the cordierite-bearing granite (Li ~220 ppm, F ~0.55 wt%). Such values are significantly  
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15 408 lower than that of trioctahedral micas from muscovite-bearing (Li ~740 ppm, F ~2.30 wt%) and  
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17 409 Li-mica-bearing (Li ~7,500 ppm, F ~3.90 wt%) granites (Fig. 6). The Li content (~160 ppm) of  
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19 410 biotite in the Ordovician orthogneiss is comparable to that from metasedimentary rocks.  
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21 411 However, biotite from Cadomian orthogneisses (especially the leucogneiss) reaches distinctly  
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23 412 higher Li (740-1,630 ppm) and F (0.75-1.40 wt%) concentrations (Fig. 6). Biotite from  
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25 413 Cadomian orthogneisses is also enriched in other rare-metals such as Cs (80-230 ppm), W (5-  
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27 414 11 ppm), Sn (40-80 ppm), Nb (100-260 ppm) and Ta (10-30 ppm). Those concentrations are  
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29 415 similar to or below that of trioctahedral micas from the Li-mica-bearing Fabras granite and  
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31 416 above that of the cordierite-bearing Velay granite (Online Resource 3, Fig. S7).  
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### 38 417 *Geochemical modeling of Li-F enrichment in crustal melts*

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41 418 In this section, we explore the behavior of F and Li during crustal melting using geochemical  
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43 419 modeling. We aim at unraveling the respective role of different key parameters which include  
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45 420 temperature, pressure, melt extraction (restite melting scenario), protolith composition and H<sub>2</sub>O  
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47 421 activity on the F-Li enrichment of anatectic silicate melts.  
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### 51 422 *Li partitioning in cordierite*

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55 423 As shown by our mineral/mineral partitioning data (Fig. 5, Table 2), Li is readily incorporated  
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57 424 in cordierite relatively to biotite whereas cordierite does not incorporate substantial amounts of  
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59 425 F. The mean  $K_{d_{\text{Li}}^{\text{Crd/Bt}}}$  values range from 1.8 to 2.8 in anatectic metasedimentary rocks and is  
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426 of 1.3 in the cordierite-bearing granite. As Li is mildly incompatible to compatible in biotite  
427 ( $0.4 \leq K_d^{Bt/melt} \leq 1.7$ ; Villaros and Pichavant 2019),  $K_{Li}^{Crd/melt}$  must be above 1. Our data are  
428 not consistent with the experimental results of Evensen and London (2003) which suggest that  
429 Li preferentially partitions into biotite over cordierite, and that Li is incompatible in the latter.  
430 However, our data are in agreement with previous data on natural rocks which show  $K_d^{Crd/Bt}$   
431 values from ~2 to 4, including felsic volcanic rocks not susceptible to retrograde re-  
432 equilibration and peraluminous granites that host cordierite with up to 3,000 ppm Li (Fig. 5d)  
433 (Gordillo et al. 1985; Bea et al. 1994; Černý et al. 1997; Acosta-Vigil et al. 2010; Alasino et al.  
434 2010; Simons et al. 2017). Actually, the positive Na-Li correlation in cordierite observed from  
435 our dataset is consistent with the classical substitution scheme ( $Na^{+Channel} + Li^{+Oct} \rightarrow (Mg^{2+},$   
436  $Fe^{2+})_{Oct}$  (Online Resource 3, Fig. S8). Therefore, the following geochemical modeling will rely  
437 on natural cordierite/mineral partitioning data.

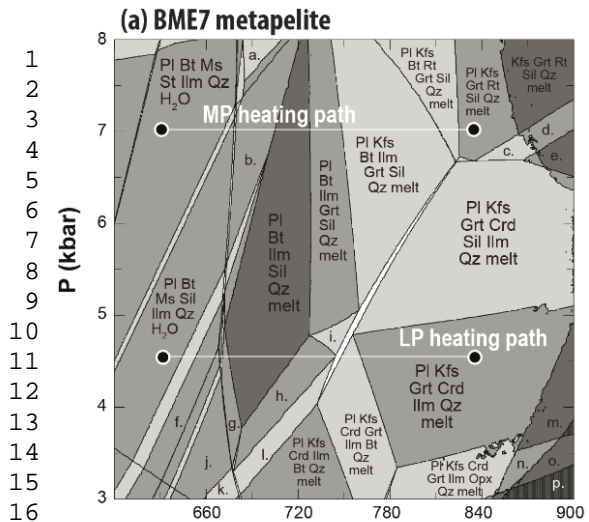
#### 438 *Modeling approach*

439 Following the methodology of Mohammadi et al. (2016) and Janoušek and Moyen (2020), the  
440 Li-F content of modeled melts and solid residues were estimated along two P–T paths  
441 mimicking different melting scenarios (Fig. 7). Paths MP and LP correspond to isobaric heating  
442 from 650 to 850°C at 7 and 4.5 kbar, respectively. The phase proportions were obtained via  
443 PerpleX. The set of partition coefficients (Table 3) was built on the experimental data compiled  
444 by Villaros and Pichavant (2019) and on  $K_d^{biotite/mineral}$  values from the Velay samples. The  
445 compositions of melts and residues were calculated using the batch melting equation, as  
446 fractional melting is probably not realistic considering the relatively high viscosity of granitic  
447 magmas.

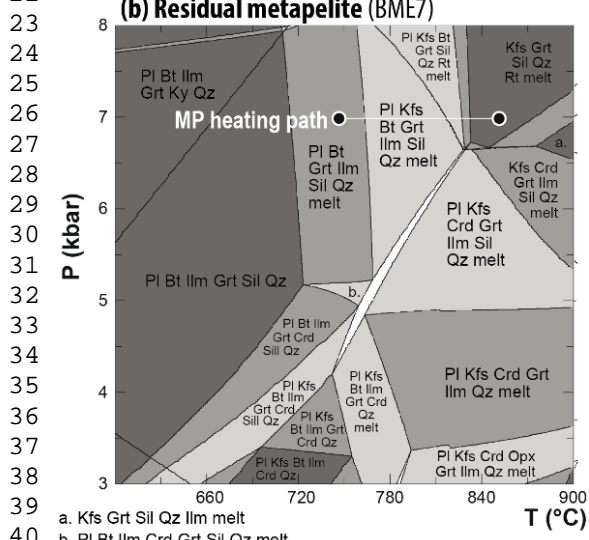
448 Metasedimentary rock melting modeling was done using as a protolith the subsolidus  
449 metapelitic sample BME7 (Fig. 7a), with 70 ppm Li and 0.081 wt% F. H<sub>2</sub>O was settled at 1.8

450 wt%, based on the modal abundance of micas in the rock and considering 5 wt% H<sub>2</sub>O in micas,  
1  
2 451 to firstly reproduce “fluid-absent” melting conditions ([Online Resource 3, Table S1](#)). Re-  
3  
4 452 melting of a biotite-rich residue left after melt extraction from a BME7-like source was also  
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6  
7 453 simulated at 7 kbar to test the restite melting scenario ([Fig. 7b](#)) and more details on the modeling  
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9  
10 454 approach are given below. Orthogneiss partial melting was modeled at 7 kbar using the CHA15-  
11  
12 455 35 leucogneiss as a starting composition ([Fig. 7c](#)). The H<sub>2</sub>O content of the leucogneiss was set  
13  
14 456 to a value of 0.68 wt% corresponding to melt saturation at the 7 kbar solidus (based on a T-  
15  
16  
17 457 X(H<sub>2</sub>O) section, [Online Resource 3, Fig. S9](#)), a value close to the LOI. The initial bulk Li-F  
18  
19 458 concentrations of the orthogneiss was set to 70 ppm Li and 0.081 wt% F (i.e., the composition  
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21  
22 459 of BME7 metapelite) in order to only evaluate the effect of protolith mineralogy on melt  
23  
24 460 compositions.

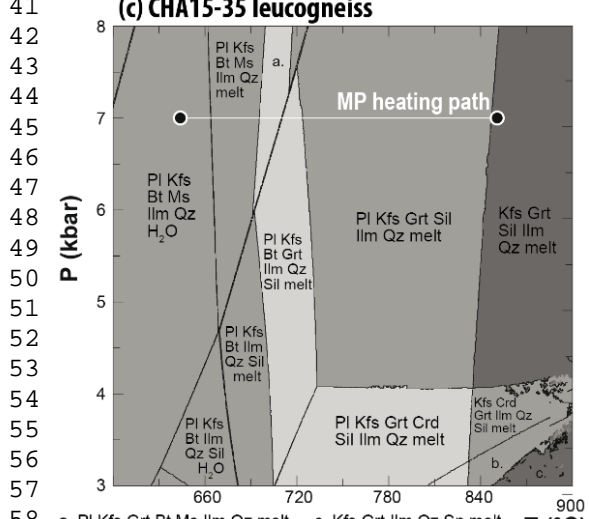




- a. PI Bt Ms Grt Ky Qz Ilm melt
- b. PI Bt Ms Sil Qz Ilm melt
- c. PI Kfs Grt Sil Qz Rt Ilm melt
- d. Kfs Grt Sil Qz Rt Ilm melt
- e. Kfs Grt Sil Qz Ilm melt
- f. PI Bt Ms Sil Qz Rt H<sub>2</sub>O
- g. PI Bt Sil Qz Ilm melt H<sub>2</sub>O
- h. PI Bt Crd Sil Qz Ilm melt
- i. PI Bt Grt Crd Sil Qz Ilm melt
- j. PI Kfs Bt Sil Qz Ilm H<sub>2</sub>O
- k. PI Kfs Bt Crd Sil Qz Ilm H<sub>2</sub>O
- l. PI Kfs Bt Crd Sil Qz Ilm melt
- m. Kfs Grt Crd Qz Ilm melt
- n. Kfs Grt Crd Opx Qz Ilm melt
- o. Kfs Grt Crd Opx Ilm melt
- p. Kfs Crd Opx Ilm melt



- a. Kfs Grt Sil Qz Ilm melt
- b. PI Bt Ilm Crd Grt Sil Qz melt



- a. PI Kfs Grt Bt Ms Ilm Qz melt
- b. Kfs Crd Grt Ilm Qz Sp melt
- c. Kfs Grt Ilm Qz Sp melt

**Fig. 7** Pseudosections for a Velay metapelite (BME7, **a**) and calculated residual equivalent **b**, as well as for a Cadomian leucogneiss (CHA15-35, **c**). The medium pressure (MP) and low pressure (LP) paths, along which phase proportions and Li-F melt/residue partitioning were calculated, are indicated. Pseudosection **b** represents the residual metapelite, after the extraction of 25 vol% melt from BME7, that was calculated in order to model restite melting.

**Table 3** Partitioning data for Li and F used for partial melting models.

	Li			F		
	Min	Pref	Max	Min	Pref	Max
Kd Bt/melt	0.41 <sup>a</sup>	0.55 <sup>a</sup>	1.67 <sup>a</sup>	1.56 <sup>a</sup>	2.25 <sup>a</sup>	4.00 <sup>a</sup>
Kd Crd/Bt	-	2.00 <sup>b</sup>	-	-	-	-
Kd Bt/Grt	-	6.00 <sup>b</sup>	-	-	-	-
Kd Bt/Ms	-	5.00 <sup>b</sup>	-	-	-	-
Kd Crd/melt	0.82 <sup>c</sup>	1.10 <sup>c</sup>	3.34 <sup>c</sup>	0.01 <sup>d</sup>	0.01 <sup>d</sup>	0.01 <sup>d</sup>
Kd Grt/melt	0.07 <sup>c</sup>	0.09 <sup>c</sup>	0.28 <sup>c</sup>	0.01 <sup>d</sup>	0.01 <sup>d</sup>	0.01 <sup>d</sup>
Kd Ms/melt	0.08 <sup>c</sup>	0.11 <sup>c</sup>	0.33 <sup>c</sup>	0.94 <sup>a</sup>	1.00 <sup>a</sup>	1.92 <sup>a</sup>

Pref: preferred; a: experimental Kd data compiled by Villaros and Pichavant (2019); b: values based on Velay rock samples (this study); c: values calculated using experimental Kd Bt/melt and Velay rock Kd mineral/mineral values; d: assumed values. The Kd of all other minerals was fixed to 0.01.

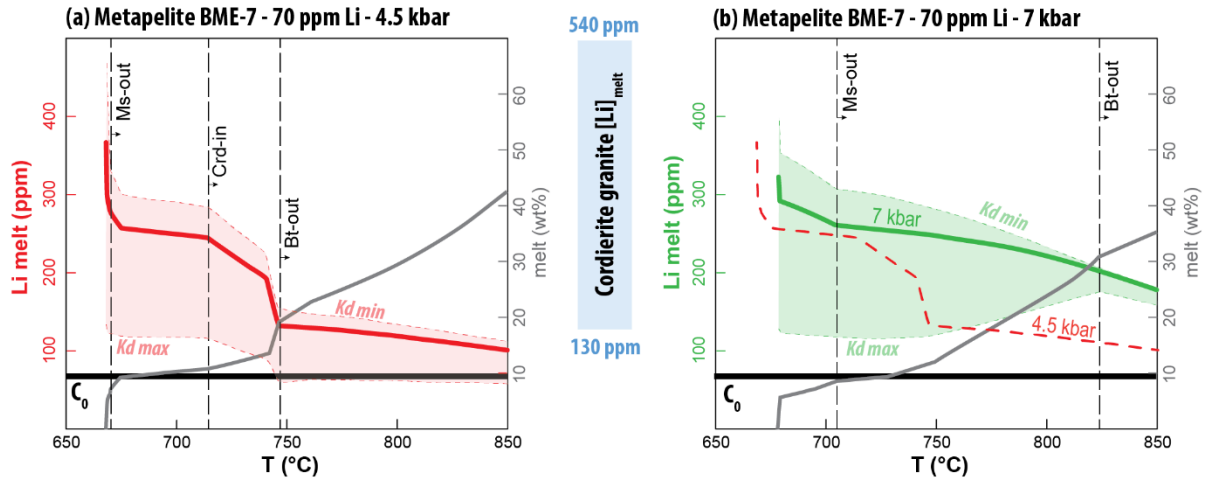


479 *Metapelite melting model and the impact of pressure and cordierite crystallization upon Li*

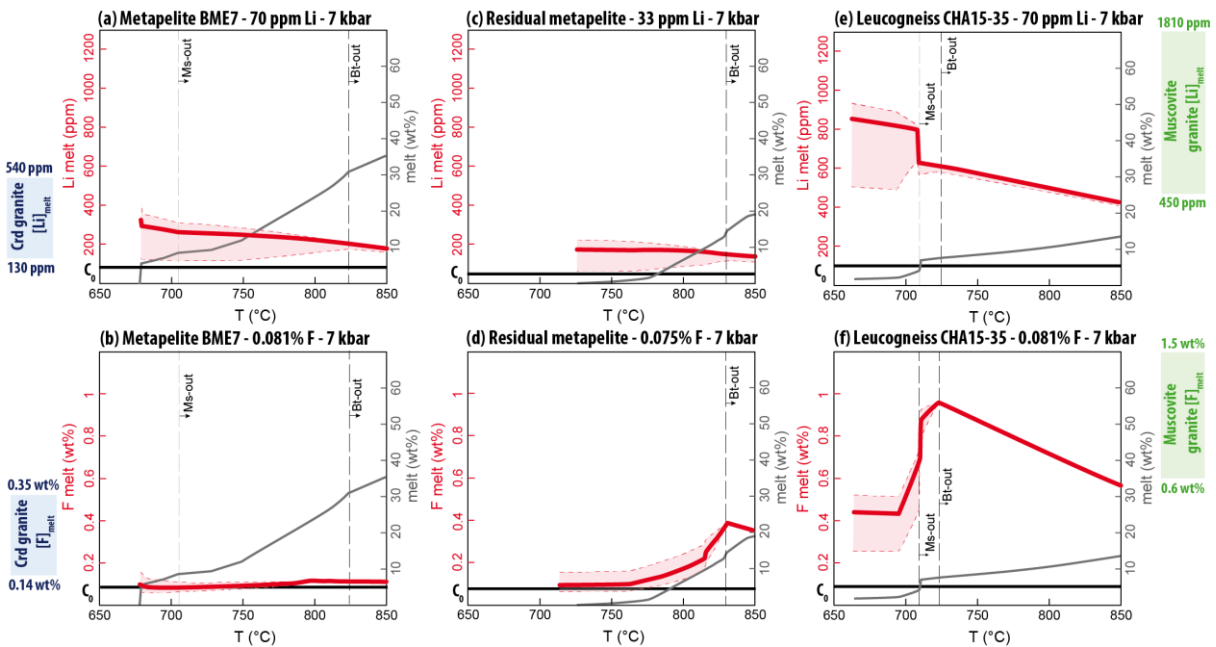
480 *enrichment in silicate melts*

481 The compatibility of Li in cordierite inhibits Li enrichment in the melt during the low-pressure  
482 dehydration melting reaction of biotite below ~5-6 kbar ( $Bt + Qz + Pl = melt + Kfs + Crd$ ),  
483 contrary to garnet ( $Bt + Qz + Pl = melt + Kfs + Grt$ ) which does not incorporate significant  
484 amounts of Li. The modeled Li content of liquids produced during metapelite anatexis are  
485 shown in Figure 8. At both low (Fig. 8a) and medium (Fig. 8b) pressure (i.e., within and outside  
486 the stability field of cordierite, respectively), the melt is enriched in Li relatively to the residue  
487 and the protolith. With increasing temperature, the Li concentration in the melt decreases as the  
488 melt proportion increases (dilution effect). The muscovite-out reaction occurs at low  
489 temperature around 670°C for the LP path, explaining its absence in the investigated anatectic  
490 metasedimentary rocks having minimum peak temperatures around 700°C (Fig. 6). At 7 kbar,  
491 this reaction occurs at slightly higher temperature around 700°C. Similarly, the biotite-out  
492 reaction occurs at lower temperature along the LP path (~750°C) than along the MP path  
493 (~825°C). The first significant amounts of melts (~10 wt%) produced below 700°C have similar  
494 Li concentrations around 250-300 ppm at low and medium pressure. However, above 700°C,  
495 peritectic cordierite crystallization along the LP path induces a stronger decrease of melt Li  
496 concentrations relatively to the melt produced at higher pressure. At ~750°C, the difference  
497 between LP (~125 ppm) and MP (~250 ppm) melts is maximum and reaches a factor 2.

498 As cordierite crystallization cannot inhibit F enrichment of the melt, F partitioning  
499 during metapelite melting was only modeled at 7 kbar. In contrast to Li (Fig. 9a), the modeled  
500 F concentration of the melt remains similar to the protolith (~0.08 wt%) from ~670 to 750°C  
501 and then slightly increases up to ~0.10 wt% around 800 °C (Fig. 9b).



**Fig. 8** Lithium concentrations in melt versus temperature diagrams illustrating the results of batch melting modeling for a typical metapelite (BME7) from the Velay dome with H<sub>2</sub>O concentration in the protolith settled at 1.8 wt%. Partial melting was simulated at **a** 4.5 kbar and **b** 7 kbar within and outside the stability field of cordierite, respectively. The light-colored fields show deviations related to the use of minimum and maximum  $Kd^{biotite/melt}$  values from the literature. Melt amounts are shown as grey curves. The blue field represents the range of Li composition of the melt in equilibrium with the biotite of the cordierite-bearing granite based on maximum and minimum  $Kd$  values (Table 3).  $C_0$  represents the initial composition of the metapelite.



**Fig. 9** Lithium and F concentrations in melt versus temperature diagrams comparing results of batch melting modeling for a metapelite (1.8 wt% H<sub>2</sub>O) **a-b**, a residual metapelite **c-d**, and a leucogneiss (0.7 wt% H<sub>2</sub>O) **e-f** from the Velay dome at 7 kbar. Melt amounts (wt%) are shown as grey curves. Blue and green fields represent the range

514 of Li and F compositions of melts in equilibrium with the biotite of the cordierite- and muscovite-bearing granites,  
1  
2 515 respectively.  $C_0$  represents the initial composition of the protoliths.  
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#### 4 516 *Restitic metapelite melting model*

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7 517 It has been proposed that granitic melts enriched in rare-metals including Li and halogens such  
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10 518 as F can be produced by re-melting of a biotite-rich residue (restite) (e.g., [Simons et al. 2016](#);  
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12 519 [Michaud et al. 2021](#)). To test this hypothesis, we modeled the re-melting of the solid residue  
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15 520 left after extraction of ~25 vol% melt at 750°C and 7 kbar from the BME7 metapelite. We  
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17 521 considered that 1 mol% melt was retained in the source following [Korhonen et al. \(2013\)](#). The  
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20 522 solid residue is composed of Qz + Bt + Pl + Sil + Grt + Ilm ([Fig. 7b](#)). The residue contains  
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22 523 0.075 wt% F, but only 33 ppm Li because the Li-rich melt was lost along the prograde path.  
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25 524 Fluid-absent melting of such restitic metapelite between ~750 and 800°C produces a  
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28 525 melt with a nearly constant Li concentration of ~175 ppm at 7 kbar, relatively close to that of  
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30 526 the fertile metapelite, and slightly decreases down to ~100-150 ppm after biotite exhaustion  
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33 527 around 830°C ([Fig. 9c](#)). In contrast, the F concentration of the melt produced by restite melting  
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35 528 significantly increases with temperature from ~0.1 to 0.4 wt%, and the maximum content is  
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38 529 attained at the Bt-out isograd ([Fig. 9d](#)). Such F melt composition is higher than that produced  
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40 530 during fertile metapelite melting ( $\leq 0.1$  wt%, [Fig. 9b](#)).  
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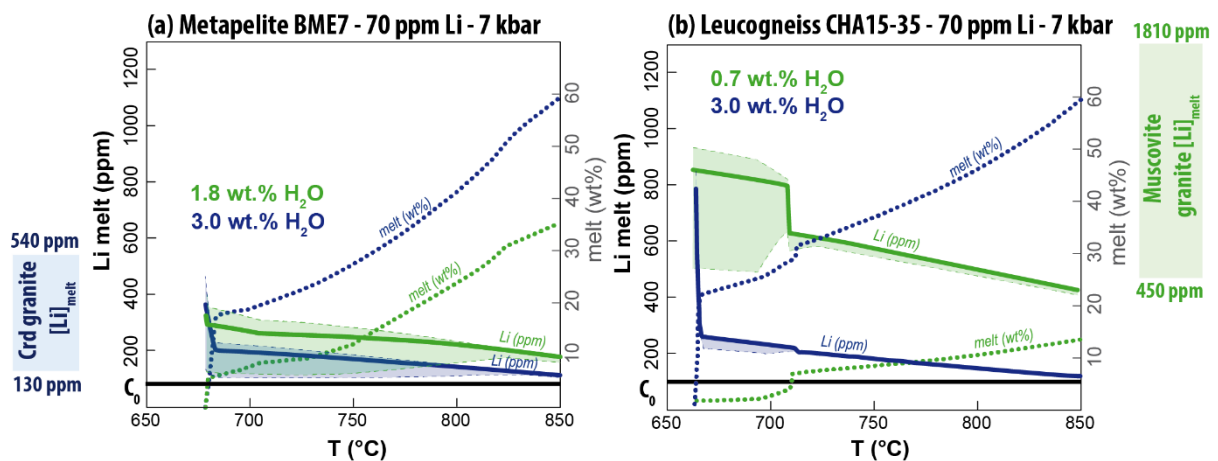
#### 43 531 *Orthogneiss melting model*

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46 532 As observed for the metapelite, partial melting of the orthogneiss produces a melt enriched in  
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49 533 Li compared to the protolith (and residue), and the Li concentration of the melt decreases with  
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51 534 increasing melting degree and temperature ([Fig. 9e](#)). However, the Li concentration of the melts  
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54 535 produced from the orthogneiss source is significantly higher than that generated from the  
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56 536 metapelite source, with a factor of enrichment above 2 (600 ppm versus 250 ppm) at ~710°C  
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59 537 ([Fig. 9a,e](#)). This is because the orthogneiss protolith has a lower mica proportion than the  
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538 metapelite. Therefore, the complete breakdown of muscovite and biotite for the orthogneiss  
 539 occurs at relatively low temperature of ~730°C and produces ~10 wt% melt enriched in Li. By  
 540 comparison, biotite-out for the metapelite occurs around 825°C at 7 kbar and can produce up  
 541 to 35 wt% of melt, but this melt is Li-poor due to dilution. Moreover, the model indicates that  
 542 a strong enrichment of F up to ~1 wt% occurs in the melt at ~720°C simultaneously with high  
 543 concentrations of Li (~600 ppm) during orthogneiss melting (Fig. 9f).

#### 544 *Fluid-absent versus water-fluxed melting*

545 The effect of water-fluxed melting versus fluid-absent melting (Figs. 8 and 9) on Li enrichment  
 546 in anatectic melts is evaluated by increasing the initial bulk H<sub>2</sub>O content of metapelitic and  
 547 orthogneissic protoliths (Fig. 10). For the metapelite BME7, the evolution of Li melt  
 548 concentrations produced using an initial bulk H<sub>2</sub>O content of 1.8 wt%, is compared to that  
 549 produced using higher bulk H<sub>2</sub>O content of 3.0 wt%, a value close to the LOI (Fig. 10a). For  
 550 the leucogneiss CHA15-35, the bulk water concentration was also increased from 0.7 to 3.0  
 551 wt% for sake of comparison (Fig. 10b). The respective pseudosections for both protoliths at  
 552 higher bulk water contents are provided in Online Resource 3, Fig. S10.



553  
 554 **Fig. 10** Lithium concentrations in melt versus temperature diagrams illustrating the effect of increasing whole-  
 555 rock H<sub>2</sub>O concentration of the protolith on batch melting modeling results for a metapelite **a** and leucogneiss **b**  
 556 from the Velay dome at 7 kbar. The green and blue curves represent Li melt concentration evolutions for low (1.8

557 wt% in **a**; 0.7 wt% in **b**) and high (3.0 wt%) water contents in each protoliths, respectively. The dashed curves  
1  
2 558 indicate the melt proportion in wt%. The Li and F compositions of melts in equilibrium with the biotite of the  
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4 559 cordierite- and muscovite-bearing granites are indicated as fields.  $C_0$  represents the initial composition of the  
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6 560 protoliths.  
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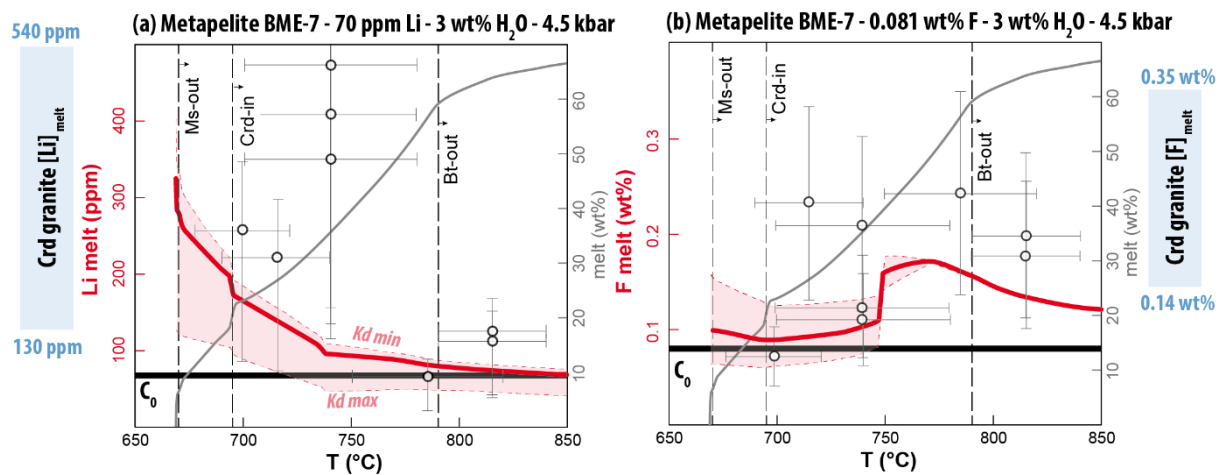
8  
9 561 Similarly to the “fluid-absent” melting scenarios, the Li melt concentrations decrease as  
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11 562 a function of temperature when more water is added to both protoliths, but concentrations are  
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13 563 lower at a given temperature during “water-fluxed” melting. From ~670 to 850°C, the Li melt  
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15 564 concentrations produced from the metapelite decrease from ~200 to ~100 ppm at high-water  
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17 565 content, whereas concentrations decrease from ~300 to ~175 ppm at low-water content, which  
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19 566 corresponds to an enrichment factor of ~1.5-2.0 from “wet” to “damp” conditions (Fig. 10a).  
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21 567 The Li concentration gap between melts generated upon “fluid-absent” and “fluid-fluxed”  
22  
23 568 melting conditions is significantly higher for the leucogneiss (factor of ~4, Fig. 10b). In the  
24  
25 569 temperature range of 660 to 850°C, Li melt concentration decreases from ~300 to 100 ppm if 3  
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27 570 wt% H<sub>2</sub>O is settled in the protolith, whereas concentrations decrease from ~850 ppm to 400  
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29 571 ppm at “damp” conditions (0.7 wt% H<sub>2</sub>O). For both protoliths, the decrease of Li melt  
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31 572 concentrations in function of their water content is due to dilution, as adding water to the  
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33 573 protolith significantly increases melt proportions. From “damp” to “wet” conditions, maximum  
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35 574 melt proportions at 850°C increase from ~35 to 60 wt% and from ~15 to 60 wt% in the case of  
36  
37 575 the metapelite and leucogneiss, respectively. The leucogneisses are indeed more sensitive to  
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39 576 this effect because of their “near-eutectic” composition (Couzinié et al. 2021).  
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## 48 577 **Discussion**

### 49 50 51 578 *Biotite compositions as proxies of Li-F enrichment in anatectic silicate melts: comparison* 52 53 54 579 *with whole-rock data and modeling results*

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56  
57 580 The Li contents of biotite and cordierite from suprasolidus metasedimentary rocks from the  
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59 581 Velay anatectic dome decrease by a factor of ~3 above 750°C (Fig. 6a). Based on available  
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582  $K_d^{Bt/melt}$  values (Table 3), we calculate that the Li contents of silicate melts in equilibrium with  
 583 biotite decreased from ~200-400 ppm to 60-100 ppm with the progress of the biotite-breakdown  
 584 melting reaction from migmatites to restitic nodules (Fig. 6a). In contrast, the F concentrations  
 585 of biotite from suprasolidus metasedimentary rocks remain constant or tend to increase with  
 586 temperature; the estimated equilibrium melt F content ranging from ~0.07 to 0.25 wt% (Fig.  
 587 6b). The relative melt concentration evolutions of F and Li recorded by biotite are in agreement  
 588 with the results of “water-fluxed” metapelite melting modeling at 4.5 kbar, i.e., the conditions  
 589 relevant for the Velay anatectic dome (Fig. 11). This, together with above-solidus Ti-in-biotite  
 590 temperatures ( $\geq 700$  °C, Table 1, Henry et al. 2005) and uniform biotite-cordierite Li  
 591 partitioning data (Fig. 5 and Table 2), suggests that the Li-F compositions of minerals were not  
 592 re-equilibrated at sub-solidus conditions. Biotite compositions are thus good proxies of melt  
 593 compositional evolutions upon crustal anatexis in the Velay dome.



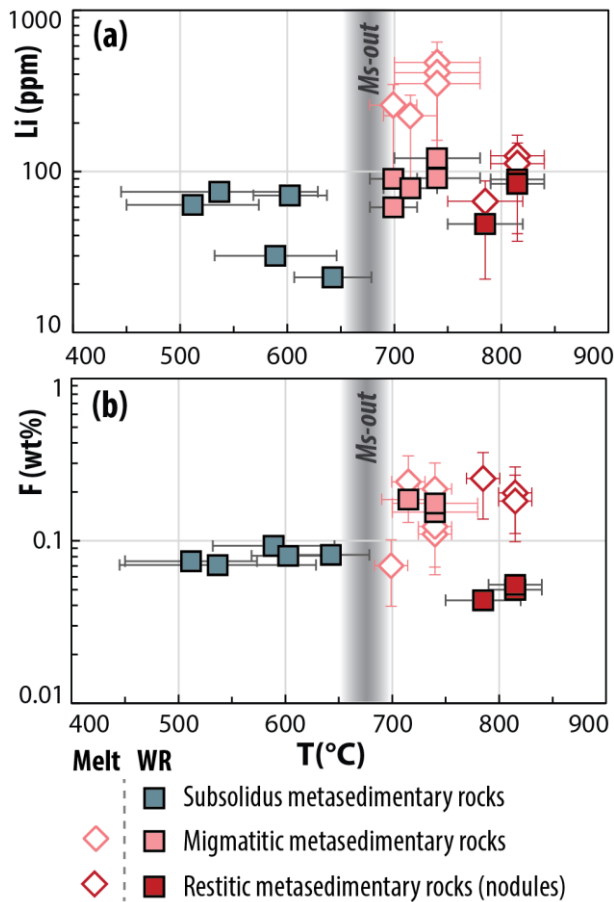
594  
 595 **Fig. 11** Lithium **a** and F **b** concentrations in melt versus temperature diagrams illustrating the results of batch  
 596 melting modeling for the BME7 metapelite at the conditions relevant from the Velay dome (i.e., 4.5 kbar and  
 597 “wet” conditions with H<sub>2</sub>O content in the protolith settled at 3 wt%). The melt concentrations in equilibrium with  
 598 biotite from anatectic metasedimentary rocks (white points) and cordierite granite (blue field) from the Velay  
 599 dome, calculated based on preferred, minimum and maximum Kd values (Table 3) are shown for comparison. The  
 600 grey curves show the melt proportion and C<sub>0</sub> represents the initial composition of the protolith.

601 Both modeling and biotite compositions support a contrasted behavior of Li and F  
1  
2 602 during partial melting of metapelites. This is true at low pressure < 5 kbar (Fig. 11) but also at  
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4 603 higher pressures (Fig. 9a,b). Lithium behaved incompatibly with respect to residual silicate  
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6 604 minerals and the Li-richest melts (200-400 ppm) were produced at low temperature  $\leq 750^{\circ}\text{C}$   
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8 605 during muscovite- or incipient biotite-breakdown. In contrast, F behaved more compatibly; F  
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10 606 melt concentrations (~0.1-0.2 wt%) remained relatively stable with temperature with a slight  
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12 607 concentration increase at  $T > 750^{\circ}\text{C}$ . Similar behavior for both Li and F were reported for biotite  
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14 608 from sub- to supra-solidus metasedimentary rocks from the Ivrea Zone in the European Alps  
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16 609 and the Langtang Himalaya in Nepal (Kunz et al. 2022), as well as for metamorphic rocks from  
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18 610 the Rogaland metamorphic aureole in Norway (Finch and Tomkins 2017) (Online Resource 3,  
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24 611 Fig. S11).

27 612 Whole-rock data alone do not allow to trace with the same accuracy the behavior of  
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29 613 both elements upon partial melting, but are complementary to silicate mineral compositions. In  
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31 614 the Velay dome, bulk Li contents are roughly similar for para-derived migmatites (60-120 ppm)  
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33 615 and restitic nodules (50-90 ppm) due to the abundance of peritectic cordierite in the latter (~50  
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35 616 vol%, Fig. 4d) for which Li is compatible (Fig. 12a). Therefore, calculated melt concentrations  
36  
37 617 in equilibrium with biotite are enriched relative to corresponding bulk migmatites at  $< 750^{\circ}\text{C}$   
38  
39 618 but melt and whole-rock contents are almost equivalent for restitic nodules at  $> 750^{\circ}\text{C}$  (Fig.  
40  
41  
42 619 12a). Regarding F, whole-rock concentrations decrease significantly from 0.15-0.18 wt% to  
43  
44 620 0.04-0.05 wt% above  $750^{\circ}\text{C}$ . This is due to the progress of the biotite-breakdown reaction and  
45  
46 621 the absence of other mineral phases incorporating F, such as apatite, in restitic nodules (Fig.  
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48 622 12b). Melt and whole-rock F concentrations are similar at  $< 750^{\circ}\text{C}$  but melts are enriched  
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50  
51 623 relative to bulk restitic nodules at  $> 750^{\circ}\text{C}$ , as F behave more incompatibly at these  
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53  
54 624 temperatures. In the Ivrea zone, the whole-rock Li concentrations of metasedimentary rocks  
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56  
57  
58  
59 625 decrease with temperature, similarly as biotite Li contents (Bea and Montero 1999; Qiu et al.



626 2011; Kunz et al. 2022) (Online Resource 2, Fig. S11). Contrary to the Velay area, melt  
 627 equilibrated with biotite are always enriched in Li relative to whole-rock samples, as cordierite  
 628 is generally not stable at the melting conditions of the Ivrea zone (> 5 kbar).



**Fig. 12** Evolution of the whole-rock (WR) Li **a** and F **b** concentrations of metasedimentary rocks from the Velay dome as a function of peak temperature, and comparison with calculated melt compositions in equilibrium with biotite (using  $K_d$  values from Table 3).

641

### 642 *Factors of Li-F enrichment in granitic melts during anatexis*

643 Silicate mineral records and modeling results indicate that metapelite-derived melts  
 644 systematically show modest Li contents, globally in the range of the concentration of the melt  
 645 in equilibrium with biotite from the cordierite-bearing Velay granite (i.e., 130-540 ppm Li  
 646 considering maximum and minimum  $K_d^{Bt/melt}$  values, Figs. 8 to 11). Notwithstanding, “fluid-  
 647 absent” melting favors the Li enrichment of anatectic melts relatively to “fluid-assisted”  
 648 melting. An enrichment factor around 2 is observed for Li by changing the water concentration  
 649 of the metapelite protolith from 3.0 to 1.8 wt% (Fig. 10a). This is because decreasing the water



650 contents reduces the dilution effect by changing the range of melt proportions from ~20-60 wt%  
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2 651 to ~10-35 wt%. Similarly, the crystallization of peritectic cordierite during LP crustal melting  
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5 652 limits the Li enrichment of silicate melts by a factor of 2 (Fig. 8).  
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8 653 Metapelite-derived melts relatively enriched in F (~ 0.15 wt% F) are produced at  
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10 654 temperatures > 750°C near the biotite-out isograd (Figs. 9b and 11b). Such melts could be even  
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13 655 more enriched (~0.4 wt%) if low temperature melts < 725°C are extracted from the melting  
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15 656 zone (i.e., restite melting, Fig. 9d). However, the melts produced during restite melting are  
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17  
18 657 relatively Li poor  $\leq 200$  ppm (Fig. 9c), because Li, which is less compatible in biotite than F  
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20 658 (Table 3), was removed/scavenged by lower temperature melts. Restite melting is, thus, not a  
21  
22 659 viable process to generate Li-rich melts. Similarly, dehydration of restitic biotite-bearing deep  
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25 660 crustal rocks in the presence of mantle-derived CO<sub>2</sub>-rich fluids at granulite-facies conditions  
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27 661 (Cuney and Barbey 2014) may generate a F-rich fluid but this media might not be especially  
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29  
30 662 enriched in Li due its major loss upon prograde melting at relatively low temperatures.  
31  
32 663 Therefore, it is still unclear whether such metamorphic fluids could trigger the formation of Li-  
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35 664 F-rich magmas during fluid-fluxed crustal melting in late-orogenic settings.  
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38 665 Modeling results indicate that fluid-absent melting of a peraluminous leucocratic  
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40 666 orthogneiss can generate a melt that is concomitantly enriched in both F (~1 wt%) and Li (~600  
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42  
43 667 ppm) at relatively low temperature (< 750°C, Figs. 9e,f and 10b). This is possible because (i)  
44  
45 668 the small amounts of melt produced (~10-15 wt%) limit metal dilution, and (ii) the complete  
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48 669 breakdown of both muscovite and biotite occurs within a narrow range of temperature (710-  
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50 670 730°C, Fig. 9e,f). This is consistent with our natural dataset as the melt in equilibrium with  
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53 671 biotite from a Velay anatectic augen gneiss with peak temperature of 660-730°C (Couzinié et  
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55 672 al. 2021) is characterized by concentrations of Li (~1,350 ppm) and F (~0.35 wt%), which are  
56  
57 673 significantly higher than those of melts equilibrated with biotite from anatectic paragneisses  
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60 674 (Fig. 6). The Li-F concentrations of orthogneiss-derived melts remain below that of the melt in  
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675 equilibrium with trioctahedral micas from the Fabras Li-mica-topaz granite (4,490-18,290 ppm  
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2 676 Li; 1.0-2.5 wt% F) but are similar to that of the melt equilibrated with biotite from the  
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5 677 muscovite-bearing granite (450-1,810 ppm Li; 0.6-1.5 wt% F).  
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### 8 678 *Implications for the formation of peraluminous rare-metal granites and pegmatites*

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10  
11 679 Our natural dataset and the results of geochemical modelling show that F-Li decoupling is  
12  
13 680 expected during metapelite melting: the Li-richest melts would be produced at low temperature  
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16 681 (< 750°C) whereas the F-richest melts are more likely to be generated at > 750°C (Figs. 6, 9,  
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18 682 11, and Online Resource 3, Fig. S11). Such decoupling might affect other elements typically  
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21 683 enriched up to economic levels in RMGPs. As for Li, the concentrations of W, Be and Cs in  
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23 684 biotite from suprasolidus metasedimentary rocks decrease with increasing temperature (Online  
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25 685 Resource 3, Fig. S7). Therefore, the melt rare-metal contents decreased as prograde melting  
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27  
28 686 proceeded, resulting in the production of the melts with the highest contents of W, Be and Cs  
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31 687 at temperatures < 750°C, by muscovite breakdown or incipient biotite breakdown. In contrast,  
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33 688 Sn, Nb and Ta behaved like F as their concentrations in biotite remained constant or increased  
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35 689 as melting reactions proceeded, suggesting that the richest melts were produced at temperatures  
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38 690 > 750°C.  
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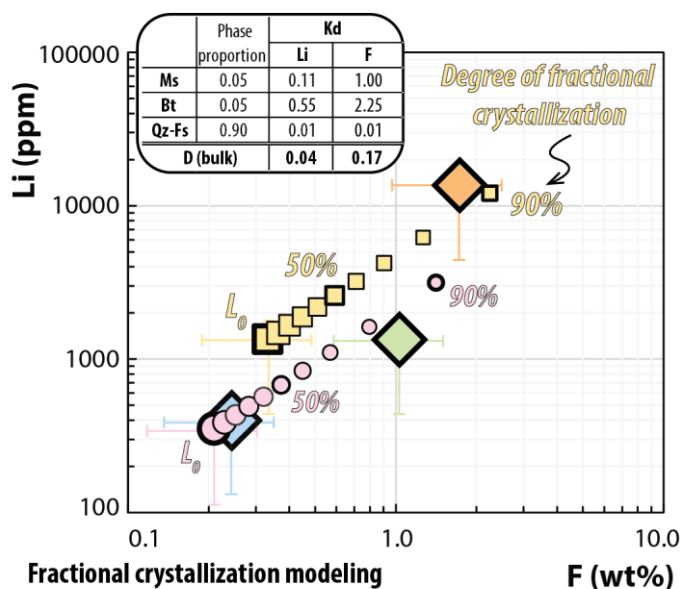
41 691 Consistently, partial melting experiments performed on a biotite-rich paragneiss  
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43 692 indicate that Li, Cs and W are enriched in the melt relatively to the protolith upon biotite-  
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45 693 dehydration melting whereas the opposite is true for Nb and Ta (Michaud et al. 2021).  
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48 694 Moreover, Zhao et al. (2022) predicted using a modeling approach that W-rich melts are  
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51 695 generated at lower temperature (< 700°C) than Sn-rich ones (> 800°C) during metapelite  
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53 696 melting. Mobilization of Sn only at high temperature (corresponding to biotite breakdown  
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55 697 conditions), was also predicted by Wolf et al. (2018) based on the analyses of leucosomes and  
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58 698 associated residuum of Variscan migmatites from Iberia. Therefore, Li-W-Be-Cs and F-Sn-Nb-  
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60 699 Ta decoupling during partial melting of metapelites indicates that the latter are not adequate  
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700 sources for the generation of RMGPs which are characteristically enriched in *all* those elements.  
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2 701 Low- and high temperature melts could-be aggregated and mixed together in a same magmatic  
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4 702 reservoir. In this case, however, dilution will occur, and the resulting hybrid melt will be  
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7 703 depleted in rare-metals and F. Finally, a recent study showed that staurolite melting reactions  
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10 704 can generate Li-rich melts (200-1,000 ppm) from a metapelitic protolith at MP conditions of 6-  
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12 705 8 kbar (Knoll et al. 2023). Nonetheless, although staurolite may have high Li contents, it does  
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14 706 not incorporate significant amount of other rare-metals (Nb, Ta, Sn, Cs) or F (Dutrow et al.  
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16 707 1986; Konzett et al. 2018; Knoll et al. 2023). Therefore, staurolite breakdown reactions (which  
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19 708 are only relevant in metapelite systems) are likely not able to generate typical RMGPs as those  
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22 709 encountered in the FMC.

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25 710 In contrast, fluid-absent mica breakdown of a relatively biotite-poor and muscovite-rich  
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27 711 peraluminous orthogneiss from 710 to 730°C generates a melt that is simultaneously enriched  
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30 712 in both Li and F (Fig. 9e,f). Such melts would also be enriched in other metals incorporated in  
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32 713 micas, such as Cs, Be, W, Nb, Ta and Sn. This is suggested by partial melting experiments  
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35 714 performed on a muscovite-rich orthogneiss (Michaud et al. 2021) and our natural data indicating  
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37 715 that orthogneiss biotite (and muscovite) has elevated Sn, Cs, W, Nb and Ta contents (Online  
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39 716 Resources 2 and 3, Fig. S7). However, modeling the uptake of W, Sn, Ta and Nb by the melt  
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42 717 phase remains elusive as these elements are also hosted in Fe-Ti oxide minerals (e.g., ilmenite,  
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44 718 rutile) for which mineral/granitic melt partitioning data are scarce.

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47 719 Despite the low melt fraction (~10 wt%, Fig. 9) produced by partial melting of  
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50 720 orthogneisses, rare-metal-rich melts are expected to be readily extracted from their source.  
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52 721 Indeed, considering melt H<sub>2</sub>O and F contents of 8 and 1 wt%, respectively, yields a melt  
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55 722 viscosity of ~10<sup>4</sup> Pa.s at 700°C (calculated using the model of Giordano et al. 2004). This value  
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57 723 is low enough to ensure melt extraction from migmatitic sources during deformation (e.g.,  
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59 724 Vigneresse et al. 1996), and further rare-metal enrichment may occur by differentiation during  
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725 magma ascent and storage in magmatic reservoirs at upper crustal levels. Fractional  
 726 crystallization modeling was performed to assess the capability of an orthogneiss-derived  
 727 primary melt to reach the composition of the liquid equilibrated with the trioctahedral mica  
 728 from the Fabras Li-mica-topaz granite (Li ~13,500 ppm, ~1.73 wt% F, Fig. 13). This is indeed  
 729 possible moderating 80-90 wt% of fractional crystallization of an assemblage consisting of 5  
 730 wt% Ms, 5 wt% Bt and 90 wt% Qz-Fsp. In contrast, for the same degree of fractional  
 731 crystallization, a metapelite-derived melt would only reach the composition of the melt in  
 732 equilibrium with biotite from the muscovite-bearing granite (~1,350 ppm Li, ~1.03 wt% F, Fig.  
 733 13). Since the melt in equilibrium with trioctahedral mica from the Fabras granite features Li-  
 734 F contents higher than or similar to those observed in economic grade RMGPs (e.g., the apical  
 735 facies of the Beauvoir granite, with bulk Li and F of ~4,000–10,000 ppm and 1.5-2.5 wt%,  
 736 respectively, Cuney et al. 1992; Raimbault et al. 1995), we conclude that orthogneiss melting  
 737 followed by extended magmatic differentiation is a viable mechanism to form RMGP deposits.



**Fractional crystallization modeling**  
**Starting liquid ( $L_0$ )**  
 ■ Suprasolidus augen gneiss : CHA15-65 (melt in equilibrium with Bt)  
 ● Suprasolidus metapelite: N102-14-3 (melt in equilibrium with Bt)  
**Granites: melt in equilibrium with Bt**  
 ◆ Li-mica-bearing granite (Fabras)    ◆ Muscovite-bearing granite  
 ◆ Cordierite-bearing granite

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739 **Fig. 13** Li vs. F concentration diagram illustrating the effect of fractional crystallization of micas and quartz-  
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2 740 feldspar on the composition of primary melts ( $L_0$ ) in equilibrium with trioctahedral micas from an anatectic  
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4 741 metapelite and augen orthogneiss from the Velay dome. The degree of fractional crystallization is shown by  
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6 742 increment of 10 wt% and the compositions of the melt in equilibrium with biotite from regional granites are  
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8 743 reported for comparison. Error bars for granite melts and starting liquid compositions show deviations related to  
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10 744 the use of minimum and maximum  $Kd^{biotite/melt}$  values from the literature. Modeling parameters including phase  
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12 745 proportions and  $Kd$  (preferred values of [Table 3](#)) are presented in inset.

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15 746 ***The role of protracted crustal differentiation to generate Li-F-rich peraluminous rare-metal***  
16  
17 747 ***granites and pegmatites***

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20 748 Collectively, our results suggest a felsic meta-igneous source for Li-F-rich granites and possibly  
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22 749 for RMGPs in general; their parental melts would derive from low temperature ( $< 750^\circ\text{C}$ )  
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24 750 melting of pre-existing peraluminous (meta-) granitic rocks followed by extended fractional  
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26 751 crystallization. Such model would readily explain the abundance of RMGPs in the European  
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28 752 Variscan belt since peraluminous orthogneisses constitute a major component of the pre-  
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30 753 orogenic basement ([Ballèvre et al. 2012](#); [Chelle-Michou et al. 2017](#); [García-Arias et al. 2018](#)).  
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32 754 They correspond to former S-type (volcano-) plutonic complexes that were formed during  
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34 755 polycyclic crustal melting episodes extending from the Late Ediacaran to the Late Ordovician  
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36 756 (550–445 Ma), i.e., 50–150 Ma before the onset of the Variscan orogeny. The oldest igneous  
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38 757 rock suite (550–535 Ma) was emplaced in back-arc basins at the aftermath of the Cadomian  
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40 758 accretionary orogeny ([Linnemann et al. 2014](#); [Mezger and Gerdes 2016](#); [Couzinié et al. 2017](#)).  
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42 759 Additionally, many peraluminous granitic plutons and felsic volcanic rocks are remnants of a  
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44 760 second, protracted (490–445 Ma) magmatic event ([García-Arias et al. 2018](#)) triggered by crustal  
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46 761 extension coeval to the opening of the Rheic ocean ([Nance et al. 2010](#)).  
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55 762 A similar relationship between polycyclic crustal differentiation, involving repeated  
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57 763 stages of granite melting followed by fractional crystallization, and the fertility of Archean  
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59 764 terranes for Li-Cs-Ta pegmatites was highlighted by [Černý \(1989\)](#) and [Kendall-Langley et al.](#)



765 (2020). Therefore, we infer that the amenability of a given crustal segment to produce RMGPs  
1  
2 766 during an orogenic cycle would necessarily be tied to its pre-orogenic evolution: terrains having  
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4 767 experienced protracted crust differentiation with multiple episodes of crustal melting are  
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7 768 expected be more rare-metal-fertile, as also proposed for U-rich leucogranites (Ballouard et al.  
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9 769 2018).

## 770 **Conclusions**

771 Geochemical analyses of silicate minerals from samples of the Velay anatectic dome, combined  
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18 772 with geochemical modeling, allowed us to decipher the crustal melting conditions and protoliths  
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21 773 amenable to generate Li-F-rich anatectic melts and RMGPs.

24 774 “Fluid-absent” melting favors the Li enrichment of anatectic melts relatively to “water-  
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26 775 fluxed” melting because it produces lower melt amounts and thus limits the dilution of rare-  
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29 776 metals. Low-pressure anatexis (< 5 kbar) leads to the crystallization of peritectic cordierite,  
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31 777 which acts as a Li sink and hampers the Li transfer to silicate melts.

34 778 During metapelite anatexis, melts with the highest Li concentrations of 200-400 ppm  
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37 779 are produced at temperature < 750°C upon muscovite breakdown or incipient biotite  
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39 780 breakdown. The melt Li/F ratio decreases with increasing temperature and such decoupling  
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41  
42 781 precludes the formation of Li-F-rich melts with RMPG signatures. Restite melting at T > 750°C  
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44 782 produces melts with the highest F contents (up to 0.4 wt%). However, prior loss of Li during  
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47 783 the extraction of low temperature melts again impedes the generation of Li-F-rich silicic liquids.

49 784 “Fluid-absent” melting of a peraluminous orthogneiss at P > 5 kbar can produce melts  
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52 785 simultaneously enriched in both F and Li due to near-concomitant muscovite and biotite  
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55 786 breakdown within a narrow range of temperature (710-730°C) and the low amount of melt  
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57 787 produced (~10 wt%), which limits dilution. An orthogneiss-derived melt with ~1,350 ppm Li  
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59 788 and 0.3 wt% F (values estimated for a Velay anatectic orthogneiss based on biotite

789 compositions) can reach the Li-F enrichment of a peraluminous rare-metal granite (~10,000  
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2 790 ppm Li and 2 wt% F) after ~80-90 % of fractional crystallization. Given the composition of  
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5 791 orthogneiss biotite and muscovite, the low-temperature orthogneiss-derived melts are also  
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7 792 expected to be enriched in Cs, Be, W, Nb, Ta and Sn.  
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10 793 Therefore, the role of the protolith, especially the remelting of peraluminous granite  
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12 794 along with further fractional crystallization, appears critical for the generation of Li-F-rich  
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15 795 peraluminous granitic melts and RMGPs in general. This highlights the key role played by  
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17 796 crustal recycling processes and tectonic-magmatic inheritance on the rare-metal fertility of a  
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20 797 given crust segment.  
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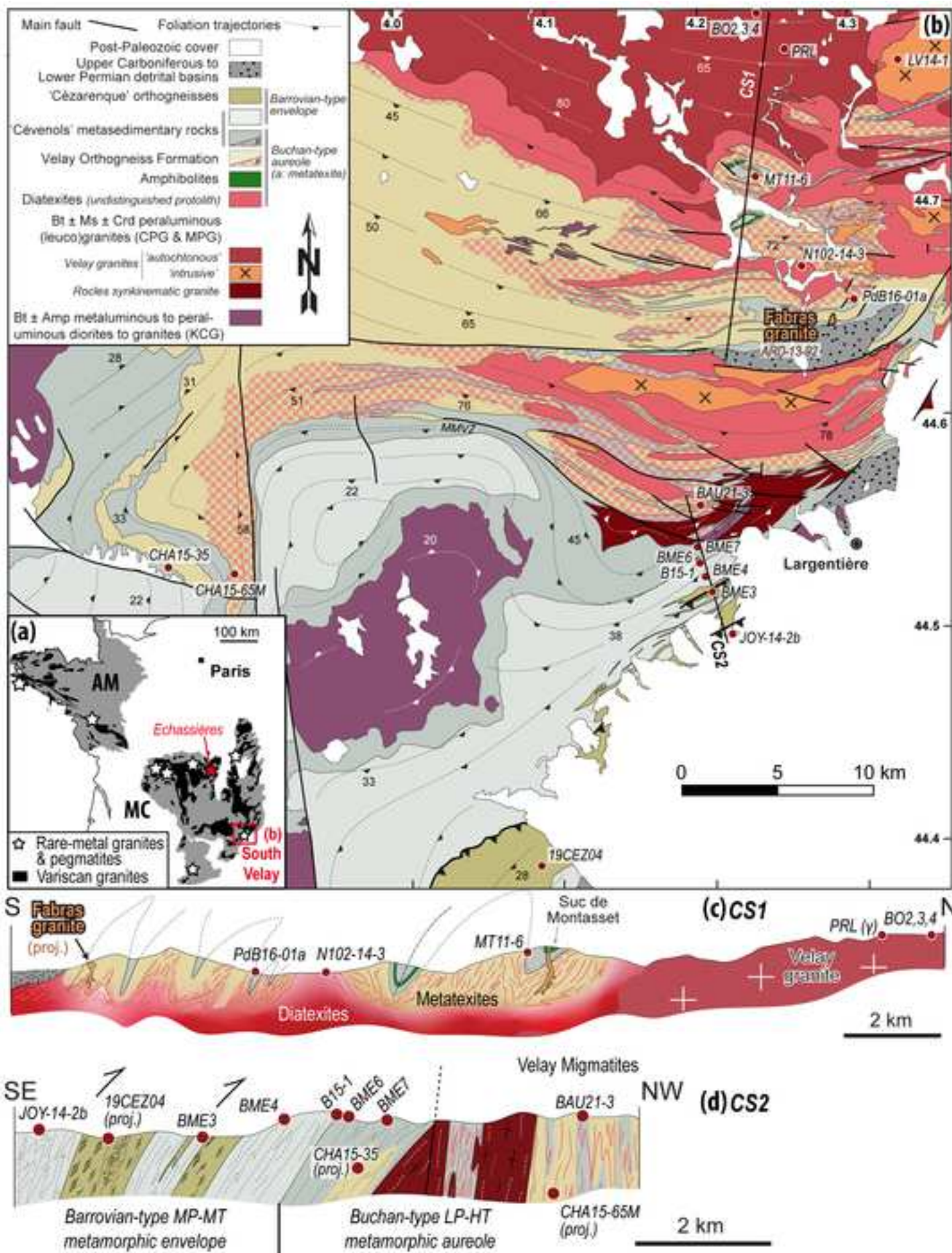
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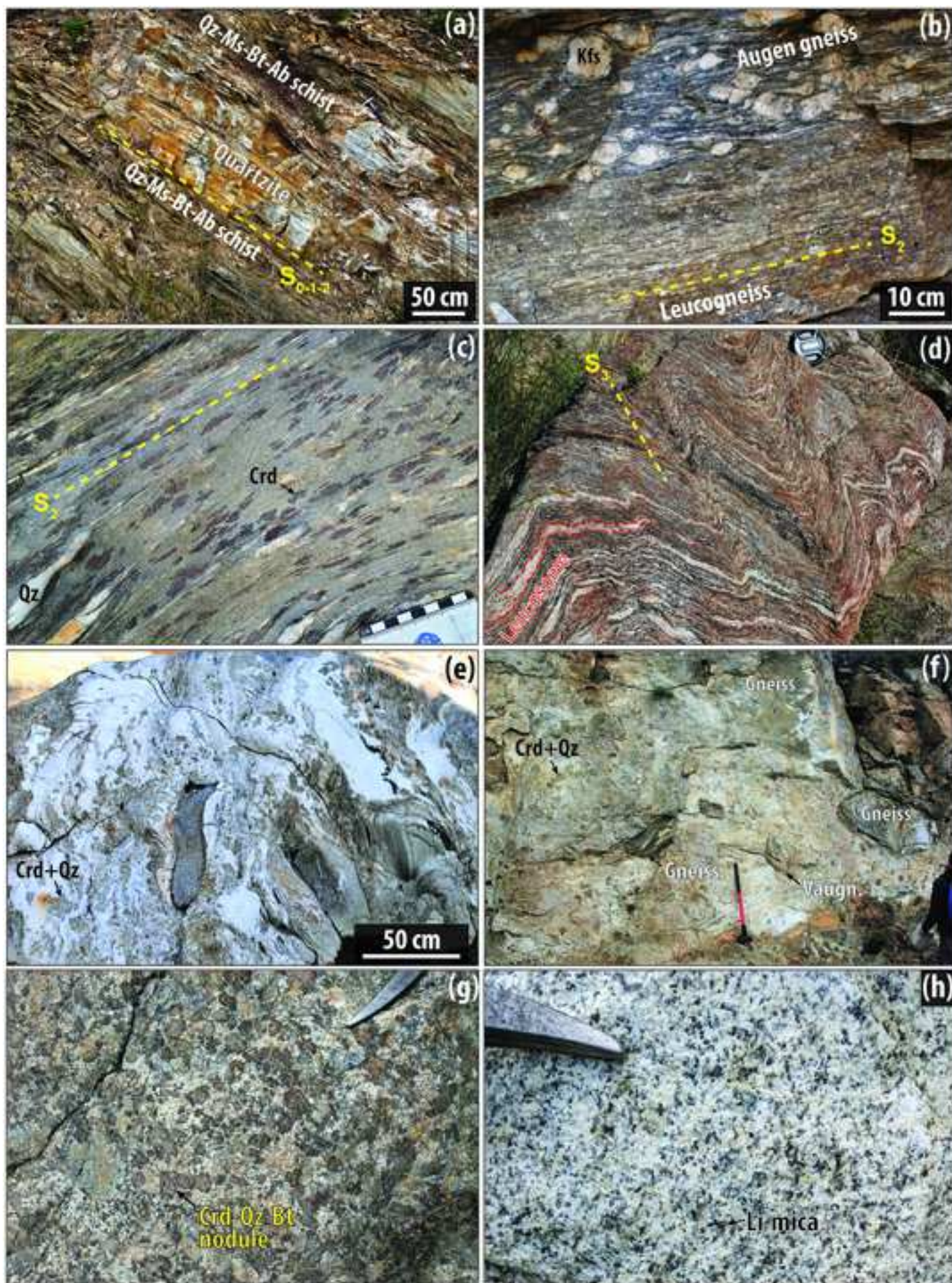
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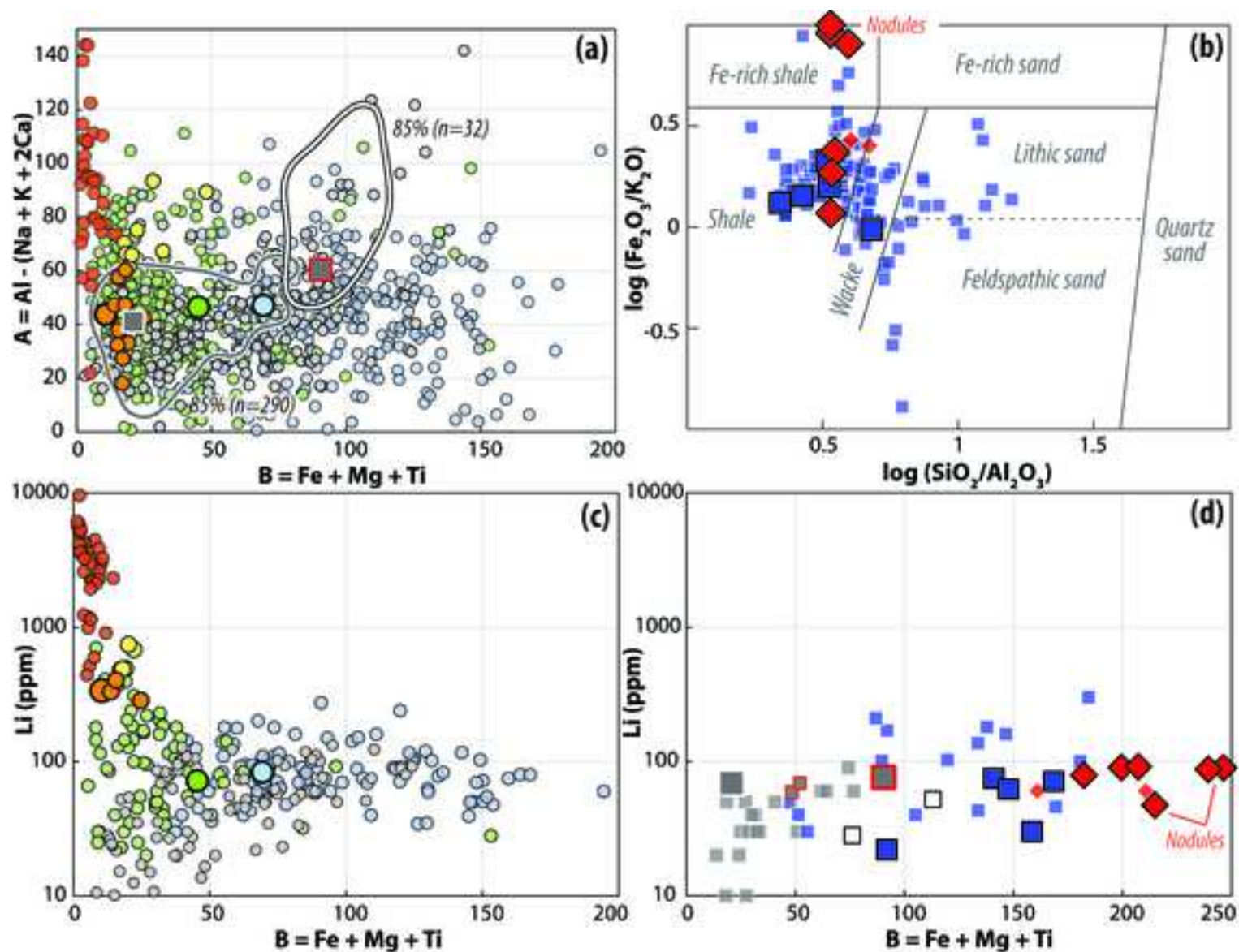
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*Eastern Massif Central (Velay area)*

● Muscovite-bearing peraluminous granites (MPG)

○ Cordierite-bearing peraluminous granites (CPG)

○ ■ Cadomian orthogneiss (■ *anatectic*) ○ □ Ordovician augen gneiss

● Fabras Li-mica-topaz-bearing peraluminous granite

○ Velay granites (undistinguished)

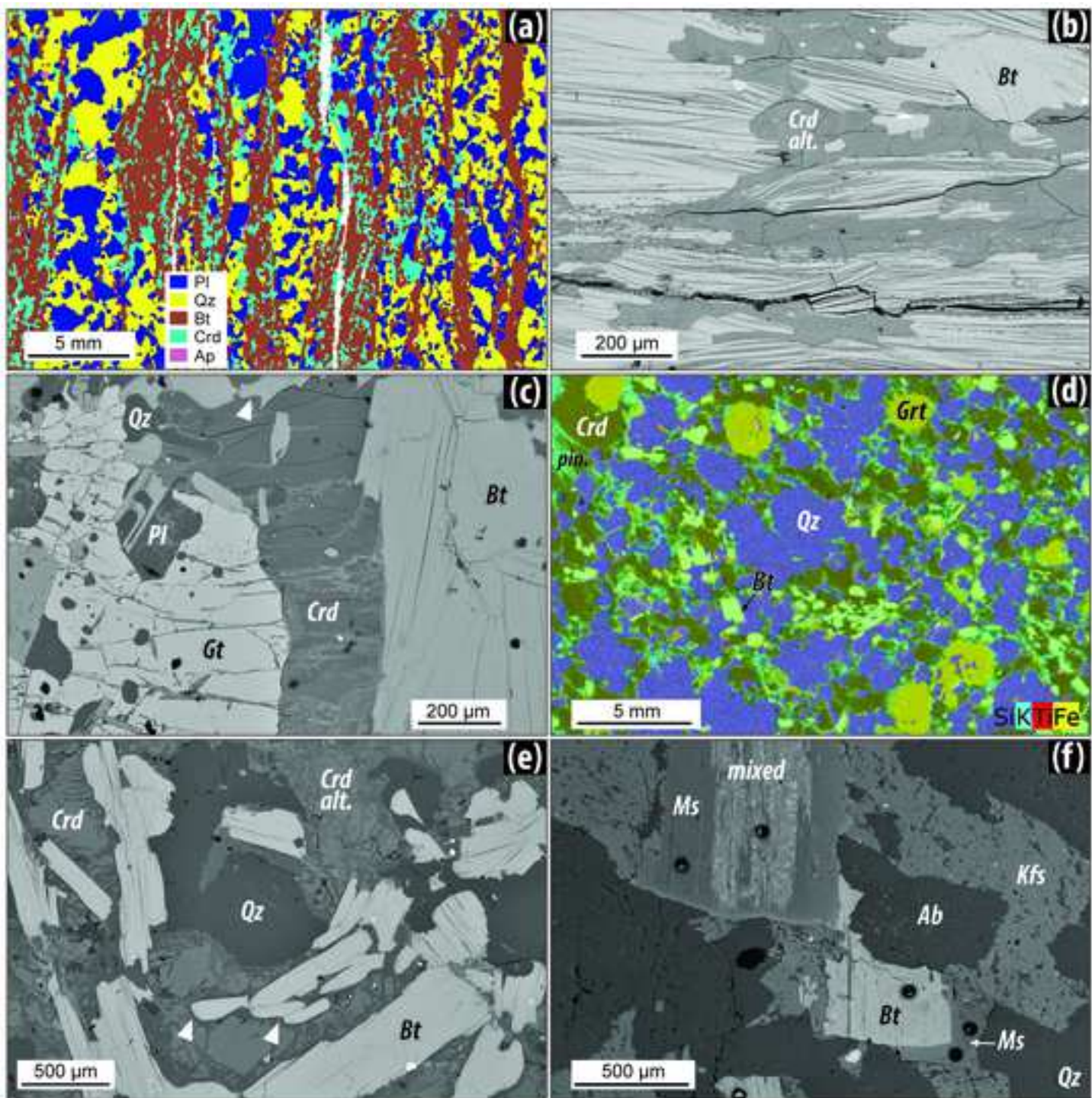
■ Metasediments (◆ *anatectic*)

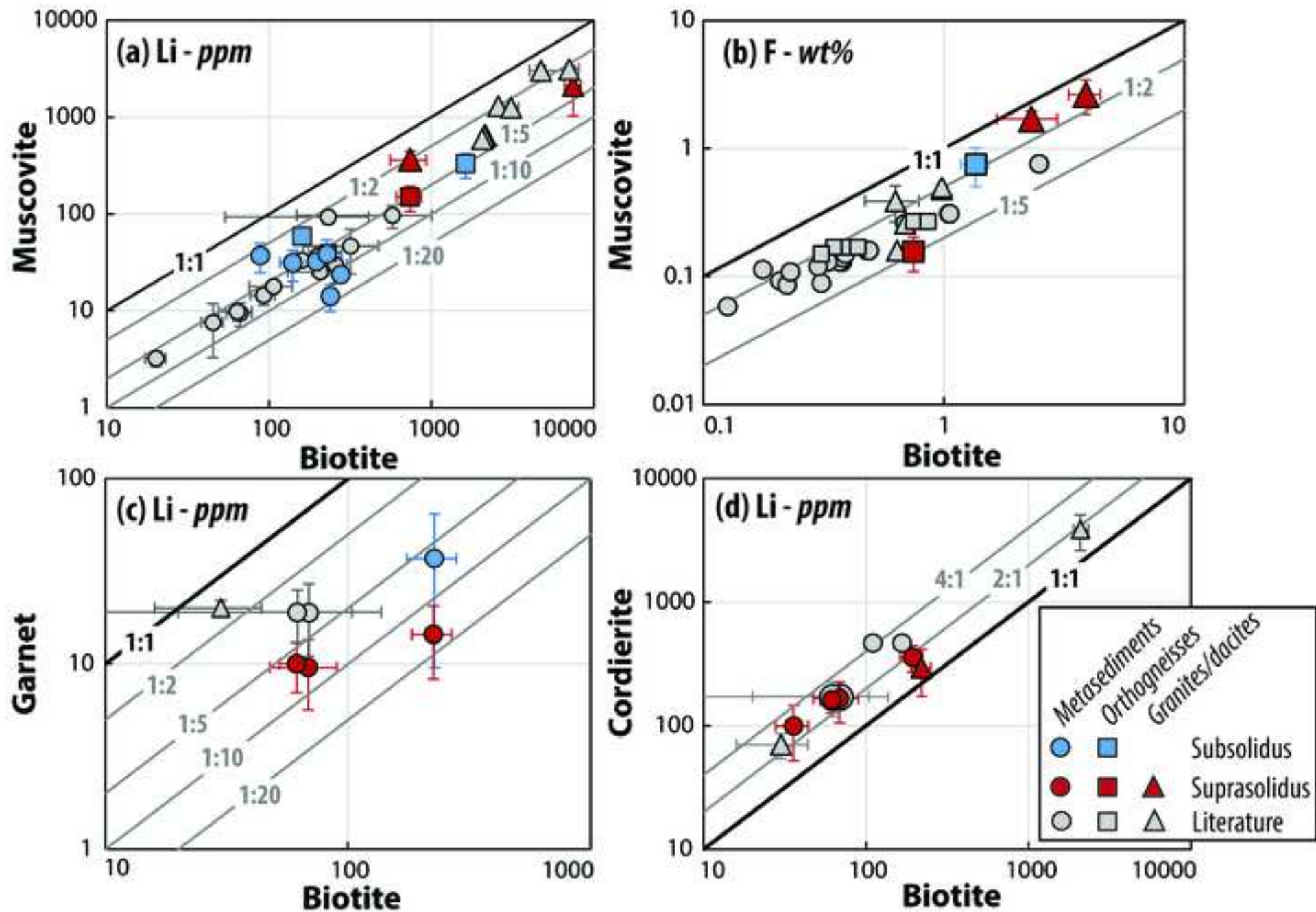
*Echassières district, northern Massif Central*

● Beauvoir lepidolite-bearing peraluminous rare-metal granite (RMG)

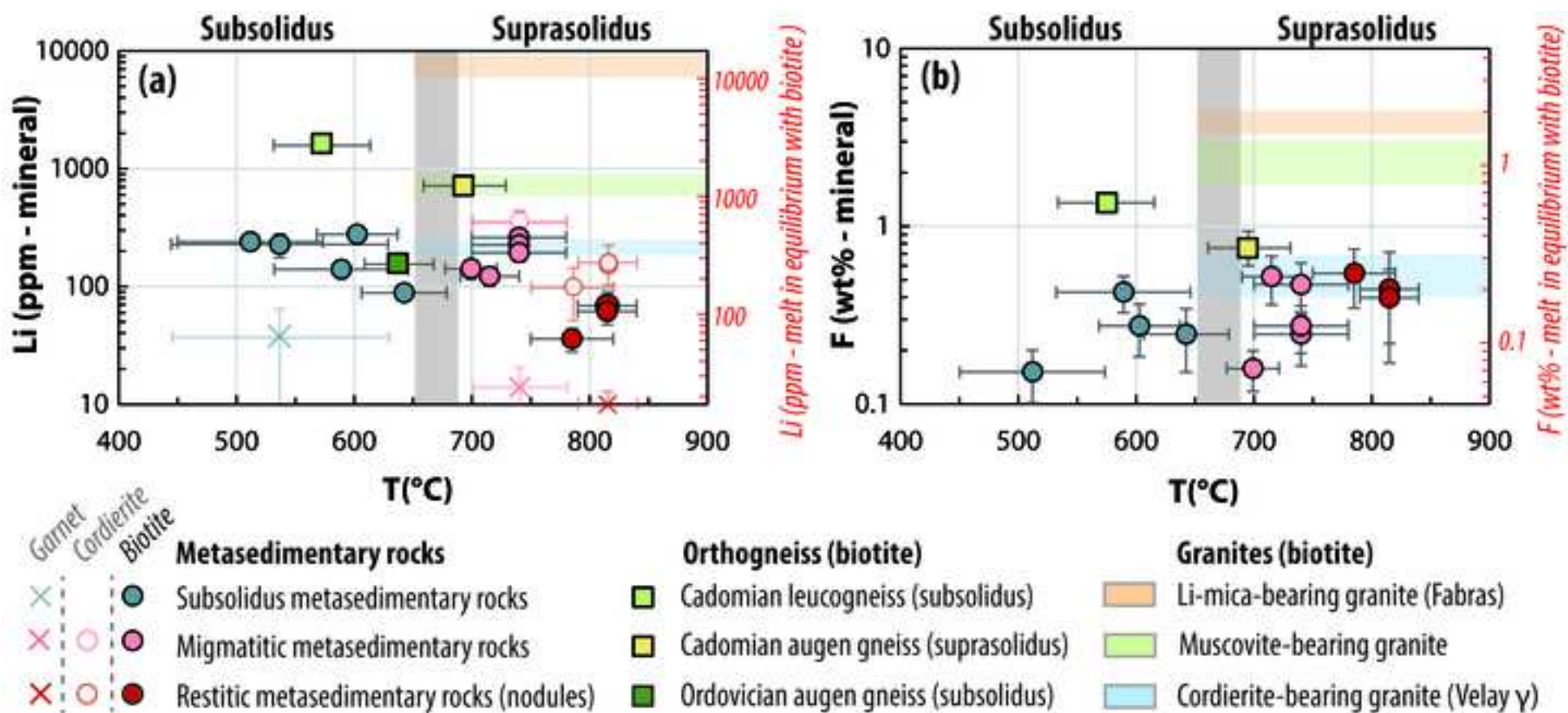
● Colettes Li-mica-bearing peraluminous granite

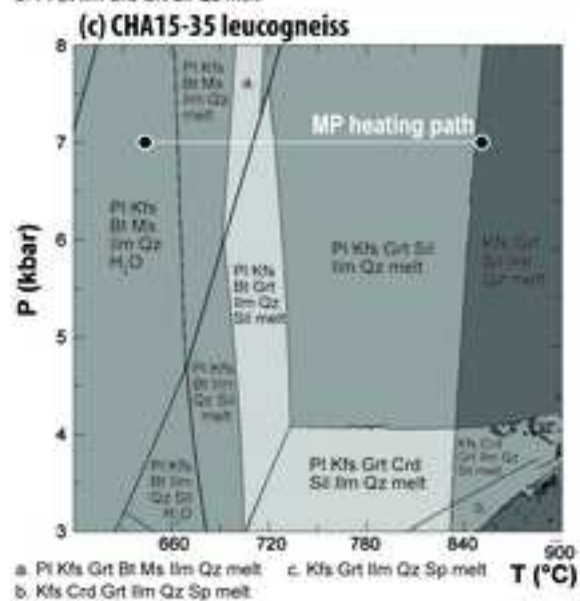
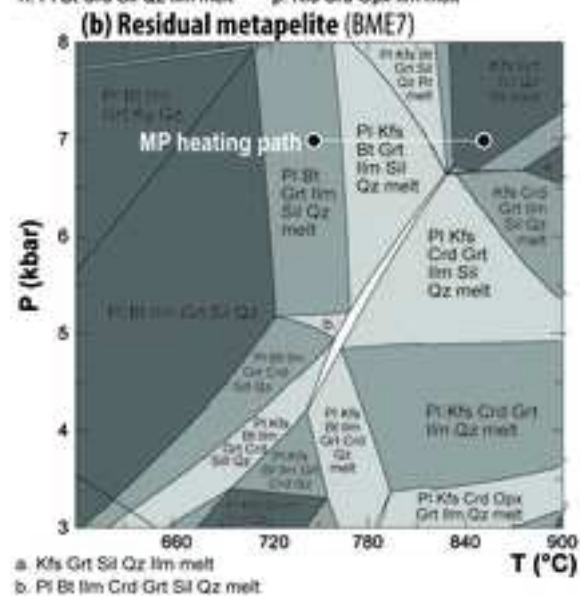
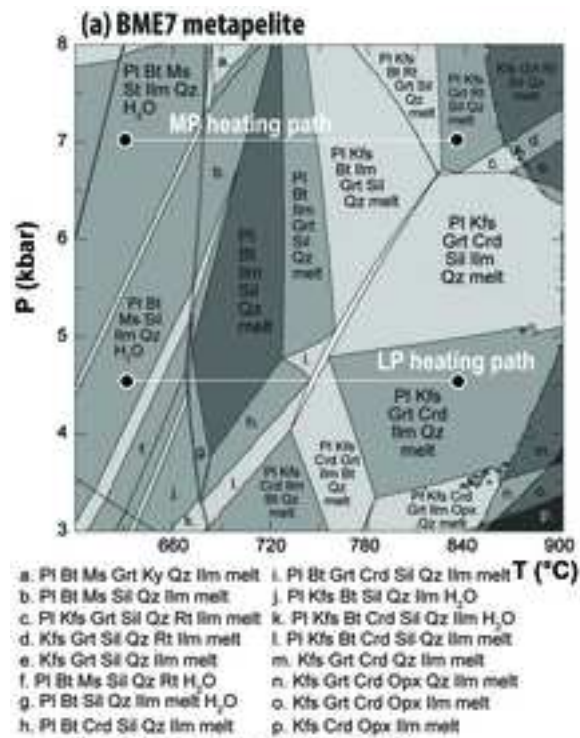


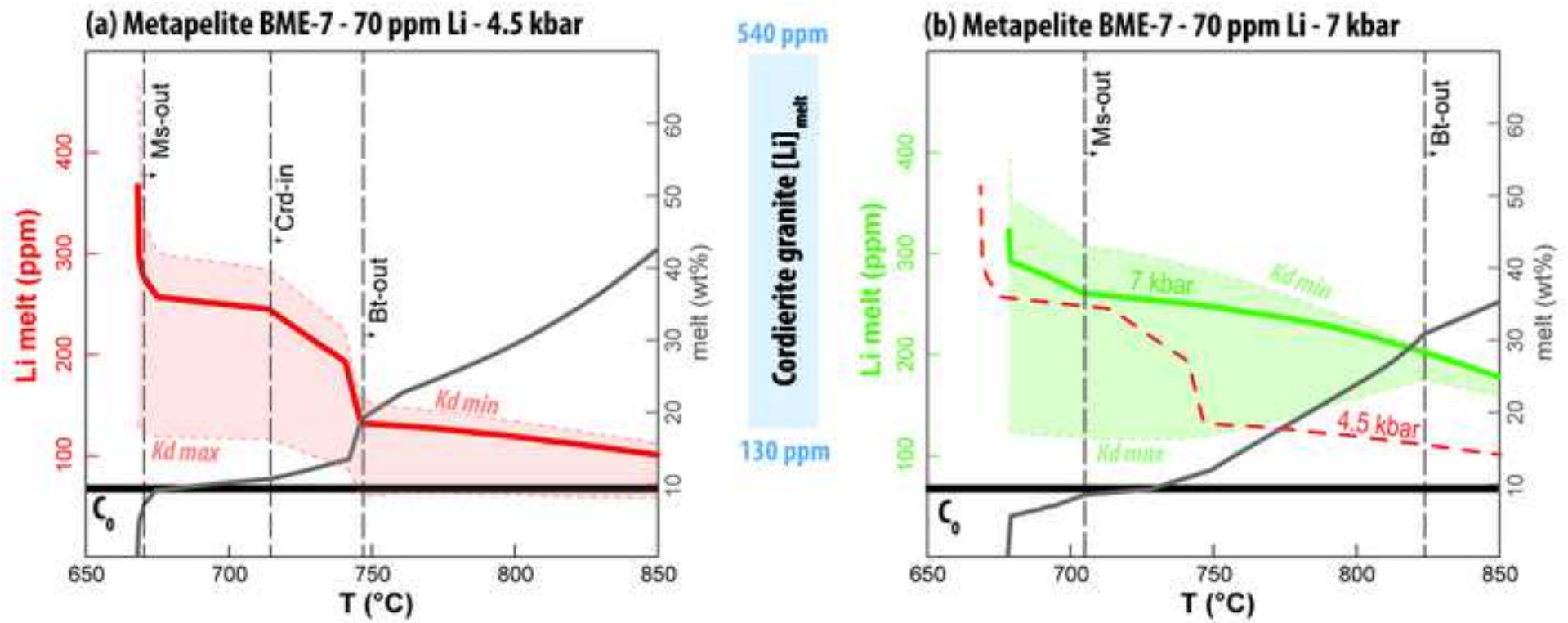


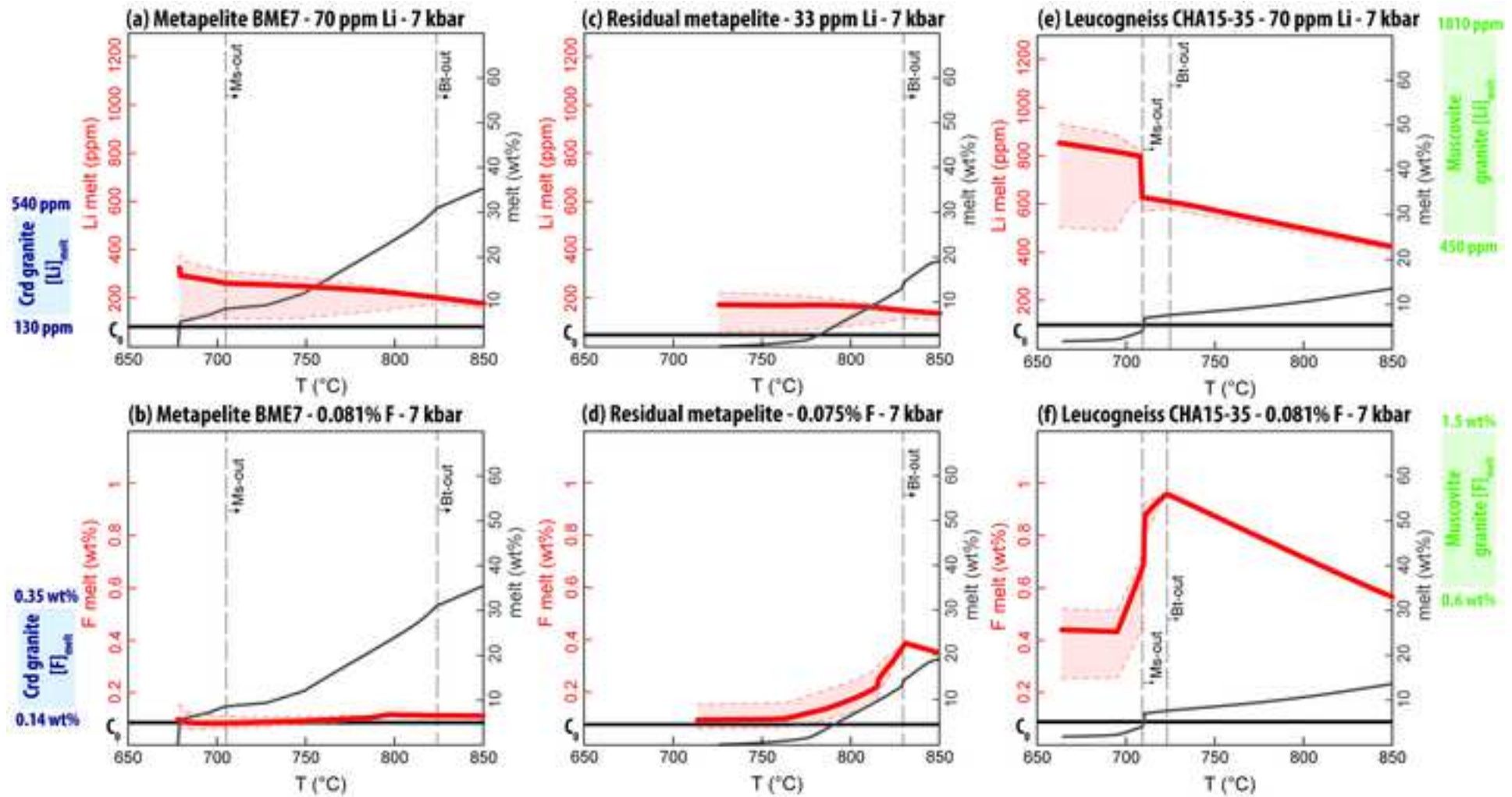




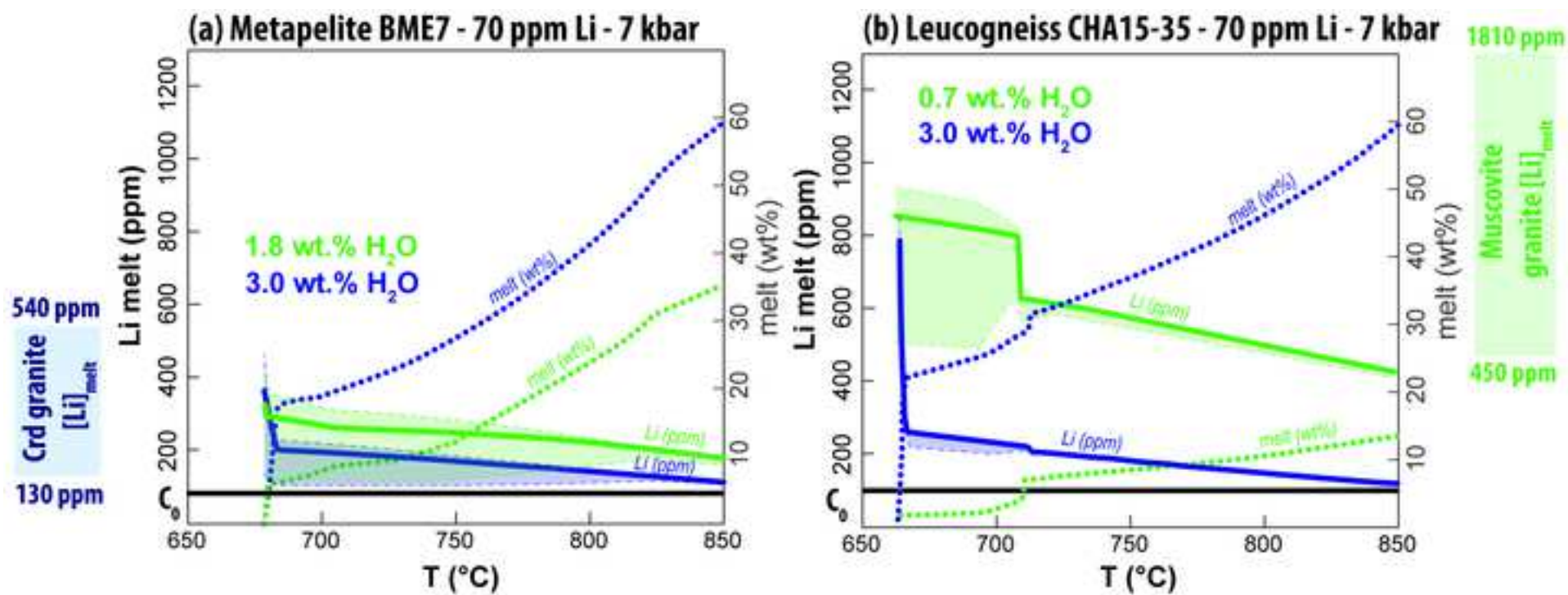




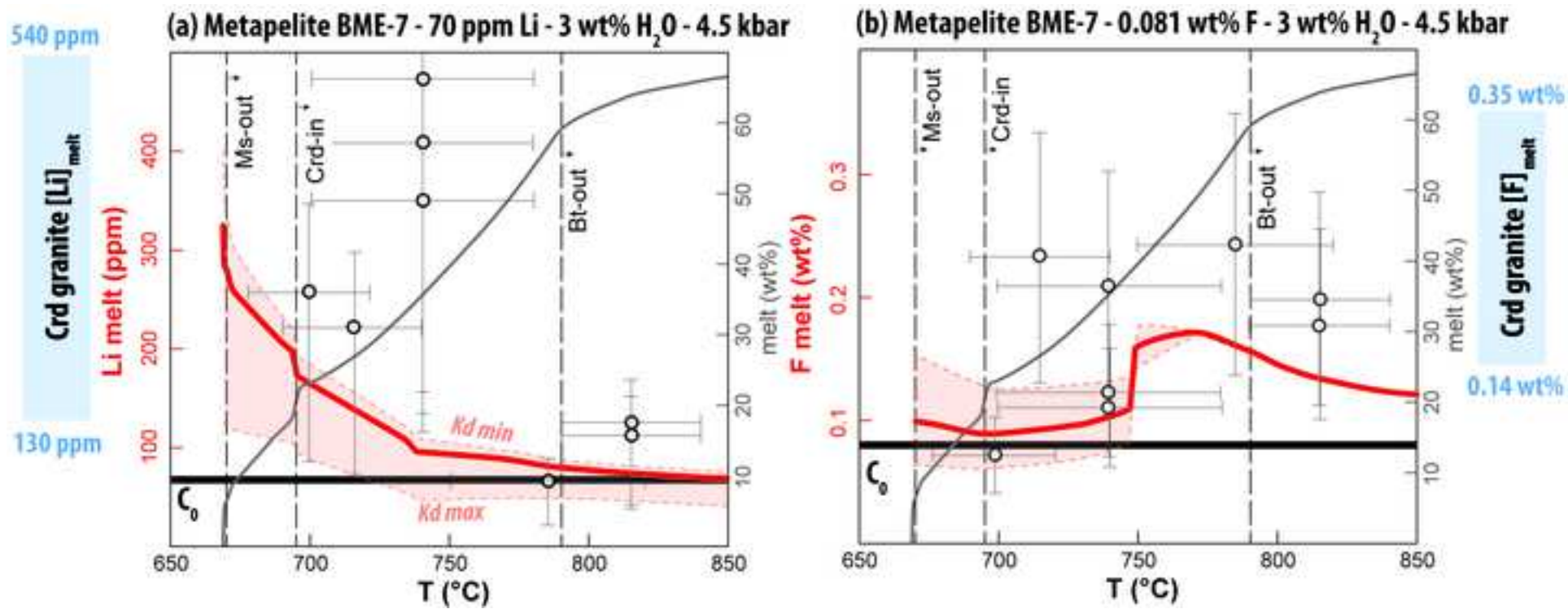


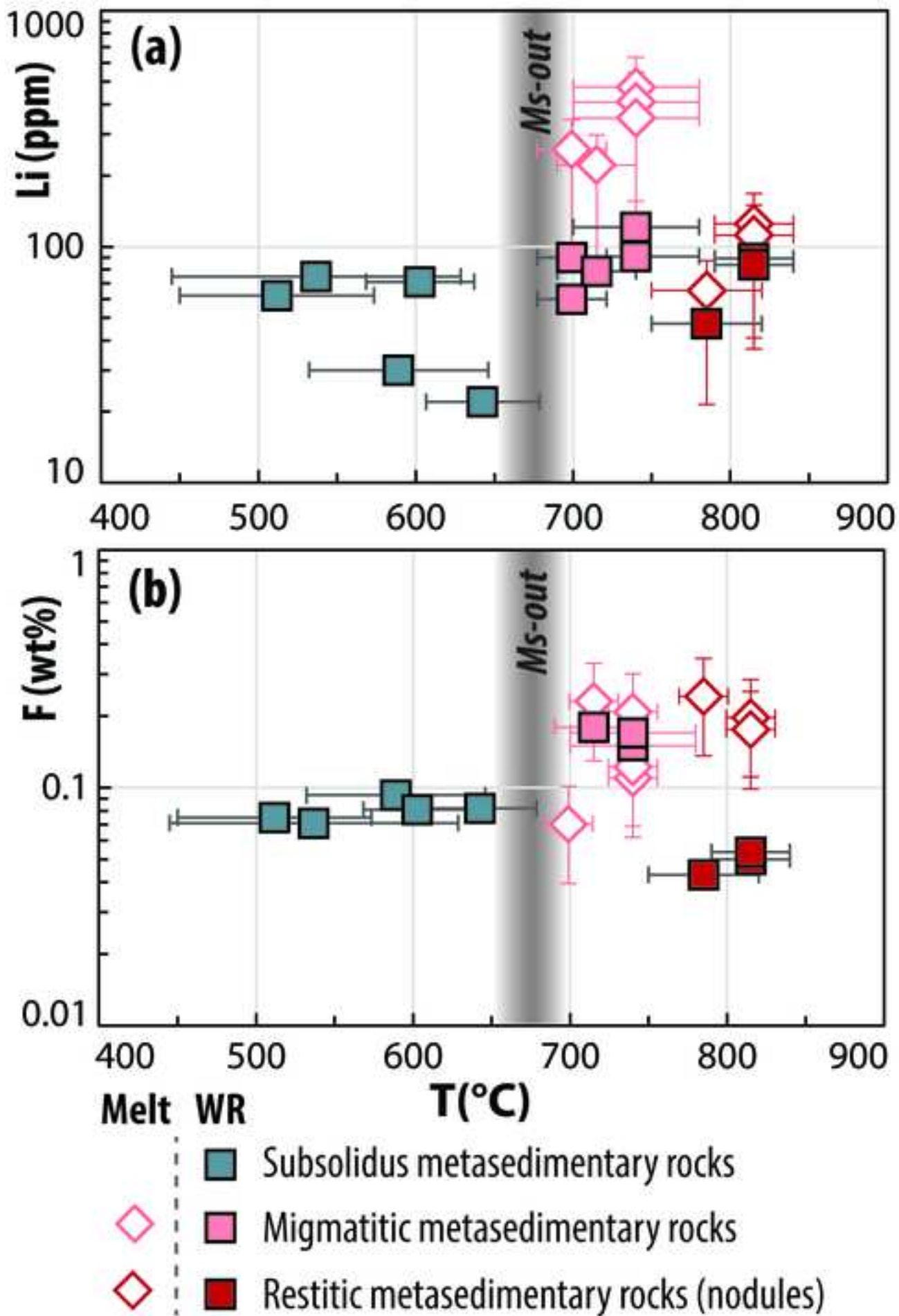


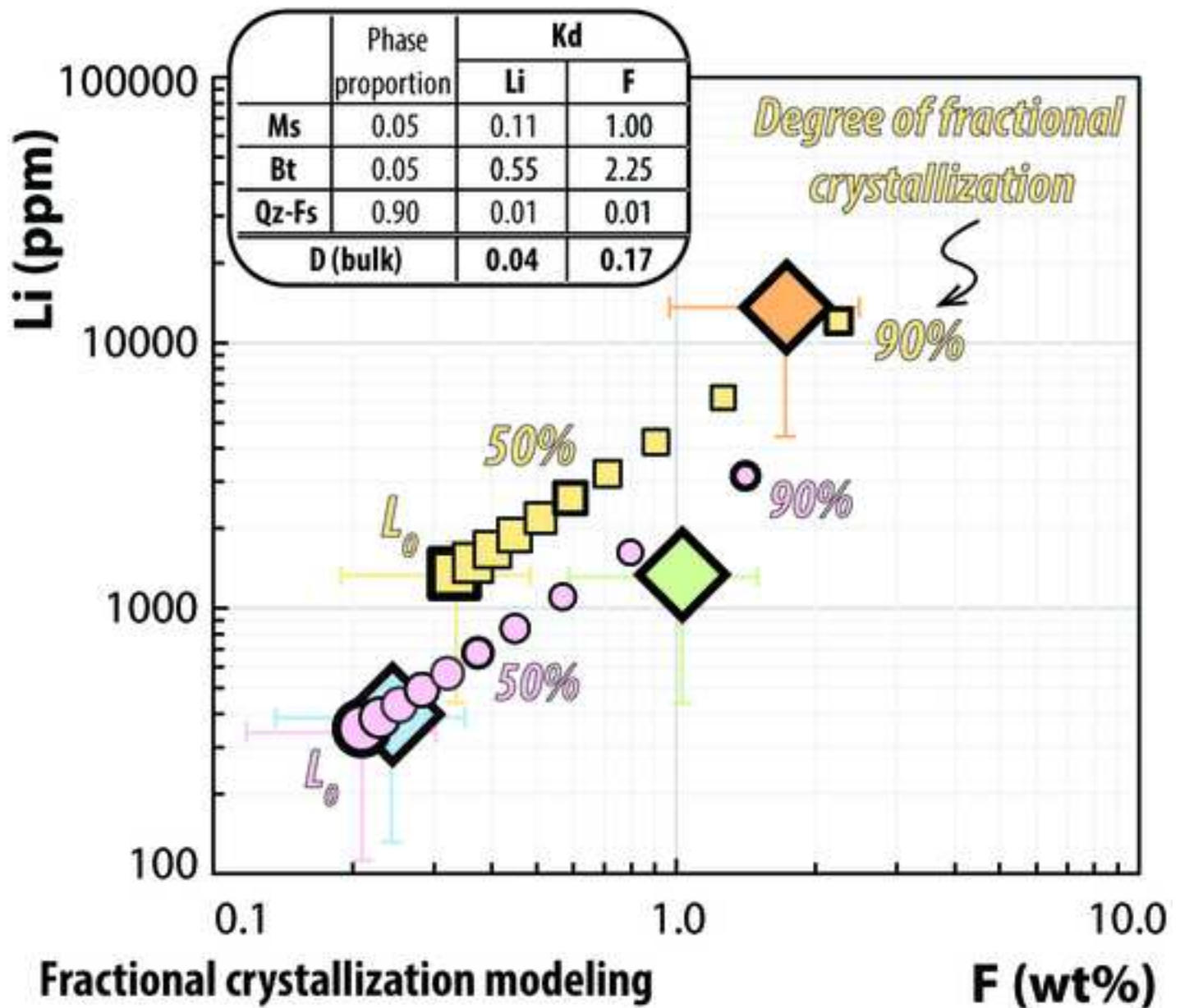












**Starting liquid ( $L_0$ )**

■ Suprasolidus augen gneiss : CHA15-65 (melt in equilibrium with Bt)

● Suprasolidus metapelite: N102-14-3 (melt in equilibrium with Bt)

**Granites: melt in equilibrium with Bt**

◆ Li-mica-bearing granite (Fabras)    ◆ Muscovite-bearing granite

◆ Cordierite-bearing granite

**Table 1** Summary of P–T estimates obtained for the migmatites investigated in this study.

Sample	Ti-in-Bt (H05)	Ti-in-Bt ; $4.5 \pm 1.0$ kbar (W15)	Na-in-Crd (T18); GASP (H01)	Grt-Bt (H00); GASP (H01)	Grt-Crd (B93); GASP (H01)	Pseudosection analysis
PdB16-01a	699±22°C; n=16	647±53°C; n=16	-	-	-	-
MT11-6	704±29°C; n=37	669±58°C; n=37	-	-	-	700-770°C < 4.6 kbar
BAU21-3a	695±25°C; n=40	647±51°C; n=40	-	-	-	-
BAU21-3b	711±50°C; n=27	689±61°C; N=27	-	736°C 5.4 kbar	-	700-780°C > 5 kbar
N102-14-3	717±7°C; n=15	711±22°C; n=15	-	-	-	690-780°C < 4.5 kbar
BO2	732±23°C; n=30	747±66°C; n=30	760±20°C; n=12 > 4.4 kbar	739°C > 4.2 kbar	753°C > 4.3	790-835°C 4-5 kbar
BO3	736±20°C; n=18	744±42°C; n=18	761±19; n=17 > 4.7 kbar	723°C > 4 kbar	755°C > 4.5 kbar	790-835°C 4-5 kbar
BO4	733±26°C; n=19	727±51°C; n=18	758±28°C; n=15 -	-	-	750-820°C 4-5 kbar

H05 and W15 refer to the Ti-in-biotite thermometers of [Henry et al. \(2005\)](#) and [Wu and Chen \(2015\)](#), respectively. The italic values represent pressures calculated via the GASP barometer ([Holdaway 2001](#)) at temperatures obtained by Na-in-cordierite ([Tropper et al. 2018](#)), Grt-Bt ([Holdaway 2000](#)) and Grt-Crd ([Bhattacharya 1993](#)) thermometers. Uncertainties are two standard deviations. GASP barometry along with Grt-Bt and Grt-Crd thermometry relied on average mineral compositions calculated for each sample, as all minerals were chemically unzoned. When sillimanite is absent from the mineral assemblage, the calculated value represents a minimal pressure.

**Table 2** Mineral-mineral partitioning data of Li and F for Velay samples.

Sample	Li						F					
	$Kd^{Bv/Ms}$	$2\sigma$ (+)	$2\sigma$ (-)	$Kd^{Crd/Bt}$	$2\sigma$ (+)	$2\sigma$ (-)	$Kd^{Bv/Grt}$	$2\sigma$ (+)	$2\sigma$ (-)	$Kd^{Bv/Ms}$	$2\sigma$ (+)	$2\sigma$ (-)
<i>Subsolidus metasedimentary rock</i>												
BME4	4.5	3.6	1.7	-	-	-	-	-	-	-	-	-
JOY14-2b	5.9	6.2	2.7	-	-	-	6.2	23.2	3.4	-	-	-
B15-1	2.4	1.5	0.8	-	-	-	-	-	-	-	-	-
BME6	16.9	9.3	5.0	-	-	-	-	-	-	-	-	-
BME7	11.7	3.7	2.6	-	-	-	-	-	-	-	-	-
<i>Subsolidus Ordovician orthogneiss</i>												
19CEZ04	2.7	0.9	0.6	-	-	-	-	-	-	-	-	-
<i>Subsolidus Cadomian orthogneiss</i>												
CHA15-35	5.0	2.8	1.5	-	-	-	-	-	-	1.8	1.3	0.6
<i>Suprasolidus metasedimentary rock</i>												
BAU21-3b	-	-	-	-	-	-	15.7	16.7	6.7	-	-	-
N102-14-3	-	-	-	1.8	0.9	0.6	-	-	-	-	-	-
B02	-	-	-	2.4	2.4	1.2	7.2	8.8	3.7	-	-	-
B04	-	-	-	2.8	2.5	1.6	-	-	-	-	-	-
B03	-	-	-	2.6	1.1	0.8	6.1	4.0	2.1	-	-	-
<i>Suprasolidus Cadomian orthogneiss</i>												
CHA15-65M	5.0	3.3	1.8	-	-	-	-	-	-	4.8	2.8	1.5
<i>Cordierite-bearing granite</i>												
PRL	-	-	-	1.3	0.9	0.6	-	-	-	-	-	-
<i>Muscovite-bearing granite</i>												
LV14-01	2.1	1.3	0.8	-	-	-	-	-	-	1.4	0.7	0.5
<i>Li-mica-bearing granite</i>												
ARD13-92a	3.6	4.5	1.5	-	-	-	-	-	-	1.5	1.0	0.5

**Table 3** Partitioning data for Li and F used for partial melting models.

	Li			F		
	<i>Min</i>	<i>Pref</i>	<i>Max</i>	<i>Min</i>	<i>Pref</i>	<i>Max</i>
Kd <sub>Bt/melt</sub>	0.41 <sup>a</sup>	0.55 <sup>a</sup>	1.67 <sup>a</sup>	1.56 <sup>a</sup>	2.25 <sup>a</sup>	4.00 <sup>a</sup>
Kd <sub>Crd/Bt</sub>	-	2.00 <sup>b</sup>	-	-	-	-
Kd <sub>Bt/Grt</sub>	-	6.00 <sup>b</sup>	-	-	-	-
Kd <sub>Bt/Ms</sub>	-	5.00 <sup>b</sup>	-	-	-	-
Kd <sub>Crd/melt</sub>	0.82 <sup>c</sup>	1.10 <sup>c</sup>	3.34 <sup>c</sup>	0.01 <sup>d</sup>	0.01 <sup>d</sup>	0.01 <sup>d</sup>
Kd <sub>Grt/melt</sub>	0.07 <sup>c</sup>	0.09 <sup>c</sup>	0.28 <sup>c</sup>	0.01 <sup>d</sup>	0.01 <sup>d</sup>	0.01 <sup>d</sup>
Kd <sub>Ms/melt</sub>	0.08 <sup>c</sup>	0.11 <sup>c</sup>	0.33 <sup>c</sup>	0.94 <sup>a</sup>	1.00 <sup>a</sup>	1.92 <sup>a</sup>

Pref: preferred; a: experimental Kd data compiled by [Villaro and Pichavant \(2019\)](#); b: values based on Velay rock samples (this study); c:

values calculated using experimental Kd<sub>Bt/melt</sub> and Velay rock Kd mineral/mineral values; d: assumed values. The Kd of all other minerals

was fixed to 0.01.