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Matthieu Harlaux, Julien Mercadier, Christian Marignac, Michel Cuney, Wilédio Bonzi, et al.. Geochemical signature of rare-metal magmatic fluids exsolved from the Beauvoir granite (Massif Central, France) revealed by LA-ICPMS analysis of primary fluid inclusions. 14th SGA Biennial Meeting, Aug 2017, Quebec, Canada. hal-01668914

HAL Id: hal-01668914

<https://hal.science/hal-01668914v1>

Submitted on 20 Dec 2017

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Geochemical signature of rare-metal magmatic fluids exsolved from the Beauvoir granite (Massif Central, France) revealed by LA-ICPMS analysis of primary fluid inclusions

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Abstract. The Beauvoir granite (Limousin, French Massif Central) represents an exceptional case in the European Variscan belt of a peraluminous rare-metal granite crosscutting an early W stockwork. The latter was strongly overprinted by the rare-metal magmatic-hydrothermal fluids derived from the Beauvoir granite, resulting in a massive topazification. This work presents a complete study of primary fluid inclusions hosted in quartz and topaz from the Beauvoir granite and the metasomatized stockwork in order to characterize the geochemical composition of the early magmatic fluids exsolved during the crystallization of this highly evolved rare-metal granite. Microthermometric data show that the earliest fluid (L1) is high temperature (500 to >600°C), saline (17-28 wt.% NaCl eq) and Li-rich (Te<70°C). LA-ICPMS analyses of fluid inclusions show that its chemical composition is dominated by Li, Na, K, Cs, Sn, and Rb as major elements, with significant concentrations (10²-10³ ppm) of Nb, W and Ta. These results demonstrate that primary fluid inclusions preserved the pristine signature of the magmatic fluids in the Beauvoir granite, but also in the metasomatized W stockwork despite the distance from the granitic cupola (>100 m) and interaction with external fluids.

1 Introduction

Rare-metal deposits are mainly associated with peraluminous to peralkaline granites and pegmatites, which represent major economic resources for strategic elements such as Li, Be, Nb, Ta, Sn, W and REE (Linnen and Cuney 2005; Linnen et al. 2012). The European Variscan belt represents an important metallogenic province for rare-metal granites and pegmatites, which are located mainly in the Bohemian Massif, the Iberian Massif, Cornwall, and the French Massif Central (FMC). These deposits formed during Carboniferous to Permian times between 330 and 280 Ma in relation with the late-Variscan orogenic evolution (Chen et al. 1993; Marignac and Cuney 1999; Cuney et al. 2002; Melleton et al. 2012, 2015). In France, the Beauvoir granite represents one of the best examples of a peraluminous high phosphorus rare-metal granite (Černý et al. 2005) and was intensively studied during the 1980s-1990s, with a 900 m of continuous core drilling GPF1 from the “Géologie Profonde de la France” program (Cuney and Autran 1987).

In this study, we present a complete study of primary fluid inclusions hosted in quartz and topaz crystals from

the Beauvoir granite and the metasomatized stockwork with three main objectives: (i) to characterize the geochemical composition of the early rare-metal-rich magmatic fluids exsolved during the crystallization of the Beauvoir granite; (ii) to study the partitioning of elements between the co-existing volatile and brine phases during the magmatic-hydrothermal transition; and (iii) to determine the geochemical evolution of the magmatic fluids during their ascent and their interaction with the enclosing micaschists with distance from the granitic cupola.

2 Geological setting

The Beauvoir granite is located in the Echassières granitic complex in the NE part of the FMC in the Limousin area, which consists of a stack of metamorphic nappes emplaced during the Variscan orogeny during the Upper Paleozoic (Faure et al. 2009). The Echassières complex includes an early W-bearing quartz-vein system, the so-called La Bosse stockwork, and is composed of at least three successive granitic units that intruded into the micaschists of the Para-Autochthonous Unit (Cuney et al. 1992; Raimbault et al. 1995). From oldest to youngest, these granitic units are: (i) the La Bosse granite, which is concealed at depth and is presumed to be related to the formation of the W deposit; (ii) the Colettes granite, which is a porphyritic biotite-muscovite-cordierite granite that overprints the La Bosse stockwork; and (iii) the Beauvoir granite, which crosscuts the Colettes granite and consists of a topaz-lepidolite-albite granite with disseminated Sn, Li, Ta, Nb and Be mineralization, corresponding to accessory minerals of cassiterite, columbite-tantalite, lepidolite and Li-Be-phosphates.

The latter is characterized by a vertical internal zoning marked by the succession of three granitic units (B3, B2, B1) emplaced successively, which present a magmatic foliation underlined by lepidolite and show a progressive magmatic differentiation upwards (Cuney et al. 1992; Raimbault et al. 1995). The emplacement of the Beauvoir granite has been dated at 308 ± 2 Ma (⁴⁰Ar-³⁹Ar on lepidolite; Cheilletz et al. 1992). However, a recent U-Pb dating of columbite-tantalite yielded an age of 317 ± 6 Ma (Melleton et al. 2015), which is significantly older than the

previous age. Considering that no late, high-temperature hydrothermal alteration event is recorded at Echassières (Merceron et al. 1992), the age obtained on lepidolite is likely close to the magmatic emplacement age of the Beauvoir granite and does not represent a late, disturbed age. Thus, a possible emplacement age of 310 Ma for the Beauvoir granite seems consistent within uncertainty with the two existing U-Pb and ^{40}Ar - ^{39}Ar ages.

The La Bosse W stockwork consists in a network of up to 0.6 m-thick quartz-ferberite veins, which are hosted in the enclosing micaschists and have been dated at 334 ± 2 Ma (U-Pb on wolframite; Harlaux et al. 2017). The stockwork outcrops about 100 m above the Beauvoir granite contact and several 100 metres laterally from the cupola. It was strongly overprinted by the magmatic fluids derived from the Beauvoir granite, resulting in massive topazification of the vein system, partial dissolution of quartz, and crystallization of late Li-micas and Nb-Ta-oxides (Aïssa et al. 1987a).

3 Fluid inclusion study

Samples from the Beauvoir granite (B1 facies) and the metasomatized La Bosse stockwork were studied. Double-polished thick sections (150-200 μm) were prepared for the study of fluid inclusions in quartz and topaz. All analyses were performed at the GeoRessources laboratory (Université de Lorraine, Vandoeuvre-lès-Nancy, France).

3.1 Petrography and microthermometry of fluid inclusions

In the Beauvoir granite and La Bosse stockwork, quartz and topaz crystals contain numerous fluid inclusions, found as dense clouds of disseminated individual or clustered inclusions. This represents a severe limitation for the identification of different generations of fluid inclusions based on criteria of relative position or arrangement. Nevertheless, three main types of fluid inclusions can be distinguished in quartz and topaz based on petrography and microthermometry results (Fig. 1):

(i) *L1-type fluid inclusions*: these consist of multi-phase fluid inclusions with a dominant aqueous phase containing a vapour bubble (~40%) and small isotropic cubic solids, interpreted as halite. The fluid inclusions have irregular shapes, and range in size from 10 to 23 μm , typically. They are characterized by very low eutectic temperatures ($T_e < -70^\circ\text{C}$) and low ice-melting temperatures ($-40^\circ\text{C} < T_{m_{\text{ice}}} < -2^\circ\text{C}$). Halite melting occurred between 275 and 300°C , before total homogenization by vapour disappearance. In the Beauvoir granite, homogenization occurs to the liquid phase at temperatures from 491 to 600°C , with an average value of 542°C . They are lower in the La Bosse stockwork, where they range from 377 to 468°C , with an average value of 422°C . Estimated salinities range from 16.7 to 28.1 wt.% NaCl eq in the Beauvoir granite and from 27 to 28.7 wt.% NaCl eq in the La Bosse stockwork.

(ii) *L2-type fluid inclusions*: these comprise multi-phase fluid inclusions composed of a dominant aqueous phase with a small vapour phase (~30%) and contain multiple cubic crystals of salts, including halite. These fluid inclusions are characterized by irregular to regular shapes and have sizes between 10 and 35 μm . They have very low eutectic temperatures ($-80^\circ\text{C} < T_e < -52^\circ\text{C}$) and low ice-melting temperatures ($-42^\circ\text{C} < T_{m_{\text{ice}}} < -1.6^\circ\text{C}$). Halite melting occurred consistently before total homogenization at temperatures between 215 and 407°C , with average values of 359°C in the Beauvoir granite and 286°C in the La Bosse stockwork. Bulk homogenization occurs to the liquid phase at temperatures ranging from 377 to 542°C in the Beauvoir granite (average: 455°C), whereas they range from 305 to 439°C in the La Bosse stockwork (average: 375°C). Estimated salinities are between 32.6 and 48.2 wt.% NaCl eq in the Beauvoir granite and between 36.7 and 40.4 wt.% NaCl eq in the La Bosse stockwork.

(iii) *V2-type fluid inclusions*: these consist of two-phase fluid inclusions and contain a dominant vapour phase (>80%) with a minor liquid phase. They comprise irregularly shaped fluid inclusions and range from 12 to 24 μm in size. They have very low eutectic temperatures ($T_e < -65^\circ\text{C}$) and low ice-melting temperatures ($-19^\circ\text{C} < T_{m_{\text{ice}}} < -1.4^\circ\text{C}$). They homogenize to the vapour phase at temperatures between 375 and 595°C in the Beauvoir granite (average: 465°C) and between 342 and 490°C in the La Bosse stockwork (average: 403°C). Estimated salinities range from 4.7 to 21.9 wt.% NaCl eq in the Beauvoir granite and from 1.4 to 9.2 wt.% NaCl eq in the La Bosse stockwork.

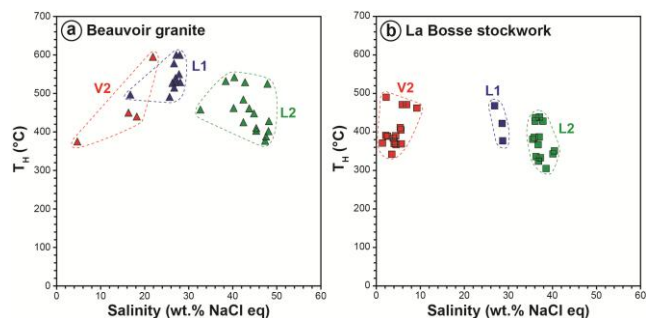


Figure 1. Salinity vs T_H diagram for the different generations of fluid inclusions identified in the Beauvoir granite (a) and the La Bosse stockwork (b).

3.2 LA-ICPMS analyses of fluid inclusions

LA-ICPMS analyses were performed on selected fluid inclusions previously studied by microthermometry using an Agilent 7500c Q-ICPMS. An example of LA-ICPMS spectrum of an L1-type fluid inclusion from the Beauvoir granite is shown in Fig. 2. The fluid inclusion signal is ca. 56 s in length and shows high signal/background ratios (10^1 - 10^4) for most of the measured elements (Na, Sn, Cs, Mg, Fe, Li, W, Nb, Ta). The salinities of fluid inclusions were used to estimate the Na content for the quantification of the LA-ICPMS signals. Results of concentrations

determined by LA-ICPMS are shown on Fig. 3. In the Beauvoir granite, L1-type fluid inclusions are characterized by high concentrations in Na (10^5 ppm), Sn (1,100-38,000 ppm), Cs (22,000-76,000 ppm), K (3,200-42,000 ppm), Mn (9,000-30,000 ppm), Fe (12,000-17,000 ppm), Rb (4,000-14,000 ppm), Li (4,500-18,000 ppm) and minor concentrations in W (900-3,000 ppm), Nb (40-1,500 ppm) and Ta (18-180 ppm). The L2- and V2-type fluid inclusions have, respectively, higher and lower concentrations for most of the elements compared to the L1-type fluid inclusions, but within the same order of magnitude. In contrast, L1-, L2- and V2-type fluid inclusions from the La Bosse stockwork have generally lower concentrations compared to those from the Beauvoir granite, except for K, Mn, Fe and Sr, which have higher concentrations.

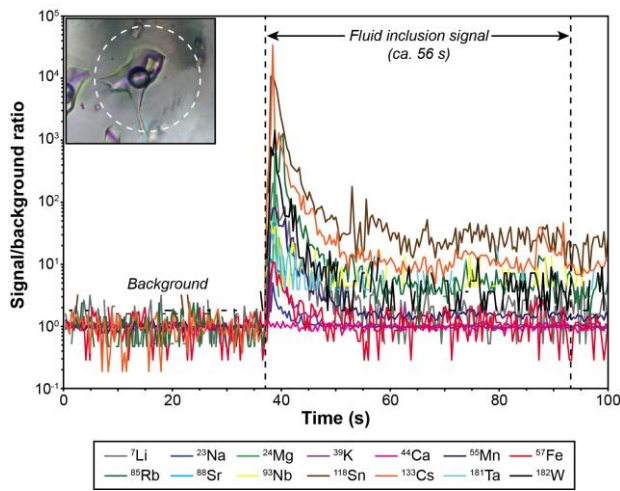


Figure 2. Typical LA-ICPMS spectrum of a primary magmatic L1-type fluid inclusion hosted in a globular quartz crystal from the Beauvoir granite. The ablated fluid inclusion (picture in inset) was 17 μm in size using a laser spot diameter of 32 μm (dashed white circle).

4 Discussion

The different types of fluid inclusions identified represent different generations of fluids trapped in primary quartz and topaz during the magmatic-hydrothermal transition of the Beauvoir granite. These data appear to be in good agreement with previously reported microthermometry results (Aïssa et al. 1987b; Cuney et al. 1992). L1-type fluid inclusions represent the earliest record of the primary fluid exsolved during the crystallization of the Beauvoir granite. Microthermometric data indicate that this fluid was high temperature (500 to $>600^\circ\text{C}$), saline (17-28 wt.% NaCl eq) and Li-rich ($T_e < -70^\circ\text{C}$). LA-ICPMS analyses reveal that the chemical composition of the L1 fluid is dominated by Li, Na, K, Cs, Sn, and Rb as major elements, and Nb, Ta, and W as minor elements. The Nb content is higher on average than the Ta content in the fluid ($\text{Nb}/\text{Ta} \sim 5$), which may indicate the higher hydrothermal mobility of Nb compared to Ta. Indeed, Nb is known to have precipitated during the topazification of the W

stockwork (Aïssa et al. 1987b). Ca was systematically below the limits of detection ($\text{LOD} \sim 3,000$ ppm) in the L1-type fluid inclusions, which indicates that its concentration was low in the primary fluid, in agreement with the low Ca content of the Beauvoir granite (Cuney et al. 1992; Raimbault et al. 1995). Moreover, the massive topazification overprinting the La Bosse stockwork at surface suggests that the L1 fluid contained high concentrations in F (not analyzed by LA-ICPMS), which is also known to efficiently increase the solubility of Nb and Ta in hydrothermal fluids (Zaraisky et al. 2010; Timofeev et al. 2015).

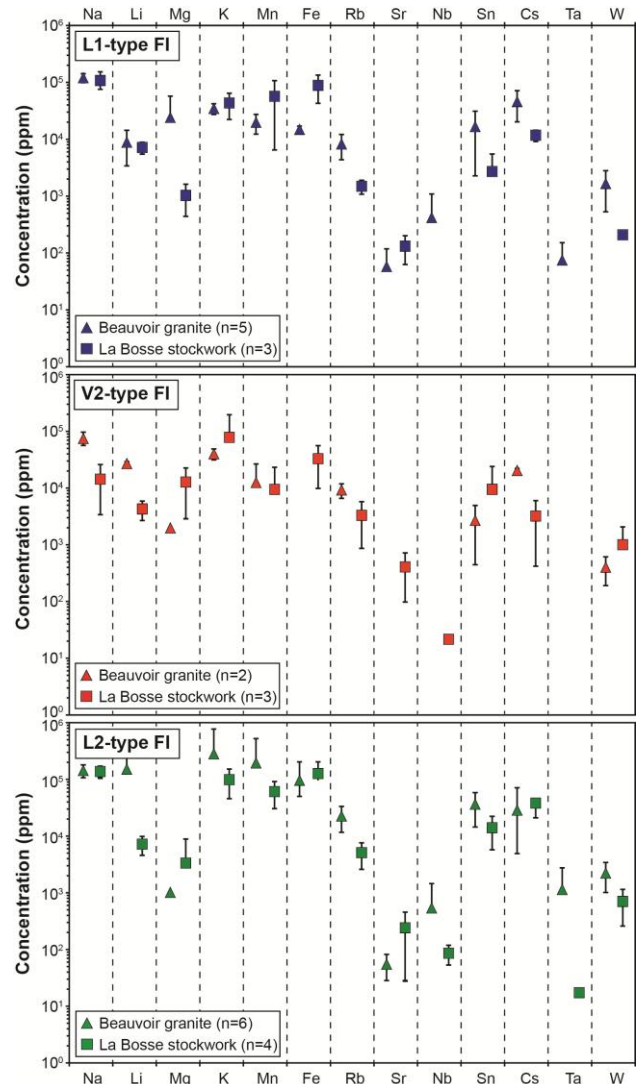


Figure 3. Minor and trace elements contents in L1-, V2- and L2-type fluid inclusions (FI) from the Beauvoir granite and the La Bosse stockwork determined by LA-ICPMS. The values represented correspond to the average and standard deviations of the concentrations determined.

Boiling of the primary L1 fluid yielded to the phase separation of a low- to moderate-salinity vapour (V2; 4.7-22 wt.% NaCl eq) and a high-salinity brine (L2; 32-48 wt.% NaCl eq) at ca. 450°C (Cuney et al. 1992). LA-ICPMS analyses of the co-existing V2- and L2-type fluid

inclusions revealed that the L2-fluid has the highest concentrations of metals and shows a preferential enrichment in most of the elements compared to the V2 fluid. This indicates that the majority of the elements partition preferentially into the aqueous phase in the Beauvoir granite. This behaviour is similar to the results of Audétat et al. (2000a,b) on the Mole granite (Australia), where most of the elements, including W, Sn, Na, K, Li and Cs, are partitioned preferentially into the brine phase.

The evolution of the exsolved magmatic fluids percolating through the enclosing micaschists with distance from the Beauvoir granite is characterized by a decrease in temperature (60–120°C) and salinity (3–10 wt.% NaCl eq), which can be interpreted in terms of cooling and thermal equilibration around the intrusion. The salinity decrease may indicate that the magmatic-hydrothermal fluids were more or less diluted by a very low-salinity fluid, which may correspond to meteoric water, considering the relatively shallow depth of emplacement (ca. 3 km) of the Beauvoir granite (Aïssa et al. 1987b). These results also show that the geochemical signature of the rare-metal magmatic fluid is preserved in fluid inclusions from the metasomatized La Bosse stockwork, despite the distance from the granitic cupola (>100 m) and interaction with external fluids. Consequently, the geochemical signature of fluid inclusions may represent a highly reliable pathfinder for the discovery of hidden rare-metal granitic cupolas at Echassières and more widely in the Limousin area, as well as elsewhere in the world.

Acknowledgements

This work was supported by the French National Research Agency through the national program “Investissements d’avenir” of the Labex Ressources 21 with the reference ANR-10-LABX-21-RESSOURCES21 and has also taken part of the project ERAMIN “New Ores”. The authors would like to thank Imerys, and especially Hubert Sauvage for their support and access to the Beauvoir quarry. We thank also Dr Chantal Peiffert and Dr Marie-Christine Boiron for technical support in providing analytical data with LA-ICPMS analyses.

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