

Origin of brines associated with the Bou Azzer silver deposit, Anti-Atlas, Morocco: A LA-ICPMS study of individual fluid inclusions

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Determination of major and trace element concentrations including metals in fluids associated with ore deposits is essential to evaluate contrasting genetic models. Such information can be obtained by LA-ICPMS analysis of individual fluid inclusions as they represent remnants of the hydrothermal fluids responsible of ore deposition. Previous studies have determined Br and Cl concentrations in high-salinity fluid inclusions using standard multi-element solutions loaded in silica glass capillaries [1] or by using scapolite solid standards [2, 3, 4]. In this work, all metal concentrations have been calibrated using NIST 610 glass. Concentration of all elements in the fluid inclusions have been calculated as described by Leisen *et al.* (2012) [5].

Fluid inclusions associated with silver mineralisation in the Bou Azzer deposit (Anti-Atlas, Morocco) are Na-K-Ca chloride brines (Na: 30,000-60,000 ppm, K: 11,000-27,000 ppm, and Ca: 12,000-85,000 ppm). Ag content ranges from tens to hundreds of ppm. Cl/Br molar ratios range from 300 to 1,000. The Cl/Br ratios determined here are in good agreement with previously published data obtained by crush-leaching techniques [6]. The chemical characteristics of the fluid inclusions indicate that the fluids originated from evaporates that later migrated through basement rocks during a major extensional episode. These geochemical signatures do not support an epithermal model as previously suggested by Levresse *et al.* (2004) [7].

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[1] Stoffel *et al.* (2004) *Am. J. Sci.* **304**, 533-557 [2] Hammerli *et al.* (2013) *Chem.Geol.* **337-338**, 75-87 [3] Seo *et al.* (2011) *Chem.Geol.* **284**, 35-44 [4] Leisen *et al.* (2012) *Chem.Geol.* **330-331**, 197-206 [5] Leisen *et al.* (2012) *Geochim Cosmochim Acta*, **90**, 110-125 [6] Essaraj *et al.* (2005) *J. Afr. Ear. Sci.* **41**, 25-39 [7] Levresse *et al.* (2004) *Chem.Geol.* **207**, 59-79

Boron behavior during silicate weathering: clues from bulk mineral and intracrystalline investigations

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How to model the behavior of a trace element in the mineral structure? What can trace elements actually tell us about the weathering conditions and history of their host mineral? In the present study, we have analyzed a series of common silicate minerals (biotite, muscovite, albite, K-feldspar) handpicked in different soil horizons developed on a granite bedrock (Morvan, France). The chemical and mineralogical weathering gradient shown by those minerals is compared with their respective B and $\delta^{11}\text{B}$ signatures. Our results evidence an excess B solubility compared to major elements in both micas, whereas it shows a relative accumulation in albite. Beside, major elements and B show parallel evolutions in K-feldspar, which is diagnostic of a stoichiometric mineral dissolution.

In order to investigate whether these distinct B behaviors are related to the B atomic environment in those minerals, we have performed solid-state ^{11}B NMR (SSNMR) analyses in similar silicate minerals. As far as we know, these SSNMR analyses are the first ones performed on such low B silicate samples (10-100 ppm). The SSNMR spectra in a B-rich plagioclase (labradorite) clearly shows a well-organized environment for B atoms but they are found in both trigonal and tetrahedral coordination whereas the mineral structure only presents tetrahedral sites. The presence of trigonal B implies the disruption of one of the tetrahedral-O bond, which should necessarily change the energy state of the B local environment. The SSNMR spectra of pristine albite and muscovite clearly demonstrate that B in those minerals is also present in both the trigonal and tetrahedral coordination, but not in well-organized environments, typically not in substitution of Si or Al in the crystal structure but rather located in crystal defects (i.e. in those crystal positions expected to be the most reactive ones).

These new observations may allow the determination of distinct B energy states in crystallographic sites and study of the differential B mobility may help characterizing processes of non-stoichiometric mineral dissolution.