# Topaz-fluorite granites from the Black Forest, Germany: Evolution of F-rich felsic magmas

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F-bearing phases such as topaz, together with fluorite, micas and apatite, appear late in the crystallization history of granitic systems. Topaz crystallizes mostly from vapor, rather than melt, although questions of magmatic vs. hydrothermal origins of topaz are still debated because its parageneses and stability involves a large number of interrelated factors. The Black Forest area in the SW part of Germany is an ideal area to study the evolution of felsic magmas and the stability of topaz because topaz as well as fluorite, micas and fluorapatite are present in variscan peraluminous granites and associated rocks (e.g. pegmatite, aplite).

Topaz-biotite granite and biotite-muscovite granite (topaz-free) contain quartz, plagioclase, alkali feldspar, fluorite, fluorapatite (up to 5 wt.% F), and zircon. Topaz granite deviates in chemical composition markedly from topaz-free granite. This peraluminous high-$SiO_2$ granite (A/CNK=1.11) is relatively rich in F (0.36 wt.%), and low in Mg, Fe and Ti. The trace element composition is characterized by anomalously high Rb and Nb, and by low Ba and Zr suggesting highly differentiated residual melts. Topaz granite contains fluor-topaz (5 vol.%; 18.3-20.3 wt.% F) in the matrix as subhedral grain (up to 800 µm) and as inclusion in quartz and plagioclase. Fluorite is present as small crystal in the matrix (<250 µm) and as aggregate in alkali feldspar and plagioclase but is not closely associated with topaz. Topaz-free granite contains fluorite as large subeuhedral crystal (up to 1 mm) in the matrix. Biotite is F-rich (0.5 to 4.3 wt.% F) in topaz granite and shows oscillatory zonation from core to rim for constant mg-number (mg#=2.4-1.8). In topaz-free granite, biotite shows small variations of F content (2.5-2.8 wt.% F, mg#=9-12). Plagioclase in topaz-granite has very low anorthite content ($<An_3$) compare to topaz-free granite ($An_{4-12}$) that may suggest plagioclase decalcification during topaz (and fluorite?) crystallization.

F-rich granites from the Black Forest batholith suggest that early crystallization of fluorite and micas may have buffered the fluorine content in the less evolved topaz-free granites. Topaz crystallized in a late magmatic stage of granite evolution and probably buffered the F content in the melt. Biotite records changes in F activity during crystallization, probably at a magmatic-hydrothermal transition stage. The presence of secondary fluorite in feldspars attests of F enrichment from the destabilization of F-rich minerals (e.g. topaz, early fluorite, and micas) or/and late hydrothermal processes with F-rich fluids.

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# Toward reconstruction of boron isotopic composition of seawater

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Atmospheric $pCO_2$ is believed to be one of the main Earth's climate driver. As chemical evolution of the oceans and long-term climate changes are linked, paleoclimatologists investigate seawater carbonate system evolution to track $pCO_2$ variations. Boron isotopes in carbonates are used as a seawater paleo-pH proxy and are therefore used to constrain $pCO_2$ in ancient times. Using boron isotopes for paleo-pH reconstruction following the paleo-pH equation [1] requires many assumptions, among which the knowledge of isotopic composition of seawater ($\delta^{11}B_{sw}$).

A first approach consists of modelling the $\delta^{11}B_{sw}$ through time. Recent studies [2] have shown that $\delta^{11}B_{sw}$ is likely to have changed by 2‰ in the last 20 Ma. Secular variations in seawater chemistry have been investigated through fluid-inclusions in halites [3]. Investigation of modern and ancient halites shows that boron is essentially associated to fluid inclusions and that the bulk $\delta^{11}B$ is that of seawater for modern ones. To explore boron residence time in seawater over the last 10 Ma, we compare $\delta^{11}B$ between present sea salts and Messinian evaporites in order to define a seawater end-member bearing the Messinian $\delta^{11}B_{sw}$.

Boron isotopes are extracted from salts after dissolution in pure water and analyzed on MC-ICPMS Neptune with a d-DIHEN system [4]. Total external reproducibility including chemical extraction process is 0.2‰ (2σ). Elemental analysis are realized on a ICP MS X-Series II and by ion chromatography. A large variability is displayed by different Messinian halite samples, owing to diagenetical fluid circulations. It remains possible to define a seawater end-member. Our results confirm that $\delta^{11}B_{sw}$ has changed along the last 6 Ma with Messinian values lower than the today ones. The change amplitude appears to be stronger than suggested by models. This study is a prerequisite for more reliable determination of seawater paleo-pH.

[1] Hemming & Hanson (1992) *Geochim. Cosmochim. Acta* (**56**) 537-543 [2] Lemarchand, Léwin, Gaillardet & Allègre, (2000) *Chem. Geol.* (**190**) 123-140 [3] Horita, Zimmerman & Holland (2002) *Geochim. Cosmochim. Acta* (**66**) 3733-3756 [4] Louvat, Bouchez and Paris (subm.)