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In situ S isotope and trace element composition of apatite from the Gaspé Copper porphyry-skarn Cu-Mo deposit

LUIS KRAMPERT, BERTRAND ROTTIER, CRYSTAL LAFLAMME AND GEORGES BEAUDOIN

Université Laval

Magmatic apatite incorporates abundant trace elements and volatiles (Cl, F, OH), including S. Previous in situ $\delta^{34}S$ measurements in apatite from arc magmas and porphyry systems show a range of ~0–10‰, attributed to fluid saturation or sulfate/sulfide crystallization, which are key controls on porphyry Cu fertility.

In this study, we performed in situ SIMS $\delta^{34}S$ coupled with EPMA and LA-ICP-MS measurements in matrix-hosted apatite from polyphase porphyry intrusions at the Gaspé Copper porphyry-skarn Cu-Mo deposit to investigate the controls on the S isotope signature in apatite. A total of 33 grains were analyzed from 12 samples taken from different generations of porphyry plugs, dikes, and sills across the district.

The Gaspé Copper deposit has two intrusive centers: Copper Mountain (CM) and Porphyry Mountain (PM). Apatite at CM and PM displays $\delta^{34}S$ values with a range of ~1.5–8‰, means of ~4.7‰, and some intra-grain variations exceeding 5‰, with no specific $\delta^{34}S$ values associated with the pre-, syn-, and post-mineralization intrusions. In some syn- and post-mineralization intrusions, apatite volatile chemistry (F, Cl, OH) indicates fluid saturation, which has no or limited impact on the apatite $\delta^{34}S$ values. Only a small fraction of apatite at CM exhibits a core-to-rim increase in $\delta^{34}S$ values (up to 5.7‰) correlating with decreasing Cl content. This pattern may be consistent with S isotope fractionation driven by the exsolution of SO_2-bearing fluids in oxidized melts. However, most investigated grains from intrusions at CM and PM, also show a large range in $\delta^{34}S$ values without a systematic relationship with volatile and trace element compositions. This suggests a minor effect of fluid exsolution on the observed range of apatite $\delta^{34}S$ values.

Apatite S isotope signature is likely controlled by magmatic replenishment and crystallization/redissolution of anhydrite during apatite crystallization. The impact of magma rejuvenation on apatite $\delta^{34}S$ values may be variable, whereas anhydrite crystallization can cause a decrease of several per mil in apatite S isotope composition. While the $\delta^{34}S$ values in apatite provide only limited evidence of fluid exsolution and mineralization at the Gaspé Copper deposit, the results illustrate the complex dynamics of S in a long-lived oxidized magmatic system.