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# Calcium Isotopes in Scheelite and Skarn Systems: Advances, Complexities, and Future Directions

**MICHAEL A. ANTONELLI**[1], DREW SYVERSON[2], EDWIN SCHAUBLE[3], ADEDAPO NOAH AWOLAYO[4], GUY N EVANS[5], CYRIL CHELLE-MICHOU[6] AND WILLIAM E SEYFRIED JR.[7]

[1]University of Houston
[2]UNC Charlotte
[3]University of California, Los Angeles
[4]McMaster University
[5]University of Minnesota
[6]ETH Zürich
[7]University of Minnesota - Twin Cities

Archetypal skarn deposits are formed through the interaction between magmatic fluids and crustal carbonate bodies (e.g., limestones, marble, etc.). Acidic fluids exsolved from the magma drive hydrothermal dissolution-precipitation reactions in the host carbonates ('exoskarns') that generate permeability and promote additional fluid flow, leading to metasomatic formation of calc-silicates and precipitation of economically-important ore minerals, including scheelite ($CaWO_4$). Given the Ca-rich nature of these deposits, stable Ca isotopes ($\delta^{44}Ca$) have the potential to be used as precipitation-rate proxies [1] to better understand the duration of mineralization events in skarn systems. Faster precipitation rates lead to greater mineral-fluid isotopic disequilibrium, whereas slow precipitation rates approach equilibrium values, which are governed mainly by temperature. Extracting absolute precipitation rates from natural $\delta^{44}Ca$ data requires knowledge of the degree of isotopic disequilibrium along with several difficult-to-constrain parameters, including the kinetic (forward) & equilibrium mineral-fluid fractionation factors and the far-from-equilibrium mineral dissolution rates.

To help better constrain some of these parameters and explore what can be learned from $\delta^{44}Ca$ data in natural skarns, we present $\delta^{44}Ca$ data from hydrothermal scheelite precipitation experiments (300-400 °C, ~0.4 kbar) and compare these with new *ab-initio* predictions. Fluid time-series and final scheelite precipitates can be modelled with single fractionation factors ($1000\ln\alpha_{sch\text{-}fluid}$ of -0.45 and -0.20 at 300°C and 400°C, respectively) suggesting formation near isotopic equilibrium. The difference between $1000\ln\alpha_{sch\text{-}fluid}$ at 300°C *vs.* 400°C (-0.25) also agrees well with *ab-initio* predictions (-0.21), yet both experimental values are offset from our predictions by approx. +0.3‰. We find a similar offset when comparing our *ab-initio* predictions for anhydrite with previous hydrothermal experiments [2].

Given that mineral-fluid predictions are tied to the assumption that $1000\ln\alpha_{calcite\text{-}water} \approx 0$ at high-temperatures, the consistent offset we observe points to a possible inversion in the fractionation factor between calcite and water at hydrothermal temperatures, potentially due to increasing $Ca^{2+}$ coordination in fluids [3]. Open questions and implications from the experimental and *ab-initio* data will be discussed alongside data from two skarn deposits, where calc-silicate minerals record $\delta^{44}Ca$ variations >1‰.

[1] DePaolo, 2011 (GCA) [2] Syverson et al., 2018 (GCA) [3] Moison et al., 2024 (J Phys Chem B)