

# **Cracking the sulfate isotopic determination problem in ancient hydrothermal systems: a pilot assessment of the use of the carbonate-associated sulfate (CAS) method.**

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Sulfur isotope analysis of sulfate and sulfide minerals is very useful for unravelling the ore genesis of hydrothermal systems. However, its application is hampered by a lack of sulfate phases in many deposits. Our research indicates that a method previously applied to sedimentary and diagenetic settings, extraction of bound sulfate from sedimentary carbonate, also has application to high temperature carbonate. The method (1) has been used extensively in recent delineations of the pre-Phanerozoic seawater sulfate curve. In this new application, we have adapted the CAS method to hydrothermal vein carbonates.

Our approach provides a new mineral phase to use for sulfur isotope studies, one that is far more common than mineral sulfate. Carbonate-associated or CAS sulfate was chemically extracted in our laboratory. We focussed on vein and replacement carbonates from anhydrite-free, moderately oxidized, porphyry Cu-Au and iron oxide Cu-Au systems. Enough sulfate (10-300 ppm S) was found to be present to allow chemical extraction from veins and determine the sulfur isotopic determination. Isotopic data from co-existing sulfides and the CAS was then used to calculate paleotemperatures; these compared well with external T estimates for the veins.

Total hydrothermal sulfate abundance in vein carbonate was much lower than values reported for sedimentary carbonates (up to 1% S (1)). This is consistent with sulfate substitution being proportional to numbers of crystal defects, since defect formation is less favoured at higher temperatures of crystal formation. Microprobe mapping showed sulfur to be evenly distributed in our samples, although anomalous zones appear to correlate with zones of micro-cracking.

The method is a promising new approach for the determination of paleotemperature, sulfur source, oxidation state and even paleopressures in hydrothermal, metamorphic and igneous carbonate-bearing systems, greatly broadening the application of sulfide-sulfate isotopic methods beyond the few systems with mineral sulfate.

## **References**

(1) Burdett, J.W et al. (1989) A Neogene seawater sulfur isotope age curve from calcareous pelagic microfossils: EPSL: 94, 189–198.