

## Trace element systematics of pyrite from submarine hydrothermal vents

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Submarine hydrothermal sulfide deposits occur at mid-ocean ridges, island arcs, and in back-arc basins. It is believed that the different wall rocks and potential magmatic volatiles [1] influence the metal budget of the hydrothermal fluid and the composition of the sulfide precipitates to variable degrees.

Pyrite is the dominating mineral in these precipitates and thus, the trace element composition of pyrite may reflect the different metal sources. However, the physicochemical composition of the fluid phase and processes such as phase separation [2] largely control the solubility and transport of metals and hence, metals enriched in the wall rock or magmas may not necessarily be concentrated in the sulfides.

Here we report on a systematic study of major and trace element concentrations on pyrites from active and inactive hydrothermal fields including the Indian and Mid-Atlantic Ridges, the Tonga-Kermadec arc, Lau back-arc, and the central Okinawa Trough. Preliminary results indicate that the pyrites show significant variations in their trace element contents irrespective of the surrounding host rocks. Pyrites from single locations have highly variable concentrations of elements like Cu, Sb, Ag, Au and Co that are most likely related to fluid evolution and changes in fluid compositions. Elements like Sb, Ag and Au have a characteristic affinity to As and Pb in pyrite, Cd correlates closely with Zn. High temperature (>240°C) As-Cu-pyrites are often enriched in Co and Au, while Ni seems to be unaffected by temperature variations. The incorporation of Co and Ni into pyrite is wall rock-independent. Bismuth appears to be enriched in pyrites from settings associated with sediments [3] and Mo may be concentrated due to seawater mixing [4].

These results indicate the complexity of trace metal contents in pyrite as a function of the physicochemical composition of the fluid phase rather than their source.

[1] de Ronde *et al.* (2011) *Miner Deposita*, **46**, 541-584. [2] Koschinsky *et al.* (2008) *Geology*, **36**, 615-618. [3] Zierenberg *et al.* (1993) *Econ Geol.*, **88**, 2069-2098. [4] Trefry *et al.* (1994) *J Geophys Res.*, **99**, 4925-4936.

## Clumped isotope geochemistry of travertine carbonates in the 22-95 °C temperature range

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The formation temperature of carbonates can be estimated using both the conventional carbonate-water paleothermometry and the newly developed clumped isotope method of [1]. However, there is still a large uncertainty in the published clumped-isotope based temperature calibrations.

In this work recent travertines forming from natural springs and wells between 22 and 95 °C from Hungary, Turkey and Italy were studied for stable- and 'clumped' isotopes. Clumped isotope data showed an excellent correlation with temperature indicating equilibrium precipitation close to the spring orifice.  $\Delta_{47}$  values decreased with increasing distance from the springs, which may be related to kinetic isotope fractionation due to CO<sub>2</sub> degassing in the different depositional sub-environments (e.g. channel, terrace-pool, cascade).

All vent travertine samples show a strong  $\Delta_{47}$ -temperature relationship ( $r^2 > 0.9$ ) defining an empirical equation with a slightly lower slope (i.e. lower temperature sensitivity) than that of Ghosh *et al.* [1]. This empirical calibration significantly extends the calibration range of the clumped isotope thermometer to temperatures of 95 °C and can be used to derive the oxygen isotope composition of travertine-depositing waters from ancient deposits to reconstruct glacial-interglacial variations in meteoric water compositions and the paleohydrological regimes of the study areas.

[1] Ghosh, P. *et al.* (2006) *Geochim. Cosmochim. Acta* **70**, 1439-1456.