

Carbon and oxygen isotopic composition of brachiopod shell calcite: physiological and environmental controls

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This contribution aims to unravel the environmental and physiological controls on the stable isotope composition of modern brachiopod shell calcite. Based on SEM studies of the shells, a three dimensional high resolution sampling (< 500 µm) was performed on various modern brachiopod species (*Terebratalia transversa*; *Neothyris*; *Fallax*) in order to investigate carbon and oxygen isotope variations.

The primary shell layer as well as the outer part of the secondary shell layer of the thick shells of *Terebratalia* and *Neothyris* display large and variable negative offsets in comparison to calculated equilibrium values (as high as 6‰ for δ¹⁸O and 7‰ for δ¹³C in *Terebratalia*, and 3‰ for δ¹⁸O and 5‰ for δ¹³C in *Neothyris*). The positive correlation between δ¹⁸O and δ¹³C values (r²>0.8) suggests that the stable isotope composition of these shell domains are mainly controlled by kinetic isotope fractionation effects. The isotopic offsets from equilibrium values preclude to calculate oceanic temperatures. However, ontogenetic variations in δ¹⁸O and δ¹³C (δ¹⁸O≈4‰ and δ¹³C≈5‰ in *Terebratalia*; δ¹⁸O≈2‰ and δ¹³C≈3‰ in *Neothyris*) observed in the outer part of the secondary layer can be used to plot growth curves for these specimen. Further analyses show increasing stable isotope compositions from the outer towards the inner part of the secondary layer, where the values reach expected equilibrium. This suggests a deceleration of calcite secretion during shell thickening.

In comparison to *Terebratalia* and *Neothyris*, the very thin shell of *Fallax* displays carbon and oxygen isotope values close to equilibrium with seawater, and kinetic effects seem to be of minor importance.

In conclusion, we suggest that isotopic studies of modern or fossil brachiopod shells should be combined with SEM observations of shell microstructure, which provide valuable information with respect to growth rate and processes during shell growth. A 3D sampling procedure should be used in order to isolate the shell parts less affected by physiological effects, *i.e.* more reliable for environmental reconstructions.

Magmatic anhydrite in the Cu-porphyry-related magma at Santa Rita, New Mexico (U.S.A.)

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The formation of sulfides and immiscible sulfide melts is drawing increasing attention in research related to Cu-porphyry deposits (e.g., Halter et al., this session). It has been suggested that such sulfide phases act as temporary "storage medium" for chalcophile metals like Cu and Au (thus preventing them to be incorporated at trace-levels in other minerals), and supply the metals to the mineralizing fluids during a later stage of sulfide oxidation. Recent reports on the abundance and chemical composition of sulfide phases in natural systems seem to support this model of metal enrichment^{1,2}.

Here we present petrographic and analytical evidence for the occurrence of anhydrite in the ore-forming magma at Santa Rita, New Mexico. A pre-mineralization quartz-monzodiorite dike related to the mineralized stock contains anhydrite inclusions within apatite microphenocrysts. The rock also contains 1-2 vol-% cavities that, on the basis of petrographic relationships, can clearly be identified as former anhydrite phenocrysts. The stable assemblage of quartz + magnetite + sphene indicates a magmatic oxygen fugacity of ≥(NNO²), consistent with a lack of primary sulfides (or oxidized remains thereof)³. A similar situation has been reported from the mineralized Yerington Batholith, where the presence of magmatic anhydrite was inferred from calculated oxygen and sulfur fugacities⁴.

These examples demonstrate that significant Cu-porphyry mineralization can be generated *without* the formation of magmatic sulfides or immiscible sulfide melts. Magmatic sulfide exsolution thus appears not to be a prerequisite for the formation of economic Cu-porphyry deposits. Common to all magmas related to porphyry-type mineralization, however, seems to be a high sulfur-content (independent of the oxidation state), suggesting that this is one of the essential conditions for the genesis of such deposits.

¹Keith J.D. et al. (1997), *J. of Petrology* **38**, 1679-1690

²Halter W. et al. (2002), *Science* (in press)

³Carroll M. and Rutherford M. J. (1988), *Am. Mineral.* **73**, 845-849

⁴Streck M.J. and Dilles J.H. (1998), *Geology* **26**, 523-526