

Minor elements in layered sphalerite record fluid origin in the giant Navan Zn-Pb orebody, Ireland

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This study aims to test whether the chemistry of sphalerite in the world-class, Irish-type, Navan ore deposit may help to decipher the nature and origin of the ore-forming fluids. Detailed electron microprobe traverses were carried out across colloform and other growth-layered sphalerite, on samples that were previously analysed for Zn, Fe and S isotopes (Gagnevin *et al.*, Goldschmidt 2011). In particular, the S isotope data enabled us to distinguish between samples that precipitated from hydrothermal, metal-bearing fluids or from cooler, bacteriogenic, sulphide-bearing fluids.

On the hand sample scale, Cd and Fe discriminate between the two fluid sources (Fig. 1); Cd, Sb, and to a lesser extent Cu, are enriched in sphalerite precipitated from hydrothermal fluids ($\delta^{34}\text{S} > 0$), while Fe and As are enriched in sphalerite precipitated from bacteriogenic fluids ($\delta^{34}\text{S} < 0$), suggesting that sphalerite chemistry is a good guide to fluid origin.

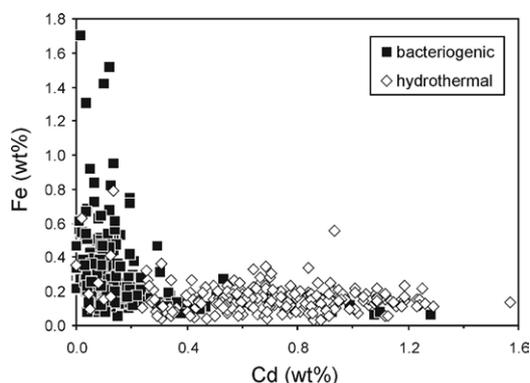


Figure 1: Cd vs Fe concentrations of layered sphalerite investigated in this study.

Frequent large (up to order of magnitude) elemental variations between successive sphalerite layers, whether colloform or not, indicate repeated influxes of hydrothermal fluids, with probable control also from kinetic effects and substitution mechanisms. Moreover, we show that sphalerite texture is sometimes, but usually not, correlated with sphalerite chemical composition.

Calcium isotopes during coral biomineralization

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A mechanistic understanding of biomineralization promises to separate biological and environmental signals in skeletal carbonates, improving the interpretation of paleoproxies. Towards this goal, we measure calcium isotope ratios of micromilled samples from modern scleractinian deep-sea coral, testing two questions in coral biomineralization. Is amorphous calcium carbonate (ACC) an important precursor during skeletal nucleation? Can reservoir effects (Rayleigh models) explain the biologically controlled variability of non-traditional stable isotopes.

Centers of calcification (COCs) are morphologically and compositionally distinct regions of the coral skeleton associated with nucleation. To test if an ACC precursor phase can explain the geochemistry of COCs, we compare the calcium isotope ratios of COCs to synthetic ACC. The $\delta^{44}\text{Ca}$ of COCs are similar to the surrounding skeleton and to inorganically precipitated aragonite, but are fractionated significantly more than inorganic ACC ($\Delta^{44}\text{Ca}_{\text{COC-seawater}} = -1.0 \pm 0.1 \text{ ‰}$ while $\Delta^{44}\text{Ca}_{\text{ACC-solution}} < -0.2 \text{ ‰}$). If ACC is involved in skeletal nucleation, then the distinct calcium isotope signature of this phase is lost during subsequent phase transformation. As calcium is the major cation in aragonite, this presumably means the minor and trace element composition of an ACC phase would be altered as well, and suggests that ACC is unlikely to explain the compositional anomalies associated with COCs in coral.

Even when grown under constant environmental conditions, metal/calcium ratios in deep-sea coral vary by more than 5%. This variability can be explained by skeletal precipitation from closed batches of seawater or a more general steady-state reservoir effect where seawater transport to the site of calcification balances precipitation. Both models make similar predictions regarding calcium isotopes, higher skeletal Sr/Ca ratios should correlate with lighter $\delta^{44}\text{Ca}$. We observe this predicted trend in preliminary results from micromilled samples, suggesting that in addition to metal/calcium ratios, reservoir effect models of coral biomineralization may also explain the variability of some isotope systems. Analysis of coral from a range of conditions will test if we can recover biomineralization corrected records of seawater isotope ratios and environmental conditions.