Micron-scale isotopic zoning in minerals: a record of large-scale geologic processes

M.A. McKibben   *Dept. of Earth Sciences, University of California, Riverside, CA 92521 USA.*

C.S. Eldridge   *Geology Dept. & RSES, Australian Nat. Univ., Canberra ACT 0200 Australia.*

Introduction

Isotopic microanalysis can reveal details of mineralizing processes that would otherwise remain undiscovered, because minerals often exhibit micron-scale isotopic zonations recording the large-scale geologic events which have affected them.

The SHRIMP (sensitive high resolution ion microprobe) performs *in-situ* $^{34}S/^{32}S$ analyses of minerals, utilizing a sampling volume that is only 15–25 μm wide and 5 μm deep. A negatively-charged oxygen primary beam is used to sputter secondary sulphur ions for analysis in the mass spectrometer sector of the instrument. The precision and accuracy of SHRIMP $\delta^{34}S$ values are $\pm$ 2‰ (2σ) (Eldridge *et al.*, 1987, 1989).

Ion microprobe analyses of S isotopic variations with the SHRIMP have documented numerous examples where *individual* minerals or mineral intergrowths exhibit micron-scale $\delta^{34}S$ variations that approach the known range of conventional bulk S isotopic compositions in nature. Moreover, the magnitudes and directions of micron-scale S isotopic zoning are often diagnostic of specific geochemical processes which have caused mineralization.

Creede Caldera moat sediments

Sedimentary and vein pyrites in the moat of the Creede Caldera show the largest stable isotopic variations ever reported in natural minerals from a single location ($\delta^{34}S$ −30 to 110‰). The diagenetic and vein pyrite are found in a moat sequence of tuffaceous lacustrine sediments and an underlying sequence of tuff and landslide breccias; the sulphides formed at temperatures of 0 to 90°C.

Within the moat sediments pyrite occurs as thin fine-grained lenses and clots composed of framboids, euhedral crystallites and polycrystalline aggregates having $\delta^{34}S$ values from −30 to 40‰. Individual pyrite masses exhibit $\delta^{34}S$ zonations ranging up to 30‰, with light cores and heavy rims, recording their growth during a transition from open system biogenic sulphate

reduction at the sediment/water interface to closed system reduction upon burial and decreasing permeability.

Within the underlying tuffs, veins of framboidal, colloform and polycrystalline pyrite occur with bladed calcite. The veinlets contain geopetal structures in the form of pyrite stalactites and graded framboidal sediments. $\delta^{34}S$ values for pyrite in these structures show an astoundingly large total range of −23 to 111‰, typically with light early values and heavy late values. In many cases the progressive zonation pattern is interrupted at textural/isotopic discontinuities, starting again at negative values and then increasing to more positive values.

The large $\delta^{34}S$ zonations in the vein pyrites record the passage of fluids whose sulphur isotopic compositions varied strongly with time. The progressive positive $\delta^{34}S$ zonations across many sequential overgrowths imply that H_2S in influxing fluids was evolving from depleted to enriched $^{34}S/^{32}S$ ratios. The sudden discontinuities and reversals in $\delta^{34}S$ values from many samples suggest that multiple, episodic pulses of isotopically distinct fluids moved into the tuff.

A single fluid packet undergoing a Rayleigh process of *in-situ* SO_4 reduction and pyrite precipitation would incorporate extremely enriched H_2S only in the last fraction of pyrite that was deposited. The relatively large amounts of extremely ^{34}S-enriched pyrite found within the veins, along with the frequent isotopic zoning discontinuities and reversals, require instead that the vein pyrites incorporated H_2S from fluids which had already experienced substantial closed-system SO_4 reduction *prior* to their arrival at the site of precipitation.

Because biogenic sulphate reduction occurred in the overlying Creede Formation, it is likely that fluids from these overlying sediments migrated down through the tuff in multiple stages, each stage having experienced varying extents of SO_4 sulphate reduction. The isotopic zoning discontinuities and reversals in the vein pyrites thus record the influx of each new fluid packet. These features

indicate that bacteriogenic reduction of aqueous SO_4 was common in the Creede moat pore fluids and likely fed reduced sulphur to the adjacent Creede hydrothermal system, as predicted from isotopic studies of base metal vein mineralization in the adjacent vein district (Rye *et al.*, 1988).

Valles Caldera moat rhyolites

In rhyolites beneath the Sulfur Springs thermal area in the Valles Caldera moat, authigenic hydrothermal pyrite crystals show heavy to light $\delta^{34}S$ zonations of up to 23‰ from core to rim, over distances of less than 75 μm (McKibben & Eldridge, 1990). The zoned pyrites occur in a section of altered, mineralized rhyolite that formerly hosted a shallow liquid-dominated hydrothermal system; the present system is vapour-dominated. The rhyolite exhibits enrichments in Au and As at the same depth as the zoned pyrites.

The progressive S isotopic depletion recorded in the zoned pyrites is opposite to Rayleigh trends expected for biochemical or thermochemical sulphate reduction. Instead, this reverse zonation likely records *oxidation* of aqueous H_2S that accompanied boiling and transition to a vapour-dominated hydrothermal system. Boiling and hydrogen loss can oxidize H_2S and preferentially partition ^{34}S into SO_4, leaving behind isotopically depleted H_2S to become incorporated into pyrite. The magnitude of the observed isotopic zoning is consistent with calculated Rayleigh effects accompanying oxidation of up to 50% of initial aqueous H_2S at 200°C. Boiling and hydrogen loss also cause deposition of gold, thus explaining the coincidence of isotopically zoned pyrite and Au enrichment in the rhyolite.

The $\delta^{34}S$ zoning in the pyrite may record boiling caused by a transition from a liquid- to vapour-dominated system, triggered by collapse of the caldera wall and draining of the former caldera lake.

Salton Sea rift sediments

Sedimentary and diagenetic sulphides in the lacustrine-deltaic sediments hosting the Salton Sea geothermal system show $\delta^{34}S$ variations up to 50‰ over distances less than 300 μm (McKibben & Eldridge, 1989). Sedimentary pyrite masses often show light to heavy $\delta^{34}S$ zonations from core to rim, consistent with biogenic SO_4 reduction during diagenesis. Low-temperature sulphur isotopic differences between intergrown sedimentary sulphide and evaporitic sulphate are preserved in spite of active sediment metamorphism to temperatures as high as 330°C.

Vein sulphides show zonations up to 10‰ due to variable degrees of thermochemical reduction of evaporitic SO_4, or to precipitation-induced fractionation in brines with low H_2S concentrations. Where later hydrothermal chalcopyrite envelops sedimentary pyrite, large $\delta^{34}S$ contrasts imply that no local recycling of sedimentary sulphide into the hydrothermal sulphide has taken place.

Viburnum Trend carbonate-hosted Pb-Zn ores

Mississippi Valley type ores from the Viburnum Trend of S. E. Missouri, U.S.A. exhibit $\delta^{34}S$ variations within and among intergrown Fe-Cu-Pb-Zn sulphides which are very large (−10 to 25‰) and indicate an extremely complex history of mineral deposition (McKibben and Eldridge, 1994).

Early FeS_2 is generally much more depleted in $\delta^{34}S$ (by $\simeq$ 20‰) than main-stage galena or late chalcopyrite. Early FeS_2 and late chalcopyrite generations *each* exhibit large, cyclic micron-scale zonations in $\delta^{34}S$ of up to 15‰. Isotopic zoning in galena crystals is comparatively negligible, but variations among *different* galena crystals encompass a large total range in $\delta^{34}S$ values ($\simeq$ 20‰), similar to the total ranges observed in early FeS_2 and late chalcopyrite.

Where later sulphides crosscut and replace earlier sulphides, the SHRIMP data indicate that there has been negligible local recycling of S from earlier sulphides in the ore-forming zone; each generation of metal appears to have brought in its own isotopically distinct and evolving batch of sulphur. During deposition of *each* metal generation, the observed $\delta^{34}S$ variations require either large cyclic shifts among isotopically distinctive distal source fluids feeding already reduced sulphur to the ore-forming zone, and/or the existence of local sulphur isotopic fractionation mechanisms producing reduced sulphur *in-situ* whose isotopic composition varied progressively with time.

In each of the cases cited above, minerals contain microscopic isotopic variations that record the large-scale geologic events which have caused mineralization. Such critical genetic information is typically masked by traditional bulk isotopic sampling and analytical methods.