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## **PRELIMINARY SCIENTIFIC RESULTS OF THE CREEDE CALDERA CONTINENTAL SCIENTIFIC DRILLING PROGRAM**

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## **SHRIMP ION MICROPROBE SULFUR ISOTOPIC STUDY OF PYRITE IN COREHOLE CCM-2: EVIDENCE FOR MULTIPLE EPISODES OF EXTREME BIOGENIC SULFATE REDUCTION**

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## INTRODUCTION

We have characterized the sulfur isotopic composition of sediment-hosted sulfide minerals in the CCM-2 drillhole using the SHRIMP ion microprobe and compared the results with those obtained by conventional bulk sampling (see Rye, Bethke and Finkelstein, Chapter G, this Open-File Report). We analyzed samples of diagenetic and vein-filling pyrite found in a 490 m thick sequence of tuffaceous lacustrine sediments (Creede Formation) and an underlying 218 m thick sequence of Snowshoe Mountain Tuff and landslide breccias (which form the floor of the moat) penetrated by drillhole CCM-2.

Samples 2R106, 2R118 and 2R140 consist of thin fine-grained lenses and clots of pyrite occurring within tuffaceous lacustrine sandstones and siltstones of the Creede Formation at depths of 1090-1426 feet (332-435 m). The authigenic pyrite occurs as disseminated framboids, euhedral crystallites, and polycrystalline aggregates, and often replaces matrix, glass shards and phenocryst fragments.

Samples 2R223, 2R224 and 2R236 consist of texturally complex veinlets of framboidal, colloform and polycrystalline pyrite occurring with bladed calcite in Snowshoe Mountain ignimbrite at depths of 670-707 m (2199-2319 feet). Many of these veinlets contain geopetal structures in the form of hangingwall pyrite stalactites and footwall graded pyrite sediments. Etching of this pyrite with nitric acid reveals an astounding array of textures, such as framboidal cores overgrown by radial coarse crystals.

## ANALYTICAL METHODS

We used the SHRIMP (Sensitive High Resolution Ion Microprobe), located at the Australian National University, to analyze the sulfur isotopic composition of the Creede Moat pyrites on a microscopic scale in polished sections. SHRIMP produces an analytical crater on polished surfaces that is 20-30  $\mu\text{m}$  wide and 5  $\mu\text{m}$  deep. SHRIMP  $\delta^{34}\text{S}$  results are reported relative to the CDT standard and have a precision of 2 ‰ at the 2 sigma level.

Conventional  $\delta^{34}\text{S}$  values, determined on sedimentary pyrite, vein pyrite and organic matter samples from several depths in CCM-2, were obtained at R.O. Rye's stable isotope laboratory the USGS in Denver. The conventional values have a precision of 0.1-0.2 ‰.

## RESULTS

A total of 37 conventional  $\delta^{34}\text{S}$  values for pyrite and organic matter samples reported by Rye. et al., (Chapter G this Open-File Report) are summarized in Figure 1. A total of 79 SHRIMP  $\delta^{34}\text{S}$  values for 6 pyrite samples are plotted versus depth in Figure 2.

## **Pyrite in Creede Formation sediments**

Disseminated and stratiform pyrite from the Creede Formation sediments shows  $\delta^{34}\text{S}$  ranges that are virtually identical for the two analytical methods:

-20 to 35 ‰ for conventional data

-20 to 30 ‰ for SHRIMP data

SHRIMP analysis of pyrite in sediments shows that many pyrite lenses, clots and concretions exhibit a zonation in  $\delta^{34}\text{S}$  values from core to rim:

2R106 - a lens zoned from -4 to 24 ‰.

2R140 - a clot zoned from -13 to -2 ‰.

In other cases a regular zonation cannot be so clearly established.

## **Pyrite in veinlets in snowshoe Mountain Tuff**

Conventional  $\delta^{34}\text{S}$  values for pyrite in veins from the Snowshoe Mountain Tuff show a relatively narrow range of 0 to 16 (Rye, et al., Chapter G this Open-File Report). By contrast, SHRIMP  $\delta^{34}\text{S}$  values for pyrite in these veins show an astoundingly large total range of -23 to 111 ‰ (Figure 3).

In sample 2R224, SHRIMP analysis of sequential pyrite over-growths reveals  $\delta^{34}\text{S}$  variations from values as low as -17 ‰ near vein walls to values as heavy as 72 ‰ near vein centers, over distances of only 100-200  $\mu\text{m}$ . In some cases the zonation pattern appears to be interrupted following a textural/isotopic discontinuity, starting again at negative values and then increasing to more positive values.

In sample 2R236 similar  $\delta^{34}\text{S}$  patterns are seen; for example a variation from about 20 ‰ in the core of a symmetrically zoned mass to about 110 ‰ near its rim, over a distance of 400 microns. Even larger textural/isotopic discontinuities of  $\approx$  130 ‰ are seen in this sample, where the outermost overgrowths of pyrite begin at  $\delta^{34}\text{S}$  values of about -20 ‰.

The  $\delta^{34}\text{S}$  variations seen in the vein pyrites from samples 2R224 and 2R236 are, to our knowledge, the largest stable isotopic zonations ever documented for natural minerals.

## **DISCUSSION**

The -20 to 35 ‰  $\delta^{34}\text{S}$  range of diagenetic pyrite in the Creede Formation sediments is very consistent with ranges for sedimentary/diagenetic Pyrite seen in recent clastic sedimentary environments in both marine and lacustrine euxinic settings (e.g., Goldhaber and Kaplan, 1974; McKibben and Eldridge, 1989; Ohmoto et al., 1990). The general isotopic zonation from light cores to heavy rims is also consistent with zonations of diagenetic pyrite in these settings, and likely reflects a transition from open-system biogenic sulfate reduction near the sediment/water interface to closed-system reduction upon burial and decreasing permeability.

These features indicate that bacteriogenic reduction of aqueous  $\text{SO}_4^-$  was common in the Creede Formation pore fluids, as predicted from the study of district vein minerals (Rye et al., 1988). Biogenic  $\text{SO}_4^-$  reduction generally

produces  $\text{SO}_4^- - \text{H}_2\text{S}$  isotopic fractionations of  $-45 \pm 20 \text{ ‰}$  (Ohmoto et al., 1990), depending on the temperature, nutrient supply and rate of reduction. A combination of variable kinetic fractionations and closed system effects acting over time could thus account for the  $-20$  to  $35 \text{ ‰}$  total range of  $\delta^{34}\text{S}$  values observed in the Creede Formation pyrites.

For example, an  $11 \text{ ‰}$  core to rim zonation seen in a single sedimentary pyrite clot in sample 2R140 could record the progressive reduction of  $\sim 20\%$  of the initial  $\text{SO}_4^-$  present in a closed pore fluid system, if the kinetic  $\text{SO}_4^- - \text{H}_2\text{S}$  fractionation was approximately  $-40 \text{ ‰}$ .

Even larger SHRIMP  $\delta^{34}\text{S}$  zonation patterns are seen in pyrites from veins in the underlying Snowshoe Mountain Tuff (Samples 2R224 and 2R236), reflecting the influx of fluids containing  $\text{H}_2\text{S}$  whose sulfur isotopic compositions varied strongly with time. The progressive positive  $\delta^{34}\text{S}$  zonations across many sequential overgrowths imply that  $\text{H}_2\text{S}$  in influxing fluids was evolving from depleted to enriched  $^{34}\text{S} / ^{32}\text{S}$  ratios. Sudden discontinuities and reversals in  $\delta^{34}\text{S}$  values seen in some samples suggest that multiple, episodic pulses of isotopically distinct fluids moved into the tuff.

Rayleigh calculations indicate that the heaviest  $\delta^{34}\text{S}$  values for pyrite in the tuff could represent  $\text{H}_2\text{S}$  derived from closed system reduction of the last remaining fraction of  $\text{SO}_4^-$  in a single fluid packet. If the fluid packet underwent complete closed-system reduction at the site of precipitation, and if pyrite precipitated continuously during reduction, then a full continuous spectrum of  $\delta^{34}\text{S}$  values would be observed with the extremely enriched pyrite comprising only a small late fraction of the total  $\text{H}_2\text{S}$  precipitated as pyrite.

Therefore, the relatively large amounts of extremely  $^{34}\text{S}$ -enriched pyrite present within some individual samples (2R224 and 2R236), coupled with the isotopic discontinuities and reversals, suggest that such pyrite incorporated  $\text{H}_2\text{S}$  from multiple fluid packets, some of which must have experienced substantial closed-system sulfate reduction prior to their arrival at the site of precipitation.

At least some pyrite that precipitated in the tuff is as isotopically light as  $-20 \text{ ‰}$ , and thus must have incorporated  $\text{H}_2\text{S}$  that was virtually the initial fraction of incipient closed system sulfate reduction acting on a fluid packet. Therefore, there is evidence for the movement of fluids into the tuff which had undergone both relatively low extents of closed system sulfate reduction and relatively large extents of closed system sulfate reduction, prior to entering the tuff.

Given the evidence that sulfate reduction occurred in the overlying Creede Formation, it seems reasonable to propose that incipiently to extensively reduced fluids from the overlying sediments migrated down through the tuff in multiple stages. The reversals and discontinuities of  $\delta^{34}\text{S}$  values seen in the pyrite in tuff likely record the initiation of new fluid influx cycles.

## ACKNOWLEDGMENTS

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## FIGURE CAPTIONS

- Fig. 1  $\delta^{34}\text{S}$  values for pyrite and organic matter determined by conventional methods by Rye. et al., (Chapter G, this Open-File Report)
- Fig. 2 Plot of  $\delta^{34}\text{S}$  values determined in this study versus depth.
- Fig. 3 Photographs of samples of vein pyrite showing  $\delta^{34}\text{S}$  values for areas analyzed by SHRIMP microprobe.

$\delta^{34}\text{S}$  values of diagenetic and vein sulfide  
in Creede Formation by conventional analyses

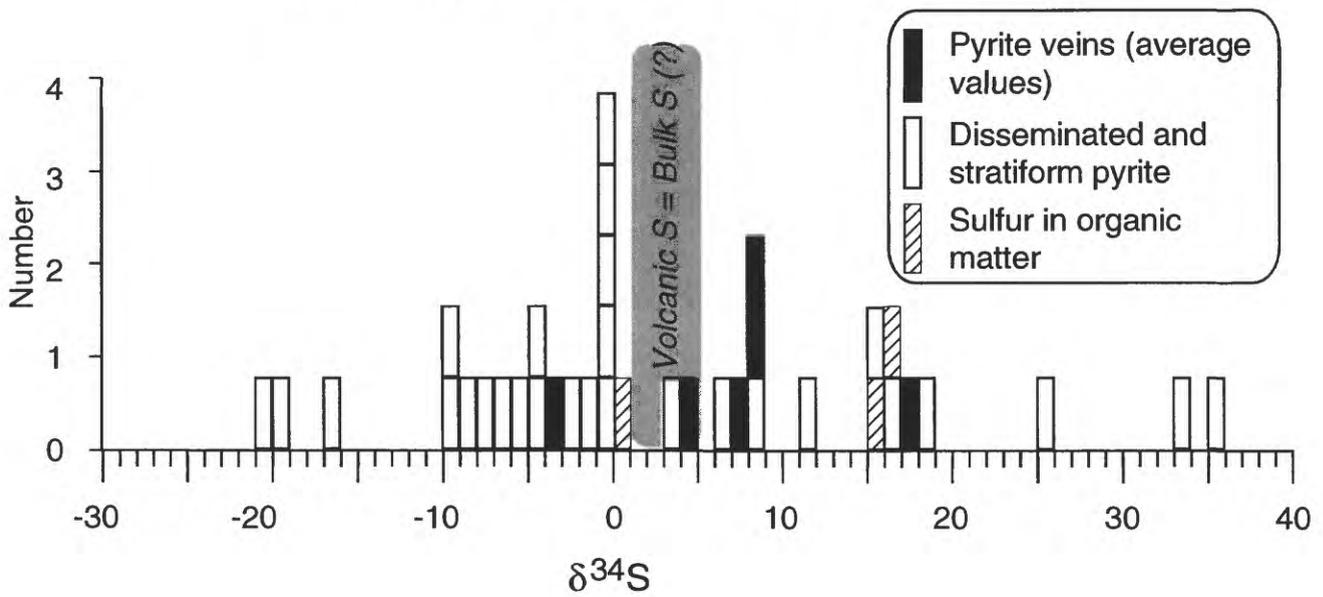


Figure 1

# CCM2 SHRIMP Data

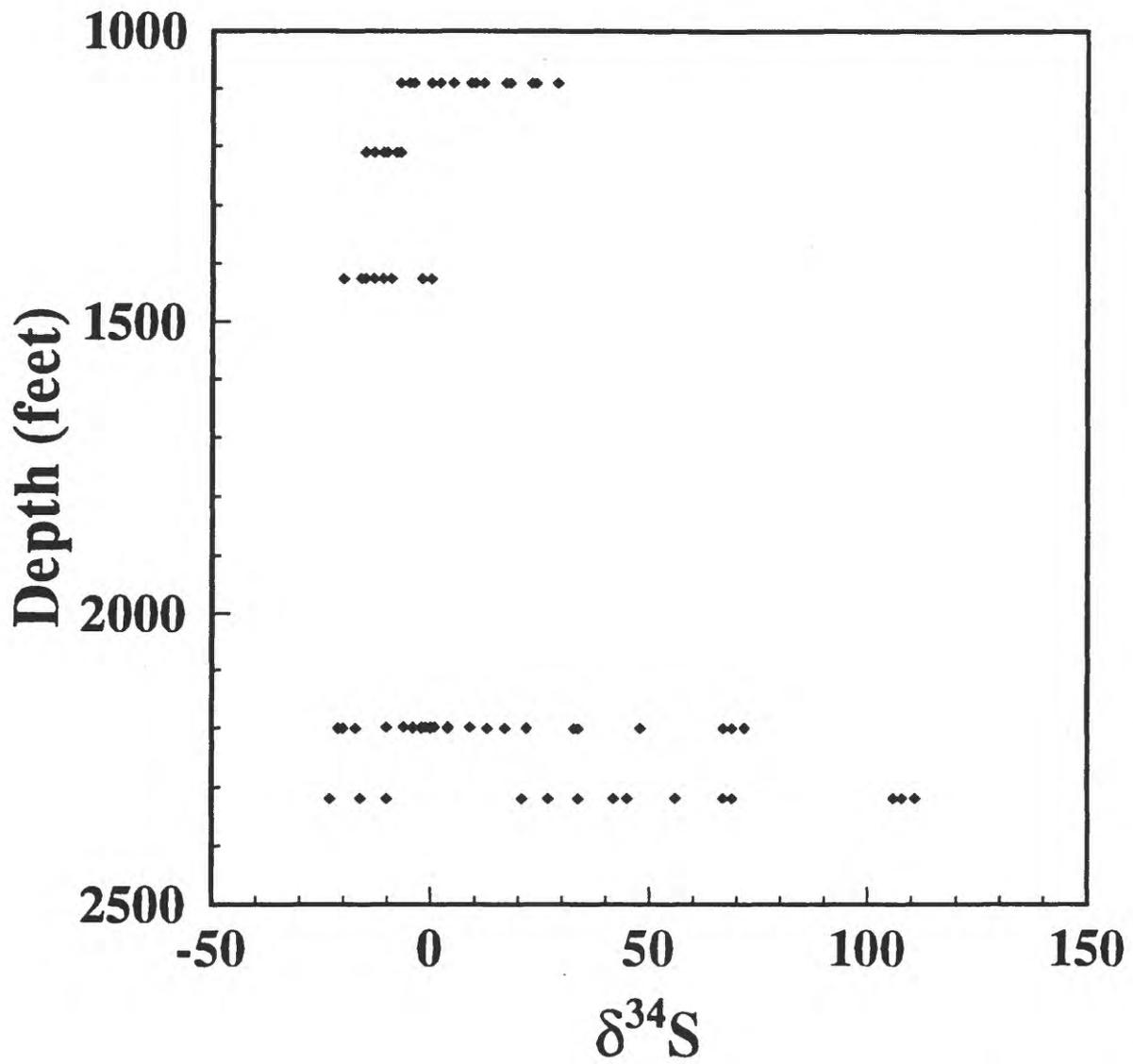


Figure 2

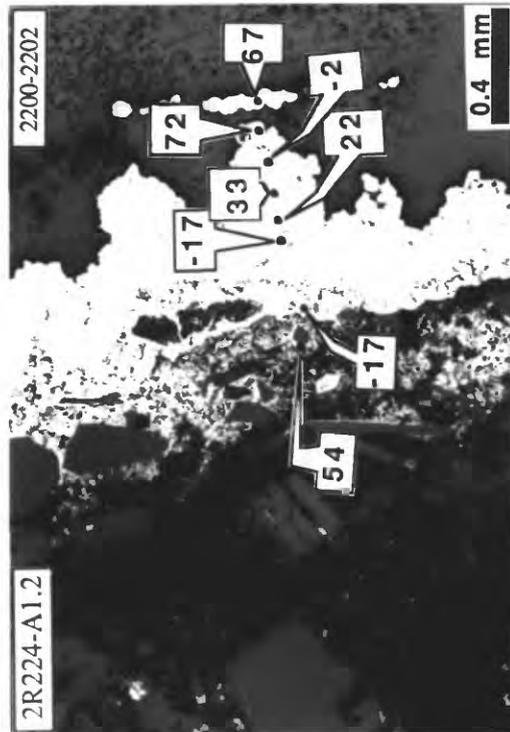
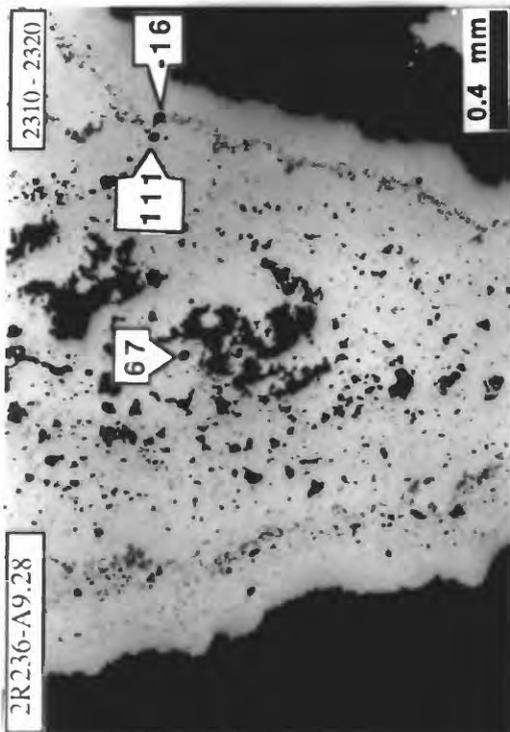
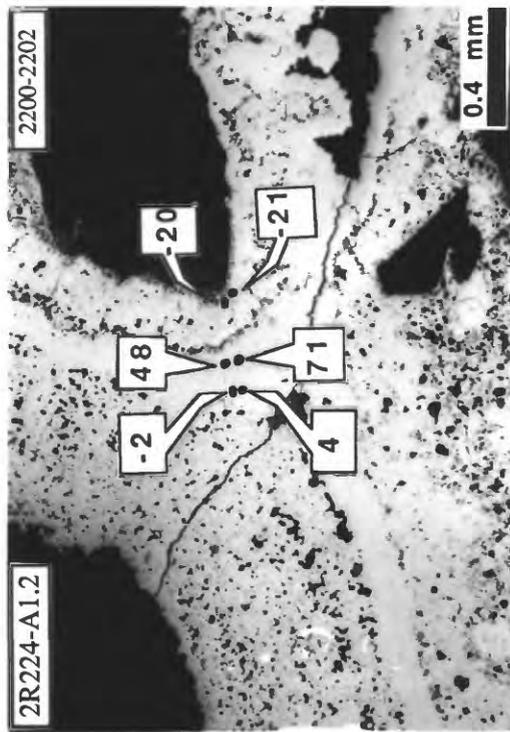
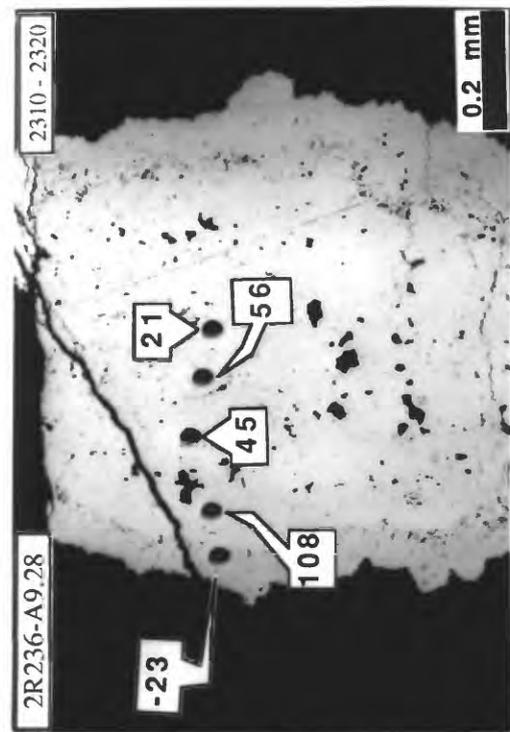


Figure 3