

## SESSION 37, T11. Sulfur Cycling in Precambrian to Recent Ocean-Atmosphere Systems

4:45 PM Varni, Michael A.

### ANOMALOUS $\delta^{34}\text{S}$ SIGNATURES IN TRACE SULFATE FROM A POTENTIAL CAP CARBONATE IN THE NEOPROTEROZOIC BAMBUI GROUP, BRAZIL

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An unusually textured unit in the Sete Lagoas Formation, Bambuí Group may be a cap carbonate atop a second as yet unrecognized Neoproterozoic glacial interval in Brazil. Textures, insoluble residues, and carbon, oxygen, sulfur, and strontium isotopic compositions of high-resolution samples from two nearby quarries outside of Belo Horizonte, Brazil were investigated. At the Samba Quarry, carbonates record a positive  $\delta^{13}\text{C}$  excursion from the base at -4 to near 0‰ some 8 meters higher;  $\delta^{18}\text{O}$  values remain relatively constant above this transition zone. Over the same interval,  $\delta^{18}\text{O}$  values appear to co-vary with carbonate  $\delta^{13}\text{C}$  abundance. Organic matter is anomalously enriched in  $\delta^{13}\text{C}$  near the base, with remarkably constant values of ca. -18 to -20‰, resulting in remarkably reduced carbon isotope fractionations ( $\Delta\delta$ ) between inorganic and organic phases. Variable, but high Sr and low Mn abundances characterize the seafloor cements at the base of the exposure. These well-preserved limestones record  $^{87}\text{Sr}/^{86}\text{Sr}$  values of 0.7074. Abundances of carbonate-associated trace sulfate range between 28 and 174 ppm. The  $\delta^{34}\text{S}$  values are strongly positive, up to +38‰ relative to CDT. Nearby carbonates collected from the Paraíso Quarry record carbonate  $\delta^{34}\text{S}$  values around 0‰. Trace sulfate concentrations range from 6 to 86 ppm. The  $\delta^{34}\text{S}$  values of samples from the Paraíso Quarry are as high as +47.5‰. The extreme enrichment in  $\delta^{34}\text{S}$  of carbonate-associated sulfate is the expected consequence of high rates of bacterial sulfate reduction in anoxic waters during Neoproterozoic ice ages. During post-glacial transgression the photosynthetic production of oxygen would have likely driven sulfate reducers back into sediments. Due to the diffusive limitation of sulfate into sediments, SRB would have been cut off from oceanic sulfate and  $\delta^{34}\text{S}$  of newly formed sulfides and carbonate-associated sulfate could have risen to values higher than contemporaneous seawater. As modern river inputs to seawater have  $\delta^{34}\text{S}$  values in the range of 6-10‰, this sulfur isotope anomaly most likely reflects oceanographic processes, rather than the sudden and intense post-glacial weathering of exposed continents under a  $\text{CO}_2$  charged atmosphere.

5:00 PM Hurtgen, Matthew T.

### THE SULFUR ISOTOPIC EVOLUTION OF NEOPROTEROZOIC SEAWATER SULFATE

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We have analyzed the sulfur isotopic composition of trace sulfate extracted from Neoproterozoic carbonates collected in Namibia, South Australia and Death Valley, CA, in order to construct the isotopic evolution of Neoproterozoic seawater sulfate. Biogeochemical processes impose significant and predictable isotopic fractionations on sulfur species as they are cycled between oxidized and reduced forms. Consequently, the isotopic composition of sedimentary sulfates are sensitive indicators of rates of these processes at a global scale. Previous secular  $\delta^{34}\text{S}_{\text{sulfate}}$  trends for the Neoproterozoic have been developed using rarely occurring evaporitic gypsum and barite deposits that provide only a low-resolution glimpse of sulfate evolution. Carbonates are significantly more abundant in the Neoproterozoic than sedimentary sulfate deposits and therefore can provide a relatively continuous marine sulfate sulfur isotopic signal that may be utilized to assess environmental change. The nearly pure carbonates contain 0 to 300 ppm sulfate.

$\delta^{34}\text{S}_{\text{sulfate}}$  and  $\delta^{34}\text{C}_{\text{carbonate}}$  values of Neoproterozoic carbonates are relatively stable until about 850 Ma, with  $\delta^{34}\text{S}$  values ranging from 10-25‰ and  $\delta^{13}\text{C}$  values near 0‰. By contrast, the mid to late Neoproterozoic (850-550 Ma) is characterized by rising  $\delta^{34}\text{S}$  values reaching 50‰ with high-amplitude short-term variation between 10‰ and 40‰. Additionally,  $\delta^{13}\text{C}$  values rise to 8‰ with sharp minima. We suggest that weathering inputs of sulfate and inorganic carbon were high during the late Mesoproterozoic and early Neoproterozoic, with an anoxic-sulfidic deep ocean supporting a moderate pyrite burial rate. By contrast, most of the late Neoproterozoic was characterized by low weathering rates and high burial ratios of pyrite/total sulfur and organic carbon/total carbon, but low burial rates.

There are no definitive trends in  $\delta^{34}\text{S}_{\text{sulfate-pyrite}}$  through this period, but a minimum of 0‰ as late as 580 Ma may indicate low sulfate concentrations and near total reduction of oceanic sulfate to sulfide. The available data cannot support or refute the proposed development of a non-photosynthetic sulfide-oxidizing biota at 800 Ma.

5:15 PM Goldhaber, Martin B.

### SUBCONTINENTAL SCALE FLUID TRANSPORT OF THE SULFIDE COMPONENT OF MISSISSIPPI VALLEY-TYPE ORES

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The midcontinent of the U.S. hosts Zn-Pb mineralization in Paleozoic carbonate rocks. These 'Mississippi Valley-Type' districts together contain hundreds of millions of tons of sulfide ore minerals and pyrite. Transport of the Zn, Pb, and other metals was by a hydrothermal flow system that extended 100's of kilometers driven by late Paleozoic Ouachita tectonism. The source of sulfide in the ores is, however, problematic, as is the site of sulfide generation; both local (district scale) and distant sources have been proposed.

An isotopic and petrographic study on over 400 pyrite-bearing ore fluid aquifer samples was conducted to determine the origin of the sulfide sulfur. Samples were from 31 core holes within an area of 25,000 Km<sup>2</sup>. This 'far-field' pyrite is a product of the passage of ore-forming fluids because: 1) the pyrite is intergrown with ore-stage vug-filling dolomite and 2) lead isotope compositions of trace lead in the epigenetic pyrite are similar to ores. The far-field sulfur isotopic data show a pronounced maximum in the range -0 to -6 ‰, which overlaps the values for ore sulfides of the geographically dispersed Tri-State, northern Arkansas, and central Missouri Districts. This isotopically light component occurs throughout the entire Ozark region in huge quantities. The enormous mass and isotopic homogeneity of this sulfide argue for formation from a gigantic source. The most likely candidate is thermal decomposition of sedimentary pyrite to form pyrrhotite +  $\text{H}_2\text{S}$  at T>300 °C in clastic sediments of the adjacent Arkoma basin. There is a secondary maximum in the data in the range +6 to +18 ‰. This range overlaps the main stage ore sulfides of the Lead Belts of southeast Missouri. The isotopically heavy sulfide occurs over a large region but only in an aquifer that fed into the Lead Belts. This heavy sulfide formed by thermochemical reduction of sulfate migrating in this aquifer. The results of this study show that production of ore sulfide was by two distinct abiogenic mechanisms and transport was by migrating hydrothermal fluids.

## SESSION NO. 38, 1:30 PM

Monday, November 5, 2001

### T15. Special Session in Honor of Half Zantop (*Society of Economic Geologists*)

Hynes Convention Center, 103

1:45 PM Sonder, Leslie J.

#### HALF ZANTOP: A DARTMOUTH EARTH SCIENCES PERSPECTIVE

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After completing his Ph.D. at Stanford in 1969, Half Zantop spent 7 years as an industry geologist involved in exploration in Spain, Argentina, and Costa Rica. He joined the Dartmouth Earth Sciences faculty in 1976. His expertise in economic geology, industry contacts, familiarity with life in Latin America, and fluency in English, German, French, and Spanish precisely met the Department's need for an economic geologist who could contribute to existing active research and teaching programs in Central America. He was promoted to Associate Professor in 1982 and full Professor in 1988. His research initially focussed on manganese and iron deposits, shifting later to stratiform/stratobound deposits and ultimately to hydrothermal precious metal deposits. At the time of his death he had nearly completed the revised second edition of International Mineral Economics: Mineral Exploration, Mine Valuation, Markets, and International Mineral Policies (co-authored with W. Gocht and R. Eggert; Springer-Verlag).

Half was renowned as a teacher in his upper-level economic geology classes and even more so in his introductory courses. Countless students were inspired to switch their major to geology after taking physical geology with Half. Many students thought he was the best professor they had at Dartmouth. Beyond being a superlative teacher in the classroom, he was a mentor without peer, caring and fair to his students. His devotion to his students was well known in the department and made him one of the most sought-after undergraduate thesis advisors. Half would take on undergraduates whose previous academic performance might have dissuaded other faculty; his faith in them and the time he invested paid off at thesis defense time when the quality of the work took everyone else by surprise.

Half maintained a cultured approach to people and life. He and his wife, also a Dartmouth faculty member (German Studies department), were frequently active in political and human rights issues beyond the scope of the Department and Dartmouth. In departmental affairs, he was our conscience, never permitting expediency to come before fairness and justice. And always, he spoke with grace, tact, and humor even when in disagreement. He left us the better, and the more honorable, for knowing him.

2:00 PM Burkins, Melody Brown

#### MINES, VOLCANOES, AND "THE STRETCH": A STUDENT TRIBUTE TO HALF ZANTOP

BURKINS, Melody Brown, Washington, DC, melody\_burkins@leahy.senate.gov

The Dartmouth College off-campus program, fondly known as "The Stretch," was made all the more special each year by the two-week segment led by Dr. Half Zantop. The segment was loved not only for its content — the study of active volcanoes and working mines throughout Central America and Mexico — but also for the unique experience of learning, working, and traveling with Half. Half engaged students in his passion for methodical and detailed field studies, sometimes spending several hours at a single outcrop as he encouraged students to sketch, analyze, and debate until a geologic story unraveled. He was also untiring, keeping students' schedules filled with fourteen-hour days of field studies based out of indestructible (almost) Volkswagen vans. Yet, amid the hard work and driving schedule, Half would purposefully carve out time — sometimes in the middle of a field day — for students to wander an historic town, buy silver earrings and bracelets, and simply experience the culture, people, and landscape around them. This presentation, a student tribute to Dr. Half Zantop's work on "The Stretch," will revisit the years he led the field program. Through collections of student photos and personal stories, the narrative will highlight Half's love of field geology, his personal connection to the volcanoes, mines, and people of the region, and his unwavering dedication to his students. "The Stretch" will not be the same without Dr. Half Zantop, but it will remember him as one of its most respected, and most beloved, professors.

2:15 PM Gemmell, J. Bruce

#### HALF ZANTOP'S CONTRIBUTION TO THE GEOLOGY AND MINERAL DEPOSITS OF THE FRESNILLO DISTRICT, MEXICO

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Half Zantop's interest in Fresnillo, the world's largest and richest silver mining district, began in the mid 1980's. He realised the importance of the district and began, along with his graduate and undergraduate students, investigating the physical and chemical processes of ore formation through geological and geochemical research. Fresnillo is located in Zacatecas state 750 km NW from Mexico City. A series of epithermal veins and replacement bodies are hosted in Cretaceous sedimentary and mafic volcanic rocks.

From the mid-1980's to 2001, Half supervised 10 thesis projects at Fresnillo, as well as conducting his own research. Initial research in the district began with a study on the geology and geochemistry of the Santo Nino vein by Bruce Gemmell (PhD, 1986) and a study on selected veins in the central part of the district by Eduardo Chico (MSc, 1986). Laurie Benton (Hons, 1987) undertook project investigating the trace element and strontium isotope compositions of the calcite of the Santo Nino vein. Janice Gardner (MSc, 1987) compared hand-held and Landsat remote sensing data for rocks and hydrothermal alteration in the district. John Lucio (MSC, 1990) investigated the Pb and Sr isotopes of ores and host rocks throughout the district. Michael McDougall (Hons, 1998) completed a Honors thesis which included a district-scale geochemical study, including pathfinder elements. Charles Lalancette (Hons, 1998) investigated the residence and depositional mechanisms of gold in the San Mateo and San Carlos veins. Edward Hughey (Hons, 1999) undertook a study of the mineral deposition, paragenesis and fluid flow in the San Carlos vein. A fluid inclusion and cathodoluminescence study of the Santo Nino and San Carlos vein systems was done by Eric Eckberg (Hons, 1999). Jennifer Flight (Hons, 2001) inferred the presence of ore at depth throughout the district via a comparison of oxygen isotope compositions and fluid inclusion temperatures at surface.