

Iron-sulfur redox and its effect on sulfur-isotope fractionation in carbonate-hosted Cu-Au replacement ores, Superior, Arizona, USA

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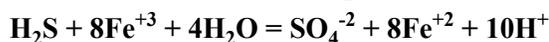
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ABSTRACT

Sulfur-isotope fractionation along an evolving redox fluid-flow path can create a sulfur-isotope pattern similar to that of a mixing line.

The porphyry-related, carbonate-replacement Cu-Au deposits at Superior, Arizona (USA) are massive specular hematite and massive sulfide ores formed when hydrothermal fluids flowed up through veins cutting relatively inert, sericitically-altered basement rocks and reacted with Paleozoic limestones and dolostones that host the ores. The massive pyrite ± chalcopyrite ± bornite pods occur within broader hematite replacement bodies and center on “feeder” veins. Field relationships and reaction-path modeling indicate these zones formed contemporaneously as concentrically-nested, outwardly-encroaching ore zones.

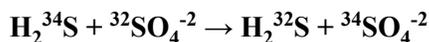
Ore fluids initially replaced carbonate rocks with hematite. Flow of fresh hydrothermal fluid from feeder veins infiltrated and replaced early hematite near veins with pyrite + chalcopyrite. Sulfidation of hematite required reduction of the iron, probably by oxidation of hydrogen sulfide (H₂S) to form sulfate (SO₄⁻²) according to the reaction:



The resulting SO₄-rich fluid continued to flow outward through the outer hematite body but contained little reduced sulfur, so only minor disseminated pyrite deposited there.

Sulfur isotopes of pyrite and chalcopyrite in sulfide-dominant ores near feeder veins range from δ³⁴S = -10.7 to -4.1 ‰, whereas pyrite at the sharp hematite-sulfide contact has δ³⁴S = 0.0‰, and disseminated pyrites within the outer hematite zone have δ³⁴S = +7.8 to +10.1‰. These sulfur isotope compositions may reflect a Raleigh distillation of sulfur isotopes that accompanied the redox reactions involved with hematite sulfidation.

Near feeder veins where pyrite replaced hematite, redox formation of SO₄⁻² may have concentrated ³⁴S in sulfate (i.e., a form inaccessible to pyrite formation) according to the reaction:



The remaining isotopically lighter H₂S would have reacted with iron to deposit ³²S-rich pyrite and stripped the fluid of some ³²S. Outward flow of the fluid carried isotopically heavier sulfur into the peripheral hematite zone. Such hydrothermal fluids were greatly depleted of reduced sulfur species, and thus deposited only disseminated pyrite using the remaining, “distilled” heavy fraction of sulfur. Isotope exchange with sulfate released by dissolution of earlier-formed anhydrite originally deposited near the carbonate-hematite reaction front may also have contributed heavier sulfur to peripheral sulfides.

Keywords: sulfur-isotope fractionation, redox, Raleigh distillation, carbonate-hosted replacement ore, porphyry

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INTRODUCTION

The carbonate-hosted massive replacement Cu-Au ores of the Superior district, Arizona, produced over 14.5 million tons of copper ore averaging 4.5% Cu (Paul and Knight, 1995). Unlike skarn deposits, these replacement ores consist of massive sulfide and massive specular hematite bodies without accompanying calcsilicate gangue.

Exploration drilling by ASARCO identified the Superior East porphyry prospect five km northeast of the Superior replacement ores (Sell, 1995). One year prior to mine closure in 1996, exploration drilling by BHP penetrated a swarm of altered porphyry dikes (Manske and Paul, 2002), and subsequent drilling delineated the large Resolution porphyry deposit 2 km to the south of the Superior replacement orebodies (Fig. 1).

Both the similarity of the replacement ores with carbonate-hosted, porphyry-related ores in other districts, as well as the general spatial association with nearby porphyry copper deposits, strongly suggests carbonate-hosted replacement ores in the Superior district are part of a porphyry copper system.

DISTRICT GEOLOGY

Proterozoic basement rocks consist primarily of Pinal quartz-muscovite schist and batholithic Ruin granite, capped by the Apache group quartzites, slates, and metadolostones (Short et al., 1943; Hammer and Peterson, 1968). Locally thick 1.1 Ga diabase sills intrude the Proterozoic section (Wrucke, 1989). These Proterozoic rocks are the primary hosts for Cordilleran vein deposits such as the Magma vein (Hammer and Peterson, 1968) and very minor carbonate-replacement ores in the Mescal limestone.

Paleozoic platform carbonate strata unconformably overly basement rocks. The Devonian Martin, Mississippian Escabrosa, and Pennsylvanian Naco Formations host the bulk of the hypogene replacement ores. Carbonate rocks in these formations contain only very minor amounts of silt, and are locally cross-bedded and oolitic. Thin shale interbeds occur throughout.

Undated, fault-bounded Mesozoic conglomerates and andesitic volcanoclastic rocks comparable to Cretaceous volcanoclastic rocks elsewhere in Arizona are concealed by younger strata (Manske and Paul, 2002). Laramide quartz monzodiorite intruded the Mesozoic clastic rocks circa ~64-63 Ma (Seedorff et al., 2005). These porphyries are linked to several centers of porphyry mineralization in a belt stretching from Superior through the Miami-Globe area.

Tertiary conglomerates unconformably overlie the Paleozoic carbonate rocks, truncating ore, and thickening to the east. The 400+ meter thick Apache Leap dacite tuff caps the sequence and has an $^{40}\text{Ar}/^{39}\text{Ar}$ age of 18.6 Ma (Ferguson et al., 1998).

Paul and Knight (1995) presented a detailed description of the replacement ores and carbonate host rocks.

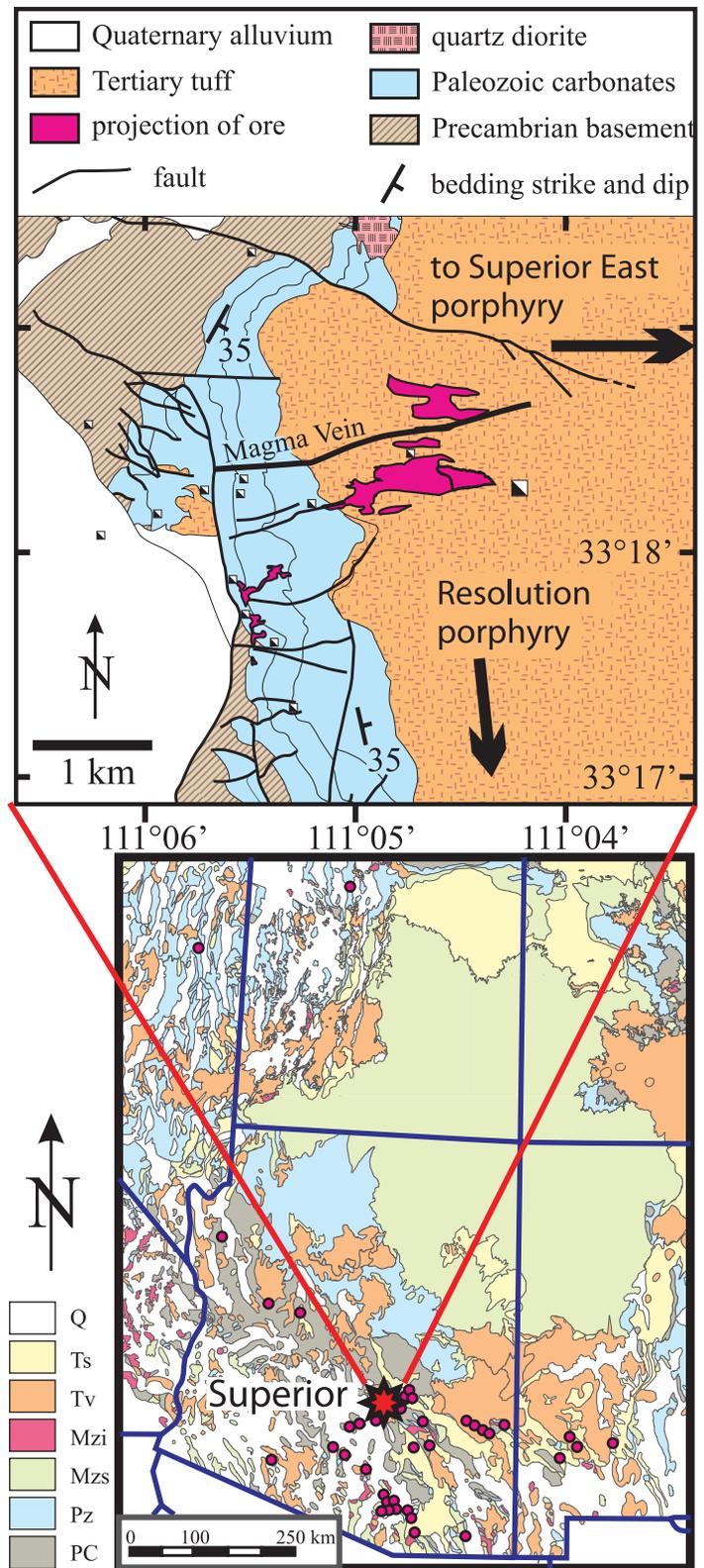


Figure 1. Location of the Superior district's carbonate-replacement ores relative to the Magma Vein and two nearby porphyry copper deposits (upper), and location of the Superior district relative to other porphyry deposits in the southwestern U.S.A. (lower; porphyry locations from Tittley, 1982). Q-Quaternary sediments; Ts-Tertiary sediments; Tv-Tertiary volcanics; Mzi-Mesozoic intrusions; Mzs-Mesozoic sediments; Pz-Paleozoic sediments; PC-Precambrian rocks.

CARBONATE-HOSTED REPLACEMENT OREBODIES

The C-bed orebody, the largest of the carbonate replacement “manto” ores, zones successively outward from a central quartz-sulfide vein, to a barren massive pyrite body, massive pyrite-chalcopyrite±bornite ore, and marginal specular hematite-hosted ore containing disseminated copper-iron sulfides (Fig. 2). The boundary between massive sulfide-gangue and massive specular hematite-gangue ores is sharp with local boundary-parallel rhythmic layering over the 10-cm-wide transition zone.

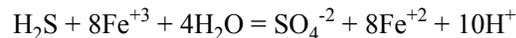
This zonation resulted from outward (northward) flow of hydrothermal fluids from the feeder vein out into reactive dolomite host rocks (Friehauf, 1998). Due to the unreactive nature of the quartzfeldspathic clastic host rocks south of the feeder vein, fluid flow did not proceed southward.

Ore fluids at the carbonate replacement front deposited hematite because the fluid contained dissolved iron, but little reduced sulfur. “Fresh” ore fluid from the feeder veins introduced iron, copper, and reduced sulfur, replacing earlier-formed hematite with massive sulfides. Ubiquitous concentricity of marginal hematite ores and central sulfide ores in all orebodies indicates both replacement zones formed simultaneously as outwardly encroaching replacement fronts (Friehauf, 1998). The bimodal distribution of sulfide- and hematite-dominant ores suggests ore fluids transported more iron

than could be deposited by accompanying H_2S and the sharp contact between these zones represent the final front where H_2S was largely exhausted.

Petrographic evidence such as relict specular hematite lathes in pyrite indicates much of the pyrite formed by sulfidation (pyritization) of hematite. Pyritization of hematite requires reduction of ferric iron (Fe^{+3}) to ferrous iron (Fe^{+2}). Basement rocks in the region include the Pinal Schist and other Proterozoic metasedimentary rocks that lack significant reduced carbon that could have caused this reduction. Similarly, the total organic carbon (TOC) of the host rock Paleozoic carbonates is near zero and so could not have reduced ferric iron.

With a paucity of local, rock-hosted reducing agents, aqueous hydrothermal sulfur species (H_2S or HS^-) were the most abundant reducing agent available in system. Iron reduction was probably accomplished by contemporaneous oxidation of reduced aqueous sulfur to form sulfate according to the reaction:



One byproduct of this reaction is the formation of hydrogen ions that further enhanced the ore fluid's ability to continue onward and dissolve carbonate at the orebody-host rock contact. The other byproduct, SO_4^{-2} , had the potential to react with Ca^{+2} at the wall rock replacement front and affect permeabilities there by precipitation of anhydrite. Anhydrite

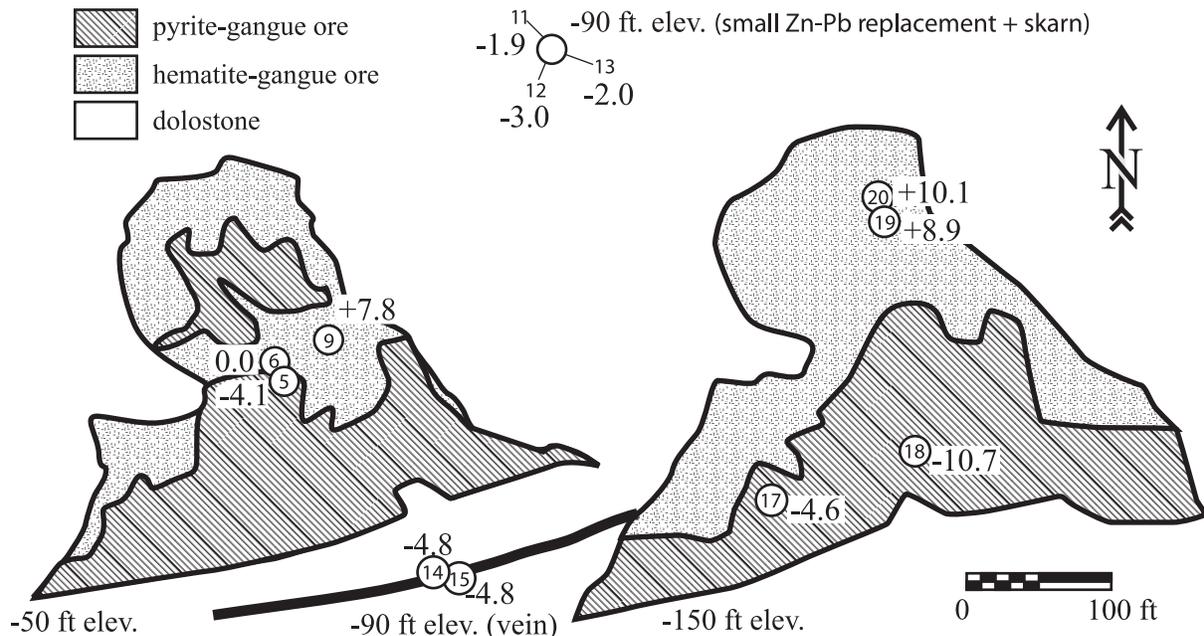


Figure 2. This composite map of vertical projections of the C-bed orebody shows the sample locations on the successively deeper 3644, 3690, and 3744 levels of the mine (50, 90, and 150 feet below sea level, respectively). Ore fluids flowed upward and northward into the dolostone from the fluid conduit at the southern boundary of the orebody. $\delta^{34}S$ results are shown with large font. Sample numbers are shown in italics. Sample locations (circles) were chosen to be representative of each ore type as a function of distance from the ore-fluid conduit vein. Samples 11, 12, and 13 occur within a small, isolated Pb-Zn replacement body. Samples 5 and 6 actually located 5 cm apart.

annealing fractures might thereby have diminished the importance of smaller fractures for fluid flow into carbonate wall rocks, resulting in the more broadly lobate ore-wallrock contact observed in the C-bed orebody.

The iron-sulfur redox reaction created two sharply contrasting aqueous sulfur environments: an inner zone in which sulfur occurred primarily as bisulfide (HS^-) or hydrogen sulfide (H_2S), and an outer zone in which the dominant aqueous sulfur species was sulfate (SO_4^{-2}). Continued outward flow of the resulting SO_4 -rich fluid through the outer hematite body, with little dissolved reduced sulfur or ferrous iron, caused deposition of only minor disseminated pyrite. Chalcopyrite in the outer hematite-gangue ores occurs primarily as replacement overgrowths on pyrite, indicating copper in solution could only precipitate chalcophile elements by replacing iron in pre-existing sulfide grains.

Variations in the sulfur isotope composition of sulfides in these two juxtaposed ore types were studied in order to find evidence for the processes leading to these different sulfur environments originating from a single fluid source (i.e., the feeder vein).

METHODS

All isotope analyses in this study focused on individual grain samples in an effort to ensure they were monomineralic and formed during only one stage of mineralization (i.e., not a composite sample of multiple grains that may have formed at different times).

I used a dental drill (courtesy of Dr. David Dettman) to excavate individual sulfide grains from polished hand samples of ore collected in the course of my underground mapping. Sample selection sought representative sulfides from each mineralization zone (vein, massive sulfide-hosted, specular-

hematite hosted, and skarn/Pb-Zn). The drill bit was thoroughly cleaned between each sampling.

I weighed approximately 100 micrograms portions of the drill "cuttings" and mixed them with 1-2 milligrams of V_2O_5 , then sealed them in capsules.

Samples were analyzed at the USGS isotope lab in Denver, Colorado (Dr. Robert Rye) by combusting them in a Carlo-Erba elemental analyzer to produce SO_2 gas, which was then admitted to a Micromass Optima mass spectrometer for the isotope measurement by the isotope ratio monitoring method. The analytical reproducibility is $\pm 0.2\%$ for sulfur. Underweight samples (i.e., those producing less than 1 nA peaks) are not reported. The hardware and procedure resemble those described by Giesemann et al. (1994).

SULFUR ISOTOPE DATA

Sulfur isotopes in the weakly-developed early garnet skarn vein and accompanying small massive pyrite-sphalerite-galena-quartz replacement pod ranged from $\delta^{34}\text{S} = -1.9$ to -3.0% (Table 1). Although these samples were taken from skarn not affected by copper mineralization, cross-cutting relationships elsewhere in the deposit indicate this type of mineralization predates main-stage copper mineralization, so these sulfur isotope values represent a different fluid stage.

The sulfur isotope compositions of pyrite and chalcopyrite grains in the massive copper-gold replacement ores show a marked gradient from light sulfur values in the feeder vein and sulfide-gangue ores ($\delta^{34}\text{S} = -10.7$ to -4.1%), to heavy $\delta^{34}\text{S}$ values in the hematite zone ($\delta^{34}\text{S} = +7.8$ to $+10.1\%$). Within the sharp contact zone between these two ore types, sulfide grains within centimeters of one another had a composition of $\delta^{34}\text{S} = -4.1\%$ on the sulfide side and $\delta^{34}\text{S} = 0.0\%$ on the hematite side (Fig. 3).

TABLE 1. SULFUR ISOTOPE DATA*

Sample	Weight (mg)	$\delta^{34}\text{S}$	Mineral	Ore type
11	0.23	-1.9	Pyrite	Pb-Zn
12	0.34	-3.0	Sphalerite	Pb-Zn
13	0.18	-2.0	Pyrite	Garnet skarn
14	0.39	-4.8	Bornite	Vein
15	0.31	-4.8	Chalcopyrite	Vein
17	0.22	-4.6	Pyrite	Sulfide (near vein)
18	0.20	-10.7	Pyrite	Sulfide
5	0.17	-4.1	Pyrite	Contact (sulfide side)
6	0.18	0.0	Pyrite	Contact (hematite side)
9	0.30	+7.8	Chalcopyrite	Hematite
19	0.18	+8.9	Pyrite	Hematite
20	0.21	+10.1	Pyrite	Hematite

*All samples are of individual sulfide mineral grains in the C-bed orebody, Superior, Arizona. Ore types based on mineralogy of massive replacement gangue.

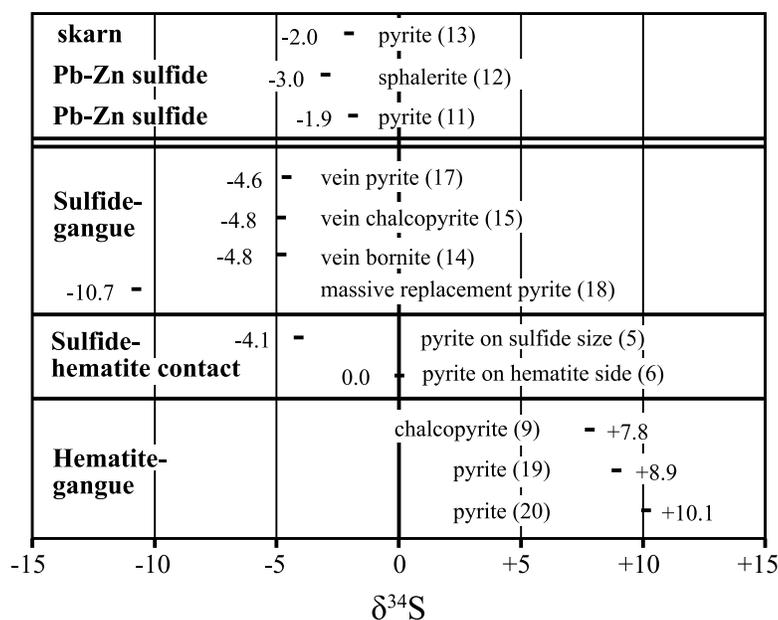
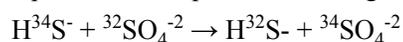


Figure 3. Sulfur-isotope values of sulfide-mineral grains in early skarn, and later massive replacement ores. Replacement ore samples grouped according to dominant gangue mineral to show characteristically light sulfur in massive-sulfide ores, near-zero $\delta^{34}\text{S}$ values in the sample at the sharp contact between ore types, and heavy sulfides in the outer hematite-gangue ores. Sample numbers are noted in parentheses.

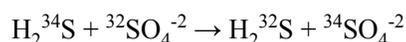
All three clusters of values – light sulfur in the sulfide zone, near-zero values at the contact, and heavy sulfur in pyrite in the hematite zone – arose from deposition from the same initial sulfur source. These differences therefore reflect fractionation processes in the fluid as it proceeded outward from feeder vein into the orebody.

SULFUR ISOTOPE FRACTIONATION BETWEEN SULFATE AND SULFIDE SPECIES

Sulfur isotopes fractionate between sulfur species in solution and sulfur-bearing minerals. The fractionation factor (α) describes how ^{34}S and ^{32}S are distributed between two coexisting species as a ratio of isotope ratios $(^{34}\text{S}/^{32}\text{S})_X / (^{34}\text{S}/^{32}\text{S})_{\text{H}_2\text{S}}$ where X is a sulfur-bearing species such as pyrite, HS^- , or SO_4^{-2} . Positive values of $\ln(\alpha)$ indicate the species X preferentially concentrates heavy sulfur ^{34}S . The magnitude of $\ln(\alpha)$ indicates the magnitude of this preference. Due to differences in the vibrational energies of the sulfur-oxygen bond compared to the sulfur-hydrogen bond, sulfate species concentrate heavy sulfur (^{34}S) much more so than do bisulfide or hydrogen sulfide. Experimentally determined fractionation factors (e.g., Ohmoto and Rye, 1979) quantify the strong preference of sulfate for ^{34}S , relatively mild preference of pyrite for ^{34}S , and weak preference of HS^- for light ^{32}S relative to H_2S (Fig. 4). In solution, sulfur isotopes exchange between aqueous sulfur species according to the reactions:



and



Pyrite precipitation from solution draws sulfur primarily from the reduced species in solution and has a sulfur isotope composition similar to the relative light HS^- or H_2S and not the isotopically heavy sulfate (Fig. 4).

COMBINED REDOX - FRACTIONATION EFFECT DRIVES RALEIGH DISTILLATION

The wide range and consistent spatial pattern of sulfur isotope compositions of sulfides in the C-bed orebody can be explained as the result of a Raleigh distillation of sulfur isotopes during progressive precipitation of sulfide minerals accompanied by contemporaneous oxidation of aqueous sulfur from a single sulfur source.

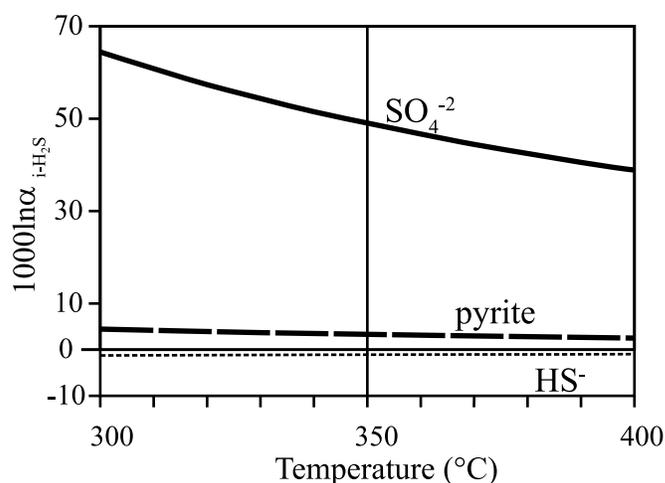


Figure 4. This plot of fractionation factors (α) for aqueous sulfate (SO_4^{-2}), pyrite, and bisulfide (HS^-) relative to $\text{H}_2\text{S}(\text{aq})$, plotted as functions of temperature, illustrates: (1) a strong preference of sulfate for ^{34}S , (2) relatively mild preference of pyrite for ^{34}S , and (3) weak preference of HS^- for light ^{32}S relative to $\text{H}_2\text{S}(\text{aq})$. In an aqueous fluid, sulfate ion will preferentially concentrate heavy ^{34}S , leaving lighter sulfur ^{32}S for HS^- ion and H_2S (data from Ohmoto and Rye, 1979).

Initial fluid composition

Similarity of the geology of the orebody at Superior with replacement ores clearly linked to porphyry copper systems (e.g., Bisbee, Bingham, and Yauricocha) and slightly negative sulfur isotope compositions of sulfide minerals in the feeder veins in the Superior district suggest a magmatic sulfur source at Superior with this initial bulk sulfur isotope composition, although a value nearer zero cannot be excluded. The dominant aqueous sulfur species was H_2S or HS^- based on thermodynamic consideration of the mineral assemblages in the feeder veins (Friehauf, 1998).

Origin of light sulfur isotopes in massive sulfide zone

Isotopically very light sulfides in the inner massive sulfide zone of the replacement ores (e.g., sample 18 – Fig. 3) may have resulted from fractionation between aqueous sulfur species during oxidation. Initially, both ^{32}S and ^{34}S occurred as hydrogen sulfide (H_2^{32}S and H_2^{34}S). Oxidation converted some H_2^{34}S to $^{34}\text{SO}_4^{-2}$, thereby making that heavy sulfur unavailable for pyrite formation (Fig. 5). Oxidation also converted some H_2^{32}S into $^{32}\text{SO}_4^{-2}$. Because isotope exchange between aqueous sulfur species preferentially concentrates heavy sulfur in sulfate, the exchange reaction

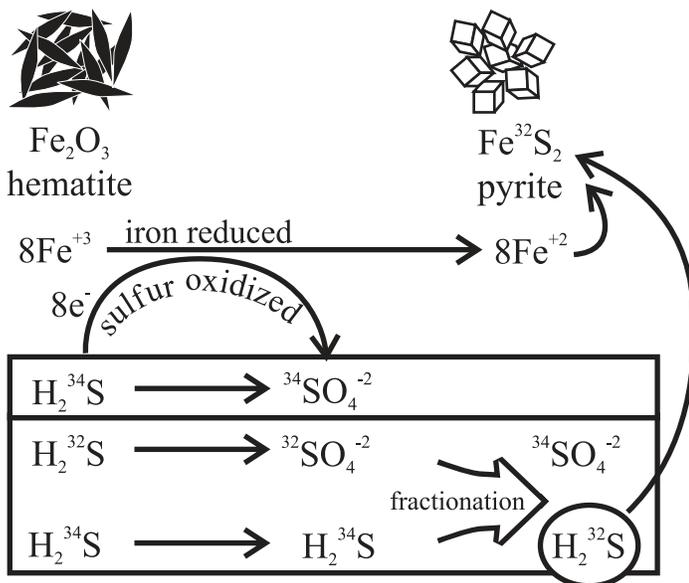
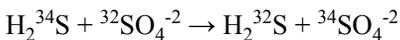


Figure 5. Pyritization of hematite requires reduction of ferric iron by accompanying oxidation of bisulfide. Oxidation of heavy H_2S forms heavy sulfate (SO_4^{-2}), which is not involved with pyrite formation. Oxidation of light H_2S forms light SO_4^{-2} . Isotope exchange between light SO_4^{-2} and heavy H_2S forms light H_2S which deposits as isotopically light pyrite in the massive pyrite zone and depleting the fluid of light sulfur. The fractionated fluid then continues to travel outward to deposit isotopically heavy pyrite in the outer hematite zone.

strongly favored isotopically light H_2S (Fig. 4). Since pyrite formation drew primarily from this reduced aqueous sulfur species, pyrite in this inner replacement zone was enriched in isotopically light sulfur. The remaining fluid, however, was depleted of ^{32}S relative to ^{34}S .

Origin of heavy sulfur isotopes in massive-hematite zone

Continued outward flow of this ^{32}S -depleted, ^{34}S -enriched fluid into the hematite zone and subsequent pyritization of hematite along this flow path would continue to increase the bulk $\delta^{34}\text{S}$ of the fluid. Pyrite precipitated from this "isotopically-distilled" fluid would have the high positive $\delta^{34}\text{S}$ values observed in the outer, hematite-rich zone (Fig. 6). Isotope exchange with sulfate released by dissolution of earlier-formed anhydrite deposited near the carbonate-hematite reaction front may also have contributed to heavier sulfur in the ore fluid in peripheral regions.

WATER-ROCK REACTION MODEL

Initial iron-rich, sulfide-poor ore fluid formed small hematite replacement mantos by dissolution of dolostone and contemporaneous hematite \pm anhydrite precipitation (Fig. 6A). The sulfide-poor nature of the fluids during this initial hematite-carbonate replacement may have been the result of depletion of reduced sulfur due to interaction with iron in basement diabase (Friehauf, 1998) or due to a more oxidized, sulfate-dominant fluid composition of the source during early mineralization.

As basement rocks lost their sulfur-fixing ability (due to sulfidation of wall rock iron), subsequent ore-fluids that flowed into the manto contained greater amounts of sulfur as H_2S . Replacement of hematite by pyrite oxidized some of this H_2S , forming byproduct aqueous sulfate not available for precipitation in pyrite (Fig. 6B). The redox reaction oxidized both light and heavy sulfur H_2S , but fractionation between aqueous H_2S and SO_4^{-2} favored deposition of light, negative $\delta^{34}\text{S}$ pyrite in the inner zone from the reduced sulfur species (H_2S). The isotopically heavy, residual ore fluid flowed outward through the hematite zone, precipitating isolated, disseminated pyrite grains from the remaining H_2S in the ^{34}S -enriched solution (Fig. 6C).

In addition to precipitation from an ore fluid which had been partially stripped of light sulfur, the ore fluid in the peripheral hematite zone may also have been enriched in heavy sulfur by dissolution of earlier-deposited anhydrite and subsequent isotope exchange (Fig. 6D).

The net result was the formation of isotopically light sulfides (negative $\delta^{34}\text{S}$) in the massive sulfide zone near the feeder vein, and less abundant, disseminated, isotopically heavy sulfides (positive $\delta^{34}\text{S}$) in the outer hematite zone (Fig. 6D).

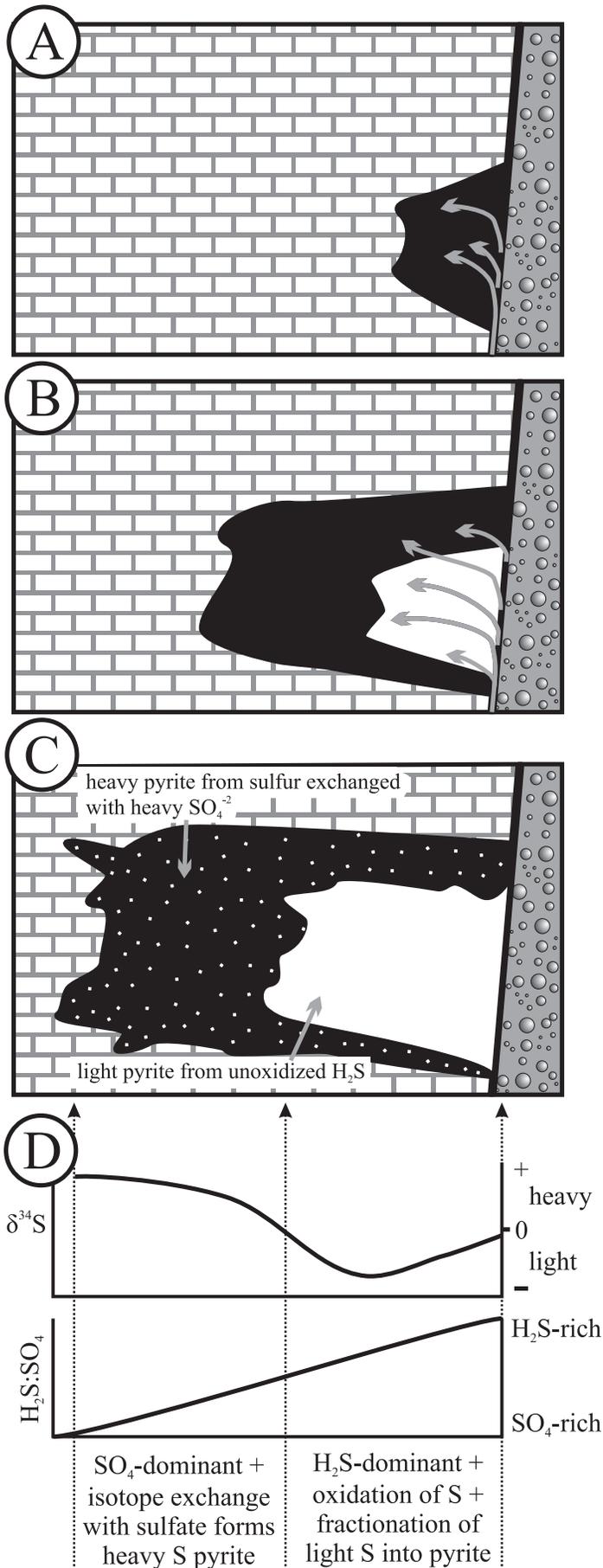


Figure 6. (A) Initial replacement of dolostone by sulfur-poor fluid formed massive specular hematite bodies. (B) Continued flow of sulfur-bearing ore fluid formed inner massive sulfide zone by pyritization of hematite. Ore fluid enriched in heavy sulfur from the pyritization process continued to flow out into the outer hematite zone. (C) Final sulfur isotope distribution with negative $\delta^{34}\text{S}$ sulfides in the massive pyrite zone and high positive $\delta^{34}\text{S}$ sulfides in the hematite zone. (D) Unscaled sketch of the sulfide mineral $\delta^{34}\text{S}$ values and aqueous speciation of sulfur in hydrothermal fluid at different positions within the orebody.

CONCLUSION

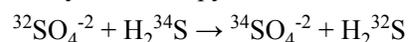
The lack of biogenically reduced, isotopically light sulfides in the basement, the absence of high $\delta^{34}\text{S}$ evaporites in the basement and wall rocks, and the probable genetic relationship to a porphyry center providing magmatic sulfur suggest the bimodal pattern we see in the carbonate-hosted massive replacement deposits of the Superior district probably does not reflect a mixing of multiple sulfur sources. The sulfur isotope distribution at Superior more probably resulted from a Rayleigh distillation of sulfur from an ore fluid that had a single, magmatic source of sulfur reservoir with $\delta^{34}\text{S} \sim 0\text{‰}$, combined with the necessary redox reactions required for pyritization of hematite.

- Initially, hydrothermal fluids flowed through major veins in basement rocks until they encountered reactive carbonate wall rocks. Initial replacement of carbonate rocks formed massive specular hematite bodies due to an abundance of dissolved iron, but relative lack of reduced sulfur. The lack of reduced sulfur may have resulted from pyritization of iron rich basement rocks early in the process, but the capacity of basement rocks for fixing sulfur was ultimately limited and an H_2S -dominant ore fluid with bulk $\delta^{34}\text{S} \sim 0\text{‰}$ ultimately encountered the early hematite body.

- As H_2S -bearing hydrothermal fluids flowed into the initial hematite-rich orebody, some heavy sulfur H_2^{34}S oxidized during reduction of ferric iron in hematite, forming heavy sulfur sulfate ($^{34}\text{SO}_4^{-2}$) that was unavailable for pyrite formation.

- Some light sulfur H_2^{32}S also oxidized to form light sulfur sulfate ($^{32}\text{SO}_4^{-2}$) which was also unavailable for pyrite formation.

- Isotope exchange between aqueous sulfur species caused light sulfur in sulfate to preferentially exchange with heavy sulfur in unoxidized H_2S , thus forming light sulfur H_2S available for pyrite formation and reducing the availability of heavy sulfur for pyrite formation:



H_2S in the ore fluid reacted with reduced iron to form pyrite with negative $\delta^{34}\text{S}$.

5. ^{32}S -depleted ore fluid continued to flow outward from the feeder vein through the hematite-hosted ores, creating an environment enriched in ^{34}S for deposition of disseminated positive $\delta^{34}\text{S}$ pyrite in the hematite zone.

The relatively wide range and spatially systematic variation in sulfur isotope compositions of sulfides in the C-bed orebody at Superior demonstrates the importance of fractionation in ore systems where sulfidation of iron oxides is a major process. Negative $\delta^{34}\text{S}$ do not necessarily indicate biogenic processes, nor do positive $\delta^{34}\text{S}$ values indicate involvement of evaporites or sea water. Ore deposits showing a strong spatial correlation with $\delta^{34}\text{S}$ therefore do not necessarily indicate ore fluid mixing from different sulfur sources.

Similar distillations might be present in similar systems in which sulfidation of iron oxides is a major process (e.g., Iron Oxide Copper-Gold, BIF-hosted gold, etc.), especially lower temperature systems in which fractionation is greatest.

ACKNOWLEDGMENTS

I would like to very heartily thank Dr. Mark Barton (University of Arizona) for allowing me to piggy-back these sulfur isotope samples with the big IOCG project suite and for taking me in as a vagrant post-doc during which time we had many excellent discussions! Thanks also go to Dr. David Dettman for loaning us his drilling lab.

I am also forever in debt to Dr. Marco Einaudi (Stanford University) for making the Superior project possible, as well as Drs. Mark Sander, Eric Seedorff, and Scott Manske (formerly of Magma Copper Co.).

Finally, I thank Drs. Timothy Marsh, Guillermo Pareja, and Craig Johnson for feedback in preparation of this abstract, and Drs. Robert Kamilli and Jon Spencer for their support.

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