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Title: IRON-SULFUR REDOX AND ITS EFFECT ON SULFUR ISOTOPE FRACTIONATION IN CARBONATE-HOSTED CU-AU REPLACEMENT ORES, SUPERIOR, ARIZONA

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Author 1 (CONTACT AUTHOR)
Name: Kurt Friehauf
Org: Kutztown University
Country: USA

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Abstract: The porphyry-related carbonate-replacement Cu-Au deposits at Superior, AZ are located near the giant Laramide-age Resolution porphyry deposit to the south and the Superior East porphyry to the east. The massive specular hematite - massive pyrite±chalcopyrite±bornite ores formed when ≈350°C acidic hydrothermal fluids flowed up through veins cutting relatively inert, sericitically-altered basement rocks and reacted with Paleozoic limestones and dolostones that host the ores.

Massive sulfide pods within broader hematite replacement bodies center on "feeder" veins and zone outward from central massive bornite-pyrite to chalcopyrite-pyrite ores before an abrupt, 10 cm wide transition to outer hematite-dominant ores. 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 bisulfide (HS^-) to form sulfate (SO_4^{-2}) according to the reaction:

$$HS- + 8Fe^{+3} + 4H_2O = SO_4^{-2} + 8Fe^{+2} + 9H^+$$

Continued outward flow of the resulting SO_4-rich fluid through the outer hematite body contained little reduced sulfur or ferrous iron, so deposited only minor disseminated pyrite there.

Sulfur isotopes of pyrite and chalcopyrite in sulfide-dominant ores near feeder veins range from $\delta^{34}S = -10.7$ to -4.1 per mil, whereas pyrite at the sharp hematite-sulfide contact has $\delta^{34}S = 0.0$ per mil, and disseminated pyrites within the outer hematite zone have $\delta^{34}S = +7.8$ to +10.1 per mil. These sulfur isotope compositions may reflect a Raleigh distillation of sulfur isotopes resulting from the redox reactions involved with hematite sulfidation.

Near feeder veins where pyrite replaced hematite, redox formation of SO_4^{-2} may have concentrated ^{34}S in sulfate (i.e., a form inaccessible to pyrite formation).

$$H^{34}S^{-} + {}^{32}SO_4^{-2} \rightarrow H^{32}S^{-} + {}^{34}SO_4^{-2}$$

The remaining isotopically lighter HS- would have reacted with iron to deposit ^{32}S-rich pyrite and stripped the fluid of some ^{32}S. 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 that originally deposited near the carbonate-hematite reaction front may also have contributed to heavier sulfur in the peripheral sulfides. The bimodal distribution of sulfide- and hematite-dominant ores suggests ore fluids transported more iron than could be deposited by accompanying HS^{-} and the sharp contact between these zones formed at the reaction front where HS^{-} was exhausted.