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IMPLICATION OF SPHALERITE COMPOSITION AT A CENTRAL TENNESSEE MISSISSIPPI VALLEY TYPE DEPOSIT

Indiana State University

Meszaros, N.[1], Magnin, B.[1], Kile, B.[2], Brake, S.[2], Unger, D.[3], and Latimer, J.[2]

[1]Department of Geosciences, DePauw University; [2] Department of Earth and Environmental Systems, Indiana State University; [3] NuLegacy Gold Corp, Reno Nevada

ABSTRACT: The Central Tennessee Zinc District (CTZD) hosts Mississippi Valley Type (MVT) mineralization. The origin of the CTZD deposits remains ambiguous due to the complexities of ore fluid genesis, movement, evolution, and interaction with country rock. The CTZD is hosted within Lower Ordovician, nearly horizontal platform carbonates located along the paleo-structural highs of the Nashville Dome and Cincinnati Arch. Samples of sphalerite were collected from the Cumberland Mine in the CTZD where sphalerite ore occurs with barite, calcite, fluorite, and pyrite gangue. Sphalerite mineralization is present in two forms: open space filling in dolomite collapse breccia and replacement ore hosted in limestone. This study uses inductively coupled plasma optical emission spectrometry to investigate element compositional heterogeneity between nine breccia ore samples and six replacement ore samples. Analysis detected Zn up to 99 wt%, Fe up to 0.3 wt%, Mg up to 1,600 ppm, Mn up to 560 ppm, Mo up to 14 ppm, Cu up to 1,500 ppm, Pb up to 190 ppm, Cd up to 4,400 ppm, Co up to 22 ppm, and Ti up to 14 ppm. Arsenic, Sr, Ba, Cr, Sn, and Ag were below detection limit. Concentrations of Fe, Cd, and Co in sphalerite are similar to other MVT deposits in the U.S. Copper concentrations commonly exceed concentrations reported in MVT districts globally. Data show that sphalerite in replacement ores is depleted in Cu, Cd, and Pb, but enriched in Mg relative to the breccia-hosted ore counterpart. A weak correlation exists between Fe and commonly substituting Mg and Mn, and a strong positive correlation (R^2=0.97) exists between Cd and Pb. The data indicate that the ores either precipitated from different compositional fluids or precipitated along different mineralizing events from a single evolved fluid. These results have important implications in understanding the nature of MVT mineralization and act as a reference for pathfinder elements when searching for such deposits.

GEOLOGIC BACKGROUND: Sphalerite samples were collected from underground workings at the Cumberland Mine (Figs. 1 and 2), a MVT deposit located in the CTZD. Mineralization is hosted mainly in the Mascot Dolomite and to a lesser extent in the underlying Kingsport Formation—situated in the upper part of the Lower Ordovician Knox Group—which is part of a nearly horizontal carbonate platform sedimentary sequence located along the hinge of the Cincinnati Arch and on the apex of the Nashville Dome (Kyle 1976), the latter a southward geologic extension of the Cincinnati Arch (Fig. 2). These structures originated along the periphery of the Middle Ordovician Blountian and Taconic fold-thrust belts, and represent paleo-structural highs along which connate brines migrated during tectonic convergence (Leach & Sangster 1993). The post-orogenic depositional setting was characterized by surficial reducing conditions (Holland & Patzkowsky 1998; Patzkowsky & Holland 1999), which may have favored dolomitization and dissolution of the underlying lower Kingsport Formation and Mascot Dolomite (Kyle 1976).

Ore at the Cumberland mine (Fig. 3) occurs as open space filling within dolomitic breccia and as replacement of limestone units (i.e., manto-style) peripheral to the breccia bodies. The dolomite breccia bodies occur at dolomite-limestone boundaries and represent collapsed breccias likely derived by dissolution of underlying limestone units and brecciation of the overlying dolomite beds during periods of karstification that predate mineralization (see Crawford & Hoagland 1968; Kyle 1976). Sphalerite is the dominant ore mineral accompanied by barite, calcite, fluorite, crystalline dolomite, and minor galena. Gangue minerals in open space filling of the breccia ore generally consist of massive white calcite with minor amounts of fluorite, galena, barite, and some coarsely crystalline dolomite. In replacement ore, gangue minerals consist mainly of coarsely crystalline dolomite. Timing of mineralization is believed to be late Paleozoic and may have occurred in three stages from an individual fluid over the course of 8 million years, based on color and textural heterogeneity in the sphalerite crystals (Gratz & Misra 1987; Misra et al. 1996). The widely accepted hypothesis for ore formation is the "mixing model" in which tectonically focused connate brines mixed with a reduced sulfide fluid associated with hydrocarbon deposits (Kyle 1976; Kesler et al. 1994; Misra et al. 1996).

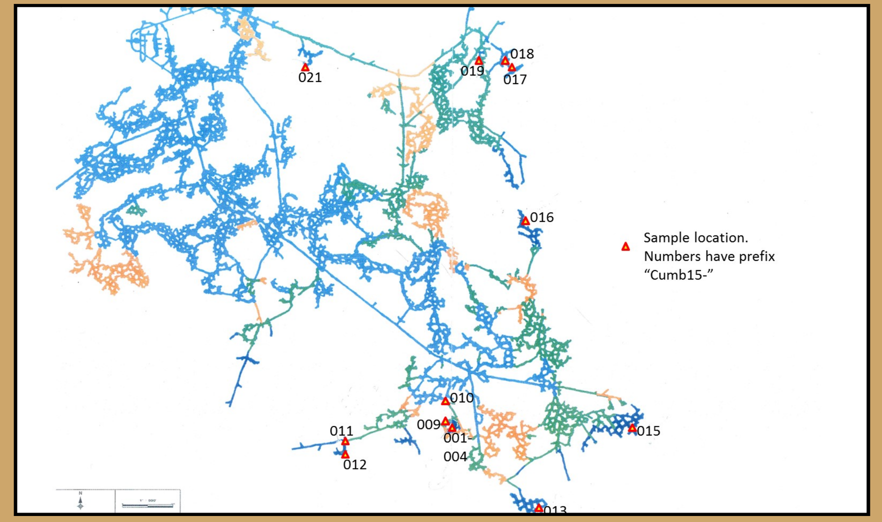


Figure 1: Location of sphalerite ore sample in underground workings at Cumberland Mine. Samples 001—004 and 009—013 = breccia ore; samples 015—019 and 021 = replacement ore.

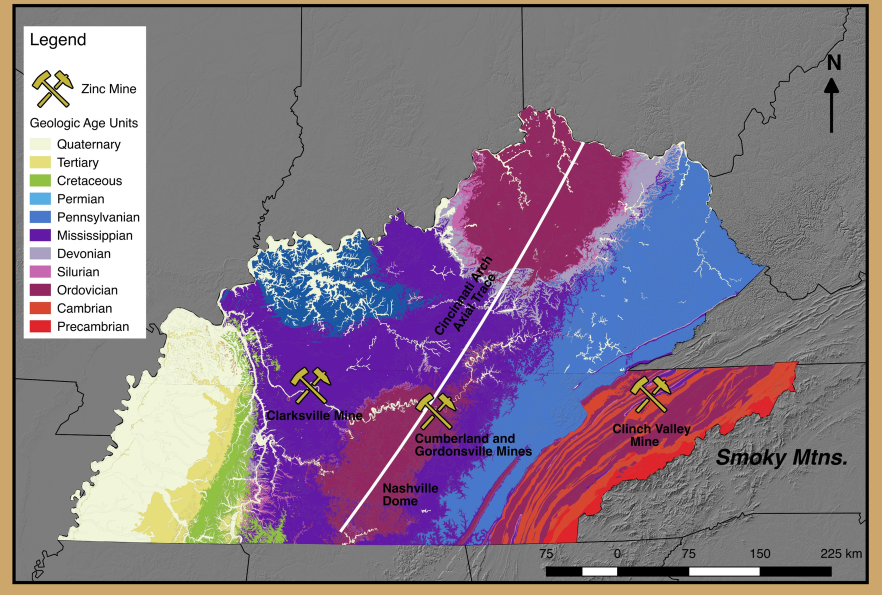


Figure 2: Regional map of mine locations in central Tennessee and notable geologic structures that influenced ore formation. White line marks axial trace of the Cincinnati Arch. Map was created with USGS GIS data available at https://mrdata.usgs.gov.

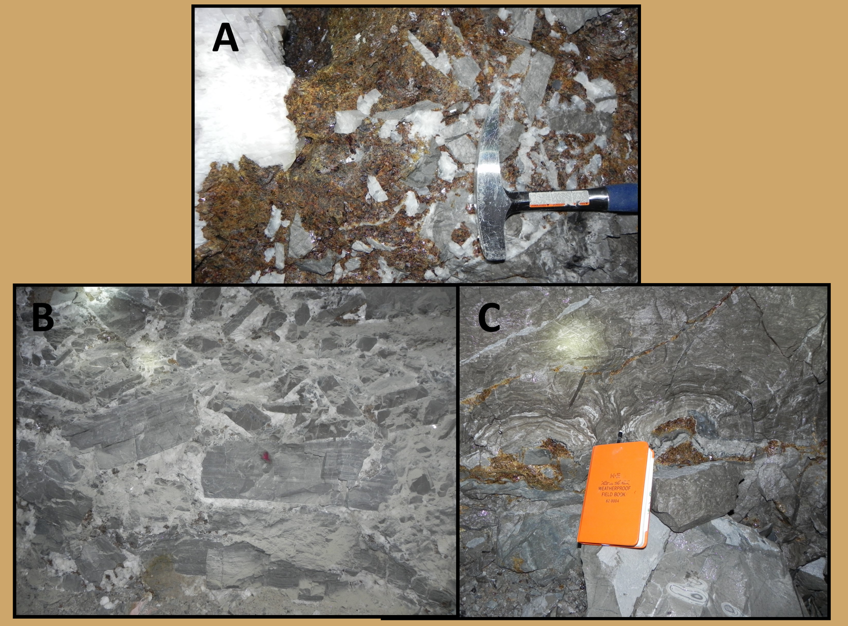


Figure 3: Photographs of sphalerite ore at Cumberland Mine. **A)** Coarse grained sphalerite surrounded by calcite gangue in collapse breccia. **B)** Dolomite collapse breccia ore (field of view = 4.5 m). **C)** Limestone replacement ore in a stromatolite layer.

PURPOSE OF STUDY: This study makes a comparison of the elemental composition of sphalerite from the Cumberland Mine with sphalerite from other MVT deposits in the U.S. and examines compositional variations at the mine between different ore occurrences (i.e., replacement vs open space filling) that would signify geochemical changes in the ore bearing fluid.

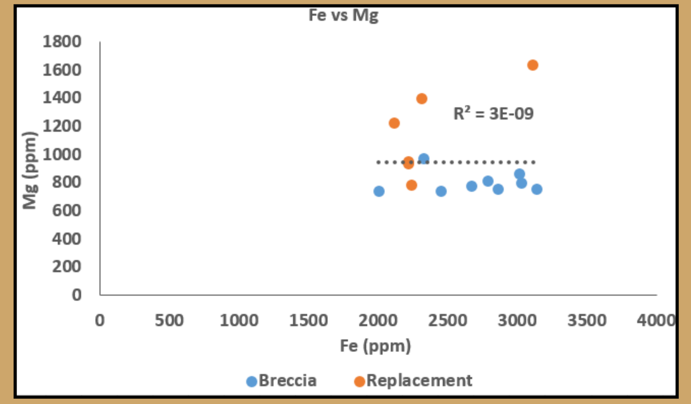
METHODS: Fifteen samples of dolomite breccia and limestone-hosted replacement ore were collected from the Cumberland underground mine. Samples were rinsed three times with reverse osmosis water to remove dust. Unmineralized rock and gangue minerals were removed from sphalerite using a hammer. Samples were then coarsely crushed with a hammer and hand-picked using a binocular microscope to form sphalerite concentrates. The concentrates were pulverized with a ceramic pestle and mortar to 100 mm size. Samples were digested in a microwave using a 1:2 HCl to HNO_3 trace metal grade aqua regia solution, consisting of 2 mL HCl and 4 mL HNO_3 diluted to 14 mL volume using Milli-Q water. The digestion solutions were then partitioned into three batches of different dilution factors for analysis: 1:1100 for Zn, 1:100 for major/minor elements (Fe, Al, Ca, Mg, and Mn), and 1:10 for trace elements (As, Ag, Mo, Sr, Cu, Pb, Ba, Cd, Cr, Co, Cu, Sn, and Ti). All digested solutions were diluted to their required concentration using Milli-Q water. Elemental abundances were quantified using an Optima 2100 DV inductively coupled plasma optical emission mass spectrometer.

RESULTS

ELEMENTAL CONCENTRATIONS IN SPHALERITE ORE

Zn (82 wt% — 99 wt%)
Mg (740 — 1,600 ppm)
Mo (8 — 14 ppm)
Cd (1,920 — 4,420 ppm)
Fe (2,000 — 3,100 ppm)
Mn (410 — 560 ppm)
Cu (570 — 1,500 ppm)
Co (20 — 22 ppm)
Al (1,100 — 4,000 ppm) *excluding an outlier of 10,600 ppm
Ca (530 — 1,800 ppm) *excluding an outlier of 4,100 ppm
Pb (12 — 190 ppm)
Ti (10 — 14 ppm)

Non-detects: Ag, As, Ba, Cr, Sn, Sr



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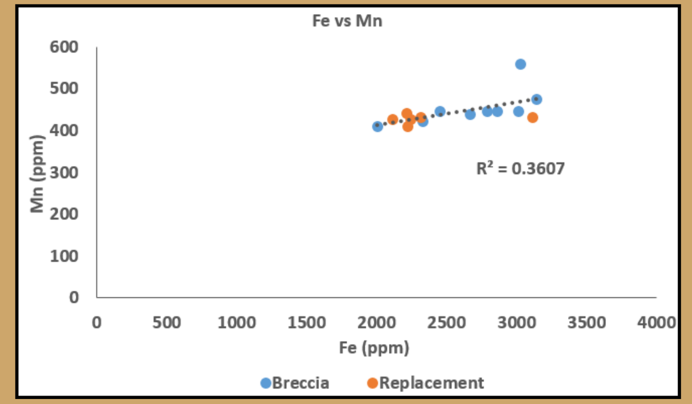

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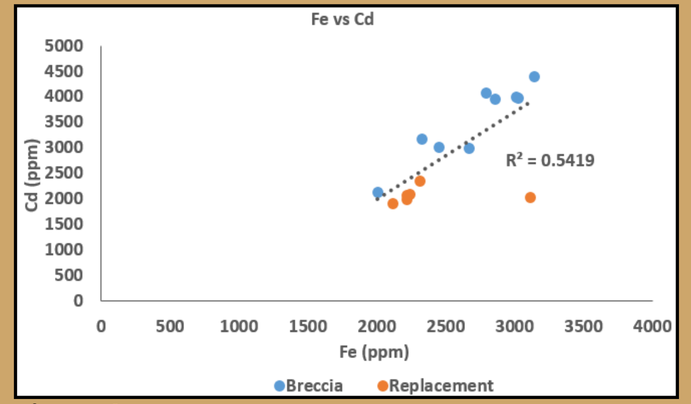

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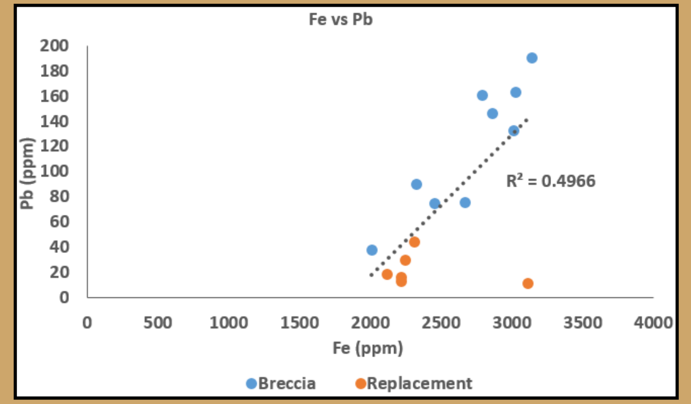

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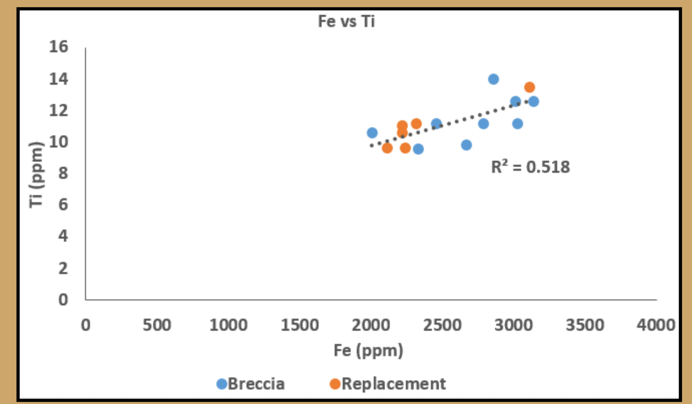

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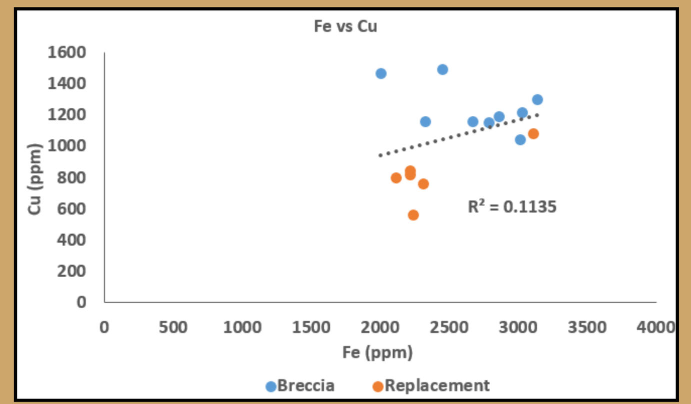

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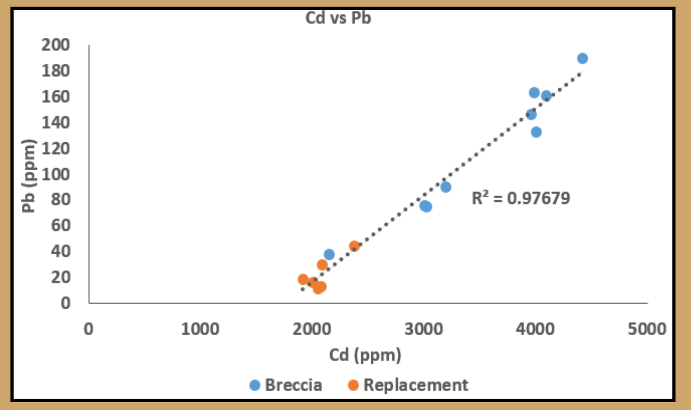

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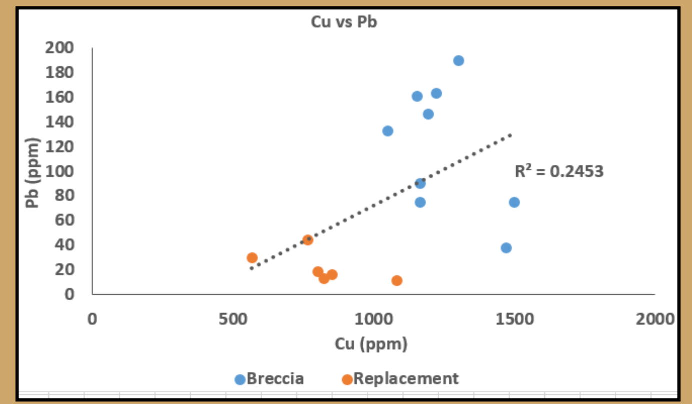

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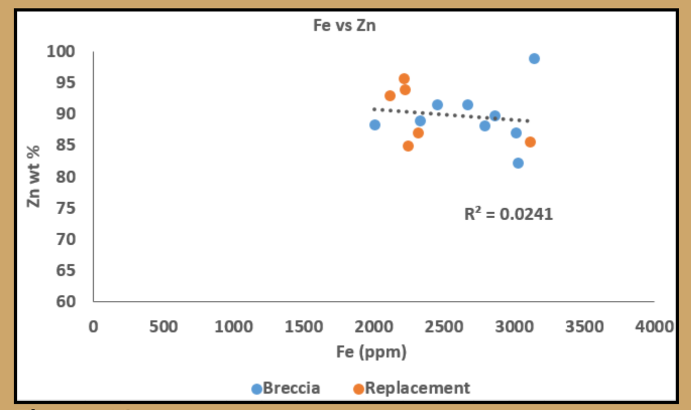

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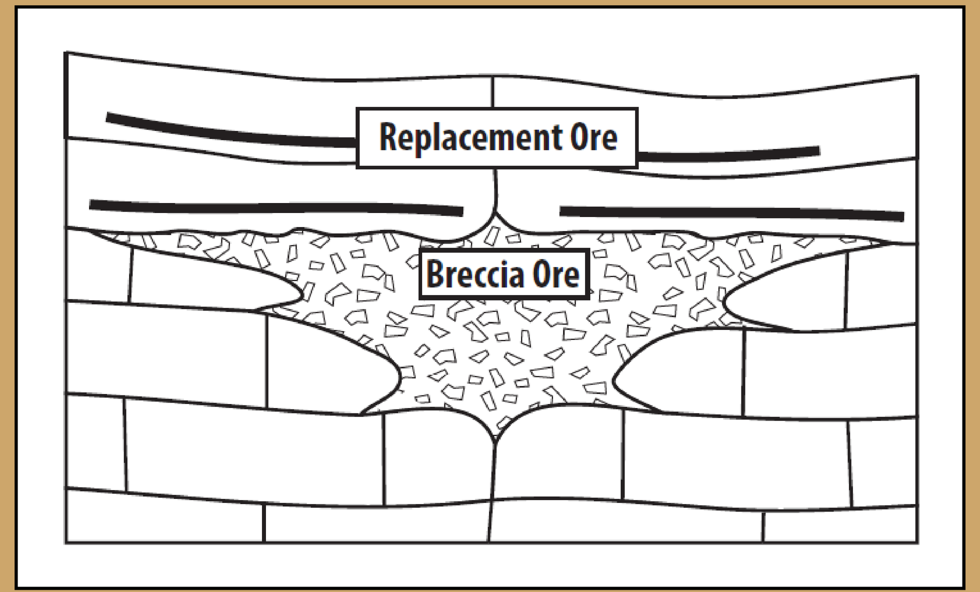

Figure 13: Idealized cross section showing the stratigraphic relationship between the breccia and replacement ores. The basin brine is believed to have precipitated the breccia ore in the paleo-karst terrain first, and then percolated upward to precipitate the manto-style replacement ore in nearly horizontal carbonate beds. In this figure the country rock surrounding both ore varieties represents carbonate rocks, which are most commonly dolostone in Cumberland Mine. Modified from Gaylord and Briskey (1983).

SUMMARY RESULTS: Plots of minor/trace elements against Fe and against Zn show similar relationships; however, most elements relate better with Fe than Zn. For this reason, relationships are discussed with respect to Fe, rather than Zn.

The data show:

- Concentrations of Fe, Cd, and Co in sphalerite are similar to other MVT deposits in the U.S (Heyl & Hall 1969; Viets et al. 1992).
- Copper and Mn concentrations commonly exceed concentrations reported in MVT districts from North America, China, Belgium, and Mexico (Viets et al. 1992; Cook et al. 2009; Ye et al. 2011; Goffin et al. 2015).
- Magnesium tends to be higher in replacement sphalerite than in breccia sphalerite (Fig.4).
- Iron, Cu, Cd, and Pb tend to be higher in breccia sphalerite than in replacement sphalerite (Figs. 6, 7, 9,11). Elevated Pb levels in breccia sphalerite is consistent with the occurrence of minor galena within the breccia ore. Interestingly, the Tennessee ores are dominantly sphalerite and not sphalerite/galena like many MVTs. Galena crystals occasionally occur along with some fluorite in the calcite matrix filling of the breccia bodies and not in the replacement ores.
- Weak positive correlations exist between Fe and Cd, Fe and Pb, and Fe and Ti (Figs. 6, 7, 8), which indicate that when the source fluid is enriched in Fe it is also enriched in Ti, Cd, and Pb (e.g., see Cook et al., 2009).
- A strong positive correlation (R^2=0.97) exists between Cd and Pb (Fig. 10) across both ore types suggesting that these elements behave similarly during substitution.
- Iron concentrations are generally higher in breccia sphalerite than in replacement sphalerite (Fig. 12).
- Plots of Fe vs Mo and Fe vs Co did not show noticeable geochemical differences between the breccia hosted ores and the replacement ores. For this reason, they are not discussed.
- Arsenic, Sr, Ba, Cr, Sn, Sr, and Ag were below detection limit.

CONCLUSIONS: Variations in minor and trace element concentrations between breccia-hosted sphalerite and replacement sphalerite may indicate the possibility of multiple geochemically distinct mineralizing events, or a single mineralizing event by an evolving fluid. We propose that the latter mechanism best explains the geochemical differences in the two ore types. As shown in Figure 13, we believe that the basin brine initially traveled upward through the more porous breccia bodies that cross-cut stratigraphy. Fluids then migrated or permeated outward into the surrounding limestones to form the replacement, manto-style ore bodies. Elements such as Fe, Cd, Pb, and Cu were more strongly substituted into early formed sphalerite in the breccia bodies resulting in depletion of these elements in the later forming replacement ore. Slightly higher Mg concentrations in the replacement sphalerite ore may be derived from initial leaching of Mg from dolomites in the breccia bodies. This Mg was then transported into the surrounding limestones where it formed coarsely crystalline dolomite—common in the replacement ore—and substituted into the sphalerite structure.

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