Copper Isotopes and Constraints on the Ore Genesis Process of Cu-Co Ore Deposits at the Idaho Cobalt Belt, USA

Nina Zaronikola 1,*,†, Elizabeth A. Holley 1, Ryan Mathur 2,*,‡ and Dan Pace 3,‡

1 Department of Mining Engineering, Colorado School of Mines, 1600 Illinois Street, Golden, CO 80401, USA
2 Department of Geology, Juniata College, 1700 Moore Street, Huntingdon, PA 16652, USA
3 Electra Batteries Material Corporation, Salmon, ID 83467, USA
* Correspondence: nina.zaronikola@eramet.com (N.Z.); mathurr@juniata.edu (R.M.)
† Current address: Eramet Ideas, 1 Av. Albert Einstein, 78190 Trappes, France.
‡ Current address: Revival Gold, Salmon, ID 83467, USA.

Abstract: Quantifying and identifying the introduction of metal in ore deposits that have experienced multiple overprinting hydrothermal events remains an elusive yet essential goal in metallogenic studies. Here, we constrain the origin of Co in the Idaho Cobalt Belt (ICB) that experienced two distinct metal-rich events that introduced Co and Cu. We performed a detailed petrographic study of sulfide ore at Iron Creek in the ICB, in concert with the quantification of trace metal element concentrations and copper isotope values to identify the introduction of Co in the system. The pyrite displays various degrees of alteration, with the highest Co concentrations (up to 6 wt.%) in less-altered pyrite grains (e.g., sharp edges, absence of altered boundaries and fissures) and highest δ65Cu isotope value. The most-altered pyrite grains (e.g., corroded grains, round and altered boundaries) have lower Co contents and lower δ65Cu isotope values that match the copper isotope values of the chalcopyrite. The least-altered pyrite shows a narrow δ65Cu range between −0.39‰ to −0.58‰. In contrast, the most-altered pyrite grains are isotopically depleted, showing a δ65Cu range from −1.35‰ to −0.90‰. Chalcopyrite shows a δ65Cu range between −1.07‰ and −0.77‰. We interpret, from the Cu isotope compositions and Co concentrations in pyrite, that the Co was originally introduced into the siliciclastic host rock package in a Mesoproterozoic SEDEX environment. The heavier Cu was then preferentially leached in a second event, resulting in isotopically lighter Cu in the altered pyrite. Remobilization of the SEDEX cobalt was likely associated with CO2-rich metamorphic fluids present in the region during the Mesoproterozoic East Kootenay orogeny, the late Mesoproterozoic Grenville orogeny, and the Late Jurassic to Late Cretaceous Cordilleran orogeny.

Keywords: cobalt-copper; pyrite; copper isotopes; alteration; overprinting mineralization

1. Introduction

The Idaho Cobalt Belt (ICB) is likely the most prospective location for cobalt production in the United States. The belt is located in central Idaho, where nearly 50 occurrences of cobalt and copper ± gold ± rare earth elements have been identified in metasedimentary rocks of the Mesoproterozoic Belt-Purcell Basin. The origin of the Idaho Cobalt Belt (ICB) mineralization has been under discussion for several decades and remains poorly understood. This lack of clarity is attributed to the fact that the mineralogical composition of the Cu-Co ore deposits and the host geological setting lack close analogs among well-studied deposits [1]. The main unanswered questions are the source of the hydrothermal fluids, the characteristics of the alteration processes, and provenance of the ore constituents. Early studies proposed that mineralization occurred in shear zones by unidentified fluids, or that sedimentary minerals were replaced by magmatic fluids [2,3]. More recent studies mentioned a syngenetic or early diagenetic metal deposition by water or magmatic fluids linked to sea-floor volcanism [4–7]. In addition, others [8,9] suggested that the hydrothermal
system was iron oxide-copper-gold-type and the sedimentary rocks replacement by marine and/or magmatic-origin fluids. Sulfur, carbon, hydrogen, and oxygen isotopes have been measured to determine that the ICB does not resemble a typical Volcanogenic Massive Sulfide (VMS) or Sedimentary Exhalative (SEDEX) ore deposit, and that the examined mineral phases show characteristics indicative of a deep environment associated with metamorphic or possibly magmatic processes [1]. Most recently, other researchers [10] used Re-Os geochronology of cobaltite to show that the ICB was affected by several episodes of mineralization beginning in the Mesoproterozoic, with metamorphic or magmatic-hydrothermal remobilization in the late Mesoproterozoic or Cretaceous.

Non-traditional stable isotopes are powerful geochemical tools to investigate and track ore forming processes and alteration events, providing indicators of both source and process. Copper has two stable isotopes, $^{63}{\text{Cu}}$ and $^{65}{\text{Cu}}$ with relative abundances of 69.17% and 30.83% in nature, respectively [11]. These two isotopes have been extensively used to track metallogenic temperature, ore-forming processes, primary versus secondary mineralization zones, and fingerprint metal circulation and source in numerous geological settings, such as copper porphyry and VMS systems [12–19]. Several studies have argued that Cu isotope fractionation is usually heterogeneous in Cu-rich mineral phases, while being sensitive to redox chemical reactions, with $\delta^{65}{\text{Cu}}$ varying from $-16.5$ to $+9.98\%$ [12,13,17,20–31]. However, Cu isotopes fractionation can be significantly affected by other parameters, including crystallography, pH, Eh, temperature, ligands, mineral dissolution and reprecipitation, adsorption of Cu in mineral surfaces and biological activity [32–34].

The purpose of this paper is to investigate the ore-forming processes responsible for Co mineralization at Iron Creek in the ICB. We utilize petrographic studies, Laser-Ablation ICP-MS trace element analyses, and Cu isotope analyses of the ore to reveal new insights on the Cu-Co ore forming processes. Our study shows how petrography, trace element concentration data, and Cu isotopes can be combined to monitor introduction and migration of metal in complexly overprinted hydrothermal systems and fingerprint the sequence of multiple alteration events.

2. Geological Setting

The ICB (Figure 1) is thought to host the most promising deposits for main-product cobalt in the United States [35,36]. The ore deposits are hosted in Mesoproterozoic metasedimentary rocks of the Lemhi Group within siltite, metasandstone and argillite of the Apple Creek Formation, and as crosscutting breccia bodies in overlying metasandstones of the Gunsight Formation [1]. The Blackbird deposit was mined for Co, Cu, and Au intermittently from 1893 to 1982 [37,38]. In the Blackbird district, ore is characterized by cobaltite, chalcopyrite, and pyrite, with pyrrhotite, marcasite, safflorite, linnaeite, and arsenopyrite as accessory phases. Additionally, gold has been identified in some deposits [1]. Recent exploration activity in the Blackbird district has focused on the Iron Creek, Ram, and Sunshine deposits. The company Jervois Mining commenced production at Ram in late 2022 and placed the operations on hiatus in March 2023 due to low cobalt prices [39]. The Iron Creek deposit is located to the southeast of the Blackbird district ICB (Figure 1). Drilling at Iron Creek has identified an indicated resource of about 6000 tons of Co and 13,000 tons of Cu [40]. The deposit consists of a shallow Co-Cu zone and a deeper Co-dominated zone with minor Cu. At Iron Creek, mineralization [40] occurs as stratabound sulfide-rich zones within argillite-siltite and quartzite metasedimentary units in the Apple Creek Formation of the Belt-Purcell Supergroup (Figure 1C). The sulfide-rich mineralization forms disseminations, massive lenses, stringers, and local shear and breccia zones. The ore mineralogy consists of chalcopyrite, cobaltiferous pyrite, magnetite, pyrite and arsenopyrite, with minor sphalerite veins [4,40].
Figure 1. (A–C) Location and geological maps of the Idaho Cobalt Belt, showing the various mineralization zones and the host lithology (modified after [40,41]), (D–H) Drill hole samples from (D) Co-Cu ore zone (IC17-28 208) from the Iron Creek deposit, (E) Co-rich ore zone (IC17-21 173) from the Iron Creek deposit, (F) Sphalerite-rich ore zone (sphalerite in veins; IC17-39 818.5) from the Iron Creek deposit, (G) Quartz-chalcopyrite drilling (IC22-03 423) from the Ruby Zone and (H) Quartz-pyrite drilling (IC22-04 657) from the Ruby Zone. Small symbols in red describe the most promising (known so far) Co-occurrences across the belt.
3. Materials and Methods

3.1. Sampling

The present study is based on representative drill core samples of massive to semi-massive sulfide minerals (Figure 1D–H). The collected samples represent the Co-Cu ore zone (Figure 1D), the Co-rich ore zone (Figure 1E) and the sphalerite veins from the Iron Creek deposit (Figure 1F). Chalcopyrite and pyrite vein samples have been also collected from drill cores coming from the Ruby Zone about 1.5 km southeast of Iron Creek (Figure 1G,H). The host rock for all the samples is a fine-grained argillite-siltite with quartzite beds. At Iron Creek and Ruby Zone, the ore grades laterally into unmineralized, chloritic rocks, where silicification is locally present [40].

3.2. Petrography

Polished 30 µm sections were prepared from the ore samples. Thin section petrography was performed at 2.5, 5, 10, 20, 40, and 50× magnification on a Carl Zeiss Axio Scope A1 polarizing microscope, in the Mining Geology research laboratory at the Colorado School of Mines. Sample mineralogy, textures, and alteration characteristics were characterized, and representative grains from each population were selected for follow-up study.

3.3. Laser-Ablation Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)

Point and map data were collected from laser ablation ICP-MS analyses at the Department of Geology and Geological Engineering at the Colorado School of Mines, on a Resolution-SE 193 nm ArF excimer laser ablation system coupled with an Agilent 8900 ICP-QQQ triple quadrupole ICP-MS. The sample aerosol was carried into the mass spectrometer using an Argon-Helium gas mixture. The laser ablation system–mass spectrometer interface is equipped with a signal homogenizing device to reduce signal noise.

The spot analyses were conducted after a 20 s background was collected. A 5 Hz laser pulse at 2.7 J/cm² was used for 30 s of signal collection. The standards and ore mineral analyses used a laser spot size of 30 µm, whereas both 30 and 60 µm were used for STDGL-3. The primary calibration for instrument drift and sensitivity was conducted using a STDGL-3 run collected at 60 µm spot size. The secondary calibration for element fractionation and spot size was completed using STDGL-3 and GSD-1g at a spot size of 30 µm. Dwell times per mass were between 0.005 and 0.02 s. The LADR software package was used to process spot analyses.

The following masses were analyzed during spot data collection: 23Na, 24Mg, 27Al, 29Si, 34S, 39K, 43Ca, 48Ti, 51V, 53Cr, 55Mn, 57Fe, 59Co, 60Ni, 65Cu, 66Zn, 71Ga, 72Ge, 73Ge, 75As, 77Se, 80Zr, 86Nb, 89Mo, 107Ag, 109Ag, 111Cd, 115In, 118Sn, 121Sb, 125Te, 137Gd, 182W, 195Pt, 196Au, 202Hg, 205Tl, 206Pb, 207Pb, 208Pb, 232Th, and 238U.

The compositional mapping was achieved by rastering a 10 µm laser square over the sample surface at 0.01 mm/s. Prior to each image, a gas blank was collected. Before each line analysis, pre-ablation was conducted with a 10 µm laser beam with a 50% spot overlap. The laser energy was 2.7 J/cm². Quantification was conducted based on STDGL-3 and GSD-1 g standard materials. Dwell times for each mass were between 0.001 and 0.01 s, for a total sampling period of 0.2 s. The Iolite v. 4.0 program (University of Melbourne, Australia) was used for data reduction, and the quantified compositional maps were constructed using the Cellspace module.

The following masses were analyzed during mapping: 23Na, 24Mg, 27Al, 29Si, 31P, 34S, 39K, 43Ca, 48Ti, 51V, 53Cr, 55Mn, 57Fe, 59Co, 60Ni, 65Cu, 66Zn, 71Ga, 72Ge, 75As, 77Se, 80Zr, 89Mo, 107Ag, 118Sn, 121Sb, 125Te, 137Gd, 182W, 197Au, 208Pb, 209Bi, and 238U.

3.4. Stable Isotope Geochemistry

Mineral samples were taken from petrographic slides with careful scratching of the thin rock wafer with a carbide tip. The separated sulfide minerals had masses ranging from 1–14 mg. Samples were dissolved in 4 mL of heated (80 °C) aquaregia overnight. The samples were dried and the dried salts from the minerals were processed with the
column chromatography in [17]. The samples were diluted to 150 ppb and measured on the Neptune plus multicollector ICP-MS at Rutgers University (Piscataway, New Jersey). The instrument was run in wet plasma mode and samples were measured in duplicate (reported values represent the mean value of 2 separate measurements of 30 ratios). On peak blanks were subtracted and mass bias was controlled by standard sample standard bracketing. The values are presented in the traditional per mil format in comparison to the international NIST 976 isotope standard. Errors for the analyses were assessed by monitoring the variations of the NIST 976 standard bracket by adjacent standards. During analytical sessions the NIST 976 std varied $\pm 0.08\%$; given this standard was measured most frequently, we assume this error for all samples. All duplicate measurements fell within this reported error. An internal lab standard the 1838 USA cent was monitored during the run generated overlapping values of $\delta^{65}\text{Cu} = -0.06 \pm 0.08\%$.

4. Results

4.1. Ore Mineralogy and Petrography

Petrographic investigation of the Iron Creek and Ruby Zone ore samples indicates that the main ore minerals are pyrite, chalcopyrite, and sphalerite. Samples from high-grade Co zones have a modal abundance of >90% pyrite. Chalcopyrite modal abundance is up to about 30% in the Co-Cu ore zone and less than 10% in the Co ore zone. Quartz occurs as the main accessory phase, up to 70% modal abundance, with lesser amounts of orthoclase and plagioclase feldspars, Fe-oxides and Fe-Mn oxides, chlorite, muscovite, and biotite. The pyrite presents various degrees of alteration and commonly occurs in association with chalcopyrite grains (Figure 2). Pyrites are divided in two groups based on textural observations; the least-altered and strongly altered pyrites. Overall, the least-altered pyrite groups present either sharp grain boundaries without evident corrosion, or they form euhedral clusters as veins. The strongly altered pyrite groups show patchy texture, weathered boundaries, and round edges, with fissures and cracks present. The least-altered pyrite generations occur as two textural types. The first is medium-grain pyrites with sharp grain boundaries (Type 3). The second type of relatively unaltered pyrite occurs as clusters of very small euhedral pyrite grains from 10 to 30 $\mu$m (Type 5), which are preferentially concentrated along beds in the sedimentary rock (Figure 2a,b). There are three types of strongly altered pyrites. The most abundant have a patchy, sponge, or resorbed appearance (Type 1; Figure 2c). The second most abundant are large crystals with fissures, fractures, and abundant inclusions (Type 2; Figure 2d). The third type of strongly altered pyrite occurs as anhedral medium-grained pyrites with smooth edges (Type 4; Figure 2e). We also identified colloform pyrite in the Ruby Zone, implying continuous hydrothermal fluid circulation (Figure 2f). In both mineralized zones, chalcopyrite typically occurs as well-formed euhedral to subhedral grains with crisp grain boundaries, commonly in the interstitial space between pyrite grains. The chalcopyrite has been observed to encapsulate euhedral or anhedral pyrite grains (Figure 2g). Sphalerite occurs along veins and is commonly surrounded by euhedral pyrite clusters (Figure 2h).

4.2. Metal Enrichment in the Pyrite and Chalcopyrite

The pyrite grains from Iron Creek contain up to 6 wt.% Co. The degree of Co enrichment is correlated with pyrite texture, where the highest Co concentrations are observed in the least-altered pyrite grains, regardless of the pyrite core or grain boundaries (Figures 3A and 4). The mean values for the least-altered pyrites in both studied drilling samples from the Iron Creek resource are 2.24 wt.% and 4.21 wt.%. Type 4 pyrite (altered pyrite) show a mean value higher than the less-altered pyrite grains in Sample 173 (Figure 4), but this includes a less-than-four spot analysis and it cannot be representative. The Co appears to be substituting for Fe in the pyrite lattice, based on the strong negative correlation between Fe and Co concentrations [41]. Copper is found in inclusions and cracks within the pyrite (Figure 3C,D). The pyrite also contains As, which generally follows the spatial distribution of Co in the studied samples (Figure 3E,F). Nickel illustrates the op-
positive behavior of Co and As; high Ni content areas are poor in Co and As (Figure 3G,H). Commonly, Ni is enriched in the core of medium-size pyrite grains (Figure 3G). Other trace elements have been found in the studied pyrite grains like Bi (Figure 3I,J) and Te, which are mainly concentrated in inclusions (Figure 3K,L). Lead is identified in inclusions and cracks (Figure 3M,N) as Cu, while Se presents a higher concentration in the core of the studied grains (Figure 3O,P). The chalcopyrite is poor in Co (Figure 5).

Figure 2. Photomicrographs of the mineralization from the Iron Creek and Ruby Zones; (a) Least-altered pyrite with sharp boundaries (Type 3) in association with large pyrite crystals (Type 2), (b) Regions of least-altered pyrite clusters (Type 5) neighboring large pyrite grains (Type 2), (c) Most-altered pyrite texture, showing a patchy appearance (Type 1), interstitial to the most-altered medium grain pyrites, (d) Altered large pyrite grains with fractures, holes, and inclusions (Type 2), (e) Pyrite (Py) intergrown with chalcopyrite (Cpy) (Type 1), (f) Pyrite (Py) intergrown with chalcopyrite (Cpy) (Type 4), (g) Chalcopyrite (Cpy) surrounded by pyrite (Py) (Type 1), (h) Sphene (Sph) in contact with chalcopyrite (Cpy) (Type 1).
(c) Most-altered pyrite texture, showing a patchy appearance (Type 1), interstitial to the most-altered medium grain pyrites, (d) Altered large pyrite grains with fractures, holes, and inclusions (Type 2), (e) Altered round medium pyrite grains with smooth boundaries, associated with interstitial chalcopyrite, (f) Colloform pyrite (g) Chalcopyrite with euhedral pyrite inclusions, and (h) Sphalerite in veins surrounded by euhedral pyrite grains. Abbreviations: Py—pyrite; Cpy—chalcopyrite; Sph—sphalerite.

4.3. Copper Isotope Signatures

The overall $\delta^{65}\text{Cu}$ range measured for all the pyrite grains of varied alteration degree is between $-1.35\%$ and $+0.13\%$ (Table 1). Chalcopyrite shows a $\delta^{65}\text{Cu}$ range between $-1.07\%$ and $-0.77\%$. The isotopic signature of the pyrite grains differs according to pyrite type (Figure 6). The least-altered pyrite shows a narrow $\delta^{65}\text{Cu}$ range between $-0.39\%$ to $-0.58\%$. In contrast, the most-altered pyrite grains are isotopically depleted, showing a $\delta^{65}\text{Cu}$ range from $-1.35\%$ to $-0.90\%$. Colloform pyrite from the Ruby mineralized zone has a value of $-0.56\%$, in the same range as the least-altered pyrite from the main Iron Creek ore system. The rest of the pyrite from the Ruby mineralized zone has a heavier $\delta^{65}\text{Cu}$ range compared to the examined pyrites from the Iron Creek resource, varying from $+0.08\%$ to $+0.13\%$. Figure 6 illustrates that the chalcopyrite from the main Iron Creek zone is depleted in $^{65}\text{Cu}$ relative to the least-altered pyrites and overlaps with the $\delta^{65}\text{Cu}$ range of the most-altered pyrites.

Table 1. Copper and Zn stable isotopes values from the Iron Creek and Ruby mineralized zones from the Idaho Cobalt belt (ICB). During analytical sessions, the NIST 976 std varied $\pm 0.08\%$; given this standard was measured most frequently, we assume this error for all samples. All duplicate measurements fell within this reported error.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mineralization</th>
<th>Pyrite Type</th>
<th>$\delta^{65}\text{Cu}$ (%)</th>
<th>No. of Replicate Analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC17-28 208B</td>
<td>Pyrite</td>
<td>1</td>
<td>$-1.28$</td>
<td>2</td>
</tr>
<tr>
<td>IC17-28 208B</td>
<td>Pyrite</td>
<td>1</td>
<td>$-1.35$</td>
<td>2</td>
</tr>
<tr>
<td>IC17-21 173A</td>
<td>Pyrite</td>
<td>2</td>
<td>$-1.01$</td>
<td>2</td>
</tr>
<tr>
<td>IC17-21 173A</td>
<td>Pyrite</td>
<td>2</td>
<td>$-0.90$</td>
<td>2</td>
</tr>
<tr>
<td>IC22_04_657A</td>
<td>Pyrite</td>
<td>2</td>
<td>$0.08$</td>
<td>2</td>
</tr>
<tr>
<td>IC22_04_657A</td>
<td>Pyrite</td>
<td>2</td>
<td>$0.13$</td>
<td>2</td>
</tr>
<tr>
<td>IC17-21 173A</td>
<td>Pyrite</td>
<td>3</td>
<td>$-0.46$</td>
<td>2</td>
</tr>
<tr>
<td>IC17-28 208B</td>
<td>Pyrite</td>
<td>3</td>
<td>$-0.39$</td>
<td>2</td>
</tr>
<tr>
<td>IC17-28 208B</td>
<td>Pyrite</td>
<td>3</td>
<td>$-0.51$</td>
<td>2</td>
</tr>
<tr>
<td>IC17-21 173B</td>
<td>Pyrite</td>
<td>4</td>
<td>$-1.01$</td>
<td>2</td>
</tr>
<tr>
<td>IC17-28 208A</td>
<td>Pyrite</td>
<td>4</td>
<td>$-1.08$</td>
<td>2</td>
</tr>
<tr>
<td>IC17-21 173A</td>
<td>Pyrite</td>
<td>5</td>
<td>$-0.54$</td>
<td>2</td>
</tr>
<tr>
<td>IC17-28 208A</td>
<td>Pyrite</td>
<td>5</td>
<td>$-0.54$</td>
<td>2</td>
</tr>
<tr>
<td>IC17-28 208B</td>
<td>Pyrite</td>
<td>5</td>
<td>$-0.58$</td>
<td>2</td>
</tr>
<tr>
<td>IC22_03_423A</td>
<td>Colloform Pyrite</td>
<td>6</td>
<td>$-0.56$</td>
<td>2</td>
</tr>
<tr>
<td>IC17-21 173A</td>
<td>Chalcopyrite</td>
<td>-</td>
<td>$-0.77$</td>
<td>2</td>
</tr>
<tr>
<td>IC17-28 208A</td>
<td>Chalcopyrite</td>
<td>-</td>
<td>$-1.07$</td>
<td>2</td>
</tr>
<tr>
<td>IC22_03_423B</td>
<td>Chalcopyrite</td>
<td>-</td>
<td>$-0.89$</td>
<td>2</td>
</tr>
</tbody>
</table>
Figure 3. Pyrite from the Iron Creek ore deposit: LA-ICP-MS maps show the distribution of Co (A,B), Cu (C,D), As (E,F), Ni (G,H), Bi (I,J) [41], Te (K,L), Pb (M,N) and Se (O,P).
4.3. Copper Isotope Signatures

The overall $\delta^{65}\text{Cu}$ range measured for all the pyrite grains of varied alteration degree is between $-1.35\%$ and $+0.13\%$ (Table 1). Chalcopyrite shows a $\delta^{65}\text{Cu}$ range between $-1.07\%$ and $-0.77\%$. The isotopic signature of the pyrite grains differs according to pyrite type (Figure 6). The least-altered pyrite shows a narrow $\delta^{65}\text{Cu}$ range between $-0.39\%$ to $1\%$.

Figure 4. Cobalt concentration by pyrite type in the Co-Cu-rich (208) and Co-rich (173) drill core samples from the ICB.

Figure 5. Comparison of metal deportment (Co, Cu and Zn) between pyrite and chalcopyrite grains from the Iron Creek deposit (ICB). Cobalt is absent in Cpy and it is hosted in Py.
This further indicates that the ore-forming processes that led to Cu isotope fractionation involved pyrites with sharp grain boundaries and the highest cobalt concentrations observed at Iron Creek. The rest of the pyrite from the Ruby mineralized zone has a heavier δ65Cu range compared to the examined pyrites from the Iron Creek resource, varying from −1.5‰ to +1‰ represent hypogene ore mineralization in the magmatic-hydrothermal environment at the time that cobalt was introduced. Based on comparisons with SEDEX systems from the ICB (Figure 6). This range shows that the copper isotope composition of Cu isotopes in combination with petrographic observations and quantification of trace metal element concentrations represent a useful geochemical tool to fingerprint combined alteration events and metal circulation in the ICB.

A range of 1.5‰ of Cu isotope fractionation has been observed in the Cu-Co ore systems from the ICB (Figure 6). This range shows that the copper isotope composition in the ores is not like VMS, sedimentary copper, or supergene copper deposits (Figure 7). This further indicates that the ore-forming processes that led to Cu isotope fractionation in VMS, sedimentary Cu and the supergene process did not operate during formation of the ICB ores. However, the observed Cu isotope range in the ICB ore samples corresponds to the ranges observed for sedimentary exhalative (SEDEX) deposits, as well as several other hydrothermal ore deposits that formed under high-temperature conditions (Figure 7).

Copper isotope variation in the studied mineral phases from the ICB clearly indicates the influence of more than one alteration event. Least-altered pyrites at Iron Creek formed with δ65Cu values of about −0.5‰. Previous studies have established that δ65Cu values between −1‰ to +1‰ represent hypogene ore mineralization in the magmatic-hydrothermal environment [17,18]. This isotopically heavy group includes bedded clusters of fine-grained euhedral pyrites and relatively low cobalt concentration (Type 5; Figure 2b). Based on the textures and compositions, we infer that the Type 5 pyrites formed in the sediments prior to the main ore-forming event. The other least-altered pyrite type comprises medium grained pyrites with sharp grain boundaries and the highest cobalt concentrations observed at Iron Creek (Type 3; Figure 2a). We interpret that these grains formed in the hydrothermal environment at the time that cobalt was introduced. Based on comparisons with SEDEX deposits elsewhere in the world, such as Mt Isa, Australia, we suggest that Type 3 pyrite
formed from circulating sub-seafloor metalliferous hydrothermal fluids that deposited cobalt, either during sedimentation or diagenesis. The Apple Creek and Gunsight formation sediments hosting the ICB ores were deposited in the Mesoproterozoic between 1445 ± 12 Ma and 1409 ± 10 Ma [37]. We infer that the first episode of mineralization occurred in the Lemhi sub-basin of the Belt-Purcell basin during this time. Syngenetic to diagenetic base-metal deposits formed elsewhere in the Belt-Purcell basin during the Mesoproterozoic, such as the giant Sullivan Pb-Zn-Ag deposit in British Columbia [7,44], and the diagenetic Sheep Creek (Black Butte) Cu-Co-Ag deposit in Montana [45].

Figure 7. Copper isotope fractionation, which has been measured in sulfide minerals from various ore systems around the globe. Significant Cu isotope fractionation has been observed in diverse mineralizing systems including SEDEX, MVT, VMS, PCD, Mt Isa and IOCG in comparison with the Cu isotope measurements from the Idaho Cobalt Belt (ICB). Copper isotope data are taken from the literature.

The combination of isotopic, geochemical, and mineralogical data provides evidence for a second hydrothermal event. The altered pyrite grains with lower cobalt concentrations (Types 1, 2, 4) are isotopically depleted, with δ⁶⁵Cu values as low as −1.35‰ in the most-altered grains, showing the selective removal of ⁶⁵Cu during alteration. We interpret that this isotopic depletion occurred during a second event that altered the earlier SEDEX pyrite, resulting in patchy textures, fissures, cracks, and resorbed boundaries. Some of the cobalt was remobilized at this time, leading to depletion of cobalt in the earlier SEDEX pyrite grain cores and redistribution into second-stage hydrothermal overgrowths (Figure 3A,B). We also see textural evidence for Ni redistribution (Figure 3G,H), suggesting that the second hydrothermal event led to formation of texturally late Co-Ni phases such as cattierite-vaesite [41]. At the Blackbird deposit, several researchers observed that Co was lost from cobaltite and redistributed into the surrounding rocks during an overprinting event [10,37].

The colloform pyrite in the Ruby zone does not occur in the same samples as the other pyrite types but is isotopically similar to the early, least-altered pyrite types in the main Iron Creek Zone (Figure 6). The studied drilling samples from the Ruby mineralized zone show a δ⁶⁵Cu variation from −0.56‰ to +0.13‰, proposing a rather primary mineralization than
a mineralization affected by multiple later events (Figure 6). Colloform pyrite can indicate continuous hydrothermal fluid circulation combined with possible mixing of fluids and the interaction with an ore-bearing fluid with changes in physio-chemical conditions [46]. Other authors have been studied the occurrence of colloform pyrite in epithermal ore systems, where it has precipitated from fluids with temperature < 240 °C, high $f_{S2}$ and $f_{O2}$, and pH < 5 [47] and in modern seafloor hydrothermal environments, resulting from the rapid mixing of high-temperature hydrothermal fluids and ambient sea water [48]. We suggest that the colloform pyrite could have formed early during the SEDEX mineralization or in a later hydrothermal overprint after the isotopic depletion that affected the SEDEX pyrite.

Chalcopyrite appears to be texturally later than most Co-bearing phases throughout the ICB. The studied chalcopyrite at Iron Creek shows a significant depletion in $^{65}$Cu, suggesting that in contrast to Co, the Cu is induced in the system later by an overprinting process and not by the initial alteration event. This is also highlighted by the fact that there is a direct overlap between the Cu isotope fractionation in the chalcopyrite and the most-altered pyrites (Figure 6) and further corroborated by the lack of Co enrichment in the chalcopyrite (Figure 5).

Finally, we discuss the potential geological origin of the second event that altered the pyrite, depleted its $^{65}$Cu signature, remobilized Co, and introduced Cu into the ICB. Similarly, other studies [10,37] suggested that the Co depletion from cobaltite that they observed at Blackbird resulted from prograde metamorphism [10,37], as has been documented in the Otago and Alpine schists in New Zealand [49]. Previous studies [10,37] have argued that the ICB underwent multiple episodes of regional metamorphism, plutonism, and metamorphic-hydrothermal mineralization. Felsic (ca. 1379–1325 Ma) and bimodal mafic-felsic plutonism (ca. 1370–1335 Ma) occurred in association with the middle Mesoproterozoic East Kootenay orogeny. Regional metamorphism occurred during the East Kootenay and the Grenville orogenies (ca. 1200–1000 Ma). The Cordilleran orogen resulted in orogenesis and plutonism from Late Jurassic through Cretaceous to early Tertiary time. The overprinting hydrothermal event recorded in our data could have occurred in association with any of these events, while metamorphic fluids could contribute the needed CO$_2$ ligands for the observed Cu isotope fractionation. Cobaltite in the Haynes-Stellite zone at Blackbird gives Re-Os ages corresponding to the East Kootenay age, whereas cobaltite in the Idaho Zone at Blackbird gives Re-Os ages that are more likely Grenvillian [10]. Those authors also observed that cobaltite was remobilized or disturbed during the Cretaceous in the Chicago zone at Blackbird, as well as at Blackpine (Figure 1). We suggest that Iron Creek Mesoproterozoic SEDEX ore would have been affected by all three events, and that the main overprint evident in the isotopic data occurred in association with the mid- to late-Mesoproterozoic East Kootenay and Grenville orogenies.

6. Conclusions

Our study in the Idaho Cobalt Belt (ICB) highlights the importance of using geochemical and petrographic data in conjunction with non-traditional stable isotopes to fingerprint complex ore-forming processes. Copper isotopes show two distinct populations of pyrite at the Iron Creek deposit. Relatively unaltered pyrites with $^{65}$Cu values around $-0.5\%$ formed during the initial cobalt mineralizing event, likely in a Mesoproterozoic SEDEX environment. A second event remobilized Co and other trace metals, and introduced Cu in the form of chalcopyrite mineralization. This second event altered the earlier pyrite, resulting in visible alteration textures and isotopically depleted pyrite with $^{65}$Cu values ranging from $-0.90\%$ to $-1.35\%$, with the most depleted values corresponding to the most-altered textures. The cobalt was removed from earlier pyrite and redistribution into overgrowth phases, and new chalcopyrite precipitated. We infer that the observed Cu isotopic fractionation resulted from the presence of CO$_2$ ligands in metamorphic fluids during a regional event. By comparison with textural and geochronological studies elsewhere in the district, we suggest that the second event occurred during the mid-Mesoproterozoic East Kootenay or late Mesoproterozoic Grenville orogeny. Further overprinting may have occurred in
association with Cretaceous metamorphism and magmatic-hydrothermal activity during the Cordilleran orogeny.

**Author Contributions:** Conceptualization, N.Z., R.M., E.A.H. and D.P.; Methodology, R.M.; Formal analysis, N.Z.; Investigation, N.Z. and R.M.; Resources, E.A.H. and D.P.; Writing—original draft, N.Z.; Writing—review & editing, E.A.H. and R.M.; Supervision, E.A.H.; Project administration, E.A.H. All authors have read and agreed to the published version of the manuscript.

**Funding:** The work was funded by NSF Growing Convergence Research 2120721 (EH), as part of the Responsible Critical Elements project.

**Data Availability Statement:** Data is unavailable due to privacy restrictions.

**Acknowledgments:** We thank Frank Santaguida, Patrick Taylor, Paul Miranda, and Mason Brevig for samples and discussion; Zhaoshan Chang and Shiqiang Huang for analyses; Kelsey Livingston and Sage Langston-Stewart for sample preparation, Katharina Pfaff for discussion, and Molly Morgan for interpreting core sample location.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**


40. First Cobalt Corp. Technical Report with Updated Estimate of Mineral Resources for the Iron Creek Cobalt-Copper Project; First Cobalt Corp: Lemhi County, ID, USA, 2019; p. 110.


45. Graham, G.; Hitzman, M.W.; Zieg, J. Geologic setting, sedimentary architecture, and paragenesis of the Mesoproterozoic sediment-hosted Sheep Creek Cu-Co-Ag deposit, Helena Embayment, Montana. Econ. Geol. 2012, 107, 1115–1141. [CrossRef]


Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.