Geogas prospecting for igneous ore deposits covered by regolith: The Zijinshan high-sulfidation epithermal Cu-Au deposit in the Cathaysia Block

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Article

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Abstract

The mining industry faces a challenge due to the scarcity of outcrop or near-surface mineral deposits, necessitating the development of low-cost and efficient prospecting methods. Inductively coupled plasma mass spectrometry (ICP-MS) has been applied to geological sample analysis, and scientists have been gradually improving the method of geogas prospecting. As a result, geogas prospecting has shown promising results in detecting underlying concealed Au, U, and Cu-Ni deposits covered by Gobi sand and Quaternary sediments. To verify the effectiveness of this method for exploring underlying concealed mineral deposits developed in igneous covered areas, the Zijinshan high-sulfdation epithermal (HSE) Cu-Au deposit, a concealed mineral deposit in southeastern China, was selected as the experimental field. Our experiments revealed nanoscale particles composed of Au, Cu-Fe, and Cu-other elements in the geogas captured above the ore bodies of the deposit. Furthermore, Cu-nanoscale particles retain the isotopic composition of copper found in both the oxidation zone and deep copper ores. The geogas samples exhibited similar C1-chondrite normalized rare earth element (REE) distributions, with right-inclined REE patterns indicating significant enrichment of LREE relative to HREE, slightly negative $\delta^{17}$Ce anomalies, and similar (La)N/(Sm)N and (Gd)N/(Yb)N ratios. These characteristics are similar to those of the gold ores, copper ores, altered rock, and bedrock near the ore bodies. These findings suggest that deep-penetration geochemical methods using geogas can be a valuable tool for uncovering underlying concealed mineral deposits in igneous covered areas.

INTRODUCTION

With outcrops of mineral deposits becoming increasingly scarce, mineral exploration has turned to Mesozoic strata-covered or Cenozoic loess-covered areas, which has made geochemical exploration technology a priority of applied geochemistry research. Early techniques, such as ammonium citrate-soluble extraction, were limited to partial element extraction, failing to distinguish mineralization anomalies from other non-mineralization anomalies. While these techniques have yielded some success in detecting underlying concealed mineral deposits, like those covered by thick sediment deposits with tens of meters in depth, other harsh geological conditions have impeded their effectiveness. More recent breakthroughs in deep-penetration geochemical methods using ICP-MS have provided promising results in finding mineral deposits concealed by Gobi sand and Quaternary sediments, detecting Au, U, and Cu-Ni deposits. Other advanced techniques, like geogas, enzyme leaching, and electrogeochemical extraction, have contributed to the recent development and success of deep-penetration geochemical methods. Further technological advances may bring deeper probing and greater exploration success.

To evaluate the effectiveness of deep-penetration geochemical methods using geogas in detecting underlying concealed mineral deposits, we conducted a study on Zijinshan high-sulfdation epithermal (HSE) Cu-Au deposit. In this study, we collected and analyzed geogas samples in the deposit cover and compared the results with previous studies on the bedrock, altered rock, and ores. Our study confirmed the applicability of deep-penetration geochemical methods using geogas in exploring underlying concealed mineral deposits in igneous covered areas. By analyzing the nanoscale particles and geogas samples, we obtained direct geological information on the type of underlying concealed ore bodies, such as nanoscale metal particles and multielement geochemical anomalies from the ore bodies. These findings imply that geogas prospecting can be a promising technique for discovering mineral deposits in covered areas.

MATERIALS AND METHODS

Deposit geology

The South China block is bisected into two distinct geological regions by the Jiangshan-Shaoxing-Pingxiang-Yushan fault, namely the Yangtze block in the northwest and Cathaysia block in the southeast. The Cathaysia Block on the southeastern coastal area of China, owing to the subduction of the paleo-Pacific plate beneath the Eurasian plate, has experienced extensive Yanshanian magmatism and mineralization, including Cu-Au, Au-Ag, Pb-Zn, and W-Sn. The Zijinshan ore field, situated on the northeastern margin of the Late Mesozoic Shanghang basin (Fig. 1a) at the intersection of the Yunxiao-Shanghang fault and the Xuanhe Anticlinorium within the interior Cathaysia, comprises a typical normal high-sulfdation epithermal (HSE) copper-gold deposit and has been considered a significant part of the porphyry Cu system. With more than 305 t Au and 2.32 Mt Cu in resources, the Zijinshan HSE Cu-Au deposit is renowned for its considerable metal reserves. Gold and copper mineralization are primarily associated with medium-fine-grained granites, porphyritic dacite, crypto-explosive breccias, and hypabyssal intrusions, forming a suite of porphyry-epithermal hydrothermal
systems with diverse mineralization types within the Zijinshan ore field (Fig. 1b) \(^{18,26-34}\). Such mineralization is closely correlated with large-scale tectono-magmatic and hydrothermal events during the Late Mesozoic period \(^{35,36}\).

The Cu-Au mineralization zone in the Zijinshan deposit has been found to extend over 1400 m vertically, from −400 m to 1000 m elevation, with drill holes identifying covellite- and digenite-dominated mineralization at a depth of −400 m elevation \(^{35}\). Intensive and pervasive alteration of igneous rocks in the Zijinshan granitic complex, comprising the Middle Jurassic Jingmei, Wulongsi, and Jinlongqiao granite batholith and Cretaceous cryptoexplosive breccia and dacitic porphyry, shows a typical high sulfdation alteration zonation (Fig. 1b). The vertical distribution of mineralization in the deposit is controlled by an upper oxidation zone, a leaching zone, and a lower primary zone, which contribute to the framework of Au and Cu enrichment (Fig. 1c, d) \(^{24}\). Weathering of the deposit has led to supergene-enrichment of gold, forming a quartz-limonite-native gold assemblage, with pyrite and limonite serving as the primary gold-bearing minerals. Copper ores occur in veins and veinlets, with chalcocite, enargite, chalcopyrite, and bornite being major ore minerals, often accompanied by local azurite occurrences \(^{37,38}\).

**Ore Features**

The Zijinshan HSE Cu-Au deposit is a complex polymetallic deposit consisting of oxide and polymetallic sulfide ores \(^{30}\). The dominant metallic component is pyrite (Fig. 2a, b), which typically occurs at concentrations ranging from 2–5%, sometimes exceeding 10%. Additionally, other metallic minerals such as chalcocite (Fig. 2d), arsenical copper minerals (Fig. 2e), and small amounts of limonite (Fig. 2c) are present in the deposit.

The primary mineral found within the gold ores of the Zijinshan deposit is native gold (Fig. 2a, b, d), accompanied by traces of gold-bearing pyrite and limonite. The ore exhibits a compact and nodular structure, with variations in gold content ranging from 1 to 10×10\(^{-9}\). Notably, the concentration of gold is even higher in the oxidized zone of the deposit.

Chalcocite and arsenical copper minerals (Fig. 2d, e) are the predominant components of the copper ore in Zijinshan, along with minor quantities of bornite (Fig. 2e), chalcopyrite (Fig. 2f), and sporadic occurrences of azurite (Fig. 2e). The copper content in these ores varies between 0.5 and 22.17×10\(^{-2}\). Significantly, the co-occurrence of gold within the copper ores is noteworthy, with an average gold content of approximately 1.95×10\(^{-9}\) in chalcopyrite and 2.85×10\(^{-9}\) in arsenical copper minerals. Consequently, the copper minerals play a crucial role in hosting gold in this deposit.

**Sampling**

To assess the potential for geogas exploration technology to detect underlying concealed mineral deposits in the Zijinshan HSE Cu-Au deposit, two geogas survey lines were arranged along NE and NW directions, intersecting above the ore body, with an average sample point distance of 25 m, half the distance above the ore body. Blank samples were collected far from the deposit as control samples (Fig. 1b). In this study, we optimized a new and rapid method for the dynamic collection of geogas \(^{41}\), using millipore-filter (MF) membranes (nitrocellulose, d ≤ 0.5 µm) to capture nanoscale particles and polyurethane foam to capture metal in the geogas collection process. The MF-membranes were pre-checked to ensure they did not contain any target elements before being used. Polyurethane foam was washed with 10% aqua regia and ultrapure water (\(\rho \geq 18 M\Omega\cdot cm, 25°C\)), and then immersed in 5% aqua regia for further cleaning \(^{42}\). Three holes were drilled using a steel chisel to 0.8 to 1.0 m depth at every sampling point for each medium, with the spacing of these holes more than 1 m apart. A spiral sampler was screwed into the holes and connected to a particulate filter, a capture device, and an air extractor by silicone tubes with ultra-filter (UF) membranes (nitrocellulose, d ≤ 200 µm) (Fig. 3). For the membrane and foam container, 3 L of gas was extracted by the air extraction pump from each hole, with the gas flow rate controlled at 1.5 L/min.

**EXPERIMENTAL**

**TEM analysis**

Nanoscale particles captured on the MF membrane were observed and analyzed using a Hitachi H9000NAR transmission electron microscope (TEM) equipped with an X-ray energy dispersive spectroscopy (EDS) capable of detecting 88 elements ranging from boron (B) to uranium (U) \(^{42,43}\). The instrument had a point resolution, lattice resolution, and minimal spot radius of 0.18 nm, 0.1 nm, and 0.8 nm, respectively, with an accelerating voltage of 300 kV and a beam spot diameter of less than 0.2 µm. To determine the composition of
the particles, we employed the EDS without reference material in this study, enabling us to obtain their elemental compositions, albeit without precise mass percentages.

**Chemical analysis**

Trace element concentrations in the polyurethane foam-captured metal from the geogas samples were measured using high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) after being ashed and dissolved in aqua regia ($\varphi > 20\%$) and adjusted to 10 mL with ultrapure water. Accuracy evaluation of the foam capture medium was challenging due to the lack of standard material. To ensure precision control, five laboratory replications were carried out for each batch of 50 samples in this study.

**Copper isotope ratios**

Copper isotope ratios were determined using a Thermo Fisher Scientific Neptune Plus MC-ICP-MS instrument, with NIST 976 Cu serving as the reference standard. The samples were dissolved in Savillex beakers using concentrated double-distilled solutions of HF + HNO$_3$, HCl + HNO$_3$, and HCl. Subsequently, the sample solution was loaded onto AG MP-1M (Bio-Rad) strong anion resin to separate the copper. Mass bias correction was performed using the sample standard bracketing method. The copper isotope ratios are reported in the standard d-notation per mil relative to NIST 976:

$$\delta^{65}\text{Cu}=\left(\frac{\delta^{65}\text{Cu}}{\delta^{63}\text{Cu}}\right)_{\text{sample}}/\left(\frac{\delta^{65}\text{Cu}}{\delta^{63}\text{Cu}}\right)_{\text{standard}} \times 1000\%$$

To minimize analytical errors, we employed the standard-sample-standard bracketing approach, comparing all copper ratios to the NIST 976 Cu standard. The $2\sigma$ error for the standard variation over two analytical sessions was determined to be ± 0.12‰.

**RESULTS**

**Nanoscale particles**

Nanoscale particles composed of Au, Cu, Fe, and other elements were observed in the geogas above the Zijinshan ore body using transmission electron microscopy (TEM), as depicted in Fig. 4. The particles exhibited a diverse array of shapes, including single grains and small nanoparticles forming aggregates with spherical, granular, oval, and polygonal shapes being typical. The metal particles’ radii ranged from several tens to several hundred nanometers. Based on their elemental composition, the particles could be classified into four types: (1) Au nanoscale particles, which represent the primary component particle (Fig. 4a), (2) Cu-Fe nanoscale particles with Al and other elements (Fig. 4b and c), the Cu-Fe nanoscale particle in Fig. 4b exhibits an ordered crystal structure, (3) Fe-Ti nanoscale particles containing Au (Fig. 4d), and (4) other complex nanoscale particles predominantly composed of Fe or Cu (Fig. 4e and f).

The particles captured from the background area contained Al, Si, K, and O, but no metal elements associated with highly siderophile element (HSE) mineralization such as Au, Cu, or Fe were detected.

**Copper isotope ratios**

Table 1 summarizes the data obtained from various samples, including nanoscale particles, pyrite, chalcocite, bornite, enarite, azurite, and chalcopyrite. Duplicate analyses were performed on copper ore samples to assess the degree of copper isotope heterogeneity within each sample. The results reveal a robust correlation between the observed variability in $\delta^{65}\text{Cu}$ values for nanoscale particles (1.97‰) and copper ore samples (2.90‰).
Table 1
Copper isotopic compositions of nanoscale particle and copper mineral samples from the Zijinshan HSE Cu-Au deposit

<table>
<thead>
<tr>
<th>Sample</th>
<th>mineral</th>
<th>Height (m)</th>
<th>δ(^{65})Cu (‰)</th>
<th>2SD</th>
<th>Sample</th>
<th>mineral</th>
<th>Height (m)</th>
<th>δ(^{65})Cu (‰)</th>
<th>2SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZJS-NP3</td>
<td>Nanoscale particle</td>
<td>834</td>
<td>-1.35</td>
<td>0.06</td>
<td>ZJS-Bn2</td>
<td>bornite</td>
<td>679</td>
<td>-0.33</td>
<td>0.05</td>
</tr>
<tr>
<td>ZJS-NP4</td>
<td>Nanoscale particle</td>
<td>837</td>
<td>0.62</td>
<td>0.02</td>
<td>ZJS-Bn3</td>
<td>bornite</td>
<td>679</td>
<td>-0.26</td>
<td>0.02</td>
</tr>
<tr>
<td>ZJS-NP7</td>
<td>Nanoscale particle</td>
<td>858</td>
<td>-0.89</td>
<td>0.02</td>
<td>ZJS-Bn4</td>
<td>bornite</td>
<td>724</td>
<td>-0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>ZJS-NP8</td>
<td>Nanoscale particle</td>
<td>839</td>
<td>0.58</td>
<td>0.03</td>
<td>ZJS-Bn6</td>
<td>bornite</td>
<td>724</td>
<td>-0.13</td>
<td>0.02</td>
</tr>
<tr>
<td>ZJS-NP11</td>
<td>Nanoscale particle</td>
<td>841</td>
<td>-0.93</td>
<td>0.02</td>
<td>ZJS-Bn7</td>
<td>bornite</td>
<td>676</td>
<td>-0.29</td>
<td>0.02</td>
</tr>
<tr>
<td>ZJS-Py2</td>
<td>pyrite</td>
<td>724</td>
<td>0.22</td>
<td>0.02</td>
<td>ZJS-Bn11</td>
<td>bornite</td>
<td>679</td>
<td>-0.52</td>
<td>0.02</td>
</tr>
<tr>
<td>ZJS-Py3</td>
<td>pyrite</td>
<td>796</td>
<td>0.57</td>
<td>0.02</td>
<td>ZJS-En3</td>
<td>enarite</td>
<td>676</td>
<td>-0.13</td>
<td>0.01</td>
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<tr>
<td>ZJS-Py5</td>
<td>pyrite</td>
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<td>-0.83</td>
<td>0.02</td>
<td>ZJS-En4</td>
<td>enarite</td>
<td>659</td>
<td>-1.95</td>
<td>0.03</td>
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<tr>
<td>ZJS-Py7</td>
<td>pyrite</td>
<td>679</td>
<td>-0.27</td>
<td>0.02</td>
<td>ZJS-En5</td>
<td>enarite</td>
<td>676</td>
<td>-0.29</td>
<td>0.01</td>
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<tr>
<td>ZJS-Cha1</td>
<td>chalcocite</td>
<td>745</td>
<td>0.18</td>
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<td>enarite</td>
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<td>0.05</td>
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<tr>
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<td>chalcocite</td>
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<td>-0.23</td>
<td>0.02</td>
<td>ZJS-En9</td>
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<td>-0.58</td>
<td>0.01</td>
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<td>ZJS-Cha8</td>
<td>chalcocite</td>
<td>736</td>
<td>0.11</td>
<td>0.02</td>
<td>ZJS-13-113*</td>
<td>azurite</td>
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<td>0.09</td>
<td>0.02</td>
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<tr>
<td>ZJS-Cha9</td>
<td>chalcocite</td>
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<td>0.23</td>
<td>0.03</td>
<td>ZJS-13-116*</td>
<td>chalcopyrite</td>
<td>652</td>
<td>-0.16</td>
<td>0.02</td>
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<tr>
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<td>chalcocite</td>
<td>676</td>
<td>-0.32</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZJS-Cha14</td>
<td>chalcocite</td>
<td>736</td>
<td>0.14</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: *from (Wu et al., 2017)

2SD = 2 times the standard deviation

The δ\(^{65}\)Cu values of nanoscale particles exhibit a variation range of 1.95‰, spanning from -1.33 to 0.62‰, which is two orders of magnitude greater than the analytical uncertainty (± 0.06‰; 2SD). Arsenical copper minerals display a more depleted copper isotope composition compared to chalcocite samples. Bornite samples exhibit δ\(^{65}\)Cu values ranging from -2.76 to 0.48‰ (n = 6), while enarite samples demonstrate a wider δ\(^{65}\)Cu range of 0.13 to 2.33‰, with an average of -1.06‰ (n = 5). The δ\(^{65}\)Cu values of the four pyrite samples range from -0.83 to 0.57‰. The data for azurite and chalcopyrite samples are sourced from a previous study. 38

The δ\(^{65}\)Cu ranges observed in the nanoscale particle samples (-1.35 to 0.62‰) and copper minerals (-2.33 to 0.23‰) are similar to or significantly larger than those reported in previous studies, which reported ranges of 0.05 to 0.29‰, -2.97 to 0.25‰, and -2.76 to 0.48‰. 38,46,47.

**Geogas samples**

Using the threshold of the sample value corresponding to the 85% cumulative frequency as outlined by 48, we delineated a total of 22 geogas samples showing geochemical anomalies. Table 2 displays trace element concentrations of these anomalous samples.
Table 2
Trace element concentrations of geogas samples, gold core, copper ore, altered rocks, and bed rocks.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Au</th>
<th>Ag</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>V</th>
<th>Ti</th>
<th>Co</th>
<th>Ni</th>
<th>Cr</th>
<th>Sn</th>
<th>Bi</th>
<th>Mo</th>
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<td>1</td>
<td>ZJg-NE04</td>
<td>1.00</td>
<td>0.79</td>
<td>0.2</td>
<td>3.7</td>
<td>1.36</td>
<td>0.35</td>
<td>0.79</td>
<td>0.013</td>
<td>0.106</td>
<td>0.22</td>
<td>11.27</td>
<td>0.018</td>
<td>0.014</td>
</tr>
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<td>2</td>
<td>ZJg-NE05</td>
<td>0.50</td>
<td>0.6</td>
<td>0.25</td>
<td>1.14</td>
<td>1.48</td>
<td>0.67</td>
<td>0.6</td>
<td>0.008</td>
<td>0.101</td>
<td>0.26</td>
<td>8.79</td>
<td>0.018</td>
<td>0.013</td>
</tr>
<tr>
<td>3</td>
<td>ZJg-NE06</td>
<td>1.75</td>
<td>0.62</td>
<td>0.19</td>
<td>1.17</td>
<td>3.07</td>
<td>0.31</td>
<td>0.62</td>
<td>0.015</td>
<td>0.106</td>
<td>0.22</td>
<td>8.99</td>
<td>0.015</td>
<td>0.013</td>
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<tr>
<td>4</td>
<td>ZJg-NE07</td>
<td>1.00</td>
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<td>1.15</td>
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<td>0.65</td>
<td>1.24</td>
<td>0.14</td>
<td>0.52</td>
<td>0.01</td>
<td>0.097</td>
<td>0.23</td>
<td>8.93</td>
<td>0.01</td>
<td>0.008</td>
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<tr>
<td>6</td>
<td>ZJg-NE09</td>
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<td>0.62</td>
<td>0.011</td>
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<td>0.009</td>
<td>0.012</td>
</tr>
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<td>11</td>
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<td>0.08</td>
<td>0.62</td>
<td>0.012</td>
<td>0.119</td>
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<td>9.78</td>
<td>0.008</td>
<td>0.011</td>
</tr>
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Note: The concentration units for Au and Ag are µg/kg, other trace elements are measured in mg/kg. No.1 to 22 are geogas samples showing geochemical anomalies above the ore body. 23 and 24 are gold cores, 25 is copper ore. 26 to 28 are altered rocks.
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Note: The concentration units for Au and Ag are µg/kg, other trace elements are measured in mg/kg. No.1 to 22 are geogas samples showing geochemical anomalies above the ore body. 23 and 24 are gold cores, 25 is copper ore. 26 to 28 are altered rocks.

Cu and Au are the primary metallogenic elements in the Zijinshan HSE Cu-Au deposit. As shown in Fig. 5, geochemical anomalies featuring Cu and Au were detected above the ore bodies, particularly the highly contrasting Cu anomaly exceeding the threshold. This implies that Cu is a high-abundance component in the endogenous mineralization system of the deposit and that Cu nanoscale particles exhibit superior penetration. Additionally, Pb, Zn, Cd, and other indicator element anomalies occur at the same locations as the Cu and Au anomalies when the ore bodies are projected horizontally. Furthermore, the boundaries of these anomalies are closely related to the alteration zone's location (Fig. 5).

**DISCUSSION**

**Provenance of nanoscale particles**

The nanoscale particles sampled from the Zijinshan HSE Cu-Au deposit demonstrate an inheritance relationship with the underlying concealed ore bodies, as evidenced by their chemical composition and morphology. Specifically, (1) different types of metal minerals exhibit different metallogenic element assemblages, with Au nanoscale particles solely present in large-scale Au deposits, (2) Cu-other elements nanoscale particles were widely dispersed, likely due to the high abundance of Cu where a sufficient Cu source can produce Cu nanoscale particles and Cu-other elements nanoscale particles, and (3) the ordered crystal structure of Cu-Fe nanoscale particles indicates that these particles are a result of endogenous mineralization, thereby suggesting that the sampled nanoscale particles originate from underlying concealed ore bodies.

**Characteristic of Copper isotopes**

Copper is a highly mobile element that undergoes significant changes in its isotope ratios during hydrothermal processes. The original copper isotope compositions in primary minerals are prone to alteration through low-temperature and secondary processes, in particular the weathering and leaching of copper-bearing rocks can lead to the remobilization, migration, and re-enrichment of supergene copper isotopes. Isotopically heavy Cu are more enriched in leaching fluids than the primary Curich minerals and can be precipitated during migration with those fluids. The copper isotope composition of copper-bearing minerals can serve as a sensitive geochemical tracer to indicate the source of ore-forming materials, the processes of mineralization, and the formation of ore deposits.
The Zijinshan Cu-Au mineralization was formed under acidic conditions and associated with highly valence sulfate such as alunite and dickite, indicating that it was formed under highly oxidizing conditions. Primary copper sulfides formed at the early ore-stage are susceptible to modification by acidic and oxidizing fluids. This process involves oxidation of Cu$^{+}$ in the sulfides and release of Cu$^{2+}$ into the fluid. Many leaching experimental studies demonstrate that the leaching fluids are more $^{65}$Cuenriched than the residual phase $^{28,56}$. As the fluids migrate away from the leach cap, and the temperature drops, and the fluid $^{65}$Cu would be precipitated and enriched via chemical reduction in the deeper zone, resulting in altered Cu isotope compositions $^{47}$.

In the Zijinshan HSE Cu-Au deposit, chalcocite and arsenical copper minerals play a dual role as both primary copper minerals and significant carriers of gold $^{27,30,31,40,47}$. Furthermore, the nanoscale particles entrapped in the overlying atmosphere exhibit a predominant composition of copper elements. Figure 6 shows that the Cu isotopes of nanoscale particles and copper minerals show distinct horizontal and vertical zoning over time, and $^{65}$Cu values for nanoscale particles is between the values of copper minerals. The above phenomenon is consistent with copper isotopes can be fractionated significantly in low-temperature aqueous reactions involving Cu oxidation, which formed different isotopic reservoirs $^{56}$. According to the Cu isotope composition of nanoscale particles and copper minerals, and their relationship with elevation, nanoscale particles, this isotopic pattern reflects the leaching of $^{65}$Cu from the upper zone and its transfer to the lower zone, resulting in spatial variations of copper isotopes. The nanoparticles not only inherit the copper isotope characteristics of copper ore in the oxidation weathering zone at 650 m, but also show a close provenance relationship with deep copper ore.

**Distribution of trace elements and REEs**

During the metallogenic process of the Zijinshan HSE Cu-Au deposit, pyrite was the most prevalent metallic mineral, constituting 15%-20% of the deposit $^{67}$. Its cubic structure enabled the incorporation of considerable amounts of trace elements (Cu, Pb, Zn, As, Se, Co, and Ni), leading to Fe and S deficiencies within the deposit $^{20}$. Furthermore, trace element analyses of pyrite provide valuable insights into ore paragenesis, metal source, and the origin of various ore deposits. Trace elements can also serve as indicators of hydrothermal ore deposits $^{17,68–70}$. Moreover, high temperatures favor Co and Ni isomorphism replacing Fe, with Co and Fe being easier to form complete isomorphism $^{67,71}$. In this study, Co/Ni values ranged from 0.09 to 1.42 across cores, altered rocks (excluding ZJal-28), and bedrock, with a mean of 0.62, which is similar to the mean of geogas samples. Bivariate plots of related trace element concentrations also exhibited parallel compositional profiles (Fig. 7).

Table 3 displays the concentrations and associated geochemical parameters of rare earth elements (REEs) for geogas samples (mean ZJg, n = 22), gold core, copper ore, altered rocks, and bedrock. As indicated in Table 2, the average $\Sigma$REE concentration in geogas samples was 0.0636 mg/kg, significantly lower than the concentrations observed in C1 (2.53 mg/kg), gold ore (1.76 to 1.88 mg/kg), copper ore (4.53 mg/kg), altered rocks (0.78 to 6.18 mg/kg), and bedrock (5.92 to 22.98 mg/kg).
Table 3
Rare earth element concentrations and associated geochemical parameters of geogas samples, gold ore, copper ore, altered rocks and bedrock.

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<th>Zjo-Au75</th>
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<td>3.27</td>
<td>3.28</td>
<td>2.89</td>
<td>2.94</td>
<td>5.17</td>
<td>2</td>
<td>3.94</td>
<td>3.41</td>
</tr>
<tr>
<td>($Gd$N/($Yb$N)</td>
<td>0.42</td>
<td>1.13</td>
<td>0.49</td>
<td>1.2</td>
<td>0.76</td>
<td>0.94</td>
<td>0.62</td>
<td>1.95</td>
<td>0.61</td>
<td>1.08</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Note: The concentration units for rare earth element are mg/kg. $\Sigma$REE = La + Ce + Pr + Nd + Sm + Eu + Gd + Tb + Dy + Ho + Er + Tm + Yb + Lu, LREE = La + Ce + Pr + Nd + Sm + Eu, HREE = Gd + Tb + Dy + Ho + Er + Tm + Yb + Lu, ($La$N/($Sm$N)+($Gd$N)), $N$ refers to normalization of C1$^{27}$.

Figure 8 exhibits the C1-normalized rare earth element (REE) distribution patterns for the aforementioned samples. The REE distribution patterns of geogas samples, gold ore, copper ore, altered rock, and bedrock formations reveal considerable enrichment in light rare earth elements (LREE) and right-inclined REE patterns, implying that these samples are predominantly enriched in LREE and relatively depleted in heavy rare earth elements (HREE).

All samples, except for the geogas samples ($\delta$Eu = 20.09), exhibited negative $\delta$Eu anomalies, accompanied by slightly negative $\delta$Ce anomalies with similar ($La$N/($Sm$N) and ($Gd$N/($Yb$N) ratios (Fig. 8, Table 3). The remarkable positive $\delta$Eu anomalies observed in the geogas samples are attributed to the variable valence nature of Eu, which is prone to fractionation from other REEs during fluid-rock interactions, especially under favorable conditions of temperature, $f_{O_2}$ and pH $^{73}$. The Zijinshan HSE Cu-Au deposit is classified as a high sulfidation epithermal (HSE) mineral deposit$^{25}$, where the abundant sulfur combines with oxygen to form SO$_2$ and SO$_4^{2-}$. Under
lower oxygen fugacity, a fraction of Eu$^{3+}$ is reduced to Eu$^{2+}$. During fluid-rock interactions, Eu$^{2+}$ tends to enter the liquid phase and migrate to the surface via the geogas. Given the extremely low concentrations of REE in the geogas samples (Table 3), the addition of a trace amount of Eu$^{2+}$ would result in the notable positive δEu anomalies observed in these samples.

**Migration model of multielement geochemical anomalies in geogas**

Simulation experiments have confirmed that metal elements in ore-bearing supercritical fluids, under extreme conditions and during pressure reduction, can be found in both the liquid and the CO$_2$-rich vapor phases, even under specific conditions (22 MPa, 250–270°C). For instance, the gold content in some vapor phase samples was higher than that in the liquid phase samples. Nanoscale metal particles are a natural occurrence in endogenous mineralization processes (Zheng and Zheng, 2002). In high reducing environments rich in hydrogen and CO, nanoscale metal particles can conglomerate at lower melting points, forming volatile and migratory carbonyl and hydride compounds with CO and H$_2$. Upon transport to an oxidizing environment, these special complexes can decompose and oxidize into nanoscale metal particles. Additionally, supergene transformation of ores can result in the formation of secondarily mobile nanoscale particles through weathering and biological actions.

Nanoscale metal particles exhibit high surface energy and can adsorb onto the surface of geogas bubbles such as CO$_2$ and CH$_4$ (Fig. 9). This mineral element transformation is beneficial for their migration and enrichment, as the particles can preserve their fundamental geochemical stability during long-distance or long-term transport. As geogas ascends, nanoscale particles can penetrate the thick covering layers and migrate to the surface (Fig. 9). Furthermore, owing to their high diffusivity, they can also vertically migrate in the gas phase directly to the surface. Upon reaching the surface, some nanoscale particles remain in the geogas, while others are captured by soil geochemical traps like clays, colloids, and oxides, resulting in multielement geochemical anomalies in geogas.

**CONCLUSION**

Evaporation is one of the methods capable of producing nanoscale particles. Conditions in geological processes such as volcanic eruption, magmatism, and hydrothermalism resemble this process and may generate abundant nanomaterials during diagenesis and mineralization. At the Zijinshan HSE Cu-Au deposit, nanoscale particles were observed in geogases above the ore body, but no Au-, Cu-, or Fe-bearing counterparts were found in samples from the background area. The particles in geogas were comparable to those in ores, exhibiting similar features regarding size, shape, assemblage, and component. Cu-nanoscale particles retain the isotopic composition of copper found in both the oxidation zone and deep copper ores. A total of 22 geogas samples demonstrated multielement geochemical anomalies above the ore body. The anomalous elements were closely linked to metallogenic elements, with the anomaly locations related to those of the ore bodies and alteration zones. Copper isotope, Trace elements, REE concentrations, and associated geochemical parameters were alike in nanoscale particles, geogas samples, gold ore, copper ore, altered rock, and bedrock. Hence, it can be inferred that nanoscale particles in geogas and ores have the same genesis, with geogas derived from ores inheriting some of their relevant characteristics related to endogenic mineralization, and with the phase and features of nanoscale particles in geogas being stable.

At the Zijinshan HSE Cu-Au deposit, these nanoscale particles can penetrate volcanic coverings and migrate to the surface by utilizing multi-battalion relays, including mantle degassing, barometric pumping, gas release from ore minerals, evaporation, capillary action, and plant uptake. These particles can be adsorbed onto bubbles and ascend along with the geogas stream to the surface, due to their considerably large surficial area. Alternatively, based on their characteristics similar to gases, particles can ascend through regolith cover independently. While some particles remain in the geogas, others become ensnared by soil geochemical traps. These particles alongside multielement geochemical anomalies constitute direct geological evidence of the underlying concealed mineral deposit (Fig. 9).

Here, the utilization of Geogas prospecting is effective in identifying locations of ore mineralization buried under thick igneous coverages. More research is required for evaluating the exact mechanism of nanoparticles release from mineral deposits and determining the applicable use of this technology for regional-scale exploration.
All data included in this study are available upon request by contact with the corresponding author.

**Author Contribution**

Quanheng Li (corresponding author) conceived and designed the study. Quanheng Li, Kequan Xu, and Shuoguo Shen performed the experiments. Quanheng Li and Rong ye analyzed the data. Kequan Xu and Yufeng Tian contributed to the interpretation of the results. Quanheng Li wrote the original draft of the manuscript. All authors reviewed and edited the manuscript.

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**References**


**Figures**
Figure 1

(a) Simplified geological map of eastern South China. (b) Expanded geological map of Zijinshan ore field showing the locations of geogas samples. (c) Simplified geological map and (d) cross-sectional profile (exploration line 3) of the Au and Cu ore bodies within the Zijinshan deposit. F1 = Jiangshan-Shaoxing-Pingxiang-Yushan fault, F2 = Yunxiao-Shanghang Fault, A1 = Xuanhe Anticlinorium, Qz zone = silicic alteration zone, Qz-Alu zone = quartz-alunite alteration zone, Qz-Alu-Dck-Ser zone = quartz-alunite-dickite-sericite alteration zone, Phy zone = phyllic alteration zone.
Upon microscopic examination, it is evident that the Zijinshan HSE Cu-Au deposit harbors native gold within its ores (a, b, d), pyrite, chalcocite and arsenical are the main gold-carrying mineral (a, d, e).

Figure 2

Figure 3
Method for dynamic collection of geogas. Different media can be used to capture nanoscale particles and metal in geogas by replacing the container\(^4\).

**Figure 4**

Nanoscale particles in geogas at Zijinshan HSE Cu-Au deposit, Au nanoscale particle (Zhang et al., 2015) (a), Cu-Fe nanoscale particle (b, c), Fe-Ti nanoscale particle (d), complex metal nanoscale particle (e, f).
Figure 5

In the north east line and the north west line, geogas samples over the Zijinshan Cu-Au ore bodies show prominent geochemical anomalies compared to the background.
Figure 6

(a) Frequency diagram of Cu isotope values of the Cu-nanoscale and copper ores. (b) $\delta^{65}_{\text{Cu}}$ distribution diagram for the Cu-nanoscale and copper ores.
Figure 7

Trace element bivariate plots of geogas samples, copper ore, gold ore, altered rocks, and bedrocks; Co/Ni (a), Au/Ag (b), Pb/Zn (c), Pb/Cr (d), Cu/Mo (e), and Cu/Bi (f) were similar among these samples.
Figure 8

*C1 chondrite-normalized REE distribution patterns for geogas samples, gold ore, copper ore, altered rock, and bedrock*.

Figure 9

*Migration modal of nanoscale metal particles carried by earth gas*