Geochemical Compositions and Detrital Minerals of Stream Sediments around the Zijinshan Copper-Gold Orefield and Their Implications

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Abstract: Regional geochemical anomalies in stream sediments often have close spatial relationships with metallogenic provinces or ore districts, but the relationships between them have not been examined in depth. In this study, stream sediments were collected around the Zijinshan Copper-Gold Orefield, Fujian Province, China. Element geochemistry, U–Pb geochronology and Hf isotope compositions of detrital zircons, and electron microprobe and LA-ICP-MS analyses of iron oxides were conducted. The aims of this study were to investigate the relationship between the provenance of the stream sediments and ore-bearing magmatic rocks in the Zijinshan Copper-Gold Orefield, and to explore the enrichment mechanism of the ore-forming elements in stream sediments. The results show that the ore-forming elements and their associated elements are most significantly enriched in stream sediments near the orefield. U–Pb ages and Hf isotopic compositions of detrital zircons in the sediments closest to the orefield carry information on the ore-bearing magmatic rocks in the orefield. However, as the stream sediments are relatively far from the orefield, the degree of enrichment of ore-forming elements and the detrital zircon U–Pb age signals of the ore-bearing magmatic rocks in the orefield rapidly weaken. This weakening of the geochemical signals may have been affected by many factors, such as lithological resistance to weathering, vegetation coverage, micro-topographic conditions, etc. In-situ elements analysis of iron oxides and elemental correlation analysis of stream sediments indicate iron oxides and clay minerals are the main carrier minerals for the migration of ore-forming elements.

Keywords: stream sediment; Zijinshan Copper-Gold Orefield; detrital zircon; U–Pb age; Hf isotope; mineral

1. Introduction

Geochemical surveying and mapping of stream sediments play major roles in ore prospecting. Regional geochemical anomalies in stream sediments often have close spatial relationships with metallogenic provinces or ore districts [1–4]. Geochemical anomalies in stream sediments over an area >1000 km2 have been defined as geochemical blocks representing an area with high concentrations of metal elements in rocks, soils and stream sediments [4,5]. For example, the spatial distribution of Cu geochemical blocks with Cu content greater than 30 ppm in stream sediments of South China is very consistent with that of famous metallogenic belts in China, such as the Middle and Lower Yangtze Metallogenic belt [3]. Large geochemical blocks are linked to giant and large ore deposits in terms of their spatial distribution pattern. In China, all known gold deposits with proven reserves >50 tons are associated with large gold geochemical blocks [4]. Based on geochemical data of stream sediments of the Fujian Province (1:500,000) and the Zijinshan Copper-Gold Orefield (1:200,000) in China, Wang et al. [6,7] delineated eight gold geochemical blocks and five copper geochemical blocks using 2.5 ppb and 15 ppm, respectively, as the lower limits of anomalies. The Zijinshan Copper-Gold Orefield is located at the intersection of all
these anomalies of different elements [8]. Therefore, geochemical blocks are presumed to have provided some amount of metallogenic materials for the formation of ore districts [9], but the relationships between them have not been explored in depth.

Many studies have been conducted using the U–Pb ages and Hf isotope compositions of detrital zircons from stream sediments to trace major geological events and the crustal growth and recycling processes within river catchments [10–16]. However, no previous research has applied detrital zircon to trace the sources of geochemical anomalies in regional exploration geochemistry.

Therefore, stream sediment samples were collected around the Zijinshan Copper-Gold Orefield, Fujian Province, China in this study. Geochemical analyses including element geochemistry, detrital zircon U–Pb chronology together with Hf isotope geochemistry were conducted, in addition to in-situ elemental analyses of iron oxides in stream sediments. The aims of the study were to investigate the provenance of stream sediments, and to explore the enrichment mechanisms of ore-forming elements in stream sediments around the Zijinshan Copper-Gold Orefield. The results could provide constraint data for research on the relationships between the spatiotemporal distribution of geochemical blocks and ore districts, and the accumulation mechanisms of ore-forming elements in stream sediments.

2. Orefield Description, Sampling, and Analysis

2.1. Orefield Description

The Zijinshan Copper-Gold Orefield located in Shanghang County, Fujian Province, China is an epithermal-porphyry ore district dominated by copper, molybdenum, and gold [17]. The Zhenghe–Dapu fault zone controls the distribution of the metallogenic belt on a regional scale [18,19], and a northeast-trending compound anticline is the primary structure controlling the host magmatic rocks and ores within the orefield [20]. Polymetallic mineralization in the Zijinshan Copper-Gold Orefield is considered to be genetically related to Cretaceous magmatic-tectonic activity [21]. Two stages of the magmatism and metallogenesis occurred during 142 Ma–125 Ma and 110 Ma–92 Ma, respectively [21]. A short magmatic quiescence lasting from 125 Ma–110 Ma separated the two stages mentioned above [21]. Representative deposits include the superlarge Zijinshan copper-gold deposit, the large Luoboling copper-molybdenum deposit, and the large Yueyang silver polymetallic deposit [17] (Figure 1). The main ore-bearing magmatic rocks include the Zijinshan granite complex and Luoboling porphyry [22]. The Zijinshan granite complex is located in the central area of the Zijinshan Copper-Gold Orefield and is mainly composed of the Jingmei intrusion, the Wulongsi intrusion, and the Jinlongqiao intrusion [23]. Its lithological composition is characterized by fine- to coarse-grained granite, in addition to Late Yanshanian volcanic rocks, subvolcanic rocks, cryptoexplosive breccia, and dacite porphyry [20,24]. Gold-copper ores occur in medium- to fine-grained granite, dacite porphyrite, and cryptoexplosive breccia [21]. The zircon U–Pb ages of medium- to fine-grained granite in the Wulongsi intrusion are divided into ~1000 Ma, 168 Ma ± 4 Ma, and 119 Ma ± 15 Ma, which represent the ages of inherited zircons, the crystallization age of the pluton, and the age of large-scale Cu-Au mineralization, respectively [25]. The Luoboling porphyry is dominated by a suite of amphibolitic biotite granodiorite porphyry and biotite granodiorite porphyry with a formation age between 103.7 Ma ± 1.2 Ma and 97.6 Ma ± 2.1 Ma [22,26]. The Re–Os isochron age of molybdenite in the Luoboling copper-molybdenum deposit is 104.9 Ma ± 1.6 Ma, which is in agreement with the formation age of the granodiorite porphyry [27]. Therefore, both magmatism and metallogenesis in the Luoboling copper-molybdenum deposit occurred during the Early Cretaceous [27,28].

Mesozoic strata are the most widely exposed in the study area, whereas Paleozoic and Sinian strata are less exposed. The outcropping strata mainly comprise dacitic, trachyandesitic, rhyolitic lava, and pyroclastic rocks of the Zhaixia Formation of the Shimaoshan Group (Kz), purple-red fine-grained clastic rocks of the Shaxian Formation of the Chishi Group (Kc), littoral clastic rocks of the Lindi Formation (Cl), neritic-littoral clastic rocks of the Tianwadong (Dt) and Taozikeng formations (Dtz), and neritic metamorphic fine
clastic rocks of the Louziba Group (Zl) [29–32] (Figure 1). The Zhaixia Formation of the Shimaoshan Group (Kz) is distributed near the Zijinshan Copper-Gold Orefield and serves as vital ore-bearing strata of copper, gold, and silver [20].

Figure 1. (a) Simplified geological map of eastern South China (modified after Zhao et al. [33]). (b) Sampling sites of stream sediments and geological map of the Zijinshan Copper-Gold Orefield (modified from 1:200,000 geological map of Fujian Province, China).

2.2. Sample Collection and Analysis

Twenty-seven stream sediment samples were collected from rivers flowing through the Zijinshan copper-gold deposit and the Luoboling copper-molybdenum deposit in 2018 (Figure 1). We collected samples near the confluence between the trunk stream and tributaries, before and after the tributaries merge into the mainstream, and in the mountain gullies around the orefield. Approximately 3 kg of surface sediments were collected at each sampling location from the newly deposited riverbank. Fine stream sediments mainly composed of sandy and muddy sediments were generally collected. Samples were mixtures of sub-samples taken from several points around each sampling site in an attempt to get representative materials from the channel at each point. After air-drying, approximately 500 g of the bulk sediment samples were used for element content analysis, detrital zircon separation, and electron microprobe analysis.

2.2.1. Geochemical Analysis of Sediments

After those samples were passed through a 60-mesh sieve, major elements, trace elements, and rare earth elements (REEs) were analyzed at the Hefei Mineral Resources...
Supervision and Testing Center, Ministry of Land and Resources, People’s Republic of China. With the exception of FeO, which was determined using the potassium dichromate volumetric method, all other major elements were tested using X-ray fluorescence spectrometry (ZSX100e; Rigaku Corp., Tokyo, Japan), and the testing method was based on the national standard GB/T 14506-1993 with an accuracy better than 0.3%. To determine trace elements and REEs contents, 0.2 g of sample powder was digested using a mixture of HF–HNO$_3$–HCl–H$_2$SO$_4$ and then analyzed using ICP-MS (X SERIES II; Thermo Fisher Scientific, Wilmington, DE, USA). When the element mass fraction was greater than 10 ppm, the accuracy was better than 5%; when the element mass fraction was less than 10 ppm, the accuracy was better than 10%.

2.2.2. EMP and LA-ICP-MS Analysis of Iron Oxides in Stream Sediments

Stream sediment samples were dried (60 °C). After drying, the samples were placed on glass slides for epoxy drip infusion and set simultaneously. Then, the samples fully filled with epoxy resin were dried for approximately 24 h (60 °C). The samples were ground flat after drying. The samples were glued to the glass slides again and put into the drying oven until the glue dried. After grinding, thinning, and polishing, the samples were made into thin sections. Mineralogical observations were conducted using a microscope. Electron Microprobe (EMP) was performed at the Analytical Laboratory of the Beijing Research Institute of Uranium Geology (Beijing, China) using a JXA-8100 electron probe microanalyzer and mineral standards (SPI, West Chester, PA, USA). The analyses of trace elements of iron oxides in stream sediments were conducted by LA-ICP-MS at the Key Laboratory of Metallogeney and Mineral Assessment of the Ministry of Natural Resources, Institute of Mineral Resources, Chinese Academy of Geological Sciences (Beijing, China). Trace element analysis was undertaken using a RESOLution S-155 193-nm ArF excimer laser ablation system (ASI, Fyshwick, Canberra, Australia) coupled to an Aurora M90 ICP-MS system (Bruker, Bremen, Germany). The analysis was performed with a laser energy density of 6 J/cm$^2$, a laser ablation frequency of 6 Hz, and an ablation beam spot size of 38 µm. In the course of laser ablation, helium was used as the carrier gas and argon was used as a compensation gas to adjust sensitivity. Each time-resolved analysis data point included a ~15 s blank signal and a 45 s sample signal. Element contents were calibrated against multiple-reference materials (BCR-2G, BIR-1G and GSE-1G) without applying internal standardization [34]. The recommended values of element concentrations for the USGS reference glasses are from the GeoReM database (http://georem.mpch-mainz.gwdg.de/, accessed on 21 November 2021). Offline processing of the analytical data was completed using the ICPMSDataCal software [34,35].

2.2.3. Isotope Analysis of Detrital Zircons in Stream Sediments

The stream sediments were sorted by electromagnetic isodynamic heavy mineral separation methods. Subsequently, detrital zircons were selected under a binocular microscope and then mounted in an epoxy resin. Cathodoluminescence images of detrital zircons were captured by Beijing Gaonian Linghang Technology Co., Ltd. (Beijing, China).

U–Pb dating of detrital zircons was conducted by LA-ICP-MS at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. Both the detailed operating conditions for the laser ablation system and the ICP-MS instrument and the data reduction process are the same as those described by [34–36]. A GeoLas 2005 laser ablation system is coupled with an Agilent 7500a ICP-MS instrument. The laser beam is focused on a spot with a diameter of 30 µm, a frequency of 8 Hz, and an energy of 70 mJ. Helium is applied as a carrier gas. Argon is used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP. Nitrogen is added into the central gas flow (Ar + He) of the Ar plasma to decrease the detection limit and improve precision [36,37]. Each analysis incorporated a background acquisition of approximately 20–30 s (gas blank) followed by 50 s of data acquisition from the sample. Zircon 91500 was used as the external standard for U–Pb dating, and was analyzed twice
every five analyses. Off-line selection and integration of background and analyte signals, and time-drift correction and quantitative calibration for U–Pb dating were performed by ICPMSDataCal [34,35]. Drawing of the U–Pb age concordia diagram and calculation of the weighted mean age for zircon samples were completed using Isoplot/Ex_ver3 [38].

Hf isotope ratio analysis of detrital zircons was conducted using a Neptune Plus MC-ICP-MS in combination with a Geolas 2005 excimer ArF laser ablation system that was hosted at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences in Wuhan. Detailed operating conditions for the laser ablation system and the MC-ICP-MS instrument and analytical methods are the same as those found in the description by [39]. The laser beam is focused to produce a spot size of 44 µm, with an energy density of 5.3 J cm\(^{-2}\) and a pulse frequency of 8 Hz. Helium is used as the carrier gas within the ablation cell and was merged with argon (makeup gas) after the ablation cell. Each measurement consisted of 20 s of acquisition of the background signal followed by 50 s of signal acquisition. The 176Hf/177Hf isotope ratios of 91,500 and GJ-1 as standard samples were 0.282735 \(\pm\) 0.000024 (2\(\sigma\)) and 0.282016 \(\pm\) 0.000020 (2\(\sigma\)), respectively. The 179Hf/177Hf and 173Yb/171Yb ratios were used to calculate the mass bias of Hf (\(\beta_{Hf}\)) and Yb (\(\beta_{Yb}\)), which were normalized to 179Hf/177Hf = 0.72000 and 173Yb/171Yb = 1.2082 [40]. Interference of 176Yb on 176Hf was corrected by measuring the interference-free 176Yb isotope and using 176Yb/175Yb = 0.7867 [41] to calculate 176Yb/177Hf. Similarly, the relatively minor interference of 176Lu on 176Hf was corrected by measuring the intensity of the interference-free 175Lu isotope and using the recommended 176Lu/175Lu = 0.02656 [40] to calculate 176Lu/177Hf. Off-line selection and integration of analyte signals and mass bias calibrations were performed using ICPMSDataCal [35].

3. Results

3.1. Element Contents of Stream Sediments

The major element, trace element, and REE compositions of the stream sediments are listed in Table 1. The stream sediments are characterized by high Si, high K, and low Mg and Ca contents. In stream sediments around the Zijinshan copper-gold deposit, the SiO\(_2\) content varies from 70.92% to 87.43% (mean: 83.14%); the Al\(_2\)O\(_3\) content ranges between 5.32% and 12.97% (mean: 7.54%); the TFe\(_2\)O\(_3\) content falls in the 0.93%–4.23% range; the MgO and CaO contents are within the 0.19%–0.52% and 0.12%–2.13% ranges, respectively; the total alkali (Na\(_2\)O + K\(_2\)O) content is in the 1.88%–2.83% range. In stream sediments around the Luoboling copper-molybdenum deposit, the SiO\(_2\) content ranges between 83.69% and 86.46% (mean: 85.49%); the Al\(_2\)O\(_3\) content is between 5.67% and 8.07% (mean: 6.54%); the TFe\(_2\)O\(_3\) content is in the 1.61%–2.41% range; the MgO and CaO content are in the 0.24%–0.53% and 0.17%–0.29% ranges, respectively; the total alkali content is 1.97%–2.75%.

Table 1. Element compositions of stream sediments in the Zijinshan Copper-Gold Orefield.

| Sample ID | ZJS01 | ZJS02-1 | ZJS05 | ZJS09 | ZJS12 | LBL03 | LBL04 | LBL06 | LBL07 | LBL09 |
|-----------|-------|---------|-------|-------|-------|-------|-------|-------|-------|-------|
| SiO\(_2\)  | 70.92 | 85.32   | 85.54 | 86.51 | 87.43 | 83.69 | 86.46 | 86.42 | 86.48 | 84.4  |
| Al\(_2\)O\(_3\) | 12.97 | 6.43    | 7.63  | 5.35  | 5.32  | 8.07  | 5.67  | 6.17  | 5.79  | 6.98  |
| TFe\(_2\)O\(_3\) | 4.23  | 1.44    | 1.19  | 1.97  | 0.93  | 2.41  | 1.61  | 1.65  | 1.72  | 2.21  |
| CaO       | 2.13  | 0.31    | 0.16  | 0.12  | 0.14  | 0.17  | 0.25  | 0.16  | 0.24  | 0.29  |
| MgO       | 0.52  | 0.35    | 0.2   | 0.19  | 0.2   | 0.33  | 0.32  | 0.24  | 0.24  | 0.53  |
| Na\(_2\)O | 0.16  | 0.55    | 0.17  | 0.42  | 0.46  | 0.2   | 0.25  | 0.2   | 0.29  | 0.35  |
| K\(_2\)O  | 1.75  | 1.78    | 1.71  | 2.06  | 2.37  | 1.77  | 1.8   | 1.7   | 1.82  | 2.4   |
Table 1. Cont.

| Sample ID | ZJS01 | ZJS02-1 | ZJS05 | ZJS09 | ZJS12 | LBL03 | LBL04 | LBL06 | LBL07 | LBL09 |
|-----------|-------|---------|-------|-------|-------|-------|-------|-------|-------|-------|
| Ba        | 355.8 | 294.4   | 143.2 | 291.4 | 324.3 | 268.8 | 251.8 | 277.3 | 304.2 | 308.5 |
| Cr        | 49.9  | 13.6    | 7.2   | 8.6   | 9.8   | 22.3  | 14.9  | 18.7  | 17.6  | 19.5  |
| Zn        | 71.0  | 28.5    | 72.7  | 30.7  | 23.9  | 71.9  | 50.9  | 45.9  | 76.4  | 62.8  |
| Pb        | 34.6  | 32.8    | 72.5  | 21.4  | 19.8  | 48.9  | 42.9  | 34.8  | 40.1  | 32.8  |
| Rb        | 101.7 | 82.4    | 105.3 | 102.6 | 112.2 | 97.4  | 92.5  | 87.5  | 98.5  | 125.6 |
| Sr        | 32.5  | 49.7    | 53.6  | 42.5  | 40.4  | 30.6  | 36.0  | 21.0  | 29.2  | 39.4  |
| Zr        | 191.7 | 80.5    | 65.8  | 88.8  | 55.6  | 134.7 | 66.0  | 73.5  | 69.0  | 101.0 |
| Nb        | 16.0  | 11.5    | 19.8  | 23.9  | 10.8  | 14.3  | 14.2  | 12.3  | 16.5  | 17.6  |
| Ag        | 84.0  | 122.0   | 430.0 | 101.0 | 67.0  | 103.0 | 90.6  | 175.0 | 16.5  | 17.6  |
| Sn        | 4.8   | 2.5     | 6.3   | 8.7   | 2.2   | 3.1   | 2.7   | 4.2   | 4.4   |
| Cu        | 26.3  | 13.2    | 36.2  | 11.6  | 8.6   | 32.2  | 23.8  | 15.5  | 14.9  | 18.3  |
| Li        | 34.6  | 19.2    | 19.4  | 17.9  | 19.7  | 31.7  | 19.3  | 15.5  | 20.9  | 21.3  |
| Mn        | 650.9 | 249.3   | 307.7 | 321.1 | 353.4 | 770.0 | 444.6 | 1073.8| 1613.7| 2291.1|

1 Unit: % for major elements; ppb for Ag, Au, and Cd; and ppm for other trace elements.

The spider diagrams of trace elements in the stream sediments are shown in Figure 2. The characteristics of trace elements in the stream sediments are very similar. Th, Sr, Zr, Hf, and Ti are depleted, whereas large ion lithophile elements are relatively enriched. The distribution patterns of REEs are displayed in Figure 3. In stream sediments around the Zijinshan copper-gold deposit, the REE content varies substantially, and the total amount of REEs is relatively low, $\Sigma$REE = 60.18 ppm–191.35 ppm. The light REE (LREE)/heavy REE (HREE) ratio is in the 1.72–3.52 range, with (La/Lu)$_N$ of 3.05–8.98, indicating enrichment of LREEs and depletion of HREEs. The distribution curves of HREEs are relatively flat, and negative Eu anomalies are evident, $\delta$Eu = 0.39–0.68. In the granite from the...
Zijinshan Copper-Gold Orefield, the total amount of REEs is between 40.41 ppm and 196.47 ppm (mean: 121.22 ppm), with (La/Lu)$_N$ of 2.99–36.65 (mean: 9.87). Negative Eu anomalies are evident, δEu = 0.29–0.65 (mean: 0.42) (Table 2). The REE patterns of the stream sediments and granite in the orefield are very similar. In stream sediments around the Luoboling copper-molybdenum deposit, the total amount of REEs is relatively low: $\sum$REE = 69.80 ppm–116.65 ppm. The REEs are weakly differentiated, with a LREE/HREE ratio of 2.70–3.31 and (La/Lu)$_N$ of 6.70–9.33. The LREEs are weakly enriched, whereas negative Eu anomalies are evident. In the granodiorite porphyry from the Luoboling copper-molybdenum deposit, the total amount of REEs is 126.6 ppm–171.6 ppm (mean: 149.3 ppm). The LREEs are distinctly enriched, with weak negative Eu anomalies: δEu = 0.91–1.03 (mean: 0.98) (Table 2).

![Figure 2](image1.png)

**Figure 2.** Primitive mantle-normalized trace element patterns of stream sediments in the Zijinshan Copper-Gold Orefield. Primitive Mantle normalized data are from [42].

![Figure 3](image2.png)

**Figure 3.** Chondrite-normalized REE patterns of stream sediments in the Zijinshan Copper-Gold Orefield. Chondrite normalized data are from [43]. (a) Stream sediments around Zijinshan copper-gold deposit; (b) Stream sediments around the Luoboling copper-molybdenum deposit. Data of ore-bearing magmatic rocks in the orefield are from [19,44].
Table 2. Comparison of rare earth element compositions of stream sediments and ore-bearing magmatic rocks in the Zijinshan Copper-Gold Orefield.

|                          | Stream Sediments | Magmatic Rocks in the Orefield * |
|--------------------------|------------------|----------------------------------|
|                          | Zijinshan copper-gold deposit |                                |
| ∑REE/(ppm)               | 99.06            | 121.22                           |
| Range                    | 60.18–191.35     | 40.41–284.20                     |
| ∑Er-Lu/(ppm)             | 4.26             | 5.67                             |
| Range                    | 2.48–6.43        | 1.21–12.88                       |
| δEu                      | 0.54             | 0.42                             |
| Range                    | 0.39–0.68        | 0.29–0.65                        |
| (La/Yb)_N                | 6.48             | 10.73                            |
| Range                    | 3.56–8.45        | 2.62–48.19                       |
| (La/Gd)_N                | 5.41             | 8.82                             |
| Range                    | 4.34–6.20        | 2.94–19.50                       |
| (Gd/Yb)_N                | 1.17             | 1.15                             |
| Range                    | 0.82–1.39        | 0.60–2.55                        |

|                          | Luoboling copper-molybdenum deposit |                                |
| ∑REE/(ppm)               | 97.57            | 149.31                           |
| Range                    | 69.8–116.65      | 126.60–171.60                    |
| ∑Er-Lu/(ppm)             | 3.78             | 3.68                             |
| Range                    | 3.16–4.18        | 3.21–4.32                       |
| δEu                      | 0.55             | 0.98                             |
| Range                    | 0.52–0.62        | 0.91–1.03                       |
| (La/Yb)_N                | 7.60             | 12.94                            |
| Range                    | 6.33–9.00        | 9.32–18.93                       |
| (La/Gd)_N                | 5.83             | 7.73                             |
| Range                    | 5.46–6.23        | 5.95–10.78                       |
| (Gd/Yb)_N                | 1.30             | 1.68                             |
| Range                    | 1.11–1.44        | 1.38–1.86                        |

* Data of ore-bearing magmatic rocks in the orefield are derived from [19,44].

In stream sediments around the Zijinshan copper-gold deposit, the Cu content varies from 8.6 ppm to 36.2 ppm (mean: 19.18 ppm); the Zn content ranges between 23.9 ppm and 72.7 ppm (mean: 45.36 ppm); the Pb content falls in the 19.8 ppm–72.5 ppm range; the Mo and Au contents are within the 0.52 ppm–3.61 ppm and 1.3 ppb–20 ppb ranges, respectively. In stream sediments around the Luoboling copper-molybdenum deposit, the Cu content ranges between 14.9 ppm and 32.2 ppm (mean: 20.94 ppm); the Mo content is between 1.4 ppm and 4.72 ppm (mean: 2.44 ppm); the Zn content is in the 45.9 ppm–76.4 ppm range; the Pb and Au contents are in the 32.8 ppm–48.9 ppm and 1.1 ppb–3.4 ppb ranges, respectively.

3.2. Ore-Forming Element Contents of Iron Oxides

It was found that the main minerals in stream sediments are quartz, feldspar, mica, pyroxene, iron oxides, and clay minerals (Figure 4). Of these, iron oxides and clay minerals are the main carrier minerals for metal elements in surface geological processes. Metal elements can not only be absorbed by iron oxides and clay minerals, but can also be carried as detrital materials of Fe-bearing minerals. Electron microprobe analysis and LA-ICP-MS in-situ element analysis were carried out on iron oxides only (Tables 3 and 4). The results show that FeO content in iron oxides varies over a large range, 56.65%–88.99% (mean: 77.69%). In the case of relatively low FeO content, the Al₂O₃ and SiO₂ contents are generally high. In addition, CuO and CdO are detected in iron oxides, suggesting that iron oxides are at least main carrier minerals for Cu and Cd (Table 3). Furthermore, the contents of ore-forming elements are extremely uneven in the iron oxides and are greater than the averages of ore-forming elements in stream sediments (Table 4). For example, the Cu content varies from 12.39 ppm to 1425.31 ppm (mean: 280.1 ppm) and the Mo content ranges between 1.93 ppm and 134.33 ppm (mean: 20.75 ppm).
Figure 4. Microscopic photographs of stream sediments in the Zijinshan Orefield. (Ab, albite; Qz, quartz; Mu, muscovite; Fsp, feldspar; Mi, mica; Kfs, potash feldspar; Aug, augite). (a) Stream sediment numbered LBL01 around Luoboling Cu-Mo deposit; (b) Stream sediment numbered LBL11 around Luoboling Cu-Mo deposit; (c) Stream sediment numbered ZJS02-1 around Zijinshan Cu-Au deposit; (d) Stream sediment numbered ZJS07 around Zijinshan Cu-Au deposit.

Table 3. Electron microprobe analysis results of iron oxides in stream sediments (unit: %).

| Sample ID | Survey Point | MgO | Na₂O | FeO | CaO | Al₂O₃ | SiO₂ | TiO₂ | K₂O | MnO | P₂O₅ | CuO | CdO | Total  |
|-----------|--------------|-----|------|-----|-----|-------|------|------|-----|-----|------|-----|-----|--------|
| LBL01     |              |     |      |     |     |       |      |      |     |     |       |     |     |        |
| 1         |              |     |      |     |     |       |      |      |     |     |       |     |     | 88.77  |
| 2         |              |     |      |     |     |       |      |      |     |     |       |     |     | 88.41  |
| 3         |              |     |      |     |     |       |      |      |     |     |       |     |     | 88.99  |
| 4         |              |     |      |     |     |       |      |      |     |     |       |     |     | 80.61  |
| 5         |              |     |      |     |     |       |      |      |     |     |       |     |     | 72.58  |
| LBL11     |              |     |      |     |     |       |      |      |     |     |       |     |     |        |
| 1         |              | 0.03| 0.07 |     |     |       |      |      |     |     |       |     |     | 71.00  |
| 2         |              | 0.04| 0.15 |     |     |       |      |      |     |     |       |     |     | 71.66  |
| 3         |              | 0.06| 0.10 |     |     |       |      |      |     |     |       |     |     | 71.57  |
| ZJS02-1   |              |     |      |     |     |       |      |      |     |     |       |     |     |        |
| 1         |              | 0.40| 0.11 |     |     |       |      |      |     |     |       |     |     | 88.61  |
| 2         |              | 0.73| 0.05 |     |     |       |      |      |     |     |       |     |     | 88.34  |
| 3         |              | 0.31| 0.04 |     |     |       |      |      |     |     |       |     |     | 88.27  |
| ZJS07     |              |     |      |     |     |       |      |      |     |     |       |     |     |        |
| 1         |              | 0.05| 0.17 |     |     |       |      |      |     |     |       |     |     | 71.39  |
| 2         |              | 0.02| 0.10 |     |     |       |      |      |     |     |       |     |     | 72.10  |
### Table 3. Cont.

| Sample ID | Survey Point | MgO | Na₂O | FeO | CaO | Al₂O₃ | SiO₂ | TiO₂ | K₂O | MnO | P₂O₅ | CuO | CdO | Total |
|-----------|--------------|-----|------|-----|-----|-------|------|------|-----|-----|------|-----|-----|-------|
| ZJS13     |              |     |      |     |     |       |      |      |     |     |      |     |     | 85.62 |
| 1         |              |     |      |     |     |       |      |      |     |     |      |     |     | 83.61 |
| 2         |              |     |      |     |     |       |      |      |     |     |      |     |     | 84.31 |
| 3         |              |     |      |     |     |       |      |      |     |     |      |     |     | 88.53 |
| 4         |              |     |      |     |     |       |      |      |     |     |      |     |     | 88.75 |
| 5         |              |     |      |     |     |       |      |      |     |     |      |     |     | 88.99 |

### Table 4. LA-ICP-MS trace element analysis of iron oxides in stream sediments (unit: ppm).

| Sample ID | Survey Point | Cu  | Zn  | In  | Sn  | Sb  | Mo  | Pb  | Bi  | Cd  |
|-----------|--------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| ZJS02     | 1-1          | n.d.| 1810.19 | 0.39 | 12.59 | 11.09 | 3.30 | 408.73 | 1.65 | n.d. |
|           | 1-2          | n.d.| 1693.58 | 0.38 | 14.28 | 17.02 | 3.82 | 772.59 | 2.20 | n.d. |
|           | 1-3          | 12.39 | 1952.28 | 0.89 | 27.31 | 21.59 | 3.14 | 496.23 | 2.89 | n.d. |
| ZJS07     | 1-1          | 125.69 | 103.07 | 0.23 | n.d. | 0.30 | 7.64 | 31.24 | n.d. | n.d. |
|           | 1-2          | 93.41 | 103.66 | 0.28 | n.d. | 1.53 | 20.65 | 48.25 | n.d. | n.d. |
| ZJS13     | 1-1          | 16.76 | 364.25 | 0.23 | 10.63 | 19.74 | 1.93 | 112.43 | 0.32 | n.d. |
|           | 1-2          | 15.18 | 306.61 | 0.26 | 10.43 | 19.91 | 1.98 | 124.89 | 0.40 | n.d. |
|           | 2-1          | 290.74 | n.d. | 21.56 | n.d. | 8.60 | 1.48 | 0.08 | n.d. | n.d. |
|           | 2-2          | 263.79 | n.d. | 7.64 | n.d. | 9.42 | n.d. | 10.17 | n.d. | n.d. |
|           | 2-3          | 247.98 | n.d. | 12.83 | n.d. | 5.47 | 1.52 | 0.09 | n.d. | n.d. |
| LBL11     | 1-1          | 268.09 | 424.77 | 0.65 | 1.35 | 12.49 | 3.10 | 30.54 | 0.63 | n.d. |
|           | 1-2          | 85.59 | n.d. | 3.14 | n.d. | n.d. | n.d. | n.d. | 9.64 | n.d. |
|           | 1-3          | 263.80 | 376.14 | 0.65 | 1.69 | 14.13 | 8.34 | 22.93 | 2.27 | 3.51 |
|           | -1           | 22.64 | 34.14 | n.d. | 7.07 | n.d. | 3.23 | 25.66 | 0.63 | n.d. |
| LBL01     | 1-2          | 85.98 | 67.40 | 0.10 | 7.12 | 0.57 | 3.74 | 368.72 | 6.87 | n.d. |
|           | 1-3          | 190.90 | 44.23 | 0.09 | 1.94 | n.d. | 5.43 | 122.06 | 1.03 | n.d. |
|           | 2-1          | 1035.56 | n.d. | 0.18 | n.d. | 0.93 | 119.56 | 377.44 | 2.89 | n.d. |
|           | 2-2          | 1425.31 | 19.84 | 0.23 | 0.37 | 1.22 | 143.33 | 300.91 | 3.76 | n.d. |
| Average   |              | 280.10 | 506.42 | 0.35 | 9.33 | 10.04 | 20.75 | 202.85 | 1.84 | 7.77 |
| Average for stream sediments in the orefield | 20.06 | 53.47 | 0.049 | 4.14 | 0.68 | 1.05 | 38.06 | 1.45 | 0.319 |

1 Note: n.d. indicates lower than the detection limit.

### 3.3. Detrital Zircon U–Pb Ages

Six stream sediment samples were selected for detrital zircon U–Pb dating according to the distance between the stream sediments and the orefield. One hundred zircons were randomly selected from each sample for U–Pb dating. The U–Pb ages of 600 detrital zircons were tested. 206 Pb/238 U age should be considered for zircons with ages younger than 1.4 Ga. Instead, for grains older than 1.4 Ga, the 206 Pb/207 Pb age is considered as the best age in dependent of minor error of this ratio [45,46]. The U–Pb age data with concordance >90% are selected to draw age histograms.

Some detrital zircons are long cylindrical in shape, suggesting that their sorting and rounding are relatively poor, and that the migration distance was generally short. In addition, some detrital zircons are spherical and irregular in shape with a relatively high roundness, which indicates that they may have been transported over long distances or were detrital zircons from clastic rocks. The cathodoluminescence images of some detrital zircons are shown in Figure 5. Most of the detrital zircons have the rhythmic oscillating zonal structure that is typical of magmatic zircons [47]. A small portion of detrital zircons have a planar and taxitic structure, which indicates that they likely are metamorphic zircons [48].
LA-ICP-MS U–Pb ages of detrital zircons from stream sediments are listed in Table S1. Kernel density plots are preferable to Isoplot functions for the treatment and representation of detrital zircon ages [49–52]. Stream sediment sample ZJS01 was collected upstream of the river flowing through Zijinshan copper-gold deposit, ~5.6 km away from the deposit (Figure 1). There were 98 detrital zircons with U–Pb ages satisfying the requirement of >90% concordance in this sample. The U–Pb age histogram shows peak ages at 102 Ma, 1061 Ma, and 1929 Ma, and a weaker peak appears at the age of 786 Ma (Figure 6a). There are also many Paleoproterozoic and Archean U–Pb ages. In addition, stream sediment sample ZJS05 was collected from the point where the river just flowed through the Zijinshan copper-gold deposit (Figure 1). In this sample, 89 detrital zircons with U–Pb ages of >90% concordance were obtained, and U–Pb ages varied from 109.2 ± 1.7 Ma to 2516.4 ± 10.8 Ma. Peak ages appear at 113 Ma, 449 Ma, 823 Ma, and 1940 Ma in the age histogram (Figure 6c). Moreover, sample ZJS12 was collected in the downstream of the river far from the Zijinshan copper-gold deposit, where two rivers converged. In this sample, there are 77 detrital
zircons with U–Pb ages of >90% concordance, and U–Pb ages range from 103.6 ± 1.2 Ma to 2283.3 ± 35.5 Ma. Prominent peaks appear at 150 Ma and 437 Ma in the age histogram (Figure 6e), with very few ages older than 1000 Ma.

Figure 6. Probability curves of U–Pb ages for detrital zircons of stream sediments in the Zijinshan Copper-Gold Orefield. (a) Stream sediment numbered ZJS01 around Zijinshan Cu-Au deposit; (b) Stream sediment numbered LBL02 around Luoboling Cu-Mo deposit; (c) Stream sediment numbered ZJS05 around Zijinshan Cu-Au deposit; (d) Stream sediment numbered LBL04 around Luoboling Cu-Mo deposit; (e) Stream sediment numbered ZJS12 around Zijinshan Cu-Au deposit; (f) Stream sediment numbered LBL09 around Luoboling Cu-Mo deposit.

Stream sediment samples LBL02, LBL04, and LBL09 were collected downstream of the river flowing through the Luoboling copper-molybdenum deposit, with gradually increasing distances from the deposit (Figure 1). In these three samples, there are 86, 78, and 91 detrital zircons with U–Pb ages of >90% concordance. In stream sediment sample LBL02, detrital zircon U–Pb ages range from 101.5 ± 1.5 Ma to 2013.0 ± 27.0 Ma. The ages in the histogram are highly concentrated in two intervals, 101.5 ± 1.5 Ma–167.4 ± 2.7 Ma
and 435.0 ± 6.7 Ma–484.7 ± 8.0 Ma, which correspond to peak ages at 112 Ma and 468 Ma, respectively (Figure 6b). There is a scarcity of detrital zircons older than 500 Ma. In stream sediment sample LBL04, detrital zircon U–Pb ages vary between 98.1 ± 1.4 Ma and 818.1 ± 14.3 Ma. The U–Pb ages are mainly concentrated in three intervals, 98.1 ± 1.4 Ma–127.9 ± 2.5 Ma, 142.7 ± 1.9 Ma–157.1 ± 3.3 Ma, and 427.6 ± 4.7 Ma–494.9 ± 6.7 Ma, corresponding to peak ages at 119 Ma, 145 Ma, and 455 Ma, respectively (Figure 6d). In stream sediment sample LBL09, detrital zircon U–Pb ages range between 97.6 ± 1.1 Ma and 1505.6 ± 38.6 Ma, and are mainly concentrated in two intervals, 97.6 ± 1.1 Ma–171.3 ± 3.5 Ma and 414.0 ± 4.9 Ma–474.0 ± 7.6 Ma; the corresponding peak ages are 148 Ma and 444 Ma, respectively (Figure 6f).

3.4. Detrital Zircon Hf Isotopic Compositions

The detrital zircons with high concordance and consistency with the U–Pb ages of magmatic zircons in ore-bearing magmatic rocks from the Zijinshan Copper-Gold Orefield were selected for Hf isotope analysis at a total of 145 points. The results show that the single-stage depleted mantle Hf model ages of detrital zircons from stream sediments fall in the 693.8–2563.9 Ma range, with a mean age of 1021.31 Ma. The two-stage depleted mantle Hf model ages of zircons vary between 922.2 and 3596.6 Ma, with a mean age of 1378.12 Ma. Aside from three detrital zircons with very low εHf(t), the other detrital zircons have the εHf(t) varying from −19.50 to 2.22 (mean: −5.65; Figure 7). These results are very similar to the Hf isotope compositions of magmatic zircons from ore-bearing magmatic rocks in the Zijinshan Copper-Gold Orefield [53–55]. The two-stage depleted mantle Hf model ages of magmatic zircons from ore-bearing magmatic rocks in the Zijinshan Copper-Gold Orefield range between 1092 and 2365 Ma, with a mean age of 1529.07 Ma; their εHf(t) varied from −19.03 to 8.71 (mean: −5.41).

Figure 7. U–Pb ages and εHf(t) composition diagram of detrital zircons of stream sediments in the Zijinshan Orefield. Data on magmatic zircons of ore-bearing magmatic rocks in the Zijinshan Copper-Gold Orefield derived from [53–55].

4. Discussion

4.1. Elemental Sediments Composition

There are no distinct differences in major element contents in the stream sediments of the two ore deposits. Compared with the ore-bearing magmatic rocks in the orefield, the total amount of REEs in the stream sediments is decreased, whereas the differentiation
of LREEs and HREEs is weakened and the content of HREEs is decreased in the stream sediments, and the negative Eu anomalies are more distinct (Table 2). Sr is also remarkably depleted (Figure 2). Because Eu and Sr often occur in plagioclase to replace Ca in the form of an isomorphism, the stream sediments also contain low Ca content (Table 1). Therefore, a plausible reason is that plagioclase was weathered during the process of weathering and migration.

The enrichment factor (the ratio of the contents of ore-forming elements in stream sediments to their abundances in the upper crust) is used to determine the degree of enrichment of ore-forming elements in stream sediments. The enrichment factors of ore-forming elements in stream sediments of the Zijinshan Copper-Gold Orefield are shown in Figure 8. Based on the geological map of the study area combined with the sampling locations of the stream sediments (Figure 1), it was found that the enrichments of ore-forming elements and associated elements in stream sediments near the orefield are most prominent. For example, stream sediment sample ZJS05 is the sample collected nearest to the Zijinshan copper-gold deposit, and ore-forming elements including Au, Cu, Mo, Ag, As, Bi, and Cd are the most enriched in this sample. Ore-forming elements are slightly enriched in the other stream sediments. This result suggests that the migration distance of ore-forming elements along the stream is not far, which may be related to the relatively developed vegetation and strong chemical weathering in the study area. The ore-forming elements in the stream sediments reflect the information of geological bodies at a close distance.

Figure 8. Normalized patterns of ore-forming elements of stream sediments in the Zijinshan Copper-Gold Orefield. Upper Crust normalized data are from [56].

The contents of ore-forming elements in iron oxides at most survey points are 1.27–24.37 times higher than the contents in stream sediments. In particular, the enrichment features of Cu, Zn, Sb, Mo, and Cd in iron oxides are more prominent among the ore-forming elements. Therefore, iron oxides are the main carrier minerals for ore-forming elements. Because the particles of clay minerals are relatively small, in-situ analysis was not carried out on these minerals. However, clay minerals have large specific surface areas and can adsorb large amounts of ore-forming elements. Cu and Mo have significant correlations with the $\text{Al}_2\text{O}_3$ contents in the stream sediments. This relationship suggests that clay minerals are also the main carrier minerals for ore-forming elements of stream sediments in the study area.

4.2. Implication of Detrital Zircon U–Pb Ages

In the stream sediments located upstream of the Zijinshan copper-gold deposit (ZJS01), the most prominent peak age of detrital zircons is at 1061 Ma, and 14.3% of the detrital
zircons match the ages of regional ore-bearing magmatic rocks. When the stream passes through the Zijinshan copper-gold deposit, the most notable U–Pb peak ages of detrital zircons from the stream sediment (ZJS05) change to 112 Ma, and the corresponding proportion of detrital zircons matching the ages of ore-bearing magmatic rocks is 32.6%. The peak value of 1061 Ma is almost gone, and the information of older ages (>500 Ma) rapidly weakens (Figure 6a,c). Therefore, ~112 Ma is the formation age of the ore-bearing magmatic rocks. The age information of ore-bearing magmatic rocks in the Zijinshan copper-gold deposit quickly masks the age information of detrital zircons in the upstream sediments. When the stream sediment migrates to the downstream area, sample ZJS12 is ~14 km away from sample ZJS05. The main peak age of detrital zircons from the stream sediment (ZJS12) is 437 Ma, followed by 150 Ma; 26% of the detrital zircons have ages consistent with the ore-bearing magmatic rocks, and this proportion decreases by ~7% compared with the stream sediment (ZJS05) near the Zijinshan copper-gold deposit. Another notable feature is that the proportion of old age data becomes lower with increasing distance from the Zijinshan copper-gold deposit. According to the statistics of detrital zircons with U–Pb ages >500 Ma, their proportions are 74.5% and 13.2% in stream sediment samples ZJS01 and ZJS12, respectively. The distance between these two sediment samples is ~21 km.

The same feature was observed for the U–Pb ages of detrital zircons from the stream sediments located downstream of the Luoboling porphyry copper-molybdenum deposit. The detrital zircon U–Pb ages of stream sediments near the deposit mainly represent the ages of ore-bearing magmatic rocks; farther away from the deposit, the proportion of the ages of ore-bearing magmatic rocks becomes lower. Samples LBL02, LBL04, and LBL09 are all collected downstream of the Luoboling porphyry copper-molybdenum deposit, and their distances from the deposit gradually increase. The U–Pb ages of detrital zircons from sample LBL02 mainly peak at 112 Ma and 468 Ma; 66.3% of the detrital zircon ages are coincident with the formation age of the ore-bearing magmatic rocks and the metallogenic age. The U–Pb ages of detrital zircons from sample LBL04 mainly peak at 455 Ma, 145 Ma, and 119 Ma; 19.2% of the detrital zircon ages are in accordance with the formation age of the ore-bearing magmatic rocks and the metallogenic age. The detrital zircon U–Pb ages of sample LBL09 mainly peak at 149 Ma and 444 Ma; 15.4% of the detrital zircons have ages consistent with the formation age of the ore-bearing magmatic rocks and the metallogenic age.

Furthermore, a major peak of ~440 Ma–460 Ma was found in the detrital zircon U–Pb ages of stream sediment samples ZJS12 and LBL04, whereas a secondary age peak of 440 Ma appears in the ages of samples ZJS05, LBL02, and LBL09. The main strata exposed along the lower reach of the river comprise purple-red tuffaceous glutenite, siltstone, and mudstone from the Zhaixia Formation of the Shimaoshan Group (KZ), and purple-red fine clastic rocks from the Shaxian Formation of the Chishi Group (KS) (Figure 1). However, there are no data of detrital zircon U–Pb ages of purple-red clastic rocks in the two formations. These two formations are important geological bodies that provided detrital zircons for stream sediments downstream of the orefield; therefore, it is speculated that the ~440 Ma–460 Ma peak may represent the main ages of detrital zircons in the KZ and KS formations.

The ages of ore-bearing magmatic rocks account for the largest proportion of detrital zircon U–Pb ages in the stream sediments nearest to the orefield. This proportion decreases with increasing distance of stream sediments from the orefield. Therefore, the U–Pb ages of detrital zircons from stream sediments in the study area mainly indicate the zircon U–Pb ages of the nearest geological bodies through which the streams flow.

4.3. Implications of Detrital Zircon Hf Isotope Compositions

According to the scatter plot of zircon εHf(t) values versus U–Pb ages (Figure 7), the Hf isotope compositions of detrital zircons from the stream sediments are very consistent with those of magmatic zircons from the ore-bearing magmatic rocks in the orefield. In both cases, the εHf(t) values change more toward positive values with younger zircon U–Pb age. The contribution of mantle-derived materials of ore-bearing magmatic rocks
gradually increased in the Zijinshan Copper-Gold Orefield [21]. Therefore, these findings also corroborate the inference that the detrital zircons from stream sediments, the U–Pb ages of which are coincident with the magmatic zircon U–Pb ages of ore-bearing magmatic rocks in the orefield, are the products of weathering and denudation of ore-bearing magmatic rocks in the orefield. With increasing distance of migration, the ore-bearing magmatic rocks in the orefield contribute less to detrital zircons in the stream sediments.

In the study area, the U–Pb ages and Hf isotope compositions of detrital zircons from the stream sediments closest to the orefield can also indicate the geochemical information of ore-bearing magmatic rocks in the orefield; thus, ore-bearing magmatic rocks in the orefield provided a large amount of material for the stream sediments. However, these geochemical signals weaken rapidly during the migration of sediments in the stream. This may have been affected by multiple factors, such as lithological resistance to weathering, vegetation coverage, micro-topographic conditions, and hydrodynamic conditions.

5. Conclusions
This study analyzed stream sediments of the Zijinshan Copper-Gold Orefield with regard to element compositions, detrital zircon U–Pb ages, Hf isotope compositions, and element contents of iron oxides. The following conclusions were drawn.

Compared with the ore-bearing magmatic rocks in the orefield, the total amount of REEs in the stream sediments are reduced, accompanied by weakened differentiation of LREEs and HREEs, decreased content of HREEs, and distinct negative Eu anomalies, which were possibly due to plagioclase weathering. The main minerals in stream sediments are quartz, feldspar, mica, pyroxene, iron oxides, and clay minerals. In-situ elements analysis of iron oxides and elemental correlation analysis of stream sediments indicate iron oxides and clay minerals are the main carrier minerals for the migration of ore-forming elements.

As the distance between the location of stream sediments and the orefield increases, the degree of enrichment of ore-forming elements in the stream sediments and the U–Pb age signals of detrital zircons from the ore-bearing magmatic rocks in the orefield, rapidly weaken. The detrital zircon U–Pb age and Hf isotope composition of the stream sediments closest to the orefield indicate the information of ore-bearing magmatic rocks in the orefield. Ore-bearing magmatic rocks in the orefield provided large amounts of materials for the stream sediments. The migration distance of ore-forming elements along the streams was not far in the study area. The U–Pb ages of detrital zircons from stream sediments can only indicate the formation ages of the nearest geological bodies the river flowed through.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/min12010032/s1, Table S1: Detrital Zircon LA-ICP-MS U–Pb data of stream sediments sampled around the Zijinshan Copper-Gold Orefield.

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