Crustal Mercury Addition Into the Giant Jinchuan Ni-Cu Sulfide Deposit, China, and Its Geological Implications

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Abstract  Mercury (Hg) isotopes have shown their power of tracing Hg pollution sources in ecosystems, but their potentials for petrogenetic tracing are yet to be explored. Here we conducted Hg isotope analysis for samples collected from major orebodies of the world-class Jinchuan Ni-Cu sulfide deposit, China. These samples show large variations of $\delta^{199}$Hg ($-2.65$ to $+0.19‰$) and $\Delta^{199}$Hg ($-0.16$ to $+0.19‰$). Some of the $\Delta^{199}$Hg values significantly deviate from current estimates on the primitive mantle ($\Delta^{199}$Hg: $0.0 \pm 0.1‰$, 2SD). The pronounced Hg mass-independent fractionation (Hg-MIF) signals, with significant positive ($>0.1‰$) and negative ($<0.1‰$) $\Delta^{199}$Hg values similar to marine sediments and terrestrial soils, respectively, suggests the addition of crustal materials into the Jinchuan deposit, via crustal assimilation during mantle-derived magma ascending to the crust. These samples show $\delta^{34}$S values ($-1.09$ to $+1.38‰$) identical to that of the primitive mantle ($0.0 \pm 2.0‰$), which may indicate a major sulfur source from the mantle. However, $\delta^{34}$S provides poor constraints on the sulfur source, and the early reported anomalous $\Delta^{34}$S values ($+0.12$ to $+2.67‰$) in the Jinchuan deposit support the involvement of external sulfur from Archean and Proterozoic sedimentary rocks during the formation of this deposit, similar to the case of Hg. This study shows the powerful use of Hg isotopes as a petrogenic tracer and highlights the importance of interaction between mantle-derived magmas and crustal materials on the formation of the Jinchuan Cu-Ni sulfide deposit.

Plain Language Summary  Photochemical reactions result in pronounced Hg mass-independent fractionation (Hg-MIF) signals ($\Delta^{199}$Hg $\neq 0‰$) in marine and terrestrial systems. Recent estimates on $^3$He-rich basalts suggest the lack of Hg-MIF signals in the primitive mantle ($\Delta^{199}$Hg $\approx 0‰$). This study observes non-zero $\Delta^{199}$Hg values ($-0.16$ to $+0.19‰$) in the giant Jinchuan Ni-Cu sulfide deposit, suggesting crustal assimilation during the formation of this deposit. Interaction between mantle-derived magmas and crustal materials could have played an important role in the formation of the Jinchuan Cu-Ni sulfide deposit. Hg isotopes have a great potential in understanding crustal-mantle interactions.

1. Introduction

Mercury (Hg) is a unique metal with multiple oxidation states (0, +1, and +2) and physical states (solid, liquid, and gas) in nature. It has seven natural stable isotopes (196, 198–202, 204 amu), which undergo unique mass-dependent fractionation (MDF, expressed as $\delta^{202}$Hg) and mass-independent fractionation (MIF, typically expressed as $\Delta^{199}$Hg). Hg-MDF ubiquitously is generated during physical, chemical, biological processes, Hg-MIF is formed mainly during photochemical reactions with little influence from other processes (Blum et al., 2014). Past studies have utilized Hg isotopes to constrain anthropogenic Hg pollution sources (Kwon et al., 2020) and large volcanic Hg emissions in geological history (Grasby et al., 2019; Shen et al., 2020, 2022). The development of Hg isotopes for metallogenetic and petrogenetic tracing is progressing. Recent estimates on $^3$He-rich basalts imply the lack of Hg-MIF signals in the primitive mantle ($\Delta^{199}$Hg $= 0 \pm 0.1‰$; Moynier et al., 2021). Photochemical reactions have resulted in positive $\Delta^{199}$Hg values in marine sediments (0 to $+0.4‰$; Kwon et al., 2020; Meng et al., 2019; Yin et al., 2015) and negative $\Delta^{199}$Hg values in terrestrial soils ($-0.6$ to $0‰$; Demers et al., 2013; Kwon et al., 2020; Zheng et al., 2016). Recent studies observed non-zero $\Delta^{199}$Hg values ($-0.4$ to $+0.3‰$) in low-temperature hydrothermal deposits (Au-Hg-Pb-Zn-Sb ores; Deng et al., 2021 and references therein) and magmatic rocks (Moynier et al., 2021; Wang et al., 2021), which evidence the recycling of Hg from terrestrial and marine reservoirs into the crust and mantle.
To date, Hg isotope studies regarding magmatic sulfide deposits remain lacking. Magmatic Ni-Cu sulfide deposits, containing about 56% and 5.1% of the world’s Ni and Cu resources respectively (Mudd & Jowitti, 2014; Peck & Huminicki, 2016; Singer, 2017), are economically significant ore deposits formed by the extreme separation of sulfide melts from mafic-ultramafic magma accomplished by extreme extraction of Ni-Cu from magma into the sulfide melts (Barnes & Lightfoot, 2005). Mantle magma often has low sulfur contents, and incorporation of crustal-derived components (e.g., sulfides) is considered an important trigger for the sulfide saturation of mantle-derived mafic magmas, leading to the formation of economically important Ni-Cu sulfide deposits (Li & Ripley, 2011; Ripley & Li, 2013; Stifter et al., 2016; Wei et al., 2019). An example of this is the Jinchuan deposit, China’s largest and the world’s third-largest magmatic Ni-Cu sulfide deposit in terms of Ni metal reserves (~620 Mt; Song et al., 2009). The Jinchuan deposit was generated by the melting of the enriched subcontinental lithospheric mantle (SCLM) heated by an anomalously hot plume (>1350°C, Li et al., 2005). Trace elements (e.g., Th/Ta and Th/Nb ratios, Song et al., 2006); tch(t) values and Re/Os ratios (Duan et al., 2016; Li & Ripley, 2011); whole-rock Sr-Nd isotopes and zircon Hf isotopes (Duan et al., 2016); carbon, oxygen and noble gas (He, Ar) isotopes (Lehmann et al., 2007; Zhang et al., 2013); all suggest the assimilation of crustal materials into magma to form the Jinchuan deposit.

This study conducted sulfur and Hg isotope analysis of Ni-Cu sulfides collected from four orebodies of the Jinchuan deposit, with the aims of (a) characterizing the Hg isotopic signatures of the Ni-Cu sulfide deposit; (b) understanding the geochemical fate of Hg during magmatic processes; and (c) understanding the addition of the crustal materials during the formation of the Jinchuan deposit.

2. Geological Background

2.1. Regional Geology

The North China Craton (Figure 1a) is adjacent to the Central Asian Orogenic Belt to the north and the Central Orogenic Belt (also named Qinling-Qilianshan Orogenic Belt) to the south. The Jinchuan deposit is located at the northern margin of the Longshoushan Terrane (LT), which situates at the southwestern margin of the North China Craton. As shown in Figure 1b, the northwest-striking LT is bounded by the two regional thrust faults (F1 and F2; C. Li et al., 2004; Porter, 2016). Numerous faults are also developed inside the LT. Proterozoic metamorphic rocks (mainly migmatites, gneisses, schists, and marbles) and granitic intrusions are unconformably overlain by the Cambrian-Silurian strata, which are composed of conglomerate, sandstone, and limestone (Song et al., 2012). Devonian-Jurassic sequences (mainly consisting of carbonatite and clastic rocks) are dispersedly distributed in the LT. Cretaceous and Cenozoic sediments (mainly piedmont, fluvial, and lacustrine clastic rocks) are distributed in the northwest and southeast of the LT (Porter, 2016; Song et al., 2009, 2012). A series of sulfide-mineralized mafic-ultramafic intrusions (e.g., Jinchuan, Zhangbutai, and Qingjingzi) and sulfide-poor mafic-ultramafic intrusions (e.g., Qingshiyao, Xijing, Maocaoquan, and Dongwan) are scattered found in the LT (Chen et al., 2013; Porter, 2016).

2.2. Ore Deposit Geology

The NW-SE elongate Jinchuan ultramafic intrusion (Figure 2a) steeply dips to the southwest with angles of 50–80°. Its wall rocks consist of Paleoproterozoic high-grade metamorphic migmatites, gneisses, marbles, schist, and plagioclase amphibolite (Song et al., 2006). Granitic dikes cut the metamorphic rocks and are cut by the Jinchuan intrusion (Lehmann et al., 2007). Complex fault systems, mainly including the NW-SE striking regional thrust faults (F1), the NEE-SWW striking left-lateral strike-slip faults (F6, F16, F23), the NNW-SSE striking right-lateral strike-slip faults (e.g., F23), are developed in the Jinchuan area, F6, F16, and F23 dip steeply to the southeast with angles of >70°and divide the Jinchuan intrusion into Segments III, I, II, and IV from west to east (Figure 2a; Song et al., 2006).

The Jinchuan intrusion has been dated as Neoproterozoic with the age of ~0.83 Ga (Li et al., 2005; Zhang et al., 2010). It has been divided into four segments (namely III, I, II, and IV from the west to the east) and they belong to two intrusions (namely the West and the East; Figure 2b). Segments III and I correspond to the Western intrusion, and Segments II and IV correspond to the Eastern intrusion. Three large orebodies, named No. 24, No. 1, No. 2, occur in Segments I and II (Figure 2b). A new orebody (No. 3) was recently found in Segment III.
The Jinchuan ultramafic intrusion essentially comprises lherzolite (∼80 vol.%), olivine pyroxenite (<10 vol.%), dunite, plagioclase peridotite, oxidized ore, and dolerite dykes (Naldrett, 2004). Rock-forming minerals are olivine, orthopyroxene, chromian spinel (chromite) and interstitial phase orthopyroxene, clinopyroxene, plagioclase,
phlogopite, base-metal sulfides (Figures 3a–3c) and base-metal sulfides are predominantly pyrrhotite, pentlandite, and chalcopyrite (Figures 3d–3f), which constitute 5 wt.% of the intrusion (De Waal et al., 2004). Pyrrhotite is the dominant sulfide mineral in the ore. It mainly occurs as anhedral or subhedral crystals. Pentlandite is closely associated with pyrrhotite and commonly occurs as subhedral to euhedral crystals, enclosed by anhedral pyrrhotite. Chalcopyrite is predominantly found as anhedral assemblages, disseminated within other sulfides, or as very fine veinlets, which crosscut olivine or pyroxene grains, or in small separate copper rich pods. Chalcopyrite is also seen to cut pyrrhotite and pentlandite. In some massive ore, fragments of pyrrhotite and pentlandite assemblages are enclosed within a chalcopyrite dominant groundmass. Very fine sulfide droplets (comprising pyrrhotite, pentlandite and chalcopyrite) are common in cumulus olivine and chromite crystals. Four styles of mineralization are evident in the Jinchuan complex, in decreasing order of importance, net-textured, disseminated, massive and mottled ore.

Figure 2. Map showing (a) the geology of the Jinchuan deposit, and (b) the distribution of orebodies in the cross-section O-O’ (after Song et al., 2012).
No. 1 orebody in Segment II contains ∼50% of the Ni and Cu reserves of the Jinchuan deposit (Song et al., 2012). It is lens-shaped (1,500 m long, up to 120 m thick) and extends from 200 to >1,100 m below the surface. It comprises a core of net-textured sulfide dunite with a thin margin of disseminated sulfide dunite, which is enveloped by medium-grained lherzolite (Figures 3e and 3f); No. 2 orebody in Segment II is 1,300 m long and up to 118 m thick and occurs near the base of Segment II. It is composed of sulfide-bearing dunites overlain by medium-grained lherzolite; No. 24 orebody is ∼1,300 m long and ∼20–70 m thick and situated at the base of Segment I. It comprises net-textured sulfides and disseminated sulfides from the base to the top and overlain by coarse-grained lherzolites (Chen et al., 2013; Song et al., 2012); No. 3 orebody is hosted in Segment III and dips to the southwest with thicknesses of 20–150 m. It is composed of olivine-sulfide cumulates with net-textured sulfide overlain by lherzolite with disseminated sulfide.

Figure 3. Photographs showing (a) Dunite comprises serpentinized pseudomorphs of coarse-grained olivine and interstitial altered clinopyroxene and sulfides (under polarized light); (b) Fine-grained olivine crystals enclosed in large oikocrysts of clinopyroxene in lherzolite and the clinopyroxene has been altered to chlorite (under crossed polarizer); (c) Lower unit diopside skarn consists of diopside with pseudomorph of pyroxene and minor olivine; (d) Sulfides in massive ore (under reflected polarizer); (e) Sulfides in net-texture ore (under reflected polarizer); and (f) Sulfides in disseminated ore (under reflected polarizer). Photos A–C are from Song et al. (2012). Ol, olivine; Sul, sulfides; Cpx, clinopyroxene; Cal, calcite; Diop, diopside; Sph, sphene; Po, pyrrhotite; Pn, Pentlandite; Ccp, Chalcopyrite; Mt, Magnetite.
Although the Jinchuan intrusion has experienced varying degrees of post-magmatic hydrothermal alteration and near-surface oxidation, it has been estimated that less than 1% of the metals and sulfur were lost during the alteration (Lehmann et al., 2007; Liu et al., 2021; Ripley et al., 2005; Zhang et al., 2013).

3. Materials and Methods

3.1. Sample Collection and Preparation

Twenty-nine unweathered ore samples were collected from the No. 24 (n = 7), No. 1 (n = 12), No. 2 (n = 4) orebodies, and No. 3 orebody (n = 6). These samples are net-textured, disseminated, massive and mottled ores (Table 1), representing the major ore types of the Jinchuan deposit. All samples were cleaned with 18.2 MΩ·cm water, air-dried, powdered, and homogenized, prior to chemical analysis.

3.2. Total Sulfur Content and Sulfur Isotopic Composition Analysis

Samples were oxidized in a high-temperature furnace to transform sulfur into SO$_2$ gas and the total sulfur content ($S_{total}$) was calculated according to the content of collected SO$_2$ at the ALS Minerals in Guangzhou, with an uncertainty of <0.01%. Sulfur isotope analysis was performed by MAT253 gas stable isotope ratio mass spectrometer and Flash EA 2000 elemental analyzer coupled with Conflo IV continuous flow device at the Institute of Geochemistry, Chinese Academy of Sciences (IGCAS), following a previous method (Yang et al., 2021). Sulfur isotopic composition is reported as follows (Canfield, 2001): 

$$\delta^{34}S = \left( \frac{\text{^{34}S/^{32}S}_{\text{sample}}}{\text{^{34}S/^{32}S}_{\text{V-CDT}}} - 1 \right) \times 1000$$

Measurement of standard reference materials (SRMs) IAEA-S-1 ($\delta^{34}S_{\text{CDT}}$: −0.3‰) and IAEA-S-2 ($\delta^{34}S_{\text{CDT}}$: 22.62‰) and IAEA-S-3 ($\delta^{34}S_{\text{CDT}}$: −32.49‰) yielded comparable results to certified values, with an uncertainty of <0.2‰ (2SD).

3.3. Total Hg Content and Hg Isotopic Composition Analysis

Total Hg ($Hg_{total}$) concentrations and Hg isotope compositions were measured at the IGCAS. Hg concentrations were directly determined by DMA-80 Mercury Analyzer, yielding Hg recoveries of 90%–110% (n = 6) for SRM GSS-4 (soil) and uncertainty of <10% for sample duplicates. Based on the measured Hg concentrations, at least 10 ng of Hg was preconcentrated by a double-stage tube furnace coupled with 5 mL of 40% anti aqua regia (HNO$_3$/HCl = 2/1, v/v; Zerkle et al., 2020). Standard reference material (GSS-4, soil) was prepared in the same way as the samples. All the solutions were diluted to 0.5 ng mL$^{-1}$ Hg in 10%–20% (v/v) acids using 18.2 MΩ·cm water, prior to analysis by Neptune Plus multi-collector inductively coupled plasma mass spectrometry, following a previous method (Yin et al., 2016). Hg-MDF is expressed in $\delta^{202}$Hg notation in units of permil (‰) referenced to the NIST-3133 Hg standard (analyzed before and after each sample): 

$$\delta^{202}\text{Hg}(‰) = \left[ \left( \frac{^{202}\text{Hg}}{^{198}\text{Hg}}_{\text{sample}} \right) / \left( \frac{^{202}\text{Hg}}{^{198}\text{Hg}}_{\text{standard}} \right) - 1 \right] \times 1000$$

Hg-MIF is reported in Δ notation, which describes the difference between the measured $\delta^{xxx}$Hg and the theoretically predicted $\delta^{xxx}$Hg value, in units of permil (‰): 

$$\Delta^{xxx}\text{Hg} \approx \delta^{xxx}\text{Hg} - \delta^{202}\text{Hg} \times \beta$$

$\beta$ is equal to 0.2520 for $^{199}$Hg, 0.5024 for $^{200}$Hg, and 0.7520 for $^{201}$Hg, respectively. NIST-3177 secondary standard solutions were measured every 10 samples. The overall average and uncertainty of NIST-3177 ($\delta^{202}$Hg: −0.54 ± 0.10‰; $\Delta^{199}$Hg: −0.01 ± 0.05‰; $\Delta^{200}$Hg: 0.01 ± 0.06‰; $\Delta^{201}$Hg: −0.02 ± 0.06‰; 2SD, n = 3) and GSS-4 ($\delta^{202}$Hg: −1.62 ± 0.11‰; $\Delta^{199}$Hg: −0.46 ± 0.05‰; $\Delta^{200}$Hg: 0.04 ± 0.06‰; $\Delta^{201}$Hg: −0.42 ± 0.05‰; 2SD, n = 3) agree well with previous results (Bergquist & Blum, 2007; Deng et al., 2021; Wang et al., 2021). The largest values of standard deviation (2SD) for NIST-3177 and GSS-4 were used to reflect analytical uncertainties.
4. Results

4.1. Mercury and Sulfur Concentrations

Analytical results are given in Table 1 and shown in Figure 4. The samples show an overall variation of 2.82–130 ppb for \( \text{Hg}_{\text{tot}} \). Specifically, No. 2 and No. 3 orebodies show \( \text{Hg}_{\text{tot}} \) concentrations of <10 ppb, whereas No. 1 and No. 24 orebodies mostly show relatively higher \( \text{Hg}_{\text{tot}} \) concentrations (>10 ppb), especially the net-textured ores from No. 1 orebody showing the highest \( \text{Hg}_{\text{tot}} \) concentrations (76–130 ppb).
The samples show a variation of 5.5–31.4 wt.% for $S_{\text{tot}}$. Most of the samples show consistent $S_{\text{tot}}$ concentrations of 5–15 wt.%, except the massive ores in No. 2 and No. 24 orebodies showing much higher $S_{\text{tot}}$ concentrations (24.7%–31.4%). No correlation can be observed between $Hg_{\text{tot}}$ and $S_{\text{tot}}$ in the investigated samples ($p > 0.05$, t-test, Figure 5).

### Figure 4
Variation of total mercury concentration, total sulfur concentration, $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$, and $\delta^{34}\text{S}$ in ore samples collected from four orebodies in the Jinchuan deposit.

### Figure 5
Crossplot between $Hg_{\text{tot}}$ and $S_{\text{tot}}$ in the Jinchuan deposit.

#### Figure 5
$y=(-0.06 \pm 0.04)x+(13.3 \pm 1.8)$
$R^2=0.04$, $p>0.05$, T-test

4.2. Sulfur and Mercury Isotope Compositions

The samples show narrow $\delta^{34}\text{S}$ values of $-1.09$ to $+1.38\%e$, consistent with mantle source (0.0 ± 2.0\%, Ripley et al., 2005). However, they show large variations of $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ ($-2.65$ to $+0.19\%e$ and $-0.16$ to $+0.19\%e$), which are 25 and 7 times the analytical uncertainty ($\delta^{202}\text{Hg}$: ±0.11\%; $\Delta^{199}\text{Hg}$: ±0.05\%). As shown in Figure 6a, 21 samples show $\Delta^{199}\text{Hg}$ values identical to the primitive mantle ($\Delta^{199}\text{Hg}$: 0.0 ± 0.1\%, 2SD), whereas eight samples show $\Delta^{199}\text{Hg}$ values deviated from the primitive mantle. Positive $\Delta^{199}\text{Hg}$ (+0.13 to +0.19\%e) from No. 24 and 2 orebodies and negative $\Delta^{199}\text{Hg}$ (−0.16 to −0.13\%) from No. 3 and 1 orebodies, indicating pronounced Hg-MIF signals. A positive correlation between $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$, with $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio of 1.06, can be observed in these samples, consistent with that observed during aqueous Hg(II) photoreduction ($\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg} = 1.02$; Bergquist & Blum, 2007).
5. Discussion

5.1. Hg Variability in the Jinchuan Deposit

The Jinchuan sulfides show relatively higher $Hg_{tot}$ concentrations than the primitive mantle (0.4–0.6 ppb, Canil et al., 2015), which may be due to their high sulfide contents due to the chalcophile nature of Hg. However, the lack of correlation between $Hg_{tot}$ and $S_{tot}$ ($p > 0.05$, t-test) and between $\Delta^{199}Hg$ and $S_{tot}$ ($p > 0.05$, t-test) in the studied samples suggest the decoupling of Hg and S during magmatic processes. Due to its high volatility, Hg tends to escape from the high-temperature magmatic systems via magmatic degassing (Sherman et al., 2009).

Figure 6. (a) $\Delta^{199}Hg$ versus $\delta^{202}Hg$ and (b) $\Delta^{199}Hg$ versus $\Delta^{201}Hg$ for Ni-Cu sulfide deposit samples from Jinchuan. The blue area represents positive $\Delta^{199}Hg$ values in marine sediments (Meng et al., 2019; Yin et al., 2015, 2017); the gray area represents negative $\Delta^{199}Hg$ values in soil (Demers et al., 2013; Wang et al., 2019; Yuan et al., 2020; Zheng et al., 2016); the brick-red area represents primitive mantle (Moynier et al., 2021). Black dolts represent published data on hydrothermal Au-Hg-Pb-Zn-Sb ores (Cooke et al., 2013; Deng et al., 2021; Fu et al., 2020; Xu et al., 2018; Yin et al., 2019).
The lack of $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ ($p > 0.05$, $t$-test) may also be caused by the magmatic degassing of Hg, which cause the loss of Hg in the magmatic system. The relatively higher Hg$_{tot}$ concentration in the Jinchuan sulfide orebody samples, compared to that in the primitive mantle, may also suggest the addition of crustal Hg into the Jinchuan deposit, as discussed below.

5.2. Hg Isotopes Trace Hg Sources in the Jinchuan Deposit

We here use Hg-MIF signals as a tracer of Hg sources in the Jinchuan deposit. Magmatic and postmagmatic hydrothermal processes do not trigger Hg-MIF (Moynier et al., 2021; Sherman et al., 2009). Hg-MIF is mainly generated during photochemical processes in the surficial environment (Blum et al., 2014). Aqueous Hg(II) photoreduction produces negative $\Delta^{199}\text{Hg}$ values in the product Hg (0) and positive $\Delta^{199}\text{Hg}$ values in the residual Hg (II), with a $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio of 1.02 in both Hg phases (Bergquist & Blum, 2007). The $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio of 1.06 in the Jinchuan samples highly agrees with that observed during aqueous Hg(II) photoreduction. As shown in Figure 6, primitive mantle show near-zero $\Delta^{199}\text{Hg}$ values ($0.00 \pm 0.10\%e$; Moynier et al., 2021), whereas Hg(II) photoreduction processes on Earth’s surface induce negative $\Delta^{199}\text{Hg}$ values (−0.6 to 0%e) in terrestrial soil and positive $\Delta^{199}\text{Hg}$ values (0 to +0.4%e) in marine sediments (Blum et al., 2014 and references therein). In this study, 72% (21/29) of samples show near-zero $\Delta^{199}\text{Hg}$ identical to that estimated for the primitive mantle (Figure 6a), which may suggest that a substantial amount of Hg in the Jinchuan deposit is sourced from the primitive mantle. The near-zero $\Delta^{199}\text{Hg}$ values could also be explained by the mixing of terrestrial and marine materials containing Hg with negative and positive $\Delta^{199}\text{Hg}$ values, respectively. We discuss this possibility bellow.

The significant positive $\Delta^{199}\text{Hg}$ (+0.13 to +0.19%e) from No. 24 and 2 orebodies and significant negative $\Delta^{199}\text{Hg}$ (−0.16 to −0.13%e) from No. 3 and 1 orebodies are similar to previous results on marine sediments and terrestrial soil, respectively (Figure 6a), indicating the involvement of Hg from crustal materials. Significant Hg-MIF signals with $\Delta^{199}\text{Hg}$ ranging from −0.4 to +0.3%e were recently observed in hydrothermal deposits (Deng et al., 2021; Fu et al., 2020; Xu et al., 2018; Yin et al., 2019) and magmatic rocks (Moynier et al., 2021; Wang et al., 2021), which evidence the involvement of crustal Hg during hydrothermal and magmatic processes. The observed non-zero $\Delta^{199}\text{Hg}$ may be caused by low temperature water-rock alteration and near-surface oxidation, however, the low Hg concentration in natural waters (a few ng/L, Chen et al., 2012) preclude this possibility. Although the positive $\Delta^{199}\text{Hg}$ values of natural waters can explain some of our samples showing positive $\Delta^{199}\text{Hg}$ values (Chen et al., 2012), they cannot explain those showing negative $\Delta^{199}\text{Hg}$ values. Possible processes resulting in the significant Hg-MIF signals in the Jinchuan samples include (a) recycling of sedimentary Hg into the mantle, or (b) the assimilation of sedimentary rocks during ascending of the mantle-derived magmas in the crust. Melting of the enriched SCLM, heated by an anomalously hot plume (>1350°C, X. H. Li et al., 2005), was responsible for the generation of the Jinchuan deposit. Recycling of sedimentary Hg into the mantle produce magma with pronounced Hg-MIF signals (Moynier et al., 2021; Wang et al., 2021; Yin et al., 2022), which can not explain the near-zero $\Delta^{199}\text{Hg}$ in the early mentioned twenty-one samples. The pronounced Hg-MIF signals (with $\Delta^{199}\text{Hg}$ either $\leq$−0.1%e or $>$$+0.1%e$) therefore should be explained by addition of melted sedimentary rocks via mantle magma ascending, as illustrated in Figure 7. Marine and terrestrial sediments show positive and negative $\Delta^{199}\text{Hg}$ values respectively (Blum et al., 2014 and references therein). Metamorphic marine sedimentary rocks (e.g., Paleoproterozoic marbles) and terrestrial sedimentary rocks (e.g., Paleoproterozoic argillaceous schists) are distributed in Jinchuan (Porter, 2016; Zhai & Santosh, 2011). Although the Hg isotopic composition of these rocks was not measured, as they are highly metamorphized and may not record the original Hg isotope signals of the sedimentary rocks, we argue that these rocks, prior to metamorphism, could be an important source of Hg-MIF in the Jinchuan samples. Given sedimentary rocks commonly have large Hg-MIF signals and contain Hg concentrations (10$^2$–10$^3$ ppb) 1 to 2 magnitudes higher than the primitive mantle (0.6ppb; Canil et al., 2015), we infer that even a small amount of sediments can leave Hg-MIF signals in the Jinchuan samples, without significantly changing the petrology (e.g., SiO$_2$ contents) of the Jinchuan intrusion (Figure 7). We hypothesized that the negative or positive $\Delta^{199}\text{Hg}$ values observed in different orebodies may be related to the types of sedimentary rocks (terrestrial or marine) melted by the upwelling mantle magma. In the future, a thorough investigation on the contacted wall rocks for the Jinchuan deposit are needed to verify the major sedimentary strata involving in the Jinchuan deposit metallogensis.
5.3. Crustal Assimilation as a Trigger of the Metallogenism of the Jinchuan Deposit

A modeling study demonstrated that primary magma (derived from the enriched SCLM) for the Jinchuan deposit only experienced ~18% fractional crystallization, but at least ~33% fractional crystallization was required for parental magma to become sulfur-saturated if no external sulfur was added (Duan et al., 2016). External crustal sulfur is highly expected to inject into mafic magma to promote sulfur saturation and then segregate sulfide melts (Li & Ripley, 2011; Ripley & Li, 2013; Stifter et al., 2016; Wei et al., 2019). A lack of correlation between $\Delta^{199}$Hg and $\delta^{34}$S ($p > 0.05$, $t$-test) is also observed in our samples, which may suggest the decoupling of Hg and S during magmatic processes, however, is more possibly explained by different sources of Hg and S in the Jinchuan deposit. In this study, the non-zero $\Delta^{199}$Hg values suggest the involvement of crustal materials during the Jinchuan deposit metallogenesis, whereas the $\delta^{34}$S values of our samples (−1.09 to +1.38‰) fall into range of primitive mantle, which may indicate a major sulfur source from the mantle. However, it must be noted that $\delta^{34}$S may not be an ideal source tracer of sulfur, given the overlapped $\delta^{34}$S ranges for different sulfur sources and the ubiquitous sulfur isotope fractionation during a variety of geochemical processes (Farquhar et al., 2010; Johnston, 2011). In a previous study, based on the anomalous $\Delta^{33}$S values (+0.12 to +2.67‰), Duan et al. (2016) concluded the involvement of external sulfur from Archean and Proterozoic sedimentary rocks during the formation of the Jinchuan deposit.

Mercury isotope results of this study agree well with previous studies that provide strong evidence of crustal materials involved in the Jinchuan deposit. For instance, the Jinchuan intrusion and sulfide ores have crustal-like Th/Ta and Th/Nb ratios of 2.5–6.5 and 0.15–0.6, respectively, distinctly higher than those of the primitive mantle (Th/Ta = 2.3, Th/Nb = 0.15; Song et al., 2006), indicating the addition of crustal materials into the mantle magmas at varying degrees. Positive $\gamma_{Os}(t)$ values (20–150) and high ratios for Re/Os (20–79) and negative $\varepsilon_{Nd}(t)$ values (−6 to −12) in the Jinchuan intrusion and sulfide ores (Duan et al., 2016; Li & Ripley, 2011; Li et al., 2005), also suggest assimilation of crustal materials since the crust rocks usually have distinctively high $\gamma_{Os}$ and Re/Os but negative $\varepsilon_{Nd}(t)$ values (Saal et al., 1998). Whole-rock Sr-Nd isotopes ($^{87}$Sr/$^{86}$Sr: 0.7077–0.7093) and zircon $\varepsilon_{Hf}(t)$ (−4 to −7) values indicated up to 20% of crustal contamination in the Jinchuan magma (Duan et al., 2016). All above evidence of crustal assimilation provide insights into the dynamics for the formation of the Jinchuan deposit, as shown in Figure 7. During the emplacement of mafic melts, crustal materials are melted, transported and equilibrated with the silicate magma without being fully assimilated during the emplacement of
mafic melts (Yao et al., 2019). During these processes, sulfur diffusion runs slower than metal diffusion, promoting metal enrichment in the exo-melt (Yao et al., 2019), providing metal basis for the Jinchuan deposit. Crustal assimilation may have also provided substantial amount of crustal sulfur to trigger the segregation of Cu-Ni sulfides, as supported by the observation of anomalous Δ34S values (+0.12 to +2.67‰) in the Jinchuan deposit (Duan et al., 2016).

6. Conclusion

This study investigates Hg isotopes in the world-class magmatic Ni-Cu sulfide deposit and observes large variations of −2.65 to +0.19‰ for Δ202Hg and −0.16 to +0.19‰ for Δ199Hg. The non-zero Δ199Hg values in the Jinchuan samples deviate from that of mantle-derived materials, providing clear constraints on the involvement of crustal Hg into the Jinchuan deposit. This study gives a new piece of evidence showing strong crust-mantle interactions via crustal assimilation during the formation of the Jinchuan deposit, and shows the potential of using Hg isotopes as a petrogenetic tracer in the future.

Data Availability Statement

Data set of this research can be found in a public domain repository (https://figshare.com/articles/dataset/Data_set_for_Crustal_mercury_addition_into_the_giant_Jinchuan_Ni-Cu_sulfide_deposit_China_and_its_geological_implications_/19358717).

Acknowledgments

This work was supported by the Natural Science Foundation of China (41873047).

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