

# Copper isotopic compositions of the Zijinshan high-sulfidation epithermal Cu–Au deposit, South China: Implications for deposit origin



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## ABSTRACT

The Zijinshan high-sulfidation epithermal Cu–Au deposit is located in the Zijinshan ore field of South China, comprising porphyry–epithermal Cu–Au–Mo–Ag ore systems. The Cu ore body is more than 1000 m thick and is characterized by an assemblage of digenite–covellite–enargite–alunite. Digenite is the dominant Cu-bearing mineral, which makes this deposit unique, although the mechanisms of digenite formation remain controversial. To elucidate the genesis of digenite, this paper presents the Cu isotopic compositions of Cu-sulfides in the Zijinshan high-sulfidation Cu–Au deposit. The Cu isotopic values (<sup>65</sup>Cu relative to NIST 976) of all samples range from  $-2.97‰$  to  $+0.34‰$ , and most values fall in a narrow range from  $-0.49‰$  to  $+0.34‰$ , which is similar to the Cu isotopic signature of typical porphyry systems. Copper isotope ratios of each mineral decrease with increasing depth, a trend that is also typical of porphyry deposits. The variation tendency of  $\delta^{65}\text{Cu}$  values between sulfides is consistent with the sequence of mineral formation. These observations suggest that the Cu-sulfides in the Zijinshan Cu–Au deposit have a hypogene origin.

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## 1. Introduction

Copper (Cu) is extensively involved in diagenesis, mineralization, and hydrothermal activity, and analyses of Cu isotopic compositions can provide insights into these important geological processes. Initial advances in Cu isotope analyses were made by Walker et al. (1958) and Shields et al. (1965), using thermal ionization mass spectrometry (TIMS). However, it was not until the development of MC–ICP–MS that high-precision measurements of Cu isotopes became possible (Maréchal et al., 1999). Based on improved analytical techniques, copper isotopes have been widely applied as a tool for tracing the source of Cu, inferring fluid pathways and metal precipitation mechanisms, and aiding mineral exploration (Graham et al., 2004; Markl et al., 2006; Mathur et al., 2009, 2012, 2013; Mathur and Schlitt, 2010; Braxton and Mathur, 2011; Li et al., 2010; Duan et al., 2016). Especially, an important improvement in the study of porphyry systems is the use of Cu isotopes to distinguish between the leach cap, and hypogene and supergene zones (Mathur et al.,

2009, 2012, 2013; Braxton and Mathur, 2011). For instance, minerals in the leach cap are depleted in <sup>65</sup>Cu and have light Cu isotopic compositions, whereas minerals in the supergene enrichment zone are relatively enriched in <sup>65</sup>Cu, and hypogene minerals have  $\delta^{65}\text{Cu}$  values that are close to zero (Mathur et al., 2009, 2012, 2013; Braxton and Mathur, 2011).

The Zijinshan Cu–Au deposit in South China is a high-sulfidation epithermal deposit in which secondary Au enrichment developed in the upper oxidized zone above a digenite-dominated Cu ore body that is more than 1000 m thick. The origin of digenite in this deposit is debated. Some researchers interpret the formation of digenite to be primary based on the study of mineralogy, ore structure and the huge thickness of the copper ore body (Qiu et al., 2010; Lin, 2012), whereas others consider it to have resulted from secondary enrichment because usually digenite–covellite–enargite–alunite mineral assemblage belongs to the oxidation zone of secondary enrichment (Ruan et al., 2009). To resolve this question, we analyzed the Cu isotopic compositions of 18 mineral separates from the open pit of the Zijinshan Cu–Au deposit. The results show that the majority of the Cu-bearing minerals (including digenite) are hypogene origin.

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## 2. Geological background

### 2.1. Regional geology

The South China Block comprises the Yangtze Block in the northwest and the Cathaysian Block or South China Caledonian fold belt in the southeast (Fig. 1). Farther north, the Qingling–Dabie orogenic belt lies between the Yangtze Block and the North China Block. The Yangtze Block is bounded to the west by the Tibetan Plateau (Fig. 1).

The Zijinshan ore field is located in the interior of the Cathaysian Block, at the intersection of the Xuanhe Anticlinorium and the Shanghang–Yunxiao Fault (Fig. 1), and at the northeastern margin of the Cretaceous Shanghang Volcanic Basin, approximately 17 km north of Shanghang city, Fujian Province, southeastern China (Fig. 1; Wang, 1995; Yu et al., 1995; Gao and Huang, 1998; Zhang et al., 2003, 2005; Liu and Hua, 2005; Huang, 2008; Wang et al., 2009). The ore field hosts the Zijinshan high-sulfidation epithermal deposit (So et al., 1998; Zhang et al., 2003), the Luoboling porphyry Cu–Mo deposit (Xue and Ruan, 2008; Wang et al., 2009; Zhong et al., 2011; Xue, 2013), the Ermiaogou high-sulfidation epithermal Cu deposit (Li et al., 2013), the Yueyang low-sulfidation epithermal Ag–Cu–Pb–Zn deposit (Lin, 2006; Wang et al., 2009), and the transition-type (from porphyry to high-sulfidation epithermal) Wuziqilong mesothermal Cu deposit (Zhang et al., 1996; Chen et al., 2011; Ruan et al., 2009) and the Longjiangting Cu deposit (Li et al., 2011). As of 2008, the proven reserves of the Zijinshan ore field were 323 t Au (~0.5 g/t), 2.36 Mt Cu (~0.45 wt%), 1554 t Ag (20–156 g/t), 4647 t Mo (0.032 wt%),

6279 t Pb (3.47 wt%), 1747 t Zn (3.75 wt%) and 0.1 Mt Mn (32.5 wt%) (Zhong et al., 2014). With proven resources of 305 t Au and 1.9 Mt Cu (Wang et al., 2009), the Zijinshan high-sulfidation epithermal Cu–Au deposit is the largest deposit in the Zijinshan ore field.

Exposed rocks in the region include the Neoproterozoic Louziba Group, Late Paleozoic clastic sedimentary rocks, Early Cretaceous volcanic rocks, and Quaternary alluvial sediments (Fig. 2). Northeast- and northwest-striking faults provided the main structural controls for the emplacement of magmatic rocks and the formation of Cu±Au ore deposits. The northwest-striking Shanghang–Yunxiao Fault extends downward for more than 40 km into the deep crust (Wang et al., 1993) and has a strike length exceeding 150 km. The fault is located in Fujian Province, at the southwestern margin of the Zijinshan district, where the geology is dominated by Cretaceous subaerial volcanic and sedimentary rocks (So et al., 1998).

Middle to Late Jurassic and Early Cretaceous magmatic rocks are common in the Zijinshan ore field (Fig. 2), and include the Middle to Late Jurassic Zijinshan Complex and the Caixi pluton. The Zijinshan Complex, including the Jingmei, Wulongzi, and Jinlongqiao plutons, intruded the southwestern part of the ore field. The Caixi monzonitic granite intruded the northeastern part of the Zijinshan Complex. The mineralization is genetically related to the Early Cretaceous granodiorite and volcanic rocks, which are interpreted to have formed from the mixing of mantle-derived magma and crustal rocks. These Early Cretaceous magmatic rocks include granodiorite, granodiorite porphyry, dacite porphyry, and the volcanic rocks of the Shimaoshan Group. The Sifang granodiorite intruded

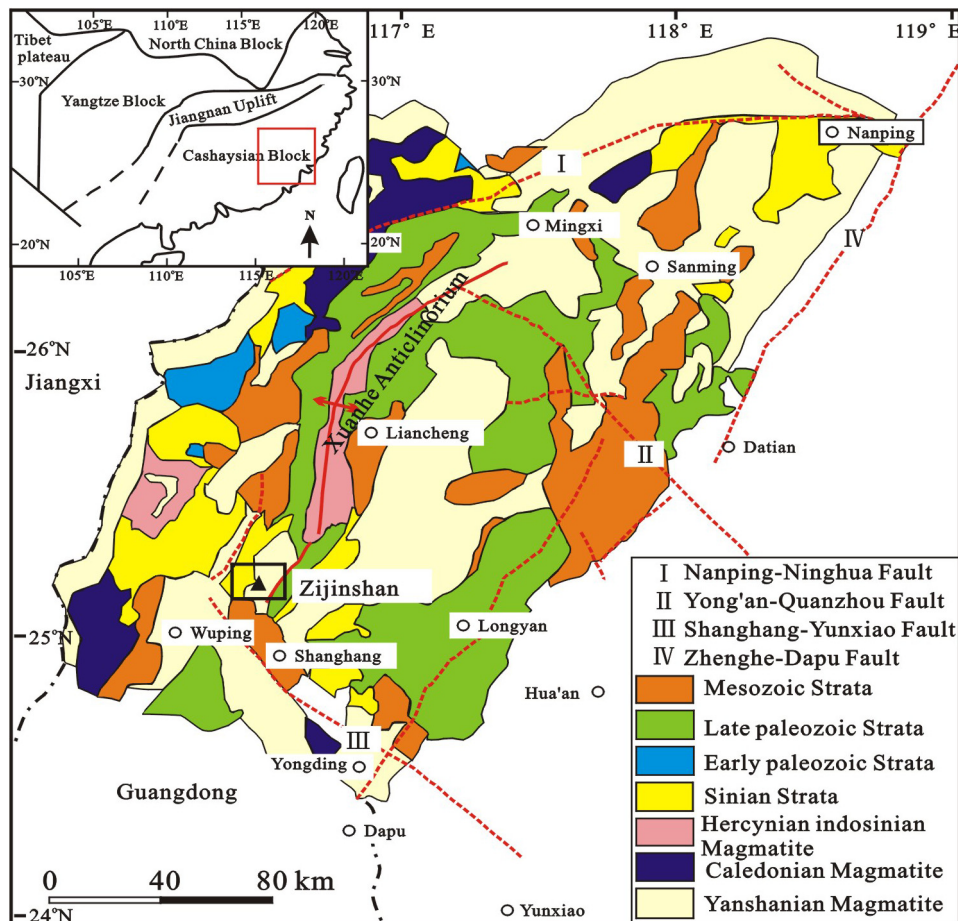


Fig. 1. Regional geological map of the Zijinshan ore field, South China (modified from Hu et al., 2012; Zhong et al., 2011).

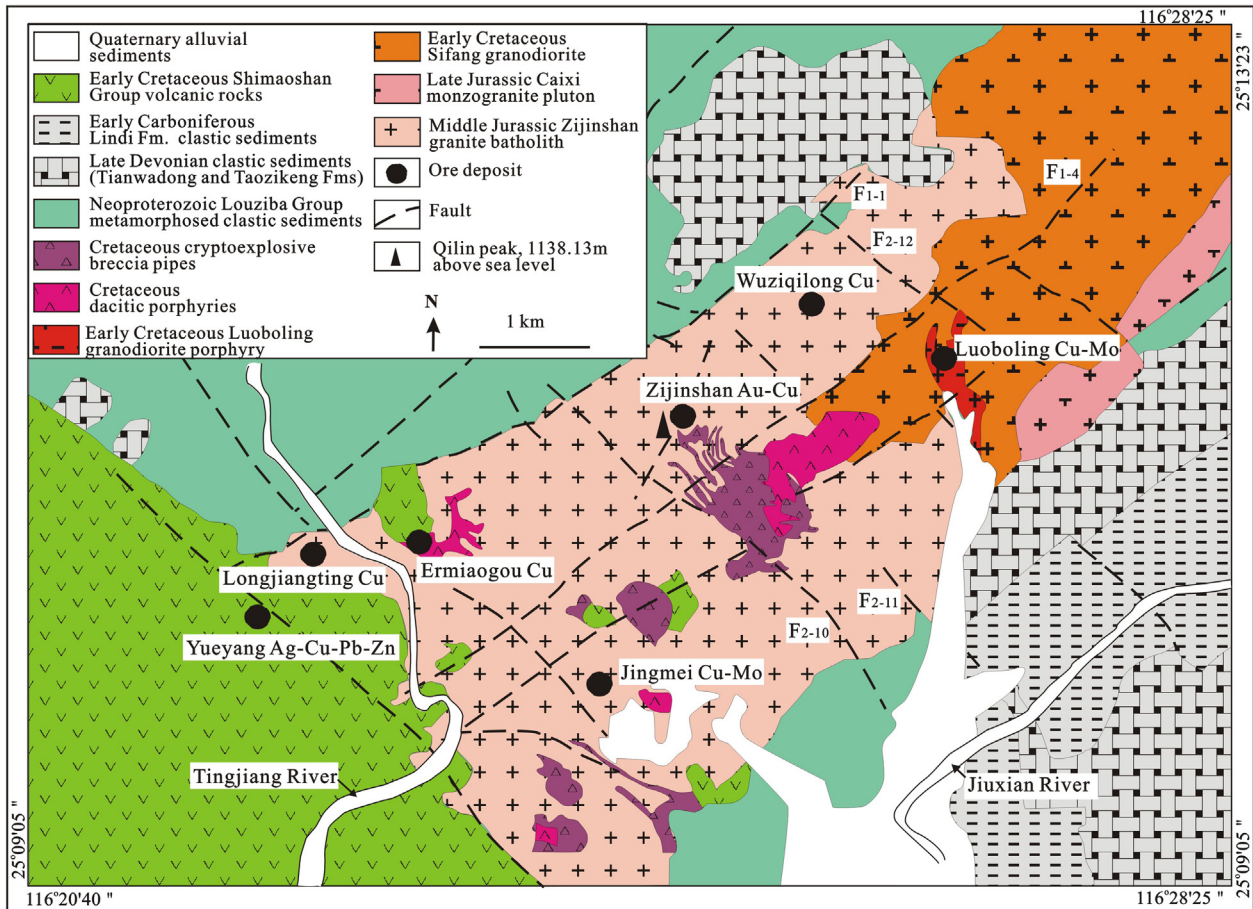


Fig. 2. Geological map of the Zijinshan ore field (modified after Zhong et al., 2014).

the northeastern part of the Zijinshan Complex and the southwestern part of the Caixi monzonitic granite, and yields a zircon U–Pb age of  $104.8 \pm 1.7$  Ma (Hu et al., 2012). The Luoboling granodiorite porphyry intrudes the Sifang granodiorite and yields a zircon U–Pb age of  $103 \pm 0.2$  Ma (Li and Jiang, 2015). Dacite porphyry occurs in the volcanic caldera of the Zijinshan ore field and yields zircon U–Pb ages of  $105 \pm 0.7$  Ma and  $105 \pm 2.2$  Ma (Hu et al., 2012). Early to middle Cretaceous volcanism resulted in the deposition of the Shimaoshan Group, which consists of dacitic to rhyolitic volcanic rocks that unconformably overlie Jurassic granite and the Louziba Group (So et al., 1998). The Shimaoshan Group yields Rb–Sr isochron ages of  $94 \pm 7.7$  Ma and  $125 \pm 9.8$  Ma (Zhang et al., 2001). The dacite porphyry hosts Cu–Au mineralization in the Zijinshan deposit, whereas the granodiorite porphyry hosts Cu–Mo mineralization in the Luoboling deposit. The fine- to medium-grained Wulongzi granite and Early Cretaceous Sifang granodiorite host Cu ore in the Wuziqilong deposit, although the mineralization is related to the Cretaceous dacite porphyry (Zhang et al., 1996). The Early Cretaceous volcanic rocks host Ag–Au–Cu mineralization in the Yueyang deposit (Zhang et al., 2001).

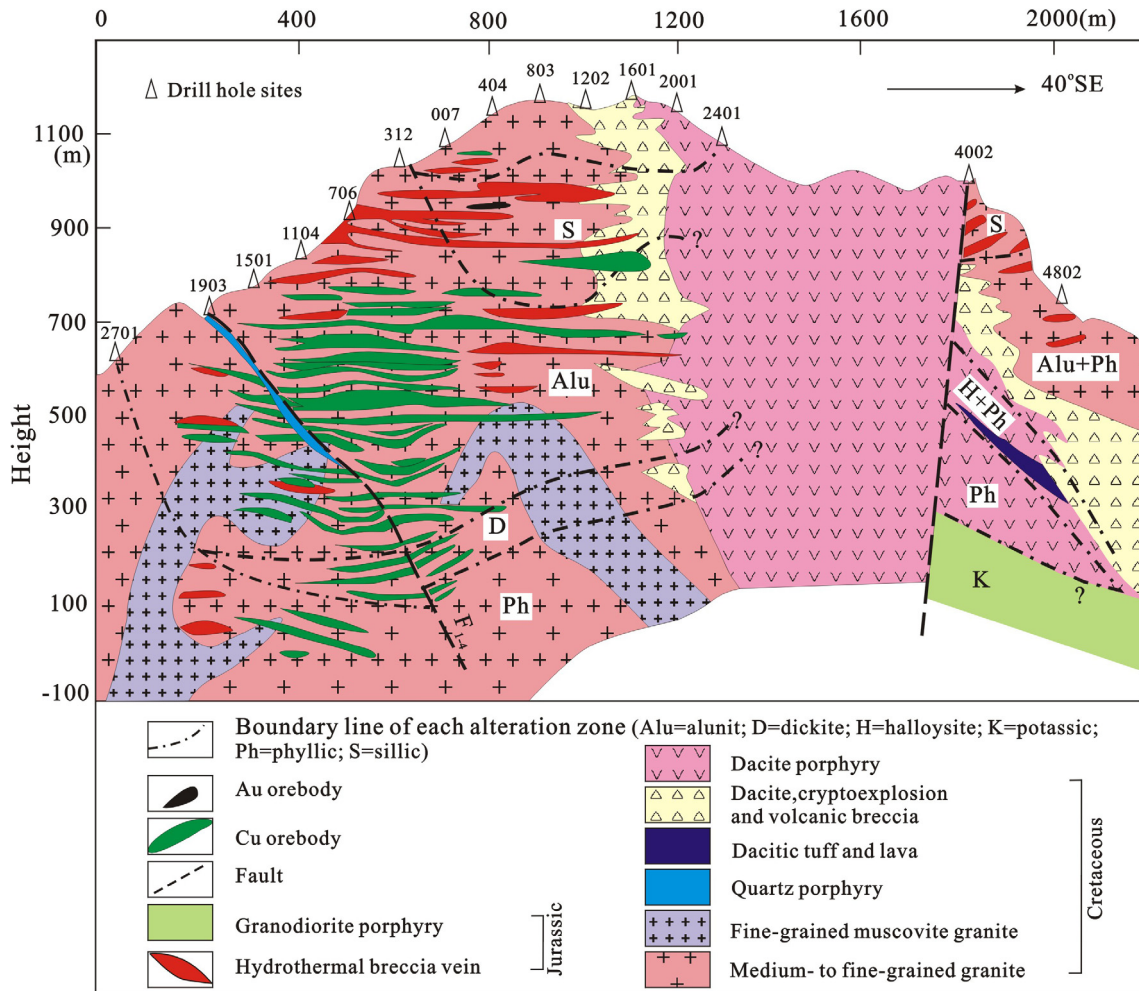
## 2.2. Geology of the Zijinshan high-sulfidation epithermal Cu–Au deposit

The Zijinshan high-sulfidation epithermal Cu–Au deposit is located in the center of the Zijinshan ore field. Dacite porphyry forms a pipe-like intrusion in the center of the deposit and is surrounded by dacitic volcanic breccia, tuff, and lava (Fig. 2; So et al., 1998). Hydrothermal alteration and mineralization are typically zoned (Fig. 3). The phyllic alteration zone occurs in the deeper

and outer parts of the system and is characterized by an assemblage of quartz–sericite–pyrite. The dickite alteration zone occurs at intermediate levels and has an assemblage of dickite–quartz–pyrite–zunyite, while the alunite alteration zone, at depths of 350–1200 m below the surface, has an assemblage of alunite–quartz–pyrite. Finally, the intense silicic alteration is dominant at levels shallower than 350 m (So et al., 1998; Zhang et al., 2001). The dacite porphyry pipe shows a transition with depth into a potassic-altered granodiorite porphyry with associated porphyry Cu mineralization. Gold and copper ore mineralization shows distinct zoning: Au mineralization is restricted to the shallow-level silicic alteration zone, whereas Cu mineralization is dominant in the alunite alteration zone at deeper levels (Fig. 3).

Gold ore bodies form disseminated and interstitial structures that are confined to the silicic alteration zone and in pipe-like hydrothermal breccias (So et al., 1998). The Au-bearing minerals are oxidized, and mainly include limonite, hematite, goethite, and covellite, with lesser pyrite, native Au, galena, bornite, and digenite. Quartz is the principal gangue mineral. Gold ore bodies tend to pinch out above the water table near a depth of 650 m, and are interpreted to have formed through secondary enrichment as a result of circulation of modern surface waters through permeable breccia ores (So et al., 1998; Zhang et al., 2001).

Copper ore bodies occur in the alunite alteration zone, at levels less than 650 m, and they form veins and stockworks that have filled in or replaced hydrothermal breccias, altered granite, and dacite porphyry. The breccias consist of angular fragments that are surrounded by a very fine-grained mineralized matrix. The fragments comprise altered wall rocks and hydrothermal ores, and the mineralized matrix consists mainly of quartz, alunite,



**Fig. 3.** Northwest-southeast cross section of the Zijinshan Cu-Au mine, showing geology and vertical alteration zoning. The cutoff grades used to outline the orebodies are 3 g/t Au for gold orebodies and 0.5 wt percent for copper orebodies.

pyrite, digenite, enargite, covellite, and minor amounts of bornite, chalcocite, chalcopyrite, and tetrahedrite. Digenite is the dominant ore mineral. The Cu mineralization is characterized by thick deposits of digenite that occur between elevations of 928 and -400 m, and exceed 1000 m in vertical thickness (Qiu et al., 2010; Lin, 2012). Ruan et al. (2009) proposed that digenite formed through secondary enrichment, whereby a strong acidic fluid dissolved Cu minerals into a sulfate solution, which then replaced other sulfides (e.g., enargite, luzonite, and tetrahedrite), forming digenite and covellite. However, other studies (Qiu et al., 2010; Lin, 2012) argue that digenite has a primary hydrothermal origin, as is typical for high-sulfidation epithermal deposits.

Fluid inclusion studies have revealed four main types of inclusions: vapor-rich, liquid-rich, liquid CO<sub>2</sub>-bearing three-phase, and liquid single-phase inclusions. The temperatures of formation of the silicic alteration and related Au mineralization range from 100 °C to 180 °C, whereas phyllic alteration formed at temperatures of 300–380 °C, dickite alteration developed at temperatures of 180–300 °C (peaking at 210 °C), and alunite alteration temperatures ranged from 160 °C to 320 °C (peaking at 190 °C and 230 °C) (So et al., 1998; Zhang et al., 2001).

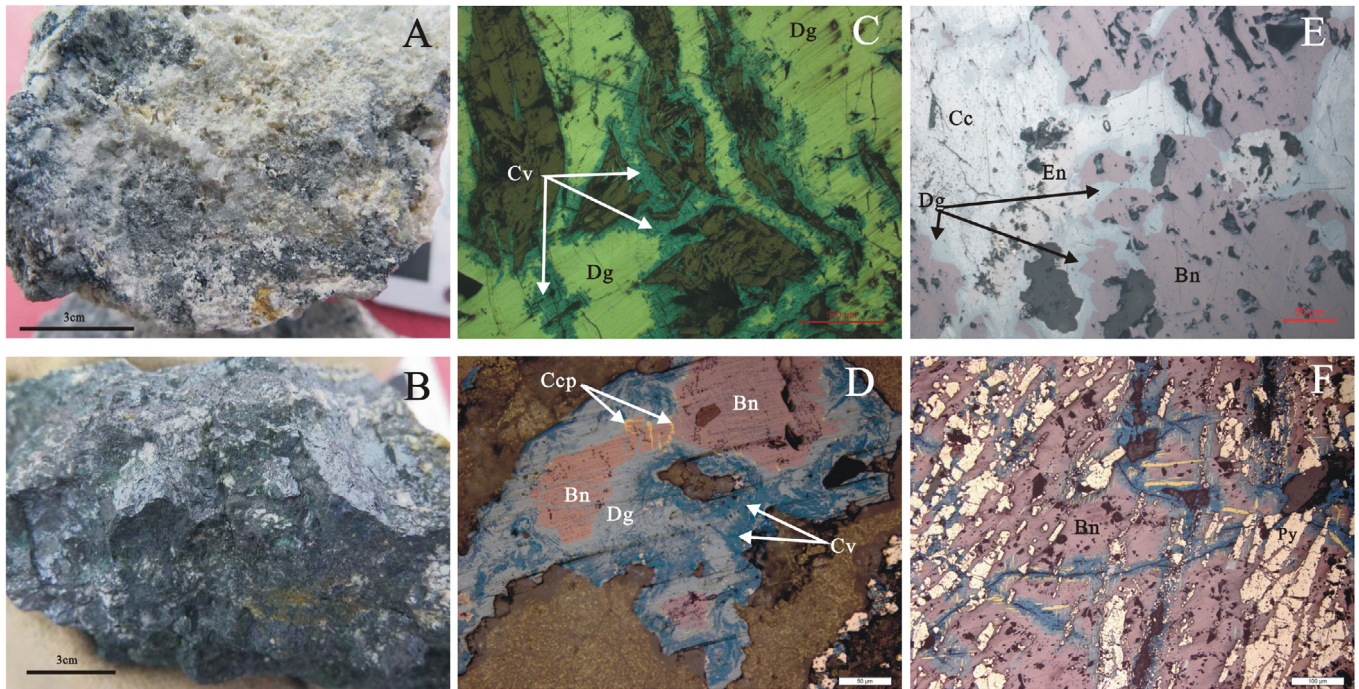
### 3. Sample preparation and analytical methods

Eighteen sulfide samples were collected from open pits of the Zijinshan high-sulfidation Cu-Au deposit, mainly from the

transition zone between the oxidized and primary ores, at heights between 650–740 m. Mineralization commonly occurs in veins, and the minerals include digenite, bornite, enargite, covellite, chalcocite, azurite, and chalcopyrite. The mineralogy of these samples were investigated by using optical microscope and electron probe microanalyser at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. Leached ores are porous (Fig. 4A), whereas other minerals are compact (Fig. 4B). After the samples were crushed, mineral chips were selected using heavy-liquid separation methods, and a subset of mineral chips was hand-picked under a binocular microscope, and finally checked using electron probe microanalyser. This work was done at the Fengzeyuan Mineral Determination Laboratory in Langfang City, China.

Copper isotope ratios were measured using a sample-standard bracketing method on a Neptune Plus™ multi-collector inductively coupled plasma mass-spectrometry (MC-ICPMS) at the Isotope Geochemistry Laboratory of the China University of Geosciences, Beijing, China. The detailed procedures for sample digestion, column chemistry, and instrumental analysis followed those of Liu et al. (2014a,b, 2015), and a brief description is given below.

Samples were first dissolved in a 1:3 (v/v) mixed solution of double-distilled HNO<sub>3</sub> + HCl. After complete dissolution, the solutions were heated to dryness at 80 °C. The samples were refluxed with concentrated HNO<sub>3</sub> and subsequently dried down at 80 °C. Then, 1 ml of 8 N HCl + 0.001% H<sub>2</sub>O<sub>2</sub> was added to each beaker



**Fig. 4.** Images of ore from the Zijinshan deposit. (A) Photograph of weakly leached ore. (B) Photograph of primary ore, without leaching. (C) Photomicrograph of ore that digenite partially replaced by covellite, reflected light. (D) Photomicrograph of ore that bornite partially replaced by digenite and covellite, reflected light. (E) Photomicrograph of ore that bornite and enargite partially replaced by chalcocite and digenite, reflected light. (F) Photomicrograph of ore that bornite replacing pyrite, with subsequent replacement by covellite and digenite, reflected light. Abbreviations: Cv, covellite; Py, pyrite; Bn, bornite; Dg, digenite; Cc, chalcocite; Ccp, chalcocopyrite; En, enargite.

and the samples were heated to dryness. This process was repeated three times to ensure that all cations were converted to chloride species prior to ion-exchange separation. The final material was dissolved in 1 ml of 8 N HCl + 0.001% H<sub>2</sub>O<sub>2</sub> in preparation for ion-exchange separation. Bio-Rad AG-MP-1 M strong anion exchange resin (100–200 mesh; chloride form) was used for separation of Cu from matrix elements. The pre-cleaned column was filled with pre-cleaned AG-MP-1 M resin, and washed with 7 ml 0.5 N HNO<sub>3</sub> and 5 ml 8 N HCl alternating with MQ H<sub>2</sub>O three times. The volume of resin was adjusted to 2 ml in 8 N HCl. 7 ml of 8 N HCl was added to the column for conditioning and then samples dissolved in 1 ml 8 N HCl (+0.001% H<sub>2</sub>O<sub>2</sub>) were loaded onto the column. Matrix elements were eluted in the first 10 ml 8 N HCl + 0.001% H<sub>2</sub>O<sub>2</sub>, and Cu was collected in the following 24 ml of 8 N HCl + 0.001% H<sub>2</sub>O<sub>2</sub>. The total procedural blank was less than 2 ng and the recovery was close to 100%.

Copper isotope data are reported in standard  $\delta$ -notation in per mil relative to standard reference material (SRM) NIST 976. The long-term external reproducibility for  $\delta^{65}\text{Cu}$  measurements is better than  $\pm 0.05\text{‰}$  (2SD), based on repeated analyses of natural samples and synthetic solutions (Liu et al., 2014a,b).

#### 4. Results

The measured Cu isotopic compositions of sulfide from the Zijinshan high-sulfidation epithermal Cu–Au deposit are presented in Table 1. The  $\delta^{65}\text{Cu}$  values of all sulfides analyzed range from  $-2.97\text{‰}$  to  $+0.34\text{‰}$ , with an overall variation of  $3.31\text{‰}$ , which is two orders of magnitude larger than the analytical uncertainty ( $\pm 0.05\text{‰}$ , 2SD). The range of Cu isotope ratios in the Zijinshan high-sulfidation epithermal Cu–Au deposit is similar to that observed in porphyry systems ( $<3\text{‰}$ ) (Mathur et al., 2013).

The  $\delta^{65}\text{Cu}$  values of bornite vary from  $-0.49\text{‰}$  to  $-0.05\text{‰}$ , and  $\delta^{65}\text{Cu}$  values of chalcocite range from  $-0.40\text{‰}$  to  $+0.29\text{‰}$ . The

**Table 1**

Copper isotopic compositions of sulfides from the Zijinshan high-sulfidation epithermal Cu–Au deposit, Fujian province, South China.

Sample	Height	Mineral	$\delta^{65}\text{Cu}(\text{‰})$	2SD
ZJS-13-92	724 m	Digenite	0.19	0.03
ZJS-13-92	724 m	Chalcocite	0.29	0.02
ZJS-13-93	724 m	Digenite	0.20	0.01
ZJS-13-93	724 m	Covellite	0.25	0.02
ZJS-13-95	724 m	Bornite	-0.06	0.00
ZJS-13-99	688 m	Chalcocite	-0.40	0.01
ZJS-13-99	688 m	Bornite	-0.49	0.07
ZJS-36-3	664 m	Enargite	-0.31	0.01
ZJS-36-3	664 m	Bornite	-0.49	0.01
ZJS-36-3	664 m	Digenite	-0.18	0.00
ZJS-13-113	652 m	Azurite	0.09	0.02
ZJS-13-116	652 m	Covellite	-2.97	0.00
ZJS-13-116	652 m	Enargite	-2.85	0.04
ZJS-13-116	652 m	Chalcocopyrite	-0.16	0.02
ZJS-13-139	736 m	Digenite	0.34	0.02
ZJS-13-139	736 m	Bornite	-0.16	0.01
ZJS-13-141	736 m	Chalcocite	0.09	0.02
ZJS-13-141	736 m	Bornite	-0.05	0.02

2SD = 2 times the standard deviation.

$\delta^{65}\text{Cu}$  values of digenite are between  $-0.18\text{‰}$  and  $+0.34\text{‰}$ , whereas enargite and covellite have  $\delta^{65}\text{Cu}$  values of  $-2.85\text{‰}$  to  $-0.31\text{‰}$  and  $-2.97\text{‰}$  to  $+0.25\text{‰}$ , respectively. The  $\delta^{65}\text{Cu}$  range of bornite ( $-0.49\text{‰}$  to  $-0.05\text{‰}$ ) identified in this study is similar to or significantly smaller than that reported in previous studies, e.g.,  $-1.07\text{‰}$  to  $+1.0\text{‰}$  (Larson et al., 2003),  $+0.28\text{‰}$  to  $+0.65\text{‰}$  (Asael et al., 2012), and  $+0.17\text{‰}$  to  $+1.39\text{‰}$  (Duan et al., 2016). Sulfides from leached ores, in which vuggy quartz is developed due to acid leaching, have more negative  $\delta^{65}\text{Cu}$  values, from  $-2.97\text{‰}$  to  $-2.85\text{‰}$ , whereas sulfides from non-leached ores yield a relatively tight cluster of  $\delta^{65}\text{Cu}$  values from  $-0.5\text{‰}$  to  $+0.4\text{‰}$  (Fig. 5a).

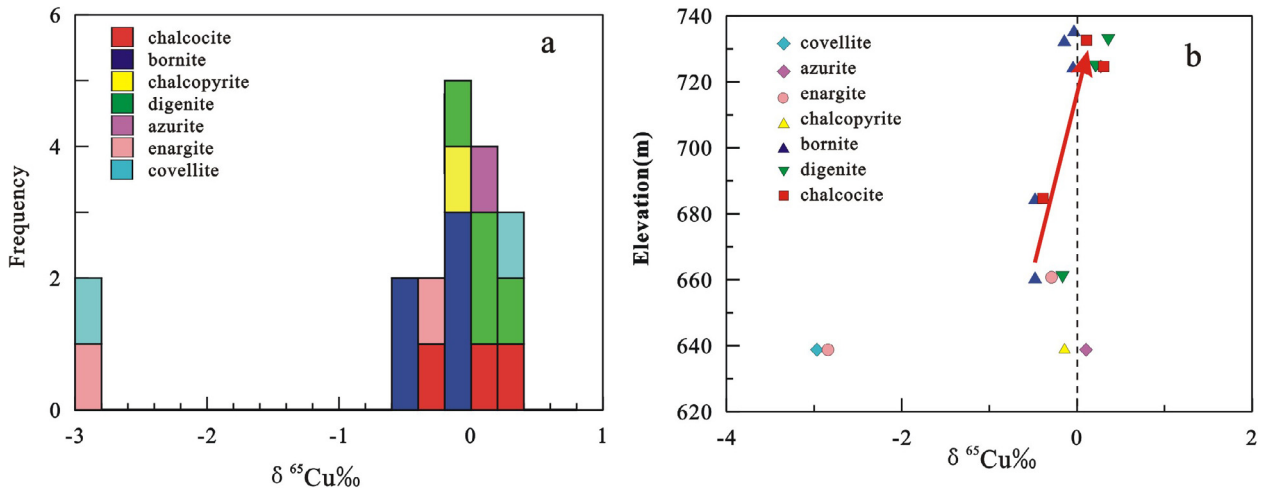


Fig. 5. a. Frequency diagram of Cu isotope values of the Zijinshan high-sulfidation epithermal Cu–Au deposit. b. Cu isotope values vs. Elevations (in m) of the Zijinshan high-sulfidation epithermal Cu–Au deposit.

5. Discussion

5.1. Cu isotope constraints on the genesis of Cu-sulfide ores in Zijinshan

Many studies of Cu isotopes have been conducted on various types of deposits worldwide (Larson et al., 2003; Graham et al., 2004; Mason et al., 2005; Markl et al., 2006; Mathur et al., 2009, 2010, 2013; Li et al., 2010; Mathur and Schlitt, 2010; Asael et al., 2012; Ripley et al., 2015; Duan et al., 2016; Saunders et al., 2016). In particular, studies have focused on Cu isotope fractionation in porphyry Cu deposits, including high-temperature hypogene sulfide mineralization, leaching, and supergene enrichment (Markl et al., 2006; Haest et al., 2009; Mathur et al., 2009, 2010, 2012; 2013; Li et al., 2010; Mathur and Schlitt, 2010; Braxton and Mathur, 2011; Wang et al., 2014; Duan et al., 2016). For example, Mathur et al. (2009) studied the Cu isotopic composition of sulfides from nine porphyry Cu deposits and determined that the  $\delta^{65}\text{Cu}$  values of hypogene chalcopyrite are between  $-1‰$  and  $+1‰$ , whereas chalcocite from the supergene enrichment zone

possesses heavier  $\delta^{65}\text{Cu}$  values of  $-0.3‰$  to  $+6.5‰$ , and Fe-oxides from the leach cap yield lighter Cu isotopic compositions of  $-9.9‰$  to  $+0.14‰$ . Chalcocite, covellite, and chalcopyrite of the Cañariaco Norte porphyry Cu deposit generally have hypogene  $\delta^{65}\text{Cu}$  values of  $-0.43‰$  to  $0.61‰$ , although both Fe-oxides and Cu-sulfides in the leach cap yield significantly low Cu isotope ratios ranging from  $-8.42‰$  to  $-2.29‰$  and  $-3.31‰$  to  $0.92‰$ , respectively (Mathur et al., 2012). In addition, experimental studies show that Cu isotope fractionation between hydrothermal fluids and sulfides is minor ( $<1‰$ ) at intermediate to high temperatures of 250–300 °C (Maher et al., 2011), and that Cu isotope fractionation in the supergene environment is significant, especially at low temperatures (Zhu et al., 2002; Ehrlich et al., 2004; Mathur et al., 2005; Pekala et al., 2011). Overall, samples of hypogene sulfides commonly have a narrow range of  $\delta^{65}\text{Cu}$  values close to  $0‰$  (mainly between  $-1‰$  and  $1‰$ ), and samples from leach caps possess the lightest  $\delta^{65}\text{Cu}$  of generally less than  $-1‰$ , whereas samples of supergene enrichment zones are enriched in  $^{65}\text{Cu}$  and have  $\delta^{65}\text{Cu}$  values exceeding  $+1‰$  (Fig. 6). Even in low-sulfidation epithermal Au–Ag deposits, the Cu isotopic compositions also show magmatic

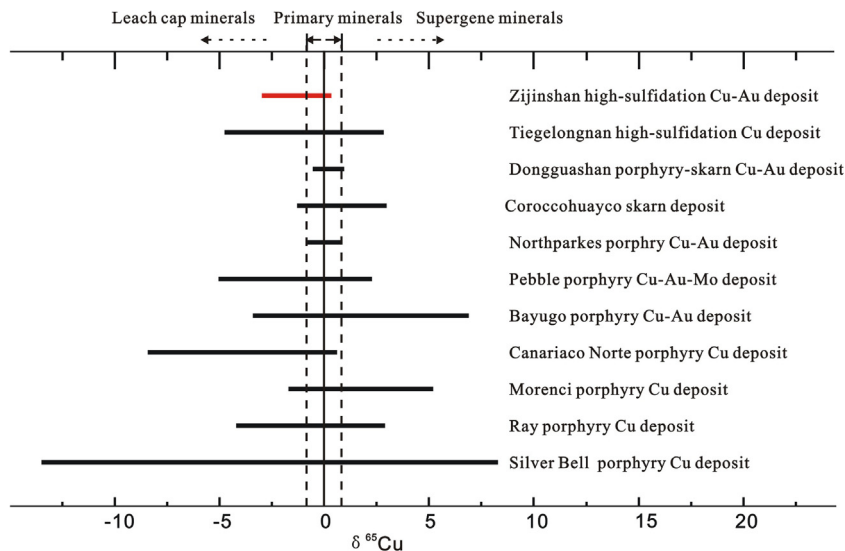


Fig. 6. Copper isotopic compositions of some porphyry, skarn, and high-sulfidation deposits in the world (data for other deposits are from Maher and Larson, 2007; Li et al., 2010; Mathur et al., 2010, 2012, 2013; Braxton and Mathur, 2011; Wang et al., 2014; Duan et al., 2016).

source of metals though their ore-forming solutions are consisted primarily of heated meteoric waters (Saunders et al., 2016).

The Zijinshan Cu–Au deposit is a typical high-sulfidation deposit (Zhang et al., 1991; So et al., 1998) with typical alteration zoning (such as silicification, alunite, dickite, and phyllic alteration) and mineral assemblage (e.g. vuggy quartz, digenite–covellite–enargite–alunite etc.) (Liu et al., 2011; Huang et al., 2014). The  $\delta^{65}\text{Cu}$  values of sulfides from the Zijinshan deposit range from  $-2.97\text{‰}$  to  $0.34\text{‰}$ , but the majority are between  $-0.49\text{‰}$  and  $0.34\text{‰}$ , which is consistent with typical Cu isotopic signatures of hypogene sulfides from porphyry deposits (Markl et al., 2006; Mathur et al., 2009, 2010, 2012; Li et al., 2010; Braxton and Mathur, 2011; Wang et al., 2014). Therefore, the Cu isotopic compositions indicate that most of the sulfides in the Zijinshan deposit are hypogene in origin.

Dendas (2016) studied Cu isotopes in chalcopyrite from the Bingham Canyon Mine, Utah, porphyry Cu–Mo–Au deposit, and reported that as alteration temperatures decrease from potassic alteration to propylitic alteration and through to argillic alteration,  $\delta^{65}\text{Cu}$  values progressively increase. Mathur et al. (2013) also observed a systematic variation in Cu isotopic compositions with depth at the Pebble porphyry Cu–Mo–Au deposit, Alaska, whereby  $\delta^{65}\text{Cu}$  values of hypogene samples increase from deeper to shallower levels in the deposit. This systematic variation was due to isotope fractionation at different alteration zones and different temperatures. In this study, we demonstrate that  $\delta^{65}\text{Cu}$  values of each mineral decrease with depth (Fig. 5b) in the Zijinshan deposit, which is consistent with relationships between depth and  $\delta^{65}\text{Cu}$  values in hypogene minerals from other porphyry deposits (Dendas, 2016; Mathur et al., 2013). Therefore, the sulfides in the Zijinshan deposit may be hypogene in origin.

In summary, based on Cu isotopic compositions and the relationship between  $\delta^{65}\text{Cu}$  value and depth of sulfides from the Zijinshan Cu–Au deposit, the majority of digenite, covellite, and other Cu-sulfides are probably of hypogene origin. It seems that Cu and Au in both high-sulfidation and low-sulfidation epithermal deposits have magmatic reservoir origin, no matter whether the ore-forming fluids themselves are primarily magmatic or meteoric waters.

## 5.2. Cu isotope fractionation between coexisting minerals

The  $\delta^{65}\text{Cu}$  values of coexisting minerals, including digenite, covellite, bornite, chalcocite, and enargite, are presented in Table 2. In all samples, the inter-mineral Cu isotope fractionation ranges from  $0.05\text{‰}$  to  $0.5\text{‰}$ . The Cu isotope fractionation between most coexisting minerals is less than  $0.18\text{‰}$ , except for up to  $0.31\text{--}0.5\text{‰}$  fractionation between digenite and bornite. This is consistent with fractionation values ( $\sim 0.4\text{‰}$ ) between bornite and other Cu-bearing minerals reported in moderate- to high-temperature porphyry deposits (Larson et al., 2003; Graham et al., 2004).

Experimental studies show that  $^{63}\text{Cu}$  tends to be transferred into minerals from solution, which changes the Cu isotopic composition of the solution as the reaction proceeds (Pekala et al., 2011). Aqueous Cu released from leached Cu(I)-sulfides during abiotic oxidation has also been demonstrated to be isotopically heavier than the starting composition of the mineral, and the leached mineral is isotopically lighter (Mathur et al., 2005; Fernandez and Borrok, 2009; Kimball et al., 2009). Moreover, experimental studies also show that at intermediate pH (4–7) and low pH leached mineral have lighter Cu isotopes than the initial starting mineral at  $250\text{ °C}$  and  $300\text{ °C}$  (Maher et al., 2011). In the Zijinshan Cu–Au deposit, bornite was replaced by digenite and covellite (Fig. 4D–F), and by chalcocite (Fig. 4E), and digenite was replaced by covellite (Fig. 4C). And it is supposed that the ore-forming fluids have  $\text{pH} < 6$  (Huang, 1994). Therefore, according to the sequence of mineral formation, the expected relationships between the Cu isotopic compositions of the key minerals in the deposit are:  $\delta^{65}\text{Cu}_{\text{bornite}} < \delta^{65}\text{Cu}_{\text{digenite}}$ ,  $\delta^{65}\text{Cu}_{\text{bornite}} < \delta^{65}\text{Cu}_{\text{chalcocite}}$ , and  $\delta^{65}\text{Cu}_{\text{digenite}} < \delta^{65}\text{Cu}_{\text{covellite}}$ , which are consistent with the  $\delta^{65}\text{Cu}$  values measured in this study (Table 2). These observations further suggest that most of these minerals were not significantly modified by post-mineralization leaching and thus are of hypogene origin.

## 6. Conclusions

Copper isotopes may be used to distinguish between primary and secondary mineralization processes. In this study, we analyzed the Cu isotopic compositions of digenite, bornite, covellite, enargite, chalcocite, and chalcopyrite from the Zijinshan high-sulfidation epithermal deposit. The results show that the majority of the Cu-bearing minerals have a hypogene origin, and that the majority of digenite is primary. High-sulfidation and low-sulfidation epithermal deposits may all have a deep, primitive metal source, irrespective of whether the ore-forming fluids themselves are primarily magmatic or meteoric waters. Together with previous studies (Graham et al., 2004; Markl et al., 2006; Mathur et al., 2009, 2012, 2013; Mathur and Schlitt, 2010; Braxton and Mathur, 2011; Li et al., 2010; Duan et al., 2016; Saunders et al., 2016), our results suggest that Cu isotopes could potentially provide important insights into metal precipitation and fluid flow in medium- to high-temperature deposits.

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**Table 2**  
Copper isotope fractionation between coexisting Cu-sulfides.

Sample	Location	Mineral	$\delta^{65}\text{Cu}(\text{‰})$	2SD	Mineral	$\delta^{65}\text{Cu}(\text{‰})$	2SD	$\Delta$
ZJS-13-92	724 m platform	Chalcocite	0.29	0.02	Digenite	0.19	0.03	0.1
ZJS-13-93	724 m platform	Covellite	0.25	0.02	Digenite	0.20	0.01	0.05
ZJS-13-99	688 m platform	Chalcocite	-0.40	0.01	Bornite	-0.49	0.07	0.09
ZJS-13-141	736 m platform	Chalcocite	0.09	0.02	Bornite	-0.05	0.02	0.14
ZJS-13-139	736 m platform	Digenite	0.34	0.02	Bornite	-0.16	0.01	0.5
ZJS-36-3	664 m platform	Digenite	-0.18	0.00	Bornite	-0.49	0.01	0.31
ZJS-36-3	664 m platform	Enargite	-0.31	0.01	Bornite	-0.49	0.01	0.18
ZJS-36-3	664 m platform	Digenite	-0.18	0.00	Enargite	-0.31	0.01	0.13
ZJS-13-116	652 m platform	Enargite	-2.85	0.04	Covellite	-2.97	0.00	0.12

2SD = 2 times the standard deviation.

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