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Gold mineralization in the Guilaizhuang deposit, southwestern Shandong Province, China: Insights from phase relations among sulfides, tellurides, selenides and oxides

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ABSTRACT

The Guilaizhuang gold deposit is composed of limestone- and breccia-type ores. In the limestone ores, gold is hosted by pyrite, As-bearing pyrite and arsenopyrite, whereas in the breccia ores, tellurides are the main gold carriers. Selenium often isomorphously substitutes for sulfur in sulfides in the limestone ores, but occurs as selenides in the breccia ores. Hematite is the only oxide in the breccia ores, associated with barite and other tellurides. In this paper, the thermodynamic parameters, especially the Gibbs free energies of formation and reaction, of related sulfides, tellurides, selenides and oxides are computed to explain the distinct mineral styles in the limestone- and breccia-type ores. We construct the phase relations among minerals delineated by phase diagrams at 250 °C, the temperature for gold precipitation in the Guilaizhuang deposit. According to the phase relations between sulfides and selenides, we propose that gold has been transported as $[Au(HS,HSe)_2]^-$, and released during rapid formation of pyrite, As-pyrite and arsenopyrite, at $\log fS_2(g)$ between −12.8 and −11.4 (250 °C). In the breccia ores, $\log fTe_2(g)$ and $\log fSe_2(g)$ are constrained within −12.9 to −9.4, and −12.4 to −6.9 (250 °C), respectively, based on the mineral assemblages observed in the ores. The phase relations between tellurides and selenides indicate that calaverite, the only stable gold telluride mineral in nature, was not stable in the breccia ores at 250 °C during the gold precipitation. Based on EMPA analysis, the so-called "calaverite" revealed from microscopic observations is in fact Au–Ag telluride, probably derived from the decomposition of sylvanite ($AuAgTe_4$) and petzite ($AuAg_3Te_2$), the only two stable Au–Ag tellurides in nature at high temperature. However, we do not exclude the possibility that calaverite occurs in this deposit, which may have precipitated in early relatively high tellurium concentration stage preceding gold mineralization. Selenium was not detected in gold-bearing tellurides, implying that selenide is unrelated with gold precipitation directly in the breccia ores, but can buffer the tellurium fugacity, and thus influence the gold precipitation indirectly. Furthermore, in $\log fO_2(g)$ range of > -35.4 at 250 °C, the majority of the tellurides and selenides can be stable in the breccia ores, but residual sulfides are proposed to be oxidized into sulfate minerals, which could also free some gold into ores, although less important relative to that formed from telluride decomposition.

1. Introduction

Sulfides, mainly pyrite, As-bearing pyrite and arsenopyrite, are the main carriers of gold in most gold deposits (Benning and Seward, 1996; Boullier et al., 1998; Clark and Williams-Jones, 1990; Emsbo et al., 2003; Fortuna et al., 2003; Gammons and Williams-Jones, 1997; Hofstra and Cline, 2000; Jugo et al., 1999; Kesler et al., 2002; Lang and Baker, 2001; Pokrovski et al., 2008; Zezin et al., 2011). However, gold-bearing tellurides, selenides and oxides have also been reported from many epithermal Au–Te deposits, telethermal selenide vein-type gold deposits, and epithermal Au–Ag deposits in the subaerial volcanic environments (Afifi et al., 1988; Alderton and Fallick, 2000; Cook and Ciobanu, 2004; Liu et al., 2000; Mills, 1974; Nasar and Shamsuddin, 1990; Simon and Essene, 1996; Simon et al., 1997).

Tellurides and selenides of Au, Ag, Cu, Fe and other elements are commonly reported as trace minerals associated with gold (Ciobanu et al., 2006; Cooke and McPhail, 2001). The association among tellurium, selenium and gold has long been recognized by economic geologists, and is the most evident in the prevalence of Au–Ag-tellurides–selenides in some ore deposits (Ciobanu et al., 2006). A comprehensive study of tellurides, selenides, oxides and sulfides is significant for understanding the processes of gold mineralization. Previous studies have used

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thermodynamic properties to calculate relative stabilities of native elements, sulfides, tellurides, selenides and oxides as a function of fugacity of S_2(g), Te_2(g), Se_2(g) and O_2(g) (Afifi et al., 1988; Liu et al., 2000; Simon and Essene, 1996; Simon et al., 1997). However, most of these studies principally focus on the thermodynamic characteristics of chemical complexes. In this paper, we provide a more simplified approach with potential application to ore-forming processes.

The Guilaizhuang gold deposit, southwestern Shandong Province, China, is primarily composed of sulfidized limestones and oxidized breccias (Hu, 2005; Teng, 1994; Yu, 2010). In the limestone ores, gold is invisible and hosted by pyrite, As-bearing pyrite and arsenopyrite. In the breccia ores, sulfides are absent, and the main gold-bearing minerals are tellurides and oxides, with less selenides (Hu, 2005; Yu, 2010). In order to understand the geochemical significance of these mineral assemblages for gold precipitation, we have calculated relative stabilities of native elements, especially Au, sulfide, selenide, telluride and oxide minerals as a function of fugacity of S_2(g), Te_2(g), Se_2(g), and O_2(g) through thermodynamic approach. Our study provides a better interpretation of the diversity in gold mineralization between the two type ores in this deposit.

2. Geological setting and ore geology

The Guilaizhuang gold deposit is located in the eastern margin of the Luxi Block affiliated with the Eastern Block of the North China Craton, and is bounded by the continental Tan-Lu Fault to the east (Fig. 1a). The Luxi Block is composed of Neoarchean gneisses, amphibolites and tonalitic-trondhjemitic-granodioritic gneisses (TTGs), Paleoproterozoic granitoids, Paleozoic marine carbonates interbedded with clastic rocks, Mesozoic and Cenozoic continental clastic rocks, volcaniclastics, intermediate-basic igneous rocks, mafic dykes, carbonatites and alkaline rocks (Fig. 1b) (Lan et al., 2012; Zhang et al., 2005; Zhao et al., 2001, 2005). The Tongshi intrusive complex is the most important magmatic body in this region (Fig. 2), composed of the fine-grained quartz monzodiorite, porphyritic quartz monzodiorite, and coarse- to fine-grained porphyritic syenites. LA-ICPMS zircon U–Pb ages show that this complex was emplaced at 180.1–184.7 Ma (Lan et al., 2012). Previous researchers inferred that the porphyritic syenites were genetically related with the Guilaizhuang gold deposit (Hu, 2005; Teng, 1994; Yu, 2010).

The Guilaizhuang deposit is hosted by the Cambrian–Ordovician carbonate rocks, limestone and dolomite, and controlled by the W–E trending fault (Fig. 3a, b). The gold resource is estimated to be >30 tonnes with an average grade of 8.10 ppm (Hu, 2005; Hu et al., 2004, 2005; Shen et al., 2001; Yu, 2010). The ores in the deposit can be subdivided into two sub-types, limestone- and breccia-type ores. In the limestone ores, gold is predominantly contained by sulfides, mainly As-bearing pyrite and arsenopyrite, which occurs as disseminations in limestone (Fig. 4a). The breccia ores, main gold producer in this deposit, are composed of various kinds of breccias, including porphyritic syenite, monzodiorite, carbonate rocks and sandstone, which are cemented by lithic fragments with the same lithology as the breccias (Fig. 4b). Calaverite ($AuTe_2$) and hessite (Ag_2Te) in the breccias are the main gold-bearing minerals in the deposit, except the native gold associated with them. Some other telluride minerals were also found in the deposit by previous researchers (Hu, 2005; Yu, 2010), including weissite, altaite and coloradoite. Minor hematite, barite, and tiemannite are closely associated with tellurides. Gold-related fluoritization is extensively developed in the deposit, which is followed by carbonatization. Silicification was observed locally, but the relationship between the gold mineralization and silicification is unclear. The paragenetic sequence of minerals in the limestone and breccia ores is illustrated in Fig. 5.

3. Methods

3.1. Mineralogical analysis

Electron microprobe analysis is used to characterize and identify the chemistry of the sulfides, tellurides, oxides and selenides observed in the deposit.

The analyses were performed on MonoCL equipment (Gatan, Germany), scanning electron microscope (SEM) (Leo145VP, Germany) equipped with BSD detector, energy dispersive spectrometer (EDS) (Inca Energy 300, Oxford Instruments, UK) and EMPA (JXA-8100, JEOL Company, Japan) equipped with five X-ray wavelength dispersive spectrometers (WDS), respectively, at the Institute of Geology and Geophysics, Chinese Academy of Sciences. For CL analysis, BSE imaging, and X-ray energy spectroscopic determination, the voltage was 10–20 keV, and the beam current was adjusted to the voltage (from 0.1 to 10 nA). For EMPA analyses, Fe, S, As, Sb, Se, Bi, Ag, Cu, Te, Hg and Au were detected in sulfide, telluride and selenide minerals using a 20 keV accelerating voltage, 10–20 nA beam current and a 10s-counting time. Standards used were natural marcasite for Fe and S, GaAs for As, stibnite for Sb, galena for Pb, cinnabar for Hg, bismuthite for Bi, and native gold, silver, tellurium, copper, zinc, nickel, cobalt, and selenium for Au, Ag, Te, Cu, Zn, Ni, Co, and Se, respectively. The detection limits for the target elements in this study are: Fe 0.03%, S 0.05%, Au 0.04%, Ag 0.04%, As 0.03%, Te 0.05%,

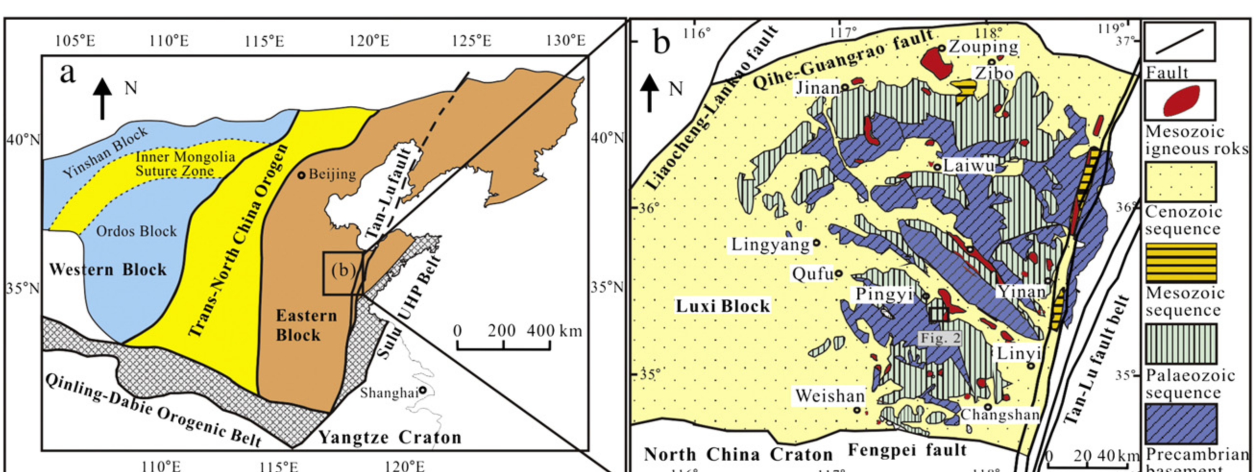

Fig. 1. (a) Tectonic setting of the Luxi Block, modified after Zhao et al. (2005) and (Santosh (2010). (b) Geological and tectonic map of the Luxi Block and the location of the Guilaizhuang gold deposit, modified after Lan et al. (2012).