Incorporation mechanism of structurally bound gold in pyrite: Insights from an integrated chemical and atomic-scale microstructural study

LEI MENG1,2, SANYUAN ZHU3, XIAOCHUN LI4, WEI TERRY CHEN5, HAIYANG XIAN4, XINYU GAO6, AND TAIPING ZHAO1,2,*

1Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
2CAS Center for Excellence in Deep Earth Science, Guangzhou 510640, China
3State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
4Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China
5State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China
6Guangdong Polytechnic of Water Resources and Electric Engineering, Guangzhou 510635, China

Abstract

Pyrite is one of the most important carriers for Au in hydrothermal deposits, but the incorporation mechanism of structurally bound Au has long been a matter of debate. This is due to a poor understanding of the chemical state and coordination environments of Au in the pyrite structure. Arsenian pyrite is the dominant Au-hosting mineral from the Shanggong Au deposit (130 t Au) in the southern margin of the North China Craton. Our EPMA and LA-ICP-MS results show that the arsenian pyrite has remarkably high Au (0.05–0.78 wt%) and As (0.39–4.60 wt%) contents. Au is negatively correlated with Fe but positively correlated with As. Z-contrast HAADF-STEM imaging reveals that Au atoms sit at the Fe atom sites in the arsenian pyrite structure. Our μ-XANES results and previously reported data suggest that Au and As in arsenian pyrite are predominant of chemically bound Au⁺ and As⁵⁺, respectively. We thus propose that Au⁺ and As⁵⁺ are both structurally bound and sit at the Fe and S atom sites of pyrite, respectively. As may not be necessary but favorable for the incorporation of structurally bound Au in pyrite. These results have significant implications for understanding the enrichment mechanism of Au from ore-forming fluids with low-Au and low-As concentrations into arsenian pyrite and for revealing the role of As in Au mineralization of hydrothermal deposits.

Keywords: Arsenian pyrite, μ-XANES spectroscopy, Z-contrast HAADF-STEM image, Au incorporation mechanism

Introduction

Pyrite, the most common sulfide in the Earth’s crust, has long been considered to be economically significant because it hosts large amounts of Au and many other trace elements, such as As, Ti, Te, Sb, and Se (Reich et al. 2005; Deditius et al. 2014). A positive correlation between Au and As in pyrite has been well recognized and is taken to indicate the control of As on Au enrichment (Reich et al. 2005; Deditius et al. 2014; Kusebauch et al. 2019; Xing et al. 2019). Arsenian pyrite is also a common mineral in hydrothermal ore deposits such as Carlin, epithermal, and orogenic Au deposits (Fleet and Mumin 1997; Cline 2001; Reich et al. 2005; Deditius et al. 2014 and references therein). Invisible Au accounts for the majority of Au in arsenian pyrite and occurs as structurally bound Au and/or Au-bearing nanoparticles (Reich et al. 2005; Deditius et al. 2014; Filimonova et al. 2020 and references therein). Although the incorporation mechanism of structurally bound Au in arsenian pyrite has been extensively investigated (Arehart et al. 1993; Fleet and Mumin 1997; Simon et al. 1999a, 1999b; Palenik et al. 2004; Chouinard et al. 2005; Reich et al. 2005; Deditius et al. 2008), it remains a matter of debate. Precise chemical state and atomic-scale structural features of Au in the pyrite lattice are still poorly understood.

* E-mail: tpzhao@gig.ac.cn

The state of Au in pyrite has attracted many studies in the past three decades (Arehart et al. 1993; Simon et al. 1999a; Palenik et al. 2004; Deditius et al. 2008 and references therein) but is still uncertain. It was traditionally considered that structurally bound Au is likely present as Au⁺ (Simon et al. 1999a; Reich et al. 2005; Deditius et al. 2014) or Au³⁺ (Arehart et al. 1993; Chouinard et al. 2005) in the lattice of arsenian pyrite, but Au³⁺ has not been confirmed by spectroscopic data. Au⁺ and ionic Au⁺ in Au-bearing arsenian pyrite were identified by X-ray absorption near edge structure (XANES) spectroscopy with a broad beam of 15 × 1 mm (Simon et al. 1999a). However, the broad beam can potentially produce mixed spectra of different states of Au. In addition, the coupled occurrence of Au and As makes it even more difficult to identify the exact chemical state and local structure of Au in arsenian pyrite because Au XANES spectra can be partly obscured by that of As (Merkulova et al. 2019). Such issues were further addressed by using recently developed high-energy-resolution X-ray absorption spectroscopy (HERFD-XAS) (Trigub et al. 2017; Merkulova et al. 2019; Pokrovski et al. 2019; Filimonova et al. 2020). Trigub et al. (2017) reported that chemically bound Au replaces Fe in a synthesized As-free hydrothermal pyrite. In contrast, Pokrovski et al. (2019) proposed that chemically bound Au⁺ in As-poor pyrite mainly occurs in Au₄S₈ clusters. Merkulova et al. (2019) reported that chemically bound Au⁺ also replaces Fe³⁺ in the arsenian pyrite structure.