Evaluating the physicochemical conditions for gold occurrences in pyrite

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**ABSTRACT**

While noble metals often occur as minor components in host minerals in various ore deposits, little theoretical assessment exists to predict the occurrence of these metals. Here, we probe the fundamental controls responsible for the occurrence of trace elements in host minerals through first-principles calculations. We apply the theoretical model to understanding the debated issues concerning the occurrence of gold (Au) in pyrite, in which the valence of Au is ascribed to either positive or negative values. Our results indicate that (1) both positive and negative valent Au may occur in pyrite and (2) higher sulfur fugacity and lower temperature lead to more Au⁺ occupying Fe sites in pyrite. These findings suggest that chemical states and speciation of the Au in host pyrite are ultimately controlled by temperature and sulfur fugacity, providing insight into the formation conditions of ore deposits and facilitating strategy design for beneficiation.

**Keywords:** Gold-bearing pyrite, physicochemical condition dependence, gold occurrence, density functional theory, thermodynamics, sulfur fugacity

**INTRODUCTION**

Gold (Au) is not only of great importance for financial reserves but also, like other trace elements including indium, germanium, and tellurium, etc., is required in unprecedented quantities in industrial applications (Gulley et al. 2018). Due to low abundance (parts to sub-parts per million), Au, as well as other trace elements, frequently disperse in host minerals as solute constituents of solid solutions (Zhai et al. 2019). The physicochemical state and speciation that these metals assume in the corresponding hosts often carry critical information indicative of the ore formation processes (Xing et al. 2019; Du et al. 2020), in addition to being a key gauge for downstream metal recovery (Wang et al. 2008). Despite such general understanding, strategies rationalizing the occurrence of noble metals in host minerals remain largely empirical. The lack of a theoretical basis to investigate the occurrence of valuable metals impedes the interpretation of genetic information of metallocgenic processes and the high efficient recovery of these metals.

Pyrite (FeS₂) occurs in almost all metalliferous deposits and is a predominant gold-bearing mineral in many giant gold deposits such as the Carlin-type (Reich et al. 2005). Although the occurrence of Au in pyrite has been of wide concern, the chemical state and site occupation of Au are still in debate. Previous studies based on spectroscopy (Li et al. 1995; Simon et al. 1999; Cabri et al. 2000; Trigub et al. 2017; Merkulova et al. 2019; Pokrovski et al. 2019) or charge-balance consideration (Chouinard et al. 2005) focused primarily on samples from specific deposits while ignoring the substitutional mechanisms of pyrite and the physicochemical conditions under which it formed. This results in a historical paradox of the oxidation state of Au in pyrite, i.e., either positive or negative oxidation state. The positive +1 and +3 valences are interpreted from X-ray absorption near edge structure (XANES) spectroscopy and charge-balance consideration (Simon et al. 1999; Cabri et al. 2000; Trigub et al. 2017; Merkulova et al. 2019; Pokrovski et al. 2019), while the negative oxidation state of gold is confirmed by X-ray photoelectron spectroscopy (XPS) and Mössbauer spectroscopy (Li et al. 1995, 2002). Therefore, we hypothesize that the inconsistency of the interpretation of gold occurrence in pyrite may be caused by variations of site occupations and formation conditions.

Herein, we propose a theoretical framework that links the occurrence of Au in pyrite structure to its metallocgenic environments to test the hypothesis. For a host mineral, the incorporated elements are de facto impurities whose site occupancy in host minerals can be treated as a distribution of the impurity elements in a crystal field, which can be described by the Maxwell-Boltzmann distribution. In such a system, the occupation probability of the impurity elements at different lattice sites of host minerals hinges upon both the incorporation energy level and the temperature. The incorporation energy of