

Mechanisms and species of gold incorporation into crystals of cadmium, lead, and iron sulfides

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Abstract

The mechanisms and species of gold incorporation into crystals of simple sulfides are described. The concept of endocrypty in its modern treatment and the corresponding technique of experimental study were used. The technique is based on the principle of phase composition correlation and variation of parameters specifying the concentrations of active crystal defects. Gold species are determined with the method of statistical samples of analytical data for single crystals (SSADSC). The highest gold incorporation limits have been established for PbS and CdS under high sulfur fugacity ($2.4 \cdot 10^{-2}$ and $7 \cdot 10^{-3}$ wt.%, respectively) at 500 °C and 1 kbar. It is shown that in this case, the main crystal defects are metal (Me) vacancies and the gold species is a donor-acceptor pair “Me vacancy– interstitial Au”. Under low sulfur fugacity, Au incorporation might be due to sulfur vacancies, and the gold species is a pair “Au in the Me position–S vacancy”; its concentrations are lower than those at high sulfur fugacity ($\leq 10^{-3}$ wt.%). A specific feature of gold is a tendency to endocrypty. The estimated limiting contents of gold incorporated into sulfide crystals (FeS₂, CdS, PbS) at 450–500 °C vary from $n \cdot 10^{-4}$ to $n \cdot 10^{-2}$ wt.%, which is nearly two orders of magnitude higher than the “true” isomorphous capacities of these crystals. For FeS, the incorporation limit of Au does not depend on defects (Fe vacancies). This phenomenon has not been explained yet. In general, the data obtained show that not only the crystallochemical features but also geochemical parameters (first of all, temperature and sulfur fugacity) of the ore formation medium are the main factors for gold concentration in sulfide minerals.

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Introduction

The structural mechanisms of gold incorporation into minerals and inorganic sulfide and oxide crystals as well as the species and limiting contents of incorporated gold are still not studied. Experimental data on this subject are scarce. The incorporation limits and species of gold were established by Wu and Delbove (1989) only for arsenopyrite. The researchers synthesized zoned arsenopyrite containing up to 1.7 wt.% Au under hydrothermal conditions at 500°C and 2 kbar. Later on, Fleet and Mumin (1997) showed that the gold contents of such an arsenopyrite reach 3.0 wt.% and are due to the excess of As and deficit of Fe. In this case, the Au incorporation might be related to arsenopyrite vacancies, in contrast to the simple mechanism of isomorphous substitution of Fe by Au proposed by Wu and Delbove (1989). Note that both studies were

performed by electron microprobe analysis with a limited identification of gold distribution microinhomogeneity determined by its spatial resolution (a few microns). The chemical species of gold were not studied in the above works, though its contents were sufficient to apply electron spectroscopy.

Later on, the incorporation limits of Au in pyrite were estimated at 500 °C and 1 kbar (Tauson, 1999c; Tauson et al., 1998b), $(3 \pm 1) \cdot 10^{-4}$ wt.%. The authors also established the incorporation limits of Au in greenockite (α -CdS) under the same *PT*-conditions, $5 \cdot 10^{-3}$ wt.%. These data are considered the most reliable. For example, the dependence of gold solubility in As-pyrite on its As content obtained by Reich et al. (2005) is in agreement with that described by the above researchers at As content equal to zero.

The maximum contents of gold in mineral crystals were obtained in hydrothermal experiments on their synthesis in the presence of ¹⁹⁵Au (Mironov et al., 1987; Mironov and Geletii, 1978, 1979). But the experimental technique (direct cocrystallization of mineral and gold) did not ensure precise estimates

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of gold incorporation limits, which are physicochemical characteristics of the system (Tauson, 1999c).

The results of studies based on different experimental and natural data and different analytical techniques differ considerably, as seen by the example of pyrite (FeS₂). The incorporation limits of Au in this mineral vary from $\leq 10^{-6}$ to ~ 1 wt.%, i.e., by six (!) orders of magnitude (Besten et al., 1999; Fleet and Mumin, 1997; Mironov and Geletii, 1978; Tauson, 1999c; Tauson et al., 1998b). The chemical species of incorporated gold are Au¹⁻, Au⁰, Au¹⁺, and Au³⁺ (Arehart et al., 1993; Cook and Chryssoulis, 1990; Friedl et al., 1995; Laptev and Rozov, 2006; Li et al., 2003; Palenik et al., 2004; Reich et al., 2005; Simon et al., 1999a,b; Smagunov et al., 2004a; Tauson et al., 1996; Voitsekhovskii et al., 1975). Note that Au¹⁻ is an unusual species in which gold is bound to alkaline metals in intermetallic compounds (Parish, 1988). Significant chemical shifts characterizing this species in Mössbauer spectra might also be related to gold cations coordinated by some organic ligands. The reported data show that the most probable incorporation limits of Au in pyrite lie in the middle of the above range of values. The earlier data can be refined if taking into account the modern concepts of admixture element uptake by real crystals (Tauson, 1999a,b, 2005). In the works by Tauson (1999c) and Tauson et al. (1998b), structural and isomorphous Au admixtures are not separated. When trace elements (<0.1 wt.%) are considered, the difference between these admixtures and their concentrations can be considerable, which is comprehensively substantiated by Urusov et al. (1997). In accordance with the theory of trace-element uptake by real crystals (Tauson, 1999a,b, 2005), the isomorphous capacity of crystal for trace element can be estimated if the crystal defects determining the element incorporation are absent. To elucidate Au incorporation into crystals of inorganic compounds and minerals, one must determine the type of their active defects and gold incorporation limits for the maximum or specified concentrations of these defects and the isomorphous capacity of the defect-free crystals. The problem becomes more complicated if the concentrations of gold in sulfide crystals and the abundance of its nonstructural phase species, first of all, elemental form (including nanoparticles) are taken into account. Note that even the application of the most modern analytical methods for study of substances, including microbeam techniques, does not provide reliable information on the incorporation limits and species of gold in crystals. Nevertheless, the experimental and analytical techniques elaborated by Tauson et al. (2001, 2002), in particular, the method of statistical samples of analytical data for single crystals (SSADSC) (Smagunov et al., 2004b), permit one to approach the solution of this problem, though with some stipulations and assumptions.

Experimental techniques

The main experimental means for studying gold incorporation into minerals and inorganic crystals are the application of the principle of phase composition correlation (Perchuk and

Ryabchikov, 1976) (the law of element partition among phases) and variation of external parameters determining the concentration of active defects (Tauson, 1999a). Trace-element distribution in real crystals is considered in detail by Urusov et al. (1997). The principle of phase composition correlation substantiates a regular simultaneous change in compositions of coexisting minerals under the effect of temperature, pressure, and other equilibrium factors (Perchuk and Ryabchikov, 1976). Structural crystal defects influence the phase composition correlation. The defects that determine the incorporation of admixture into the crystal structure increase not only its incorporation limit (Tauson, 1999a) but also the coefficient of its interphase partition. For point defects, this phenomenon was first reported by Urusov and Kravchuk (1978), and later it was also revealed for other types of defects (Urusov et al., 1997). We proposed to distinguish between the true phase composition correlation, specific for isomorphous admixture in the crystal, and the apparent phase composition correlation, characterized by a high partition coefficient of admixture as a result of its interaction with defects (Tauson, 1989). In the first case, the partition coefficient can be calculated from thermodynamic data for corresponding isomorphous mixtures, and in the second, such a calculation is possible only when the defect properties are taken into account (Urusov et al., 1997). It is obvious that the degree of the so-called trapping effect (Urusov and Kravchuk, 1978), i.e., a relative increase in partition coefficient, can be different depending on the nature and concentration of defects differently reacting to changes in the external and internal state parameters of the system.

Two variants of experimental techniques were proposed to analyze the species and incorporation limits of element in minerals (Tauson, 1999b). In the first variant, the incorporation limit is determined as the maximum content of element admixture dispersed in the host-mineral structure under given *PT*-conditions, i.e., the part of the bulk concentration of element that remains constant as the element content in the coexisting fluid phase increases. Varying the physicochemical conditions so that they favor the generation of particular type of defects in crystals, one can follow the corresponding change in the content of structurally bound admixture and thus establish its incorporation mechanism and limit. The second variant is study of phase composition correlation in the case of element partition among the mineral under study and the reference mineral, for which the incorporation limit of the element is reliably established. Irrespective of the incorporation mechanism (via defects or in other way), there is a range of element concentrations in which the partition law is fulfilled in the same form (reflecting the mass action law) as for typical isomorphous mixtures. Parameters specifying the concentration of active defects must be fixed, thus ensuring the conditions of apparent phase composition correlation. Using the partition constant and the incorporation limit of element in the reference mineral, one can estimate the same incorporation limit for the mineral under study (Tauson, 1999b). Based on the second variant, we concluded that under equilibrium, the chemical potential of gold must be equal in

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