Available online at www.sciencedirect.com
ScienceDirect
Russian Geology and Geophysics 55 (2014) 273–289
RUSSIAN GEOLOGY AND GEOPHYSICS
www.elsevier.com/locate/rgg

Structurally and superficially bound gold in pyrite from deposits of different genetic types

V.L. Tauson *, R.G. Kravtsova, N.V. Smagunov, A.M. Spiridonov, V.I. Grebenshchikova, A.E. Budyak

A.P. Vinogradov Institute of Geochemistry, Siberian Branch of the Russian Academy of Sciences, ul. Favorskogo 1a, Irkutsk, 664033, Russia

Received 28 December 2012; accepted 10 April 2013

Abstract

The gold distribution in 32 pyrite samples and some samples of other ore minerals is studied using the method of statistical samplings of analytical data for single crystals. The samples were recovered from deposits of different genetic types within the largest gold provinces of Russia and Uzbekistan. The contents of uniformly distributed gold and the ratios of its structurally to superficially bound forms have been determined. According to the Au–As diagram for the chemical states of gold, uniformly distributed gold in pyrite is chemically bound in the overwhelming majority of cases. The previous experimental data suggest that it is partly incorporated into pyrite and partly into the structures of nanosized nonautonomous phases on the surface of the pyrite crystals. Micro- and nanoparticles of native gold might appear during postgrowth transformations of these phases. Data on the other ore minerals suggest that the dependence of the content of uniformly distributed gold on the size or specific surface area of the crystal and the superficial position of its considerable part are common to the ore minerals. It is shown for pyrite that the observed features are commonly found at deposits of different genetic types, only with differences in the slope and determination coefficients of the dependences. The size dependences of the contents of gold and other elements in pyrite are genetically significant, because they give an insight into the ore-forming processes. The data on structurally bound gold permit comparative evaluation of gold concentrations in ore fluids forming gold deposits of different genetic types.

Keywords: gold; pyrite; speciation; distribution; surface; nonautonomous phase; gold deposits

Introduction

Various and numerous hypotheses are now put forward about the character of processes giving rise to ore deposits: from exclusively magmatic to exclusively biogenic (Vinichenko, 2009, p. 233). Geology as a phenomenological science might content itself with the answer that the truth is in between. However, this answer cannot be satisfactory for geochemistry, which is based on the study of mass balance and on precise chemical laws. Therefore, the state of matter in solutions and melts is widely studied to determine the forms of chemical elements participating in the given processes and the physicochemical conditions of their existence. However, mineral phases still do not receive enough attention, and speculations on the causes and conditions of ore-deposit formation are partly due to this. We need methods which would demonstrate, for example, that the metal accumulates in the crystal structure of the ore mineral at high *TP*-parameters. It follows the distribution patterns controlled by equilibrium thermodynamics rather than the selectivity of microorganisms. Otherwise, the causes of disobedience, which might include bacterial activity, have to be searched for.

As an almost ubiquitous transient mineral, pyrite is one of the most interesting and convenient subjects for such studies. It is associated with the unsolved problem of "invisible" gold, found not only in pyrite but also in other sulfides and chalcogenides (Ciobanu et al., 2009; Reich et al., 2010). There is abundant evidence that submicroscopic gold, invisible under optical microscopes, is localized within the surface layer of pyrite crystals. A small amount of data on the Au–Ag deposits of northeastern Russia previously showed that more than 90% of invisible gold is in superficially bound form (Tauson and Kravtsova, 2002; Tauson et al., 2002). According to S.H. McClenaghan et al. (2004), invisible gold is adsorbed as submicroscopic inclusions onto As-enriched surfaces of pyrite

* Corresponding author.
E-mail address: vltauson@igc.irk.ru (V.L. Tauson)

1068-7971/$ - see front matter
http://dx.doi.org/10.1016/j.rgg.2014.01.011

and arsenopyrite in the metamorphosed Zn–Pb–Cu–Ag rocks of the Bathurst Mine (Canada). Considerably higher Au contents of the rims compared to the cores of pyrite crystals from sulfidized boundaries of dike breccias at the Mule Canyon Mine (Lander County, Nevada) were pointed out by D.A. John et al. (2003). The example of arsenian pyrite from the Twin Creeks gold deposit (Nevada) was used by G. Simon et al. (1999) to show that the highest gold contents are observed in the most fine-grained pyrite at some paragenetic stages of mineralization. Monovalent gold was found in As-enriched pyrite with grains from <2 to 10–30 μm in size. The highest content (1465 ppm) was observed in anhedral pyrite grains smaller than 2 μm in size. On the other hand, most of the data show that low-As pyrite cannot contain more than 5 ppm structurally bound Au, which is consistent with the experimentally observed Au solubility in FeS_2 at 500 °C and 1 kbar (3 ± 1 ppm) (Tauson, 1999).

Thus, fragmental and mostly qualitative evidence is available that invisible Au can be chemically bound in the structure and on the surface of pyrite crystals. This statement will be confirmed by quantitative data in the present paper.

Subjects of study

Structurally and superficially bound gold in pyrite was studied at gold deposits within the largest gold-bearing provinces in northeastern Russia (Dukat, Dal'nee, Oroch, Natalka, and Degdekan), Amur region (Pokrovskoe), East Siberia (Sukhoi Log), eastern Transbaikalia (Amurskie Daiki), East Sayan (Zun-Kholba), and West Tien Shan (Kochbulak and Kyzylalmasai). The deposits, which were of different ages and geneses, contained different types of mineralization. Gold-bearing pyrite was studied from samples characterizing productive stages and mineralization stages at deposits of conventional ore assemblages as well as unconventional mineral resources.

Northeastern Russia. Studies in northeastern Russia were conducted for Au–Ag and Au–quartz deposits. The Au–Ag deposits are localized in different metallogenic structures of the central Okhotsk–Chukchi Peninsula volcanic belt (Dal'nee, Oroch, and Dukat). The orogenic structures of the Yana–Kolyma gold-bearing belt are related to the Degdekan and Natalka sulfide-poor mesothermal Au–quartz deposits.

The Dal'nee and Oroch volcanogenic Au–Ag deposits (Late Cretaceous) have all the geologic and mineralogic features of a vein-type epithermal Au–Ag ore assemblage. The veins consist of quartz (90–95%), adularia (5–10%), sericite, hydromica, carbonate, kaolinite (1–10%), and ore minerals (1–3 %). The most widespread ore mineral is pyrite, and the principal minerals are acanthite, electrum, proustite, pyrargyrite, native Au and Ag, polybasite, and stromeyerite. Galena, sphalerite, chalcopyrite, and gray copper ores are rare (Kravtsova, 2010).

The Dukat volcanoplutonogenic Au–Ag deposit (Late Mesozoic), unlike the Dal'nee and Oroch deposits, went through a long and complicated evolution. The ores, which occur in a series of contiguous veins and mineralized zones, are characterized by multistage development and complicated composition. The principal vein minerals are quartz (50–75%), adularia (7–28%), rhodonite (up to 25%), chlorite, and rhodochrosite (up to 5%), hydromica, and sericite (1–2%). The main Ag minerals are acanthite, native Ag, kustelite, proustite, pyrargyrite, gray copper ores, and freibergite. Gold occurs as electrum. The most widespread ore minerals are galena and sphalerite as well as chalcopyrite and pyrite (Konstantinov et al., 1998).

The Natalka and Degdekan gold deposits (Late Paleozoic) are confined to the edge of a presumed granite pluton in the zone of the Ten'ka deep fault and related to a collision stage in the development of the Yana–Kolyma folded system. Both deposits are marked by complicated polygenetic and multistage development and, according to most researchers, by metamorphic-hydrothermal mineralization.

The Natalka deposit belongs to the Au–quartz ore assemblage, to a low-sulfide Au–quartz–arsenopyrite type. Despite all its diversity, mineralization at the deposit of unique extent is observed as a homotypic ore accumulation, which consists of quartz, quartz-sulfide, and quartz-carbonate veins and veinlets as well as veined and vein-disseminated metasomatic segregations. The nonmetallic minerals are dominated by quartz (70–80%), which coexists with carbonates and feldspar (20–30%). The ore minerals are dominated by pyrite and arsenopyrite, which coexist with pyrrhotite, galena, sphalerite, scheelite, chalcopyrite, native Au, and, less often, ilmenite and rutile (1–3%) (Goncharov et al., 2002).

The Degdekan deposit belongs to the Au–quartz–sulfide type of the Au–quartz ore assemblage. Two mineralization stages are defined: hydrothermal-metamorphic and hydrothermal. Productive Au-sulfide mineralization (Au-pyrite and Au-arsenopyrite-pyrite ores) formed during the initial stage of the hydrothermal process. The main ore mineral is pyrite, and arsenopyrite is less widespread. Gold mainly occurs in native form. Complex ores are still more rare, and gersdorffite is seldom observed (Mikhailov et al., 2010).

Amur region. The Pokrovskoe epithermal Au–Ag deposit (Early Cretaceous), confined to the Tygda–Sergeevka intrusive-dome uplift, is localized at the edge of the Sergeevka pluton of Early Cretaceous granitoids, which adjoins the Ulunga depression with the Pokrovka paleovolcanic structure and the Pokrovskoe deposit at the periphery. The orebodies consist of granitoids and volcanics argillized and silicified to different extents, with veined and vein-disseminated Au–Ag mineralization. The nonmetallic minerals are quartz (48–93.8%), hydromica (5–12%), kaolinite (5–7%), calcite, dolomite, ankerite (2–5%), and adularia (up to 3–5%). The ore minerals (0.5–3.5%) are pyrite, arsenopyrite, silver sulfosalts, argentite, and native Au and Ag (Khomich, 2001). Recent evidence shows the presence of nanosized Au in adularia and chalcedonic colloform quartz, with 38% nanosized gold and only 5% visible gold (Moiseenko et al., 2010).

East Siberia. The Sukhoi Log giant gold deposit is localized within the Late Proterozoic calcareous-black-shale metasedimentary rocks of the Baikal–Patom Highland. The