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Noble metal-graphite mineralization: A comparative study of the carbonaceous granite-gneiss complex and shales of the Russian Far East

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ABSTRACT

A new noble metal-graphite mineralization has been revealed in the Ruzhino amphibolite-facies rocks of the northern Khanka block. It is characterized by Au and PGE (platinum group elements) contents (up to tens g/t, Pt > Au) as high as those in world-class deposits hosted by sedimentary and magmatic rocks, but is distinguished from them by isotopic composition of carbon, hydrogen and oxygen, all suggesting a distinct mantle contribution ($\delta^{13}C_{VPDB}$ from −8.5 to −10.5‰ in graphite, δD_{VSMOW} from −82.5 to −106.7‰ and $\delta^{18}O_{VSMOW}$ from 8.2 to 10.1‰ in biotite). The Ruzhino-type mineralization is highly resistant to common chemical treatments, so that detection of their metals requires that some special methods be developed. Atomic Absorption Spectrophotometry and Inductively Coupled Plasma Mass Spectrometry following severe chemical treatments and ignition at 600–650 °C, as well as Ion Mass Spectrometry allowing a direct detection of elements in solid materials were employed in this study. These methods increased noble-metal contents of the graphitized rocks compared to standard analyses including a conventional fire assay. In addition, electron microscopy surveys discovered extremely diverse native-metal and intermetallic complexes with C, O, Cl, F, REE and other elements. The microinclusions, however, represent a minor part of the mineralization. Major constituents seem to form carbonaceous nanocompounds invisible under a microscope. These graphite-based nanocomplexes, which are especially developed in the case of Pt, seem to be responsible for the highly resistant character of the Ruzhino mineralization. They also may be present in the latent form among the common Au ± PGE ores hosted by carbonaceous shales like those we studied in the close vicinity of the Ruzhino amphibolite-facies rocks and in the northeastern Bureya–Jiamusi terrane.

1. Introduction

Noble-metal mineralization is well known in carbon-bearing sedimentary and magmatic rocks commonly metamorphosed at the greenschist facies. This is true for many of world-class deposits, including Bushveld, South Africa (Ballhaus and Stumpfl, 1985), Stillwater, U.S.A. (Volborth and Housley, 1984), Sudbury, Ontario, Canada (Wright et al., 2010), Kempirsai, Kazakhstan (Melcher et al., 1997), Sukhoi Log, Russia (Distler et al., 2004; Razvozzhaeva et al., 2008), Macraes, New Zealand (Craw, 2002), Carlin-type deposits in USA and China (Li and Peters, 1998), Coronation Hill and other epithermal sediment-hosted deposits in Australia and Brazil (Mernagh et al., 1994; Sener et al., 2002), and many others. What is more, carbon is considered to play a significant role in ore-forming processes, in particular the transportation of noble metals by C–O–H ± S ± Cl ± F fluids and their precipitation under the reducing influence of organic matter and graphite in host rocks (Ballhaus and Stumpfl, 1985; Boudreau and McCallum, 1992; Hulen and Collister, 1999; Mogessie et al., 1991; Pasava, 1993). This is supported by many experimental studies that have shown an ability of carbon to form compounds with gold and PGE under hydrothermal and sedimentary conditions (Bittencourt et al., 2008; Dunaev et al., 2008; Kubrakova et al., 2010; Plyusnina et al., 2000, 2004, 2009; Tressaud and Hagenmuller, 2001; Varshal et al., 2000). However, the major economic value of noble-metal ores is currently based on carbon-free minerals such as native precious metals, their alloys with base metals, sulfides, and oxides, as well as arsenides, tellurides, bismuthides, selenides, and antimonides (Daltry and Wilson, 1997; Kaukonen, 2008; Naldrett et al., 2008). Their particles are commonly hosted by or intergrown with quartz and other silicates, as well as base-metal sulfides and oxides. Compounds of noble metals with carbon and/or noble-metal minerals in a direct contact with hydrocarbons, amorphous carbon, or graphite are, on the other hand, quite rarely reported (e.g., Berdnikov et al., 2010; Crespo et al., 2006; Khanchuk et al., 2007; Kucha, 1981; Kucha and Plimer, 1999; Kucha and Przybylowicz, 1999).

How to explain this? Two possible scenarios exist: either the natural affinity between carbon and noble metals is not implemented in

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ores for some unknown reason, or the methods commonly applied to detect and extract carbon-bound metals are imperfect. Our studies of graphite-associated noble-metal mineralization, the results of which have been published primarily in Russian and partly translated into English (Khanchuk et al., 2004, 2007, 2009, 2010a,b), will be reviewed and summarized in this paper along with a presentation of our most recent data in order to illuminate the scientific and, possibly, economic issues of this problem. In addition, the paper develops interpretations based on all data collected.

2. Geological setting

Graphite-bearing rocks of various metamorphic grades, all located in the Bureya–Jiamusi–Khanka superterrane at the eastern termination of the Central-Asian Orogenic Belt, were the subject of the present research (Fig. 1). This superterrane is composed of the late Pan-African (500–525 Ma) granite-metamorphic complexes overlapped by the Middle Paleozoic–Jurassic subduction-related volcano-sedimentary units, collisional and post-collisional dynamo-metamorphic formations and related magmatic complexes (Dacheng et al., 2004; Khanchuk et al., 2010a,b; Mishkin et al., 2000; Wilde and Wu, 2003; Wu et al., 2007; Zhou et al., 2010). The protolith of the Pan-African metamorphic rocks has Rb – Sr, Sm – Nd and U – Pb ages ranging from 700 to 1000 Ma with a single zircon date as old as 2090 Ma, suggesting that the Khanka and Bureya–Jiamusi blocks were jointly derived from either Gondwana or the North Asian Craton (Wilde and Wu, 2003; Zhou et al., 2010). The blocks collided with the Sino-Korean Craton in the Late Permian-Early Triassic (Dacheng et al., 2004) and with the Songliao block of Central-Asian Orogenic Belt, during the Triassic-Early Jurassic (Zhou et al., 2010). Some magmatic events occurred in the region in the Mid Paleozoic time (Tsygankov et al., 2010) including intrusions of granitic and alkaline rocks associated with rare-metal-fluorite mineralization in the Voznesenka Terrane (Krymsky and Belyatsky, 2001; Sato et al., 2003).

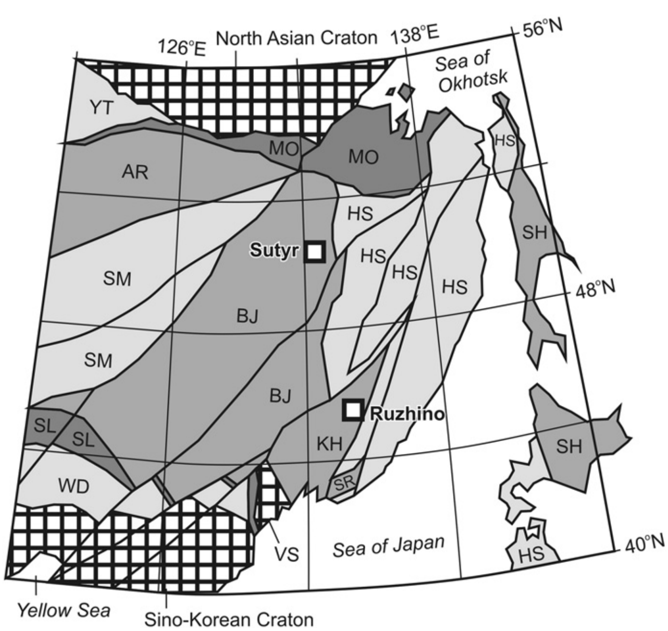

Fig. 1. The East Asia terrane scheme (simplified after Khanchuk, 2001) showing the Ruzhino and Sutyr locations (see Figs. 2 and 3 for details). Terrane abbreviations: VS — Voznesenka (Archean–Permian); BJ and KH — Bureya–Jiamusi and Khanka (Late Proterozoic–Permian), SR — Sergeevka (Cambrian–Ordovician); YT — Yenisey–Transbaikal (Vendian to Early Ordovician), MO — Mongol–Okhotsk (Devonian to Late Jurassic), AR — Argun–Idermeg (Late Proterozoic–Cambrian), SM — South Mongolia–Khingan (Ordovician to Carboniferous), SL — Solon (Carboniferous to Permian), WD — Wundurmiao (Riphean to Ordovician), HS — Honshu–Sikhote–Alin (Jurassic to Early Cretaceous), SH — Sakhalin–Hokkaido (Cretaceous).

2.1. Khanka terrane

Graphite-bearing metamorphic rocks of the northern Khanka terrane serve as a central subject of our study. They were sampled at quarries in the Lesozavodsk graphitization district, 1900 km^2 in size, established as a result of exploration performed in the middle of the 20th Century (Solonenko, 1951). We have named this area the Ruzhino noble-metal occurrence, including the Turgenevo and Tamga graphite deposits. The graphite mineralization is hosted by Proterozoic–Cambrian volcano-sedimentary rocks metamorphosed into granulites, amphibolites and green schists there.

The granulites and amphibolites form cores of narrow, tightly compressed folds of latitudinal and less often northwestern and northeastern orientation, enclosed in the larger dome-like structures, all cut by numerous faults of different strike. Gabbro and granite intrusions of the Mid Paleozoic–Mesozoic age outline the dome structure and occupy its center, whereas the Lower Paleozoic granite seems to be distributed independently.

The Ruzhino noble-metal occurrence particularly is dominated by amphibolite-facies rocks including intercalation of garnet-biotite-feldspar and biotite-quartz-feldspar crystalline schists with marble. There also are conformable injections of biotite and leucocratic granites, some of which are rich in K, as well as thin (up to 1 m) dikes of K-rich syenitic lamprophyre. Marble is altered into garnet-diopside skarn at the contacts with granite. Carbonaceous green schist-facies rocks, outcropped at the southern edge of the Ruzhino occurrence, were involved in our study for comparison. They are composed of fine-crystalline quartz, sericite, amorphous carbon, and graphite (total carbon up to 12%) with some admixture of chlorite. We will conventionally call them carbonaceous shale, black shale or just shale to emphasize their principal difference from the amphibolite-facies schists noted above.

2.2. Bureya–Jiamusi terrane

Carbonaceous shales were sampled on the left bank of the Sutyr River, the northeastern Bureya–Jiamusi terrane (Fig. 1). These rocks belong to the Upper Riphean–Lower Cambrian formation consisting of mudstones, phthanites, siltstones, sandstones, limestones, dolomites, jasper-like rocks, magnetite-hematite ores, rhyolites, rhyolitic tuffs, and basalts of 1800–2000 m in total thickness. The shales contain disseminated organic matter (1–22%) with some addition of graphite flakes 0.001–0.03 mm in size (Berdnikov et al., 2010). Fine networks of quartz veinlets were observed in some places of the sections studied. Sulfides form disseminated inclusions up to 1 mm in size, as well as veinlets and lenses 0.5–2 cm in length. They are represented by common pyrite and subordinate pyrrhotite, chalcopyrite, arsenopyrite, covellite, and marcasite. Up to 0.1 g/t Au, 0.04 g/t Pt, and 0.01 g/t Pd were previously detected in these rocks by means of semi-quantitative spectral analysis.

3. Analytical methodology

K – Ar dating of biotite was performed through isotopic analysis of argon in a continuous helium flow at the Analytical Center of FEGI FEB RAS, Vladivostok (Table 1). By this method, argon is extracted from a

Table 1
O and H isotopic compositions and K/Ar dating of biotite associated with graphite in the Ruzhino rocks.

Sample	Host rock	δD_{VSMOW}, ‰	$\delta^{18}O_{VSMOW}$, ‰	K, %	Ar_{air}, %	Ar_{rad}., ng/g	Age, Ma
Tg09/2	Granite	−106.7	8.2	6.51	5	177.1 ± 4.5	362 ± 10
Tg09/3	Granite	−82.5	10.1	7.46	2	203.7 ± 6.5	363 ± 13
Tg09/4	Schistose inclusion in granite	−90.1	9.5	6.58	8	144.8 ± 5	298 ± 11