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Significance of Late Devonian – Lower Carboniferous ages of hydrothermal sulphides and sericites from the Urals Volcanic-Hosted Massive Sulphide deposits

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ABSTRACT

Formation of the Urals Volcanic-Hosted Massive Sulphide (VHMS) deposits is considered to be related with the intra-oceanic stage of the island arc(s) development in Late Ordovician – Middle Devonian time (ca. 460–385 Ma) based on the biostratigraphic record of ore-hosting sedimentary rocks. However, the known radiometric ages of ore hosting volcanics are very limited. Here we present direct dating results of sulphide mineralisation from the Yaman-Kasy and Kul-Yurt-Tau VHMS deposits using Re-Os isotope systematics showing similar mineralisation ages of 362 ± 9 Ma and 363 ± 1 Ma. These ages coincide with the previous Re-Os dating of the Alexandrinskoe (355 ± 15 Ma) and Dergamysh (366 ± 2 Ma) VHMS deposits. This Late Devonian (Famennian) age corresponds to the late stage of the 'Magnitogorsk arc – Laurussia continent' collision event and coincides with a beginning of large scale subduction-related granitoid magmatism. The younger mineralisation age relative to the biostratigraphic ages of host rocks is interpreted as one of the latest episodes of the multi-stage history of VHMS deposits development. Ar-Ar ages of sericites from metasomatic rocks of Barsuchi Log and Babaryk deposits show even younger ages clustering around 345 Ma, and testify another late hydrothermal event in the history of the Urals VHMS deposits.

1. Introduction

The Urals is considered to be one of the world's largest Volcanic-Hosted Massive Sulphide (VHMS) deposits provinces, trailing only the Iberian Pyrite Belt VHMS Province (Spain-Portugal) in term of ore reserves. The VHMS deposits in the Urals are considered to be formed within an intra-oceanic arc setting in Late Ordovician – Early Devonian time (e.g., Herrington and Brown, 2011; Prokin and Buslaev, 1999) based on biostratigraphy of ore-hosting sedimentary rocks (e.g., Herrington et al., 2005; Artyushkova and Maslov, 2008; Puchkov, 2010).

Radiochronological U-Pb dating of zircons in the Urals is limited to intrusive magmatism (mainly granites and diorites; e.g., Fershtater et al., 2007), whereas the massive sulphide deposits are related with Ordovician to Middle Devonian magmatism mainly developed in the form of volcanic eruptions (e.g., Puchkov, 2010). The comagmatic plagiogranite intrusions, which were penetrated by some drill holes at deep levels of massive sulphide deposits, have not been studied. The Rassypnyansky tonalite-trondhjemite pluton is the only large intrusive body which has been dated, with U–Pb zircon ages from 411 ± 9 (inherited xenocryst) to 393 ± 6 Ma (Early Devonian; interpreted as crystallisation age).

Moreover, some direct Re-Os dating of sulphide ores from two VHMS deposits (Dergamysh and Alexandrinskoe) shows Late Devonian age of 366 ± 2 Ma (Gannoun et al., 2003), and Lower Carboniferous age of 355 ± 15 Ma (Tessalina et al., 2008), respectively, which are at least 25 Ma younger than the expected Early Devonian biostratigraphic ages of their hosting volcano-sedimentary sequence (Tesalina et al., 2003; Artyushkova and Maslov, 2008).

The Re-Os ages of two studied deposits (Gannoun et al., 2003; Tessalina et al., 2008) coincide with Famennian intrusive complexes that complete the island-arc evolution of the Magnitogorsk Megazone with zircon ages in a range from 360 to 368 Ma (Fershtater et al., 2007). The emplacement of these plutons marked the beginning of large-scale granitoid magmatism of the Paleozoic Ural Orogen, and was accompanied by deposition of the thick flyschoid sequence of the Zilair Formation. Interestingly, the U-Pb dating of gabbroic rocks from the Magnitogorsk megazone (38 grains) doesn't show ages older than 360 Ma (Fig. 4 in Fershtater et al., 2007).

Previous K-Ar ages for ore-related alteration sericites from nine Urals VHMS deposits are summarised by Buslaev and Kaleganov (1992) and show a range of apparent ages of 390 to 301 Ma,

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corresponding to Middle Devonian-Upper Carboniferous (Gzhelian) time interval, although K-Ar data must be considered with caution since one cannot evaluate the veracity of any given date.

These consistently younger Re-Os and K-Ar ages contradict the assumption that the VHMS ore deposits are formed in close temporal relationship with spatially associated submarine volcanism (e.g., Huston et al., 2010) and argue for either some kind of resetting/perturbation of the Re-Os and K-Ar isotopic systems, or that multiple hydrothermal events affected the VHMS deposits. However, the published Re-Os isochron ages from only two VHMS deposits do not allow a reliable test of a possible younger overprint. Similarly, the available K-Ar ages were determined >20 years ago and are not considered reliable compared to the more robust and self-assessing technique like $^{40}Ar/^{39}Ar$. To redress this problem, we studied two Urals VHMS deposits (Yaman-Kasy and Kul-Yurt-Tau) using Re-Os isotope systematics or ore sulphides, together with $^{40}Ar/^{39}Ar$ analysis of sericite from ore-bearing metasomatic rocks located at the Babaryk (Alexandrinskoe ore field) and Barsuchi Log deposits, using up-to-date analytical techniques.

2. Model of the Urals VHMS deposits formation

The formation of the Urals VHMS deposits is currently though to occur in Late Ordovician to early Devonian time in intra-oceanic arc setting (e.g., Herrington et al., 2005; Prokin and Buslaev, 1999), synchronous to the formation of ore-bearing volcano-sedimentary rocks which have been dated using biostratigraphy (e.g., Artyushkova and Maslov, 2008; Puchkov, 2010). According to current model, the formation of the Urals VHMS deposits spent a period of time of ca. 80 Ma (461–385 Ma) starting from Late Ordovician to Late Devonian, separated into several metallogenic epochs. The oldest one is related with the Ordovician Guberlya arc (Dubinina and Ryazantsev, 2008; Puchkov, 2010, 2016), hosting several VHMS deposits in Sakmara zone, including the Yaman-Kasy deposit. Next stage of the VHMS deposits formation is related with the Tagil arc, which occurs in the Northern part of Urals and not considered in this study (see Prokin and Buslaev (1999) for more details). The latest Devonian (407–392 Ma) epoch is linked to the Magnitigorsk arc and host several VHMS deposits including Kul-Yurt-Tau, Babaryk and Barsuchi Log. The geological history and chronostratigraphy of the Devonian mineralisation and related sedimentation in the Southern Urals was characterized in detail using the conodont scale (Artyushkova and Maslov, 2008), giving constrains on the age of volcanics and associated VHMS deposits, and is briefly outlined below.

During the *serotinus* Zone (Emsian, Lower Devonian; 397–407 Ma), relatively vigorous volcanism begins in the submarine extensional structures (rifts). Rhyolite-basaltic volcanogenic sequences of this age (Baimak-Buribai and Kiembai formations in the Magnitogorsk Megazone) formed and host numerous polymetallic deposits of Kuroko type (e.g., Balta-Tau, Kul-Yurt-Tau, Barsuchi Log).

A significant deepening of the basin was associated with rhyolite-basaltic volcanism in extensional settings (rifts) at the end of the *costatus* Conodont Zone and continued through the *australis* and *kockelianus* zones (Eifelian, Middle Devonian: 392–397 Ma), giving rise to the Karamalytash Formation, which hosts a large number of large and giant VHMS deposits of Uralian type within the Magnitogorsk zone (e.g., Uchali, Sibai, Alexandrinskoe).

No VHMS deposit formation is reported in rocks deposited in the period from the end of the Givetian to the early Frasnian (ca. 385 Ma), whereas the intense island-arc volcanism was still active on the territory of the East-Magnitigorsk Zone. The longest time span without any volcanic activity falls within the *punctata* – *rhenana* zones (Frasnian, Upper Devonian: 385–374 Ma), when the relatively shallow-water regime abruptly changed to a deep-water one. After a long dormant volcanic period and sedimentation the next extensive outbreak in volcanic activity falls within the Frasnian/Famennian boundary interval (ca. 374 Ma). The beginning of collision caused the accumulation of the Zilair flysch Formation in the West-Magnitogorsk zone, with volcanoclastic sediments supply from persistent volcanism in the East-Magnitogorsk Zone.

3. Geological setting and sampling

In this study, sulphide and sericite samples were collected for Re-Os and $^{40}Ar/^{39}Ar$ study from four VHMS deposits occurring in distinct geodynamic settings (Fig. 1).

3.1. Yaman-Kasy deposit

The Yaman-Kasy deposit is situated in the Orenburg district, Southern Urals (Fig. 1, location 4; Maslennikov et al., 2009) and restricted to the Sakmara zone's volcano-sedimentary bimodal sequence, which was previously interpreted as Silurian in age. Its tectonic structure however is not clear and was variously interpreted as: (a) an allochthon (e.g., Herrington et al., 2005); (b) back-arc basin (e.g., Zonenshain et al., 1990); (c) the Southern end of the Tagyl volcanic arc (Northern part of the Urals metallogenic structure; e.g. Prokin and Buslaev, 1999). Recent fauna dating (Dubinina and Ryazantsev, 2008; Ryazantsev et al., 2008) points to the Late Ordovician age and indicates that these volcanics are linked to the Ordovician Guberlya arc (Puchkov, 2010, 2016).

The mound-like Yaman-Kasy orebody (Fig. 2) consists of massive and clastic ore facies, with preserved fragments of sulphide chimneys and vent fauna. This is one of the best preserved Palaeozoic sulphide mound-like VHMS deposits, analogous to the modern black-smoker VHMS deposits. The hydrothermal chimney fragments were collected for this study, including 4 pyrite-marcasite samples from the outer wall, 2 chalcopyrite samples from the inner wall, and 1 pyrite-marcasite-sphalerite sample from the chimney core.

3.2. Kul-Yurt-Tau deposit

The studied Kul-Yurt-Tau deposit (Zaykov et al., 1988) is situated within the West-Magnitogorsk island arc (Fig. 1, location 2) and restricted to the middle part of Baimak-Buribai formation (Lower Devonian, Emsian: 397–407 Ma). This mound-like ore body occurs on the flank of a rhyolite-dacite dome within the volcaniclastic horizon. The felsic volcanic host rocks at the top and flanks of the ore body are transformed into sericite-pyrophyllite-quartz metasomatic rocks. The studied molybdenite samples form 0.1–2 mm thick coat-like aggregates in association with pyrophyllite within these metasomatic rocks (Zaykov et al., 1988).

3.3. Barsuchi log deposit

The Barsuchi Log VMS deposit is located in the Orenburg region east of the city of Orsk (Glasby et al., 2006), in the southern part of the Jusa ore field (Fig. 1, location 5). It occurs within a basalt – andesite – dacite – rhyolitic complex and is confined to the caldera of the Barsuchi Log stratovolcano, which is a part of the Karabutak Formation (ca. 395 Ma). The nucleus of the sulphide mound consists of homogenous massive copper ores surrounded by pyritized quartz – sericite – chlorite metasomatites. Banded ores are characterized by the interstratification of chalcopyrite – pyrite and sphalerite – galena layers. Sulphide ores from this deposit are generally well preserved, with relics of sulphidized fauna. Samples 9042A and B for this study were collected from sericite-bearing metasomatic rocks with sulphide veins (pyrite and minor covellite).

3.4. Babaryk deposit

The Babaryk deposit (Novoselov et al., 2006) is situated within the Alexandrinskoe ore field (Fig. 1, location 1) and considered to be the

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