Ore Geology Reviews 85 (2017) 131–139

Contents lists available at ScienceDirect

Ore Geology Reviews

journal homepage: www.elsevier.com/locate/oregeorev

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

Svetlana G. Tessalina [a],*, Fred Jourdan [a], Elena V. Belogub [b,c]

[a] John de Laeter Centre for Isotope Research, Institute for Geoscience Research (TIGeR), Curtin University, Kent St, Bentley, WA 6102, Australia
[b] Institute of Mineralogy, Urals Branch of Russian Academy of Sciences, 456317 Miass, Chelyabinsk District, Russia
[c] South Urals State University, Miass branch, 8 Iyulya St. 10, Miass, Chelyabinsk District, 456301, Russia

ARTICLE INFO

Article history:
Received 18 January 2016
Received in revised form 4 August 2016
Accepted 6 August 2016
Available online 7 August 2016

Keywords:
Urals
Volcanic-Hosted Massive Sulphide
Re-Os
Ar-Ar
Dating

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,

---

* Corresponding author.
E-mail address: Svetlana.Tessalina@curtin.edu.au (S.G. Tessalina).

http://dx.doi.org/10.1016/j.oregeorev.2016.08.005
0169-1368/

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, 2017), 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, 2017).

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 last stage of mineralisation of the adjacent Alexandrinskoe deposit. This polymetallic sphalerite-barite mineral occurrence has a subvertical structure and has undergone significant tectonic deformation. The ore-bearing metasomatic rocks and ores occur at the structural boundary between two lava flows.

The sample 5864/110.9 was collected from the ore horizon intersected by drill core and represents relatively fresh metasomatic rocks after breccia with clasts of sulphides and barites.

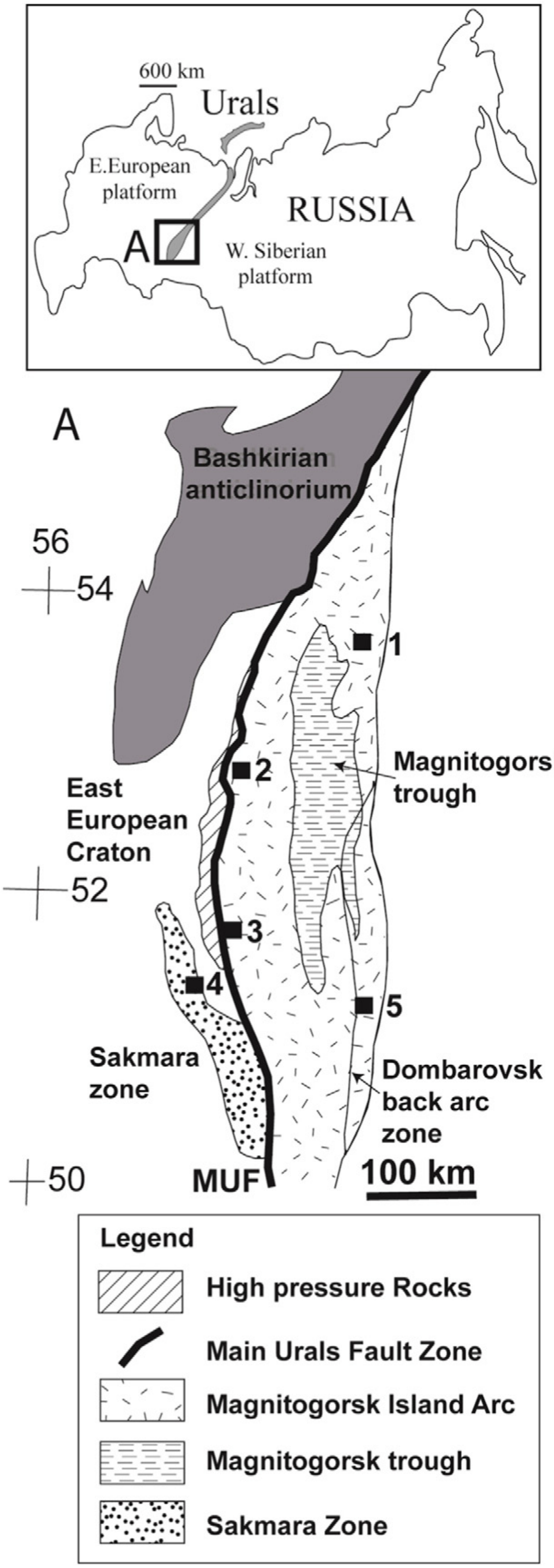

Fig. 1. Simplified geological map of the Southern Urals showing the main regions of arc volcanic sequences and the location of studied VHMS deposits. The following subdivisions are shown: (1) Main Urals Fault (MUF) suture zone with relics of ophiolite in a tectonic melange containing blocks with ages ranging from Ordovician up to Late Devonian; (2) Magnitogorsk island arc zone, consisting of volcanics and sediments of Devonian age. An intermediate "intra-arc" basin, filled by Late Devonian-Lower Carboniferous volcanics and sediments, divides the Magnitogorsk structure into the West and East-Magnitogorsk zones; (3) Sakmara zone, whose origin is not clear. Massive sulphide deposits: 1 – Alexandrinskoe and Babaryk, 2 – Kul-Yurt-Tau, 3 – Dergamysh, 4 - Yaman-Kasy, 5 – Barsuchi Log.

4. Analytical methods

4.1. Re-Os systematics

The Re and Os concentrations and the Os isotopic composition of pure sulphide samples were determined by negative thermal ionisation mass spectrometry (N-TIMS) using a Finnigan MAT-262 at the Institut de Physique du Globe de Paris. The analytical procedure was described by Birck et al. (1997). Approximately 0.1 to 0.15 g of sulphide samples were used for the analyses. Sample powders were spiked with a mixed ^{190}Os–^{185}Re spike. The sulphide samples were then dissolved in a HNO_3/CrO_3 solution. Os was extracted in liquid bromine and purified by microdistillation. The supernate was reduced by ethanol and Re was extracted and purified by liquid/liquid extraction with isoamylic alcohol and 2 N HNO_3. Total procedural blanks for Os ranged between 0.05 and 0.27 pg/g; ^{187}Os/^{188}Os values for the blanks ranged between 0.15 and 0.45. The Re blanks ranged between 5 and 10 pg/g with a mean value of 7 pg/g. Since total blank for both Re and Os was run as part of each batch of dissolutions, the appropriate blank correction for each batch was applied. For molybdenite, the same dissolution method was employed, with the only difference being a more enriched composition of mixed ^{185}Re-^{190}Os spike.

4.2. ^{40}Ar/^{39}Ar

We selected 3 samples for ^{40}Ar/^{39}Ar dating and separated homogenous, 250–300 μm-size grains of sericite. These minerals were carefully hand-picked under a binocular microscope. The selected sericite minerals were thoroughly rinsed with distilled water in an ultrasonic cleaner.

Samples were loaded into three small wells of one 1.9 cm diameter and 0.3 cm depth aluminum disc. These wells were bracketed by small wells that included Fish Canyon sanidine (FCs) used as a neutron fluence monitor for which an age of 28.294 ± 0.036 Ma (1σ) was adopted (Renne et al., 2011). The discs were Cd-shielded (to minimize undesirable nuclear interference reactions) and irradiated for 40 h in the US Geological Survey nuclear reactor (Denver, USA) in central position. The mean J-value computed from standard grains within the small pits is 0.008215 ± 0.00001561 (0.19%) determined as the average and standard deviation of J-values of the small wells for each irradiation disc. Mass discrimination was monitored using an automated air pipette and provided a mean value of 1.006299 (±0.34%) per dalton (atomic mass unit) relative to an air ratio of 298.56 ± 0.31 (Lee et al., 2006). The correction factors for interfering isotopes were $(^{39}Ar/^{37}Ar)_{Ca} = 7.30 \times 10^{-4}$ (±11%), $(^{36}Ar/^{37}Ar)_{Ca} = 2.82 \times 10^{-4}$ (±1%) and $(^{40}Ar/^{39}Ar)_K = 6.76 \times 10^{-4}$ (±32%).

The ^{40}Ar/^{39}Ar analyses were performed at the Western Australian Argon Isotope Facility at Curtin University. The samples were step-heated using a 110 W Spectron Laser Systems, with a continuous Nd-YAG (IR; 1064 nm) laser rastered over the sample during 1 min to ensure a

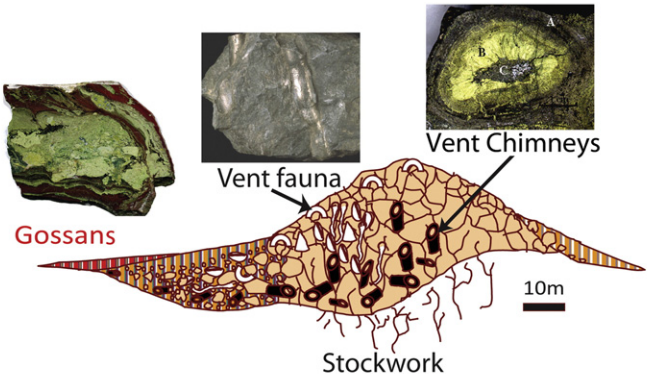

Fig. 2. Schematic cross-section across the Yaman-Kasy deposit (modified from Maslennikov et al., 2009). The fragment of hydrothermal chimney, vent fauna and clastic ore breccia with surrounding gossans are shown. Chimney consists of: A - outer pyrite-marcasite wall; B - inner chalcopyrite wall; C – pyrite-marcasite-sphalerite core.

homogenously distributed temperature. The gas was purified in a stainless steel extraction line using two SAES AP10 getters, a GP50 getter. Ar isotopes were measured in static mode using a MAP 215–50 mass spectrometer (resolution of ~450; sensitivity of 4×10^{-14} mol/V) with a Balzers SEV 217 electron multiplier using 9 to 10 cycles of peak-hopping. The data acquisition was performed with the Argus program written by M.O. McWilliams and ran under a LabView environment. The raw data were processed using the ArArCALC software (Koppers, 2002) and the ages have been calculated using the decay constants recommended by Renne et al. (2011). Blanks were monitored every 3 to 4 steps and typical ^{40}Ar blanks range from 1×10^{-16} to 2×10^{-16} mol. Ar isotopic data corrected for blank, mass discrimination and radioactive decay are given in Electronic Annex. Individual errors in Annex are given at the 1σ level. Our criteria for the determination of plateau are as follows: plateaus must include at least 70% of ^{39}Ar released. The plateau should be distributed over a minimum of 3 consecutive steps agreeing at 95% confidence level and satisfying a probability of fit (P) of at least 0.05. Plateau ages are given at the 2σ level and are calculated using the mean of all the plateau steps, each weighted by the inverse variance of their individual analytical error. All sources of uncertainties are included in the calculation.

5. Results

5.1. Re-Os in sulphides

The plot of the isotope data for the Yaman-Kasy ores on the Re-Os isochron diagram (Fig. 3; Table 1) defines a best-fit line with an age of 362 ± 9 Ma (MSWD = 3.4) and an initial ^{187}Os/^{188}Os ratio of 0.106 ± 0.016. The data indicate that scatter is present in the system, probably due to variable initial ^{187}Os/^{188}Os ratios in a seawater and hydrothermal fluid mixture (e.g., Brügmann et al., 1998), or/and to post-depositional hydrothermal fluid flow (see Discussion).

To complement the Re-Os age of sulphide ores by the isochron method, we analysed a molybdenite sample from the Kul-Yurt-Tau deposit. The absence of Os in molybdenite structure allows the direct dating because all measured Os can be ascribed to the radioactive decay of ^{187}Re isotope. The molybdenite age of 363.4 ± 1.1 Ma (Upper Devonian) for Kul-Yurt-Tau is identical within analytical error to isochron date for Yaman-Kasy (Table 2).

5.2. Ar-Ar in sericite

Two analysed sericite grains from the Barsuchi Log deposit (Fig. 4, A and B) yield two relatively precise plateau ages of 344.7 ± 2.0 Ma (MSWD = 1.6; P = 0.14) and 344.8 ± 2.9 Ma (MSWD = 1.3; P = 0.23), which include 76% and 100% of the total ^{39}Ar released, respectively. The third sample from the Babaryk deposit (Fig. 4, C) also yields a plateau age of 340 ± 7 Ma (MSWD = 0.89; P = 0.54), from 100% of the total ^{39}Ar released, but with a poorer precision compared to the other two samples, due to the small size of the grain investigated. No isochron could be calculated due to the clustering of the data near the radiogenic axis, which indicate the absence of a trapped (initial) component, and that all the ^{40}Ar released is radiogenic. All three ages agree within error.

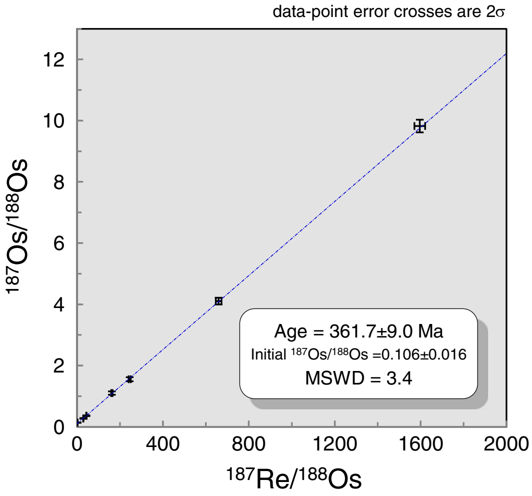

Fig. 3. Re-Os isochron diagram for the Yaman-Kasy deposit (see Table 1 for analytical dataset).

6. Discussion

The discrepancy between the age of ore-bearing volcano-sedimentary rocks and sulphide ores is rather puzzling giving that in most of the cases the Re-Os geochronology coincides with the age of ore-hosting rocks (e.g., Mathur et al., 1999), although in many cases showing scatter on Re-Os isochron diagram, and, in some cases, showing two types of fluids based on initial ^{187}Os/^{188}Os values (e.g., Lobanov et al., 2014). For example, Tharsis deposit from the Iberian Pyrite Belt was dated at 346 ± 26 (Mathur et al., 1999), which coincides with the age of ore-hosting black shales. The Altai VHMS deposits show more scatter on Re-Os isochron diagram with two possible model ages, one of which is significantly older than that of ore-hosting volcanics. The younger age was explained as metamorphic overprint (Lobanov et al., 2014).

To resolve this discrepancy between biostratigraphy and available Re-Os and K-Ar ages, and more fully understand the timeframe of volcanism versus ore formation, the application of modern radiochronological techniques for dating of ore-bearing volcanics and sulphide ores is required.

6.1. Re-Os geochronology of sulphides in geological context

The Re-Os isotope systematics are used for accurate isotopic dating and fingerprinting the source of metals. Both the parent (^{187}Re) and daughter (^{187}Os) are chalcophile and siderophile in character, leading to their enrichment in sulphide minerals relative to silicates. This is a unique combination of chemical and isotopic features which allows the direct dating of sulphide mineralisation. The common sulphide mineral molybdenite is particularly useful in this regard, because it often contains high concentrations of Re, but virtually excludes Os during crystallisation. Thus, no correction is required for the presence of initial Os.

The Re-Os isochron age for Yaman-Kasy deposit (362 ± 9 Ma) is identical to that of molybdenite dating from the Kul-Yurt-Tau deposit (363.4 ± 1.1 Ma) and is similar to the previous Re-Os isochron dating

Table 1
Re and Os concentrations and Os isotopic composition of hydrothermal chimney and clastic sulphides from the Yaman-Kasy deposit.

Ore facies	Sample #	Ore texture/ location	Mineral composition	Re (ppb)	Total Os (ppt)	^{187}Os/^{188}Os	^{187}Re/^{188}Os
Chimney	5A	Outer wall	Py-Mc	0.92	21.2	4.105 ± 0.110	659.36
	4A	Outer wall	Py-Mc	0.83	259.4	0.361 ± 0.013	43.58
	1A	Outer wall	Py	7.47	370.3	1.553 ± 0.065	245.24
	1A-2	Outer wall	Py	7.56	120.5	9.823 ± 0.207	1595.84
	1B	Inner wall	Chp	0.72	2134.5	0.137 ± 0.006	2.80
	4B	Inner wall	Chp	0.77	129.5	0.274 ± 0.011	29.31
	1C	Core	Py-Mc-Sph	0.38	15.5	1.101 ± 0.055	162.27

Note. Abbreviation used: Py – pyrite, Mc - marcasite, Sph sphalerite, Chp – chalcopyrite.

of the Dergamysh (366 ± 2 Ma; Gannoun et al., 2003) and Alexandrinskoe (355 ± 15 Ma; Tessalina et al., 2008) deposits (Table 3).

The Os isotopic composition can be used as evidence for the source of metals using the initial ^{187}Os/^{188}Os ratio from the isochron (e.g., Tessalina et al., 2008). As it was shown for the TAG hydrothermal system (Brügmann et al., 1998), the Os isotopic composition of the hydrothermal fluid approximates the Os isotopic composition of the rocks hosting the ore. The initial ^{187}Os/^{188}Os ratio of 0.106 ± 0.016 (Fig. 3) is close to that of Mid Ocean Ridge basalts (MORB; ^{187}Os/^{188}Os ~ 0.12), and indicate predominantly mantle source of Os. Moreover, the lead isotopic compositions of the Yaman-Kasy deposit (Tessalina et al., 2016) is comparable to that of the local Ordovician MORBs from the Urals (Spadea and d'Antonio, 2006), derived from highly depleted mantle metasomatized during dehydrational partial melting of subducted slab and oceanic sediments (see discussion in Tessalina et al., 2016). The Yaman-Kasy ores two-stage model ages (Stacey and Kramers, 1975) range from 400 up to 450 Ma and do not contradict to the Late Ordovician age for the ore hosting volcano-sedimentary rocks.

The Re-Os ages of ores are much younger than the biostratigraphic Late Ordovician age (ca. 461–444 Ma, Table 3) of the Yaman-Kasy hosting rocks, and ca. 40 Ma younger than the biostratigraphic Early Devonian age (ca. 400 Ma) of host rocks of the Kul-Yurt-Tau deposit (Artyushkova and Maslov, 2008; Table 3). Previously published Re-Os isotope data for the Alexandrinskoe (Tessalina et al., 2008) and Dergamysh (Gannoun et al., 2003) deposits also post-date the presumed biostratigraphic age of ore hosting volcanics by ca. 30 Ma (Table 3).

Thus, the repetitive Late Devonian Re-Os ages of sulphides for four studied Urals VHMS deposits are all younger than their respective host rocks based on biostratigraphy (Artyushkova and Maslov, 2008; Dubinina and Ryazantsev, 2008; Puchkov, 2010). This difference contradicts the assumption that the VHMS ore deposits are formed in a close temporal relationship with spatially associated submarine volcanism (e.g., Huston et al., 2010) and argue for a single event as responsible for the closure of the Re—Os 'clock' within these four Urals massive sulphide deposits. However, the Late Ordovician Yaman-Kasy deposit, with perfectly preserved initial seafloor hydrothermal facies such as chimneys and fauna, is clearly "syn-volcanic" and raises a question about what the Re-Os age actually means. In what follows, we examine several possible alternative models of the Urals VHMS systems formation to explain the meaning of the Re-Os ages.

The possible scenarios of the Urals VHMS systems formation include but not limited to: (A) deposits were formed on a seafloor of late Ordovician to early Devonian age with resetting of Re-Os and Ar-Ar by later hydrothermal activity or metamorphism; (B) the Re-Os ages reflect the true age of VHMS deposits formation, calling into question the reliability of biostratigraphic dating. However, the absence of absolute geochronological constrains for ore-hosting volcanics make us cautious while interpreting the Re-Os dating results. Resetting of Re-Os and Ar-Ar geochronometers would explain the age discrepancy between the ore-hosting rocks and mineralisation and discussed in more details below.

Table 2
Re-Os data for molybdenite from Kul-Yurt-Tay deposit, Urals. Note: all errors are 2δ absolute; decay constant uncertainty (±0.31) is included in age.

Sample	^{187}Re, ppm	^{187}Os, ppb	Re-Os age, Ma
625 KYT	6327.7	38,425 ± 106	363.4 ± 1.1

6.2. Resetting of Ar-Ar and Re-Os systems

6.2.1. ^{40}Ar/^{39}Ar system

The radioactive decay of ^{40}K to ^{40}Ar and its application in the ^{40}Ar/^{39}Ar dating method, is the basis of isotope age determination of micaceous clay minerals formed during diagenesis and hydrothermal alteration (e.g., Tessalina et al., 2015). As described in Verati and Jourdan (2014), sericite is a replacement mineral, commonly after feldspars, which yields its formation age when dated by ^{40}Ar/^{39}Ar, if the replacement level is at least 65% of the original plagioclase crystal, or date its formation age if sericite is precipitated as a hydrothermal mineral independent of feldspar replacement. The ^{40}Ar/^{39}Ar ages in sericites often show a range spanning the whole life of a hydrothermal system. This range includes the age of the end of the hydrothermal activity, which can be few Ma younger than the age of the ore formation itself. Such a phenomenon has been observed for example in the Xihuashan tungsten deposit in China (Hu et al., 2012).

The sericites selected for this study were all solid competent grains, suggesting that they formed from direct phase replacement. Further, in all cases, the flat age spectrum (Fig. 4) does not indicate any sign of post-crystallisation diffusion loss, nor recoil loss or redistribution (cf. Jourdan and Renne, 2014).

Our precise new ^{40}Ar/^{39}Ar ages from two studied deposits are ca. 20 Ma younger than Re-Os ages of sulphide ores from four VHMS deposits, clustering around 345 Ma (Fig. 4). One possible explanation for age discrepancies of ca. 20 Ma between Re-Os ages for sulphide ores and ^{40}Ar/^{39}Ar Ar ages for the metasomatised wallrocks, observed in the studied deposits, is that later phase of crystallisation of the sericite is due to relatively low-temperature (up to 150 °C) hydrothermal fluids, which precipitate the sericite that was dated in this study. Overprinting hydrothermal alteration might have occurred to alter earlier sericite in metasomatised wallrocks and form younger sericite at ca. 345 Ma (Verati and Jourdan, 2014). The relatively low temperature of the fluid required to form sericite would be too low to reset the Re-Os system in sulphides (closure temperatures in excess of 300 °C; Brenan et al., 2000), as has been proposed for some of the Japan ore deposits based on 3–12 Ma difference between Re-Os dating in molybdenite and K-Ar dating of whole rocks (Suzuki et al., 1996).

6.2.2. Re-Os system

The resetting of the Re-Os 'clock' could occur under the following circumstances: (A) post-ore re-homogenisation of Re-Os isotope system due to a metamorphic overprint; (B) incomplete homogenisation of two or more components with different initial Os ratios during ore deposition; and (C) later hydrothermal overprint leading to remobilisation of Os and/or Re.

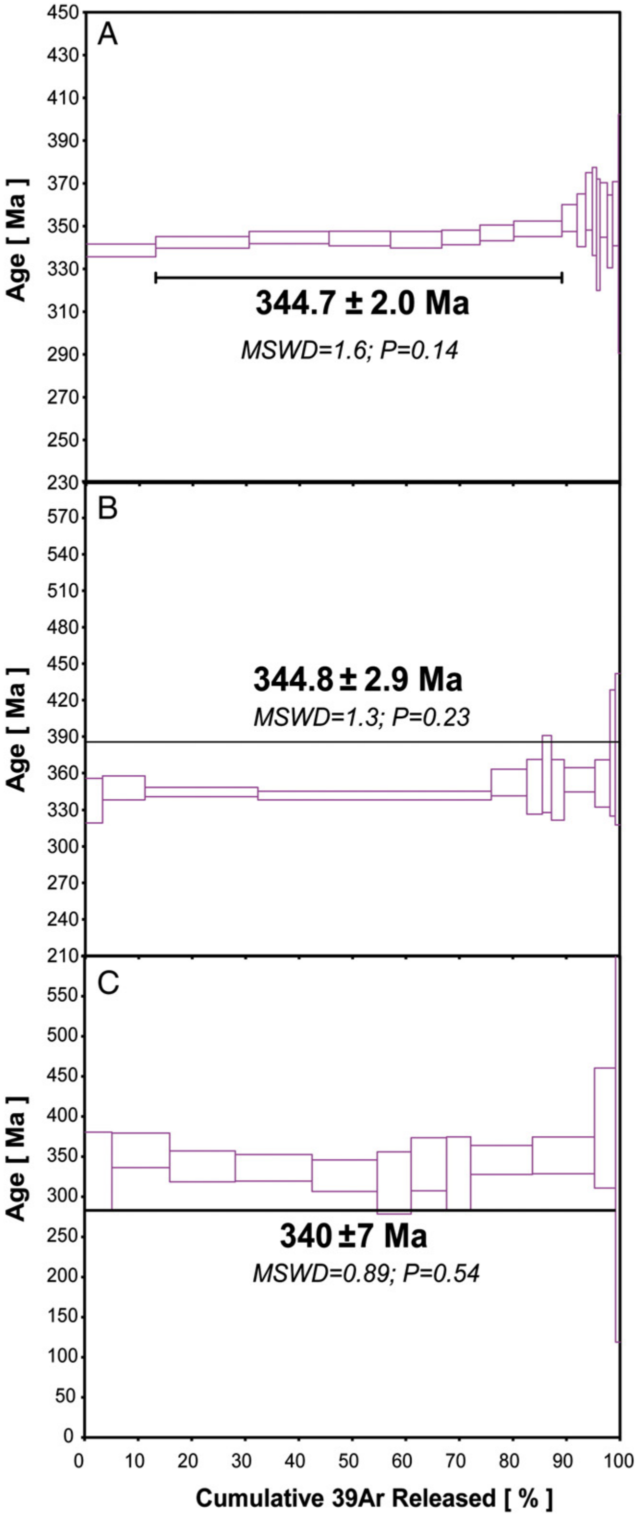

Fig. 4. ^{40}Ar-^{39}Ar age spectra on sericite from the Barsuchi Log (A and B) and Babaryk (C) deposits. The uncertainty is reported as 2σ and includes all sources of errors. The mean square weighted deviation (MSWD) and P values (probability) indicate that the reported ages are statistically valid.

(A) In the history of the Urals development, the Late Devonian (385–359 Ma) corresponds to the 'Arc-Continent' collision, which was associated with exhumation of high-pressure metamorphic complexes. This reason was recognised by Gannoun et al. (2003) as a possible cause for the young Re-Os age of the Dergamysh deposit. However, the good state of preservation of initial ore textures for the studied deposits (colloform structures, relics of hydrothermal chimneys and fauna) does not favour the metamorphic overprint.

(B) The formation of VHMS deposits is due to the mixture of at least two components represented by seawater and hydrothermal fluid, which may have different isotopic composition at the time of ore formation, with Os in hydrothermal fluids coming mostly from the leaching of host volcanic and sedimentary rocks (e.g., Brügmann et al., 1998; Tessalina et al., 2008). Mixture of hydrothermal fluid with seawater during ore formation could produce mixed isotopic characteristics at the time of ore formation, which subsequently evolved to yield linear data arrays of questionable age significance. However, the similarity of Re-Os ages for four VHMS deposits (Gannoun et al., 2003; Tessalina et al., 2008 and this study) makes this possibility very unlikely.

(C) Considering that the Re-Os 'clock' record the separate pulses of multi-stage, long-lasting hydrothermal activity, we have to conclude the existence of successive hydrothermal events which may re-mobilise Re and/or Os. This possibility is discussed below in the context of Urals development.

6.3. Implications for history of VHMS formation

Even though the rejuvenation of Re-Os ages may be due to some kind of re-setting or perturbation of the radioactive 'clock', a more likely explanation is that the four concordant Late Devonian Re-Os ages of ca. 365 Ma reflect a definitive closure of the Re-Os system and may have geological significance. According to accepted model, the formation of Southern Urals Volcanogenic Massive Sulphide deposits predates the collision event and spans a period of time from ca. 460 to 385 Ma, based on biostratigraphic studies of ore-hosting volcanic and sedimentary rocks (e.g., Herrington et al., 2005; Puchkov, 2010; Artyushkova and Maslov, 2008).

The Re-Os ages suggest that the formation of four Urals VHMS (this work; Tessalina et al., 2008; Gannoun et al., 2003) ended after the entrance of East-European (Laurussia) continent into the subduction zone, during the final stage of "Continent – Island Arc" collision. To determine the possible influences of these geological events, we summarise below the main stages of Urals island arc development in the Devonian – Lower Carboniferous period which is mainly concerned by our dating (Fig. 5).

In the Southern Urals, the initiation of intra-oceanic subduction during the Early Devonian (ca. 400 Ma) triggered the volcanism leading to the Magnitogorsk island arc development. By the Late Devonian, the young volcanic arc began to collide with the margin of the adjacent Laurussia continent. The timing of this collision event was established at 380–355 Ma, based on ^{40}Ar/^{39}Ar, U-Pb and Sm-Nd dating of high-pressure metamorphic rocks and sediments belonging to the continental margin (Beane and Connelly, 2000; Brown et al., 2006; Puchkov, 2010). The entrance of cooler and less dense continental crust into the subduction zone caused the cessation of magmatic activity for ~10 Ma (375–365 Ma; Fershtater et al., 2007) and decreased the angle of subduction slab, which in turn initiated the generation of shallow volatile-rich felsic magmas.

Felsic magma could also be formed as a result of melting of cumulates remaining from previous melting events in the mantle wedge (Nadeau et al., 2010). These cumulates may be enriched in some of the Highly Siderophile Elements (HSE: PGE, Au, Re; Nadeau et al., 2010). Metal-rich magmatic fluids released from volatile-rich felsic magmas, which are prevalent at convergent margins setting, may have contributed to the ore deposits formation (e.g., Huston et al., 2011), overprinting the previously formed sulphide edifices. The presence of magmatic aqueous-carbonic fluid with significant contents of H_2S has been detected in the Alexandrinskoe VHMS deposit (Bailly et

Table 3
Re-Os dating of selected Urals VMS deposits. Stratigraphic ages of ore hosting rocks are shown for comparison.

Deposit	*Geological setting*	*Stratigraphic age, Ma*	*Re-Os age*
Yaman-Kasy	Sakmara zone	Late Ordovician: 461–444	361.7 ± 9.0 Ma[a]
Dergamysh	Suture zone, tectonic melange	Early Devonian: 416–397	366 ± 2 Ma[b]
Kul-Yurt-Tau	West-Magnitogorsk island arc	Early Devonian-Emsian: 407–397	363.4 ± 1.1 Ma[a]
Alexandrinskoe	East-Magnitogorsk island arc	Middle Devonian-Eifelian: 392–397	355 ± 15 Ma[c]

[a] Reference - this work.
[b] Reference - Gannoun et al. (2003).
[c] Reference - Tessalina et al. (2008).

al., 1999). This fluid is typically associated with felsic magmas and capable to carry significant amounts of metals. For comparison, the Os contents of magmatic fluids from modern volcanoes (e.g., Yudovskaya et al., 2008) exceed the modern hydrothermal fluid contents (e.g., Sharma et al., 2000) by 4 orders of magnitude. It is evident that even tiny amounts of this metals-rich magmatic fluid will influence the Os (and Pb) budgets in the magmatic-hydrothermal system.

The recorded Re-Os ages for mineralisation fell into the late stage of the 'Urals island Arc – Continent' collision (380–355 Ma), which has been identified as melting of the mantle wedge and subducted crust in water-saturated conditions (Fershtater et al., 2007; Bea et al., 2002) and corresponded to large-scale granitoid magmatism. For example, the age of suprasubductional Akhunovo granites is the Mid-Famennian (365 Ma after Bea et al., 2002) and exactly coincides with the Re-Os ages of the deposits.

These intrusions would create a necessary heat source from the magma reservoir, which could promote the circulation of hydrothermal fluid in the order of a few millions years (von Quadt et al., 2011). The widespread spatial association between large subseafloor intrusions and massive sulphide deposits have been recognised for many massive sulphide districts around the world which range in age from Archaean to Cretaceous, as well as on the modern seafloor through deep-sea drilling (e.g. Galley, 2003). Only in the Precambrian, the VHMS camps spatially associated with felsic intrusions account for >90% of the aggregate sulphide tonnage (Galley, 2003). This association may be indicative for 'Mantle – Continental Crust' interaction which usually post-date the 'Arc – Continent' collision, and may be attributed to the similar tectonic processes within convergent continental margins which are responsible for ore deposit formation. Moreover, a magmatic fluid contribution from felsic intrusions has been suggested for a number of VHMS deposits (Huston et al., 2011). The magmatic-hydrothermal activity related to post-collisional magmatic processes could release HSE-rich fluids which could overprint and modify the original Re—Os isotope signature.

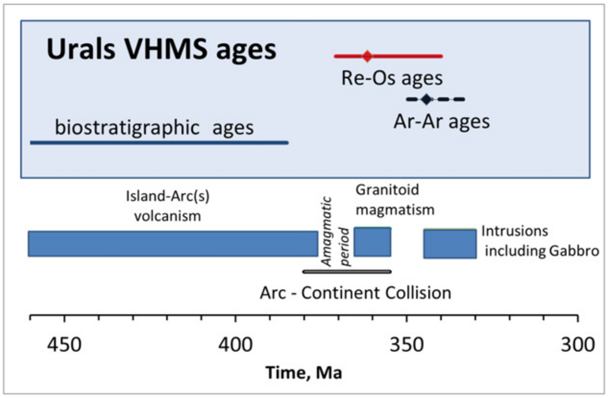

Fig. 5. Summary of available dating for the Urals VHMS deposits using the Re-Os and Ar-Ar isotopic systems (see references in the text), along with contemporaneous magmatic (Fershtater et al., 2007) and tectonic events (Beane and Connelly, 2000). Note that the time scale starts at 400 Ma, whereas the biostratigraphic ages starts at ca. 460 Ma.

However, the VHMS deposits are related to volcanic rocks, and no connection was established between Famennian intrusive complexes (mainly granites) and the VHMS deposits. Most of the VHMS deposits are cut by the gabbroic dykes. The gabbro-granite series magmatism in Magnitogorsk megazone ($n = 38$, Fershtater et al., 2007) was established in a period of time from 360 Ma to 320 Ma, with numerous intrusions including gabbroic one dated at 345–330 Ma (Fershtater et al., 2007; Fershtater, 2013a, 2013b). This age corresponds to the Ar-Ar age of studied deposits.

The geochemical signatures of the rocks belonging to the gabbro-granite series within the Magnitogorsk zone combine the marks of subduction- and rift-related origins. The initial basic magma was generated under the effect of the fluid that was released by dehydration in the subduction zone, as evidenced from distinct negative Nb and Zr anomalies and a positive Sr anomaly in gabbro (Fershtater et al., 2007). The magma crystallized with segregation of granitoid derivatives under extensional conditions of rifting that left a mark on the rock composition and caused the formation of eruptive breccia. Granitoids are characterized by elevated alkalinity and are enriched in HFSE and depleted in Sr, as is typical of rift-related igneous rocks (Fershtater et al., 2007).

More advanced studies are required to identify the exact location of VHMS deposits formation in a collisional geodynamic scenario.

6.4. Urals in a global geodynamic context

Viewed on a larger scale, the Devonian episode of volcanic and hydrothermal activity corresponds to the beginning of the Pangea supercontinent assembly by amalgamation of continental blocks. At that time, numerous microcontinents and volcanic arcs divided by basins of different character were present.

The closure of Uralian paleo-ocean corresponds to the amalgamation of Laurussia, Siberia and China-Korea paleocontinents. The fundamental plate boundary re-arrangements in the Late Devonian appears to be marked by intense magmatism under tectonic activation, manifested in island arc volcanism paired with episodic continental rifting, as well as hydrothermal activity on rifted or faulted outer continental margins, comprising large cluster of VHMS deposits in Spain and Portugal (Iberian Pyrite Belt province), Rudny Altai (Siberia), and the North American margin (Alaska) (e.g., Tornos et al., 2005; Chiaradia et al., 2006; Dusel-Bacon et al., 2004). These deposits are formed in local extensional, volcanic basins within an overall contractional geodynamic environment during or after termination of convergence by accretion of an island arc or crustal block (Huston et al., 2010), and are characterized by metal contributions from the continental crust.

The largest Iberian Pyrite Belt province was formed as a result of extension induced by oblique collision of tectonic blocks (Tornos et al., 2005), represented by an island arc and continental blocks (Gondwana and Laurentia plates) in the Late Devonian (ca. 355 Ma), about 10 Ma after the beginning of High-Pressure eclogite-facies metamorphism (365–370 Ma; Rodriguez et al., 2003).

The Devonian Rudny Altai Province (Siberia) is a host of several VHMS deposits. This terrain is a part of the Altaid orogen which formed by aggregation of Paleozoic subduction–accretion complexes and Precambrian basement blocks (e.g., Chiaradia et al., 2006).

The Zn-Pb-Ag mineralization along the ancient Pacific margin of North America (Alaska) was formed in the Late Devonian (ca. 370 Ma; Dusel-Bacon et al., 2004) in a within-plate (extensional) tectonic setting resulted from attenuation of the ancient continental margin of western North America, or as a result of development of an arc (Dusel-Bacon et al., 2004 and references therein).

Thus, the Urals represent only one example of large Devonian metallogenic province interpreted to be entirely formed within the intra-oceanic arc setting. This fact is rather ambiguous given that the modern deposits in intra-oceanic arcs tend to be small and form at low temperatures (Hannington et al., 2005). Further geochronological-field studies are needed to elucidate the place of VHMS deposits in the Urals history.

7. Conclusions

Direct dating results of sulphide mineralisation from the Yaman-Kasy and Kul-Yurt-Tau VHMS deposits using Re-Os isotope systematics show 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; Tessalina et al., 2008) and Dergamysh (366 ± 2 Ma; Gannoun et al., 2003) VHMS deposits. In the history of the Urals development, the Late Devonian (ca. 385–359 Ma) corresponds to the 'Uralian island arc – Continent' collision stage, which was associated with exhumation of high-pressure metamorphic complexes. The good preservation of initial ore textures for the studied deposits (colloform structures, well preserved relics of hydrothermal chimneys and fauna) do not favour the metamorphic overprint as was proposed previously (Gannoun et al., 2003).

The recorded Re-Os and Ar-Ar ages may reflect the multi-stage hydrothermal activity in the area. The similarity of Re-Os ages for four deposits may be related with the re-activation of the hydrothermal systems at Middle Devonian time, which was synchronous across the Southern Urals island arc structure. In the Southern Urals, this stage of island arc development has been identified as hydrous suprasubduction melting during the mantle-crustal interaction (Fershtater et al., 2007) with large-scale granitoid magmatism. These intrusions could provide necessary heat to promote the hydrothermal circulation along the existing tectonic faults. The Ar-Ar ages are ca. 20 Ma younger and may reflect the lower temperature hydrothermal event which may correspond to the emplacement of gabbroic intrusions in the area.

The Urals VHMS Province development in the Late Devonian was a part of global process on a planetary scale related to the fundamental plate boundary re-arrangements, marked by intense magmatism under tectonic activation. This is manifested in island arc volcanism paired with episodic continental rifting, as well as hydrothermal activity on rifted or faulted outer continental margins, comprising large clusters of VHMS deposits in Spain, Portugal (Iberian Pyrite Belt province), Rudny Altai (Siberia), and the North American margin (Alaska). These deposits formed in local extensional volcanic basins within an overall contractional geodynamic environment during or after termination of convergence by accretion of an island arc or crustal block (Huston et al., 2010) throughout the Devonian until Lower Carboniferous time.

Acknowledgment

This study was partly financially supported by the European Union through an INCO Copernicus Project (MinUrals ICA2-CT-2000-10011). Professor Victor V. Zaykov is acknowledged for the molybdenite sample donation from his personal collection. Professor Neal McNaughton is acknowledged for fruitful discussion of results and corrections of final manuscript. The manuscript was significantly improved by helpful reviews from Prof. Puchkov and anonymous reviewer. Olga Plotinskaya is thanked for editorial handling.

References

Artyushkova, O.V., Maslov, V.A., 2008. Detailed correlation of the Devonian deposits in the South Urals and some aspects of their formation. Bulletin of Geosciences 83(4). Czech Geological Survey, Prague, pp. 391–399.

Bailly, L., Orgeval, J.-J., Tessalina, S., Zaykov, V., Maslennikov, V., 1999. Fluid inclusion data of the Alexandrinka massive sulfide deposit, Urals. In: Stanley, et al. (Eds.), Mineral Deposits: Processes to ProcessingProceedings of the Fifth Biennial SGA Meeting and the Tenth Quadrennial IAGOD Symposium, London, United Kingdom. A.A. Balkema, Rotterdam, pp. 13–16.

Bea, F., Fershtater, G.B., Montero, P., 2002. Granitoids of the Uralides: implications for the evolution of the orogen. In: Brown, D., Juhlin, C., Puchkov, V. (Eds.), Mountain Building in the Uralides: Pangea to the Present. A.G.U. Geophysical Monograph 132, pp. 211–232.

Beane, R.J., Connelly, J.N., 2000. ^{40}Ar/^{39}Ar, U-Pb, and Sm-Nd constraints on the timing of metamorphic events in the Maksyutov Complex, southern Ural Mountains. J. Geol. Soc. Lond. 157, 811–822.

Birck, J.L., Roy-Barman, M., Capmas, F., 1997. Re–Os isotopic measurements at the femtomole level in natural samples. Geostand. Newslett. 20 (1), 19–27.

Brenan, J.M., Cherniak, D.J., Rose, L.A., 2000. Diffusion of osmium in pyrrhotite and pyrite: implications for closure of the Re-Os isotopic system. Earth Planet. Sci. Lett. 180, 399–413.

Brown, D., Spadea, P., Puchkov, V., Alvarez-Marron, J., Herrington, R., Willner, A.P., Hetzel, R., Gorozhanina, Y., Juhlin, C., 2006. Arc-Continent collision in the south Urals. Earth Sci. Rev. 79, 261–287.

Brügmann, G.E., Birck, J.L., Herzig, P.M., Hofmann, A.W., 1998. Os isotopic composition and Os and Re distribution in the active mound of the TAG hydrothermal system, Mid-Atlantic Ridge. Proceeding of the Ocean Drilling Program. Scientific Results 158, pp. 91–100.

Buslaev, F.P., Kaleganov, B.A., 1992. The age of sulfide-ore formation according to the K/Ar method. In: Prokin, V.A., Seravkin, I.B., Buslaev, F.P., et al. (Eds.), Copper-Sulfide Deposits of the Urals: Conditions of Formation. Russian Academy of Science, Ural Branch, Ekaterinburg, pp. 186–199 (in Russian).

Chiaradia, M., Konopelko, D., Seltmann, R., Cliff, R.A., 2006. Lead isotope variations across terrane boundaries of the Tien Shan and Chinese Altay. Mineral. Deposita 41, 411–428.

Dubinina, S.V., Ryazantsev, A.V., 2008. Conodont stratigraphy and correlation of the Ordovician volcanogenic and volcanogenic sedimentary sequences in the South Urals. Russ. J. Earth Sci. 10 (5), 1–31.

Dusel-Bacon, C., Wooden, J.L., Hopkins, M.J., 2004. U-Pb zircon and geochemical evidence for bimodal mid-Paleozoic magmatism and syngenetic base-metal mineralization in the Yukon-Tanana terrane, Alaska. GSA Bulletin; July/August 2004 116 (7/8), 989–1015. http://dx.doi.org/10.1130/B25342.1.

Fershtater, G.B., 2013a. The main features of the Uralian Paleozoic magmatism and the epioceanic nature of the orogen. Mineral. Petrol. 107 (1), 39–52.

Fershtater, G.B., 2013b. Palaeozoic Intrusive Magmatism of the Middle and South Urals. Ural Branch of RAS, Ekaterinburg (in Russian).

Fershtater, G.B., Krasnobaev, A.A., Bea, F., Montero, P., Borodina, N.S., 2007. Geodynamic settings and history of the Paleozoic intrusive magmatism of the central and southern Urals: results of zircon dating. Geotectonics 41, 465–486.

Galley, A.G., 2003. Composite synvolcanic intrusions associated with Precambrian VMS-related hydrothermal systems. Mineral. Deposita 38, 443–473.

Gannoun, A., Tessalina, S., Bourdon, B., Orgeval, J.-J., Birck, J.-L., Allègre, C.J., 2003. Re–Os isotopic constraints on the genesis and evolution of the Dergamysh and Ivanovka Cu (Co, Au) massive sulphide deposits, south Urals, Russia. Chem. Geol. 196 (1–4), 193–207.

Glasby, G.P., Prozherova, I.A., Maslennikov, V.V., Petukhov, S.I., 2006. Jusa and Barsuchi log volcanogenic massive sulfide deposits from the southern Urals of Russia: tectonic setting, structure and mode of formation. Resour. Geol. 57 (1), 24–36.

Hannington, M.D., de Ronde, C.E.J., Peterson, S., 2005. Sea-floor tectonics and submarine hydrothermal systems. Economic Geology 100th Anniversary Volume, pp. 111–141.

Herrington, R., Brown, D., 2011. The Generation and Preservation of Mineral Deposits in Arc-Continent Collision Environment. Chapter 6. Springer-Verlag, Berlin Heidelberg, pp. 145–162.

Herrington, R., Maslennikov, V., Zaykov, V., Seravkin, I., Kosarev, A., Buschmann, B., Orgeval, J.-J., Holland, N., Tesalina, S., Nimis, P., Armstrong, R., 2005. Classification of VMS deposits: lessons from the South Uralides. Ore Geol. Rev. 27 (1–4), 203–237.

Hu, R.-Z., Wei, W.-F., Bi, X.-W., Peng, J.-T., Qi, Y.-Q., Wu, L.-Y., Chen, Y.-W., 2012. Molybdenite Re-Os and muscovite ^{40}Ar/^{39}Ar dating of the Xihuashan tungsten deposit, central Nanling district, South China. Lithos 150, 111–118.

Huston, D.l., Pehrsson, S., Eglington, B.M., Zaw, K., 2010. The geology and metallogeny of volcanic-hosted massive sulfide deposits: variations through geologic time and with tectonic setting. Econ. Geol. 105, 571–591.

Huston, D.L., Relvas, J.M.R.S., Gemmell, J.B., Drieberg, S., 2011. The role of granites in volcanic-hosted massive sulphide ore-forming systems: an assessment of magmatic–hydrothermal contributions. Mineral. Deposita 46, 473–507.

Jourdan, F., Renne, P., 2014. Neutron-induced ^{37}Ar recoil ejection in Ca-rich minerals and implications for ^{40}Ar/^{39}Ar dating. In: Jourdan, F., Mark, D., Verati, C. (Eds.), Advances in ^{40}Ar/^{39}Ar Dating: From Archaeology to Planetary SciencesSpecial Publication 378. Geological Society, London, pp. 1–8.

Koppers, A.A.P., 2002. ArArCALC-software for ^{40}Ar/^{39}Ar age calculations. Comput. Geosci. 28, 605–619.

Lee, J.-Y., Marti, K., Severinghaus, J.P., Kawamura, K., Yoo, H.-S., Lee, J.B., Kim, J.S., 2006. A redetermination of the isotopic abundance of atmospheric Ar. Geochim. Cosmochim. Acta 70, 4507–4512.

Lobanov, K., Yakubchuk, A., Creaser, R.A., 2014. Besshi-type VMS deposits of the Rudny Altai (Central Asia). Econ. Geol. 109, 1403–1430.

Maslennikov, V.V., Maslennikova, S.P., Large, R.R., Danyushevsky, L.V., 2009. Study of trace element zonation in vent chimneys from the Silurian Yaman-Kasy volcanic-hosted massive sulfide deposit (southern Urals, Russia) using laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS). Econ. Geol. 104, 1111–1141.

Mathur, J.R., Ruiz, J., Tornos, F., 1999. Age and sources of the ore at Tharsis and Rio Tinto, Iberian Pyrite Belt, from Re-Os isotopes. Mineral. Deposita 34, 790–793.

Nadeau, O., Williams-Jones, A.E., Stix, J., 2010. Sulphide magma as a source of metals in arc-related magmatic hydrothermal ore fluids. Nat. Geosci. 3, 501–505.

Novoselov, K.A., Belogub, E.V., Zaykov, V.V., Yakovleva, V., 2006. Silver sulphotellurides from volcanic-hosted massive sulphide deposits in the southern Urals. Mineral. Petrol. 87, 327–349.

Prokin, V.A., Buslaev, F.P., 1999. Massive copper–zinc sulphide deposits in the Urals. Ore Geol. Rev. 14, 1–69.

Puchkov, V.N., 2010. Geology of the Urals and Foreurals: Topical Questions of Tectonics, Geodynamics, and Metallogeny. Dizain Poligraf Service, Ufa, Russia (280 pp. (in Russian)).

Puchkov, V.N., 2017. General features relating to the occurrence of mineral deposits in the Urals: what, where, when and why. Ore Geol. Rev. 85, 4–29.

Renne, P.R., Balco, G., Ludwig, K.R., Mundil, R., Min, K., 2011. Response to the comment by W.H. Schwarz et al. on "Joint determination of K-40 decay constants and Ar-40*/K-40 for the Fish Canyon sanidine standard, and improved accuracy for Ar-40/Ar-39 geochronology". Geochim. Cosmochim. Acta 75, 5097–5100.

Rodriguez, J., Cosca, M.A., Ibarguchia, J.I.G., Dallmeyer, R.D., 2003. Strain partitioning and preservation of ^{40}Ar/^{39}Ar ages during Variscan exhumation of a subducted crust (Malpica–Tui complex, NW Spain). Lithos 70, 111–139.

Ryazantsev, A.V., Dubinina, S.V., Kuznetsov, N.B., Belova, A.A., 2008. Ordovician lithotectonic complexes in allochthons of the southern Urals. Geotectonics 42 (5), 368–395.

Sharma, M., Wasserburg, G.J., Hofmann, A.W., Butterfield, D.A., 2000. Osmium isotopes in hydrothermal fluids from the Juan de Fuca Ridge. Earth Planet. Sci. Lett. 179, 139–152.

Spadea, P., d'Antonio, M., 2006. Initiation and evolution of intra-oceanic subduction in the Uralides: geochemical and isotopic constrains form Devonian oceanic rocks of the southern Urals, Russia. Island Arc 15, 7–25.

Stacey, J.S., Kramers, J.D., 1975. Approximation of Terrestrial Lead Isotope Evolution by a 2-Stage Model. Earth Planet. Sci. Lett. 26 (2), 207–221.

Suzuki, K., Shimizu, H., Masuda, A., 1996. Re-0 s dating of molybdenites from ore deposits in Japan: implication for the closure temperature of the Re-0 s system for molybdenite and the cooling history of molybdenum ore deposits. Geochim. Cosmochim. Acta 60 (16), 3151–3159.

Tesalina, S., Nimis, P., Augé, T., Zaykov, V., 2003. Origin of chromite in mafic–ultramafic-hosted hydrothermal massive sulfides from the Main Uralian Fault, south Urals, Russia. Lithos 70 (1–2), 39–59.

Tessalina, S.G., Bourdon, B., Maslennikov, V.V., Orgeval, J.-J., Birck, J.-L., Gannoun, A., Capmas, F., Allègre, C.-J., 2008. Osmium isotope distribution within the Palaeozoic Alexandrinka seafloor hydrothermal system in the southern Urals, Russia. Ore Geol. Rev. 33, 70–80.

Tessalina, S., Jourdan, F., Nunes, L., Kennedy, A., Denyszyn, S., Puchtel, I., Touboul, M., Creaser, R., Boyet, M., Belousova, E., Trinquier, A., 2015. Application of radiogenic isotopes in geosciences – overview and perspectives. In: Grice, K. (Ed.), Principles and Practice of Analytical Techniques in GeosciencesRSC Detection Science Series. Royal Society of Chemistry, pp. 49–93 (ISBN 1849736499, 9781849736497).

Tessalina, S.G., Herrington, R.J., Taylor, R.N., Sundblad, K., Maslennikov, V.V., Orgeval, J.-J., 2016. Lead isotopic systematics of massive sulphide deposits in the Urals: applications for geodynamic setting and metal sources. Ore Geol. Rev. 72 (1), 22–36.

Tornos, F., Casquet, C., Relvas, J.M.R.S., 2005. 4: Transpressional tectonics, lower crust decoupling and intrusion of deep mafic sills: a model for the unusual metallogenesis of SW Iberia. Ore Geol. Rev. 27, 133–163.

Verati, C., Jourdan, F., 2014. Effect of sericitization of plagioclase on the ^{40}K/^{40}Ar and ^{40}Ar/^{39}Ar chronometers: implication for dating basaltic rocks and mineral deposits. 2013. In: Jourdan, F., Mark, D., Verati, C. (Eds.), Advances in ^{40}Ar/^{39}Ar Dating: From Archaeology to Planetary SciencesSpecial Publication 378. Geological Society, London, pp. 1–8.

von Quadt, A., Erni, M., Martinek, K., Moll, M., Peytcheva, I., Heinrich, C.A., 2011. Zircon crystallization and the lifetimes of ore-forming magmatic-hydrothermal systems. Geology 39, 731–734.

Yudovskaya, M.A., Tessalina, S., Distler, V.V., Chaplygin, I.V., Chugaev, A.V., Dikov, Y.P., 2008. Behavior of highly-siderophile elements during magma degassing: a case study at the Kudryavy volcano. Chem. Geol. 248, 318–341.

Zaykov, V.V., Udachin, V.N., Sinyakovskaya, I.V., 1988. Pyrophyllite deposits. Int. Geol. Rev. 30 (1), 90–103.

Zonenshain, L.P., Kuzmin, M.I., Natapov, L.M., 1990. Geology of the USSR: a plate tectonic synthesis. Geodynamic Series 21. American Geophisical Union, Washington DC.