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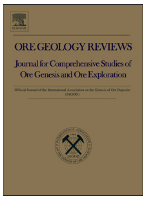

Silurian to Carboniferous Re-Os molybdenite ages of the Kalinovskoe, Mikheevskoe and Talitsa Cu- and Mo porphyry deposits in the Urals: Implications for geodynamic setting

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ABSTRACT

The Urals can be regarded as a significant Cu-Mo-porphyry province, hosting over 30 porphyry deposits. Although their geological structure and ore-forming processes have been studied in great detail, uncertainty remains about their age and related geotectonic setting. In this contribution we report for the first time the Re-Os dating of molybdenites from three Cu-Mo porphyry deposits, namely Kalinovskoe, Mikheevskoe and Talitsa. Three molybdenite samples from the Kalinovskoe deposit yield Silurian Re-Os ages ranging from 427.1 Ma to 431.7 Ma (mean 429.8 ± 4.8 Ma; 2σ standard deviation), and a Re–Os isochron age of 430.7 ± 1.3 Ma (MSWD = 0.63), which coincides with previous U-Pb zircon dating of ore-hosting diorites from the same ore field (427 ± 6 Ma). The molybdenite from the Mikheevskoe deposit gives Re-Os ages of 357.8 ± 1.8 Ma and 356.1 ± 1.4 Ma (mean 357.0 ± 2.4 Ma; Carboniferous/Tournaisian), which corresponds to previous U-Pb dating of zircons from the diorite hosting porphyry deposit (356 ± 6 Ma). The molybdenite from Talitsa Mo-porphyry deposit yields the youngest Re-Os ages of 298.3 ± 1.3 and 299.9 ± 2.9 Ma (mean 299.1 ± 2.3 Ma) at Carboniferous-Permian boundary. Thus, the studied Cu and Mo porphyry deposits are not synchronous and belong to distinct tectonic events of the Urals.

1. Introduction

The Urals host several Cu-Mo-porphyry deposits of global significance with up to 1–1.5 Mt of Cu for selected ore fields. Although the geology and mineralogy of most deposits are quite well understood (Plotinskaya et al., 2016a, and references therein), the geochronology and geotectonic setting are still controversial. The main reason is that very few porphyry deposits have been dated by modern and precise geochronological methods. Those are limited only to zircon dating of ore-hosting intrusions (Grabezhev and Ronkin, 2011; Grabezhev et al., 2013 etc.) but do not include dating of ore or wall-rock alteration. This study presents first precise Re-Os dating of porphyry mineralisation from three Urals porphyry deposits. Molybdenite samples have been collected from the Kalinovskoe porphyry Cu and Talitsa porphyry Mo deposits, which are situated within East-Uralian megaterrane; and the Mikheevskoe porphyry Cu deposit, situated on the border between the East-Uralian and Trans-Uralian megaterranes.

2. Geological setting and sampling

An overview of Urals porphyry deposits geology and geotectonic setting within the framework of Urals belt is given in a companion paper (Plotinskaya et al., 2016a). Molybdenite samples for this study have been collected from three deposits, namely Kalinovskoe, Mikheevskoe and Talitsa (see Fig. 1 for deposits locations). In what follows, we provide a short description of studied deposits and samples dated, referring to relevant publications for more details.

2.1. Kalinovskoe porphyry copper deposit

The Kalinovskoe Cu-porphyry deposit occurs within the Birgilda-Tomino ore cluster, which is situated within the East Uralian volcanic megazone (Plotinskaya et al., 2014a, 2016b and references therein). The Ordovician aphyric basaltic lavas and tuffs form the base of the visible section and host the Kalinovskoe, Tomino and Birgil'da porphyry copper deposits. Tomino and Kalinovskoe sites (Fig. 2) comprise the Tomino ore field with total reserves of 331 Mt at 0.46% Cu and 0.1 g/t Au (Volchkov et al., 2015). The Cu porphyry mineralisation is confined to an irregularly shaped diorite stock, approximately 2–3 km in size. Quartz–sericite (phyllic) alteration with chalcopyrite, molybdenite and minor bornite forms the central part of the deposit. Marginal

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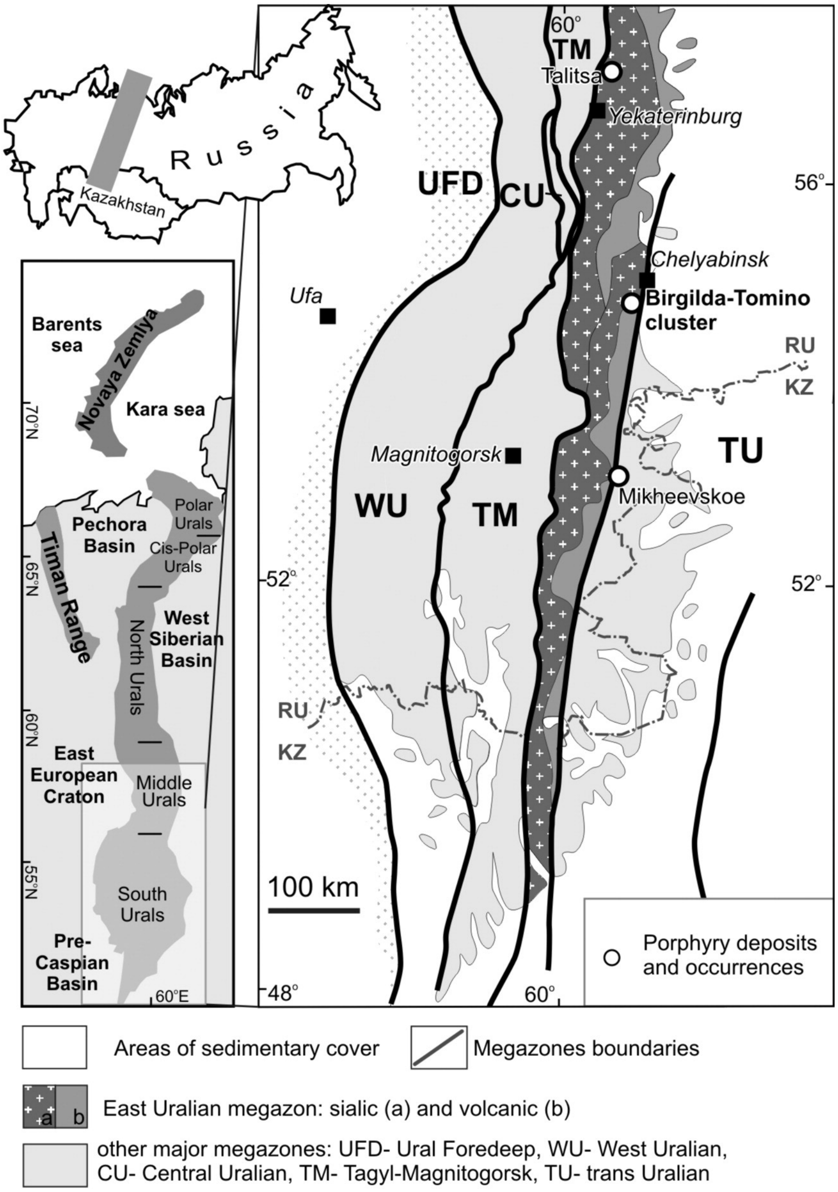

Fig. 1. Simplified tectonic scheme of the Middle and South Urals, showing locations of studied porphyry deposits (modified after Petrov et al., 2007; Puchkov, 2010; Plotinskaya et al., 2014a).

zones are composed of propylitic (chlorite, epidote, carbonate) alteration with pyrite-chalcopyrite mineralisation. Bismuth–gold–(base metal) mineralisation forms an epithermal overprint on the earlier stages. Porphyry copper deposits are associated with quartz diorite porphyry intrusions of the K-Na calc-alkaline series (Birgil'da–Tomino igneous complex) which have been recently dated at 428 ± 3 Ma and 427 ± 6 Ma (Silurian; Grabezhev et al., 2013).

Molybdenite is rare but occurs throughout the aforementioned deposits mainly within the areas of phyllic alteration. There is no published data on Mo content or Cu/Mo ratio in the Kalinovskoe deposit, however for the neighboring Tomino deposit Grabezhev (2013) reported Cu/Mo ratio from 100 to 300, occasionally 25 to 50. In the central zone of the Kalinovskoe deposit, the EMPA revealed high Re contents in molybdenite i.e. up to 0.95 wt% in a single point analysis, but normally below 0.15 wt.% (Plotinskaya et al., 2014b). In the Tomino deposit, Grabezhev and Hiller (2015) reported Re contents ranging from 0.05 to 0.4 wt.%.

The samples for Re-Os dating were collected from the drillcore 2210 located in the Northeast periphery of the deposit (Fig. 2). Samples were taken from the ore zone which is enriched in molybdenite relatively to other parts of the ore system. Samples consist of diorite with strong phyllic alteration overlapped with propylitic halo alteration minerals of sericite, quartz and chlorite. Molybdenite is present as dissemination, nests, and veinlets, (see Fig. 3a–c). Molybdenite nests are often overgrown and brecciaed by later chalcopyrite (Fig. 3, d). The EMPA data for sample K-2210/73.4 (Grabezhev and Hiller, 2015) show the Re contents near or below the detection limit (ca. 200 ppm).

2.2. The Mikheevskoe porphyry copper deposit

The Mikheevskoe porphyry Cu deposit is hosted by Late Devonian sandstones, tuffstone and basaltic andesites, overlain by basaltic lavas, tuffs and sandstones, which are cross-cut by quartz diorite stocks and numerous diorite and granodiorite porphyry dykes (Shargorodskii et al., 2005). Intrusions were previously dated using the U-Pb method in zircons at 356 ± 6 Ma (Grabezhev and Ronkin, 2011). Volcanic-sedimentary rocks rather than dykes host the ore (347 Mt of ore at 0.45% Cu and 0.1 ppm Au; Volchkov et al., 2015). For more details on geology and conditions of ore formation, we refer to the companion paper by Plotinskaya et al. (2016a).

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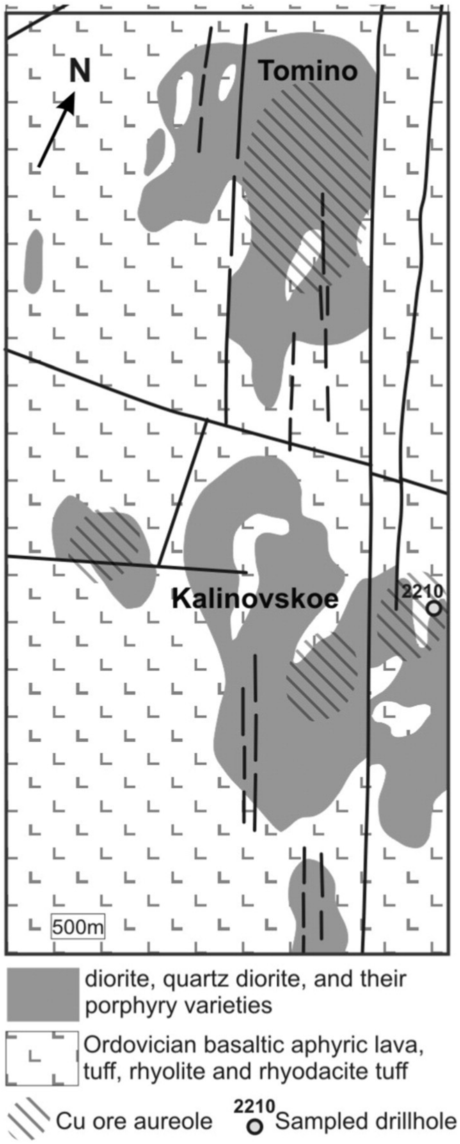

Fig. 2. Geological map of the Tomino ore field with the location of Tomino and Kalinovskoe deposits shown (simplified after Puzhakov, 1999). The location of the sampled drillcore 2210 is shown.

Molybdenites are hosted by two different types of rocks: (a) diorite with cm-size quartz veinlet with molybdenite and chalcopyrite nests up to 3 mm (sample M-11/139.1; Fig. 3f,g) and (b) basaltic andesite subjected to biotite, phyllic and propylitic alterations with stringers and nests of molybdenite up to 1–2 mm (sample M43/32.2; Fig. 3h). Grabezhev (2013) and Plotinskaya et al. (2015) reported variable Cu/Mo ratios in ores (8 to 1667) and very uneven distribution of Re in molybdenite (231–3598 ppm via spectrophotometry data), and from below the detection limit to 1.09 wt.% (via EMPA data).

2.3. Talitsa porphyry molybdenum deposit

The Talitsa porphyry Mo deposit lies on the western margin of the East Uralian terrane. It occurs within the Carboniferous intrusives of granodiorite, quartz monzonite, granite composition with minor monzodiorite, cut by granodiorite to quartz monzonite porphyry and granite porphyry stocks and dykes. The country rocks are Devonian rhyolites, basalts and serpentinite. Zones of potassic alteration (mainly K-feldspar) are confined to porphyry stocks and dykes. Phyllic (sericite and quartz-sericite) alteration is developed throughout the central zone of the Talitsa intrusion whereas propylitic alteration occurs typically on its margins. Mineralisation (0.04 to 0.34% Mo, 0.09 to 0.47% Cu, Cu/Mo = 0.5 to 3) occurs as dissemination and stockwork zones (see Azovskova and Grabezhev, 2008; Plotinskaya et al. (2016a) for more details). Grabezhev (2013) reported Re content of 187 ppm in molybdenite (spectrophotometry method). No data on Re distribution within molybdenite is available. Samples selected for Re-Os dating represent molybdenite in nests up to 3 mm in size on quartz veinlets or in surrounding K-feldspar halo within granodiorite porphyry (Fig. 3e).

3. Analytical methods

Molybdenite was hand-picked with a needle. Molybdenite separates were precisely weighed (approximately 100 mg) and transferred via funnels into Carius tubes resting in dry ice, followed by a precise amount of the mixed ^{188}Os-^{190}Os/^{185}Re spike as recommended in Markey et al. (2003). To this is added 1 ml concentrated, Teflon-distilled HCl and 3 ml concentrated, distilled HNO_3. The sealed tubes were placed in an oven at 220° and reacted for 48 h. After sample digestion, the tubes are refrozen and opened. Os is separated by solvent extraction, with a final purification of the Os by microdistillation. Rhenium was separated from a portion of the residuum liquid using anion exchange chromatography.

Re and Os aliquots were loaded onto Pt filaments and covered with the $Ba(OH)_2$/NaOH activator. Isotopic measurements were made by Thermo-Ionization Mass-Spectrometer (TIMS) Triton™ instrument for both Os and Re. All Re and most Os measurements were made using the Faraday collectors. Multiple measurements of natural Re was within analytical uncertainty of ^{185}Re/^{187}Re = 0.59; therefore, no fractionation correction was applied. Measured Os isotope ratios are first corrected for contributions from natural Os (based on preliminary isotope dilution calculations), then corrected for mass fractionation based on the ^{190}Os/^{188}Os ratio of the spike. ^{187}Os is determined from the ^{187}Os/^{188}Os of the mixture and corrected for minor contributions from total common Os (blank plus sample).

Re and Os concentrations are determined by isotope dilution using measured isotopic ratios for Os and spikes weight. Concentrations of common Os and radiogenic ^{187}Os are then calculated using the isotope dilution equations. Note that common Os is insignificant relative to that of radiogenic Os in the studied molybdenites.

Because of the basically mono-isotopic nature of Os in molybdenite (nearly all ^{187}Os), the error magnification is insignificant for the determination of ^{187}Os concentration (Stein et al., 2001). Most of the error in both the Re and Os concentrations is from the uncertainties on the spike calibrations and the mass spectrometric measurements, an error magnification factor, uncertainties on blank corrections and, for the age determination, uncertainty in the decay constant for ^{187}Re. The weighing error of the sample does not contribute to the uncertainty on the ages because of a mixed-double ^{188}Os-^{190}Os/^{185}Re spike used (Markey et al., 2003). Analytical blanks are insignificant for the age calculations, given the Re and ^{187}Os concentrations of the samples studied and the sample size used in the analyses. Blank values were 12 pg for Re and 0.8 pg for Os with ^{187}Os/^{188}Os of 0.25 ± 0.01.

Concentration data for Re and ^{187}Os are reproducible to within 0.44 and 0.91%, respectively. The uncertainty for each individual age determination doesn't exceed 1%, this includes the 0.3% uncertainty in the decay constant for ^{187}Re.

Data quality was verified by the measurement of international Reference Material of Henderson molybdenite RM 8599 with known age (Table 1). The age returned for molybdenite standard material is within the error of certified value of 27.65 ± 0.02 (Markey et al., 2007).

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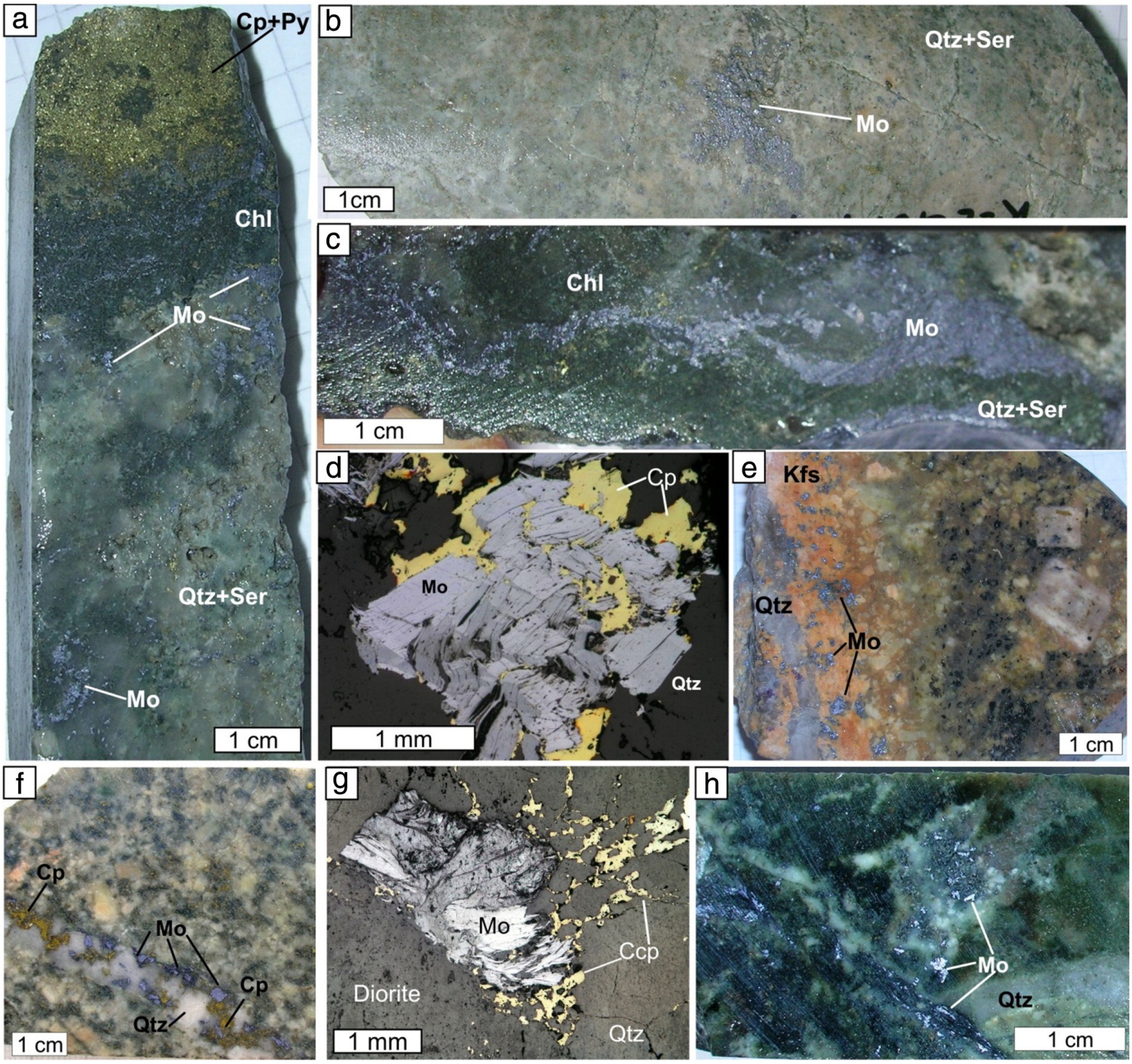

Fig. 3. Hand specimens with molybdenite studied in this work. (a) to (d) – Kalinovskoe deposit: a – sample K-2210/73.4, diorite (?) with strong phyllic alteration, molybdenite (Mo) dissemination, overlapped with pyrite + chalcopyrite (Py + Cp) with propylitic halo (Chl); b – sample K-2210/74.5, diorite (?) with strong phyllic alteration and molybdenite nest; c – sample K-2210/73.1, molybdenite dissemination and veinlets in diorite (?) with strong phyllic (Qtz + Ser) alteration, overlapped with propylitic alteration; d – sample K-2210/74.5, reflected light, molybdenite overgrown by chalcopyrite (Cp); e – Talitsa deposit, sample Tal-19/78, molybdenite nests with K-feldspar halo around quartz veinlet in granodiorite porphyry; (f) to (h) – Mikheevskoe deposit: f – sample M-11/139.1, molybdenite and chalcopyrite nests in a quartz (Qtz) veinlet in diorite; g – fragment of (f) in reflected light, molybdenite nest in quartz veinlet overgrown by chalcopyrite, chlorite and muscovite (Chl + Mus); h – sample M-43/32.2, stringers and nests of molybdenite in basaltic andesite subjected to biotite, phyllic and propylitic alterations.

4. Results

4.1. Re and Os concentrations

Among three deposits studied the lowest concentrations of ^{187}Re (10 ppm) and ^{187}Os (52 ppb) were measured for the Talitsa porphyry deposit (Table 2). Two replicates from the same sample show quite variable concentrations within 49% for both Re and ^{187}Os, possibly reflecting the inhomogeneity in the sample material.

Three molybdenite samples from the North-East periphery of the Kalinovskoe deposit display Re values of 82 to 228 ppm (see Table 2). This is in an agreement with the EMPA data for sample K-2210/73.4, where the Mo contents are below the detection limit (Grabezhev and Hiller, 2015).

Table 1
Re-Os age and abundance results for the Henderson molybdenite Reference Material (RM 8599) using ^{188}Os-^{190}Os double spike. The age of the Reference Material molybdenite (RM 8599) is within the error of the certified age of 27.65 ± 0.02 Ma.

Run	Re(ppm)	^{187}Os (ppb)	Age (Ma)	2σ
Henderson molybdenite Reference Material RM 8599 (this study)	11.07	3.19	27.56	0.10
Henderson molybdenite Reference Material RM 8599 (reported)[a]	11.08	3.21	27.65	0.02

[a] Markey et al. (2007).

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Table 2
Re-Os age and abundance results for studied samples.

Sample	Re ppm	$\pm 2\sigma$	^{187}Re ppm	$\pm 2\sigma$	^{187}Os ppb	$\pm 2\sigma$	Model Age (Ma)	$\pm 2\sigma$ (Ma)
Kalinovskoe								
K2210_73.1	228.1	1	143.3	0.2	1031.9	0.30	430.50	1.7
K2210_73.4	81.5	0.2	51.2	0.1	369.6	0.4	431.70	1.7
K2210_74.5	147.0	0.4	92.3	0.4	659.1	6	427.1	3.3
Mikheevskoe								
M11_139.1	400.0	1	251.7	0.6	1504.8	5	357.8	1.8
M43_32.2	758.9	1.8	477.0	2.2	2838.5	0.6	356.1	1.4
Talitsa								
Tal 19_78	27.3	0.06	17.1	0.04	85.9	0.7	299.9	2.9
Duplicate	16.6	0.05	10.4	0.03	52.0	0.1	298.3	1.3

The highest ^{187}Re and ^{187}Os contents were obtained for the Mikheevskoe porphyry (252 to 477 ppm and 1.5 to 2.8 ppm, respectively; Table 2). The Re contents in molybdenites from the Mikheevskoe deposit fall in the lower end of the range reported by Plotinskaya et al. (2015), with Re contents ranging from 231 up to 3598 ppm (spectrophotometry data).

4.2. Re-Os ages

For the Kalinovskoe deposit, three molybdenite samples returned Re-Os ages of 427.1 ± 3.3 to 431.7 ± 1.7 ($n = 3$). Reproducibilities in the ages for three measured samples are 0.2–0.6%, which is within the uncertainty of the individual age determination (0.4–0.8%). Variations may be caused by minor overprint of propylitic and sub-epithermal assemblages. Despite this variability, these three samples are considered to represent a single population within the analytical uncertainty. Plotted on the ^{187}Re versus^{187}Os isochron plot, these three samples yield an isochron age of 430.7 ± 1.3 Ma, with MSWD of 0.63 (Fig. 4).

Re-Os ages for two molybdenite samples from the Mikheevskoe deposit are quite similar within the analytical uncertainty, ranging from 356.1 ± 1.4 to 357.8 ± 1.8 Ma. For the Talitsa deposit, only one molybdenite sample was analysed (with duplicate), giving the Re-Os age of 299.9 ± 2.9 Ma and 298.3 ± 1.3 Ma. The reproducibility in the ages for the sample from the Talitsa deposit is 0.5% for two replicates.

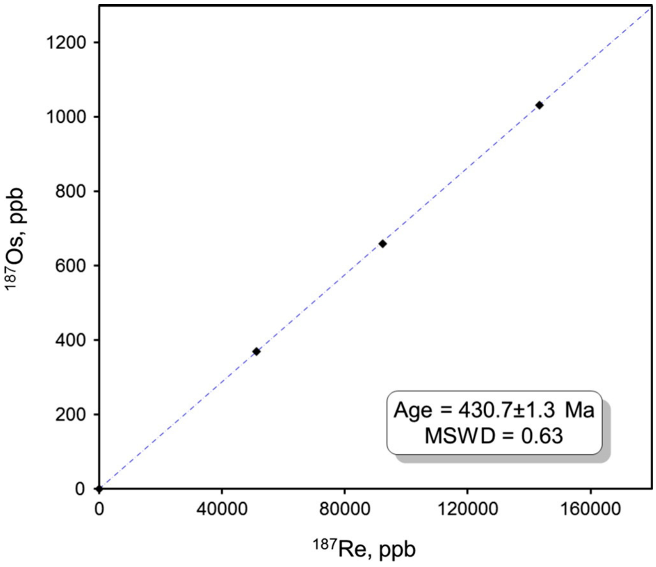

Fig. 4. An isochron plot utilizing ^{187}Re versus ^{187}Os space. Note that regression of the three analyses extrapolate to within error of the origin, so the isochron regression was fixed with initial ^{187}Os at 'zero', which is implicit in individual model age calculations (see Stein et al., 2001 for method details). By regression of only three points, the isochronous relationship is demonstrated with intercept of 1.5 ± 4.0 and age of 430.7 ± 1.3 Ma (not shown), which is well within the error of the isochron fixed through the origin.

5. Discussion

5.1. Geochronology – link between mineralisation and magmatism

5.1.1. Kalinovskoe porphyry copper deposit

Until recently, the geochronology of porphyry deposits of the Birgilda-Tomino cluster mainly relied on the biostratigraphic data summarised by Puzhakov (1999) and references therein. According to this, the Kalinovskoe and Tomino deposits, situated within East Uralian volcanic megazone, were interpreted to be Late Devonian to Early Carboniferous in age and this point of view is still officially accepted (Puzhakov et al., 2013 and references therein). Recent U-Pb zircon dating of ore-related intrusive rocks (428 ± 3 Ma and 427 ± 6 Ma), however, has changed our understanding of formation ages and related geodynamic setting of selected porphyry deposits (Grabezhev et al., 2013). This discrepancy calls for both the direct dating of sulphide mineralisation and hosting magmatic rocks, to provide a critical understanding of their geotectonic setting and evolution of ore-forming processes. We consider the geochronological data obtained by application of the Re-Os dating technique to three molybdenite samples from the Kalinovskoe porphyry deposit (model ages ranging from 427.1 Ma to 431.7 Ma (Table 2); Re–Os isochron age of 430.7 ± 1.3 Ma with MSWD of 0.63 (Fig. 4)) to closely approximate the age of the ore-bearing porphyry diorite of 428 ± 3 Ma (Grabezhev et al., 2013).

5.1.2. Mikheevskoe porphyry copper deposit

The Mikheevskoe deposit was considered to be Carboniferous because of the close spatial association with quartz diorites, diorites and granodiorite intrusives of Carboniferous age (Shargorodskii et al., 2005). Recent U-Pb zircon dating of ore-bearing quartz diorites from the ore field has revealed a Late Devonian age of 356 ± 6 Ma (Grabezhev and Ronkin, 2011). Our Re-Os model ages of 357.8 ± 1.8 Ma and 356.1 ± 1.4 Ma are the same within the analytical uncertainty. Here again, close temporal and special association is observed between magmatic activity and hydrothermal processes (e.g., Stein, 2014).

5.1.3. Talitsa porphyry molybdenum deposit

The Talitsa porphyry Mo deposit was considered to be genetically related to Carboniferous intrusives of granodiorite to quartz monzonite and granite (Azovskova and Grabezhev, 2008). Indeed, the K-Ar age of monzogranite was established to be Carboniferous/Missisippian (320 to 341 Ma ($n = 5$); Azovskova and Grabezhev, 2008). However recent SHRIMP-II dating of zircon from granite yielded an age of 297.4 ± 2.3 Ma (Smirnov V.N., personal communication), pointing to mineralisation in the Late Carboniferous to Early Permian.

Our Re-Os model ages (298.3 ± 1.3 Ma and 299.9 ± 2.9 Ma) correspond within the error to that obtained by recent zircon dating using SHRIMP. Moreover, the molybdenite from Talitsa is distinguished from other deposits by the lowest ^{187}Re and ^{187}Os contents (Table 2).

5.1.4. Spatial and temporal relationship between mineralisation and magmatism

The similarity of ages between magmatic rocks and mineralisation for all three studied deposits implies that the ore-forming magmatism and hydrothermal process leading to deposition of Re-bearing molybdenites took place synchronously. The close temporal relationship between magmatism and hydrothermal processes is common for a range of porphyry deposits as reported in a number of publications (e.g., Quadt et al., 2011; Parry et al., 2001; Stein, 2014). These studies report coeval magmatism and related mineralisation, with time gaps usually of less than 1 Ma, and often within the analytical uncertainty of the age measurements. This short time frame is especially applicable for the

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Late Mesozoic and Cenozoic Cu-porphyry deposits, which constitute the major part of this particular ore deposit type (see Grabezhev et al., 2013 for literature review). The older (Lower Mesozoic to Paleozoic) Cu-porphyry systems may have a longer interval between magmatism and related mineralisation, as is the case for some Siberian porphyry deposits (Berzina et al., 2012). For example, the La Cariadad ore field in Mexico is characterised by two-phases of mineralisation and related ore-bearing granitoids separated in time by ca 5 Ma (Valencia et al., 2008).

5.2. Source of metals

It has been advocated that the Re contents in molybdenite provide evidence for the origin of a deposit (e.g., Stein et al., 2001). It has been noted that the high Re concentrations are typical for deposits with mantle origin of metals, involving mantle underplating and metasomatism, or melting of mafic or ultramafic rocks. In contrast, the low Re concentrations are more typical for deposits whose metal origin is related to crustal rocks or sedimentary sequences (Stein et al., 2001).

The porphyry Cu-Mo deposits are typically rich in Re, with Re contents reaching hundreds to thousands of ppm (0.01–0.1 wt%; e.g., Stein et al., 2001). The Re contents in molybdenite also reflect the abundance of molybdenum in a system, since almost all Re is scavenged into the molybdenite structure (MoS_2) where it substitutes for molybdenum. Indeed, a strong positive correlation (correlation coefficient 0.94) has been established between Re and Mo contents within the Mikheevskoe Cu-Mo porphyry deposits by Plotinskaya et al. (2015). The Mo/Re ratio in ores of this deposit varies from 38 up to 987. Our data also show the high Re contents in the Mikheevskoe deposit (400–759 ppm), followed by the Kalinovskoe deposit (82–228 ppm), with the lowest contents encountered in the Talitsa deposit (17–27 ppm).

High Re contents in the Kalinovskoe and Mikheevskoe Cu-Mo porphyry deposits may indicate a predominantly mantle source of metals, which is confirmed by independent isotopic studies. For example, the unradiogenic Sr isotopic composition ($^{87}Sr/^{86}Sr = 0.7042–0.7051$; Grabezhev, 2009) of diorites of the Birgilda-Tomino igneous complex together with depleted Nd values ($\varepsilon Nd = 6.5–7.5$) indicates that the ore-hosting rocks and related fluids were originated predominantly from a mantle source, possibly near the Crust–Mantle boundary (Grabezhev, 2009). Similar isotopic signatures were reported for the Mikheevskoe deposit: $^{87}Sr/^{86}Sr = 0.7050–0.7059$ and $\varepsilon Nd = 3.4–4.1$ (Grabezhev, 2009).

The Talitsa deposit is characterised by the highest Mo contents and lowest Re concentrations which may be 'diluted' by the large quantity of molybdenite according to mass balance considerations. The intrusive rocks from Talitsa deposits are characterised by low initial Sr isotopic compositions (0.7043) and slightly lower ε_{Nd} values (2.2–3.7), which possibly indicate an increasing amount of crustal (continental) component (Grabezhev, 2009).

5.3. Implications for tectonic setting

Although tectonic setting is considered in more details in the companion paper by Plotinskaya et al. (2016a), in what follows we briefly summarise the main conclusions arising from dating of molybdenites.

5.3.1. Kalinovskoe deposit

The studied Kalinovskoe deposit together with two other porphyry Cu deposits (Birgilda and Tomino) form an ore cluster named Birgilda-Tomino (Plotinskaya et al., 2014b and references therein) within the East Uralian Volcanic terrane (Fig. 1). These deposits are hosted by Ordovician basalts (Grabezhev et al., 1998; Puzhakov, 1999), but were thought to be related to Late-Devonian to Early Carboniferous porphyry intrusions (Grabezhev et al., 1998). These younger ages are in good agreement with the presence a Late-Devonian to Early Carboniferous Andean-type volcanic arc formed above the subduction zone dipping westward under the East Uralian continent at this time (Samygin and Burtman, 2009; Puchkov, 2013).

The molybdenites from the Kalinovskoe deposit display the oldest Silurian age (430.7 ± 1.3 Ma; Fig. 4) corresponding in age to diorites from the same ore field (428 ± 3 Ma and 427 ± 6 Ma; Grabezhev et al., 2013). This dataset requires reassessment of the geodynamic position of this ore field and points to the Silurian oceanic volcanic arc which could have been the southern end of the Tagil arc or developed independently (Yazeva and Bochkarev, 1995; Puchkov, 2016). See also (Plotinskaya et al., 2016b) and references therein for farther discussion.

5.3.2. Mikheevskoe deposit

The Mikheevskoe porphyry Cu deposit (see Plotinskaya et al., 2016a) occurs within a transitional structural zone between the East- and Trans-Uralian mega-terranes. It is restricted to Late Devonian – Early Carboniferous volcanic and sedimentary rocks, which are cross cut by stocks and dikes of diorite porphyritic diorite and plagiogranodiorite porphyry. The latter was recently dated using the U-Pb method in zircons at 356 ± 6 Ma (Grabezhev and Ronkin, 2011). This age is in a good agreement with our Re-Os age of molybdenites (357.8 ± 1.8 Ma and 356.1 ± 1.4 Ma; Table 2). This age correspond to the activity of the Andean-type arc on the margin of the East Uralian microcontinent (see Section 5.3.1) but petrochemical affinity of intrusions (see Plotinskaya et al., 2016a for details) indicates the presence of an ocean-type volcanic arc. Such arc is not discussed in present-day models of Urals evolution and its exact position, tectonic history, as well as the subduction direction remains unclear.

5.3.3. Talitsa deposit

The Talitsa deposit is hosted by a Carboniferous granodiorite within the East Uralian megaterrane (Fig. 1). The K–Ar biotite age of the ore-hosting granodiorite yielded 320–341 ± 8 Ma (Azovskova and Grabezhev, 2008) and suggests its relation to the relatively small and short-living Verkhisetsk subduction zone dipping eastward under an Andean-type margin of the East-Uralian continent in Serpukhovian (Fershtater, 2013). However, the Re-Os ages of molybdenite (299.9 ± 2.9 Ma and 298.3 ± 1.3 Ma; Table 2) are much younger, which is supported by unpublished zircon dating (297.4 ± 2.3 Ma; Smirnov V.N. personal communication). This younger ages point to an early stage of 'continent – continent' collision (Puchkov, 2016). However, the limited dataset (one sample) does not allow us to firmly constrain its age and geodynamic position.

6. Conclusions

Three molybdenite samples from Kalinovskoe deposit yield the Silurian Re-Os ages ranging from 427.1 to 431.7 Ma (mean 429.8 ± 4.8 Ma; 2σ standard deviation); with a Re–Os isochron age of 430.7 ± 1.3 Ma (MSWD = 0.6), which coincides with previous U-Pb dating of ore-hosting diorites from the same ore field (427 ± 6 Ma; Grabezhev et al., 2013).

The molybdenite from Mikheevskoe deposit gives Re-Os ages of 357.8 ± 1.8 and 356.1 ± 1.4 Ma (mean 357.0 ± 2.4 Ma; Carboniferous/Tournaisian), which corresponds to previous U-Pb dating of zircons from the diorite hosted porphyry deposit (356 ± 6 Ma; Grabezhev and Ronkin, 2011).

The molybdenite from Talitsa Mo-porphyry deposit yields the youngest Re-Os ages of 299.9 ± 2.9 and 298.3 ± 1.3 Ma (mean 299.1 ± 2.3 Ma) at Carboniferous-Permian boundary.

For all three studied porphyry deposits, a close spatial and temporal relationship with magmatism was established. All three studied deposits belong to the distinct stages of Urals metallogenic province development, starting from an inferred Silurian volcanic arc (Kalinovskoe deposit); subduction of the Late Devonian oceanic island arc (Mikheevskoe deposit); and the Late Carboniferous-Early Permian collision between the East European plate and the Kazakh continent.

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