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LETTER

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Re–Os ages for the Shameika porphyry Mo deposit and the Lipovy Log rare metal pegmatite, central Urals, Russia

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Abstract The ages for pegmatite rare metal and beryl (emerald) deposits, as well as porphyry Mo deposits in the Hercynian Uralide orogen, are not well known. Five molybdenite samples from the Lipovy Log pegmatite Ta–Nb–Mo deposit and 11 molybdenite samples from the Shameika porphyry Mo deposit were selected for Re–Os dating. Both mineral occurrences are spatial-temporally associated with the Adui composite granite pluton, a well-known rare metal-related granite intrusion. A Re–Os isochron age of 262.0 ± 7.3 Ma was obtained for the Lipovy Log pegmatite Ta–Nb–Mo deposit. The Shameika porphyry Mo deposit, associated with the Malyshevo leucogranitic stock and surrounding hornfels, provided isochron ages of 273 ± 5 and 282 ± 6 Ma, for two groups of molybdenite (within stock and within hornfels). All of these Re–Os ages are consistent with presumed Hercynian ages for the granite intrusions, formed in a post-collisional setting within the Uralide orogen.

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Introduction

Pegmatite rare metal deposits, beryl (emerald) deposits, and a porphyry Mo deposit occur at the eastern and southern contacts of the Late Paleozoic Adui granitic pluton in the vicinity of Malyshevo settlement, 55 km northeast of Yekaterinburg. Although the deposits have been mined for several decades and some have been closed, their metallogenic ages are not well known, but have been inferred as Hercynian–Uralide (Fershtater et al. 1997; Levin et al. 2000). We have sampled molybdenite from the Shameika porphyry Mo deposit and the Lipovy Log pegmatite Ta–Nb–Be–Mo deposit for Re–Os dating in order to determine the age of mineralization.

Geological setting

Polymetallic and emerald deposits are distributed mainly along the eastern and southern exocontact zones of the Adui granitic pluton, a member of the Kamensky, Adui, and Murzinka granitic block (Fig. 1) within the paleocontinental belt in the Central-Southern Urals (Fershtater 2000).

The Adui granite pluton consists of high-K biotite–orthoclase granite and two-mica microcline granite enriched in Rb, Li, and Cs (Fershtater 2000; Levin et al. 2000). Both plutons are inferred to be part of a larger granitic batholith hidden at depth (Levin et al. 2000). The country rocks for the Adui granitic pluton are Precambrian migmatites and biotite orthogneiss to the immediate west, and Paleozoic volcano-sedimentary rocks in the east. Twelve pegmatite rare metal deposits and beryl (emerald) deposits, in addition to a stockwork Mo deposit, are distributed along the eastern and southern contacts of the Adui granitic pluton (Fig. 2). The Adui granite pluton is intruded by the Malyshevo two-mica leucogranite, which is spatially and genetically associated with the Mo porphyry mineralization of Shameika.

The Malyshevo leucogranite stock, about 6×2 km, is hosted by both the Adui granite pluton and the Paleozoic volcanic and sedimentary rocks (Levin et al. 1995). The leucogranite consists of albite–oligoclase, latticed microcline, quartz, biotite with Fe/(Fe + Mg) ratios of 0.44–0.58, and muscovite. It is enriched in fluorite, especially within the mineralized area (Levin et al. 2000). The Shameika porphyry Mo deposit is located along the eastern contact of the Malyshevo leucogranitic stock (Fig. 3).

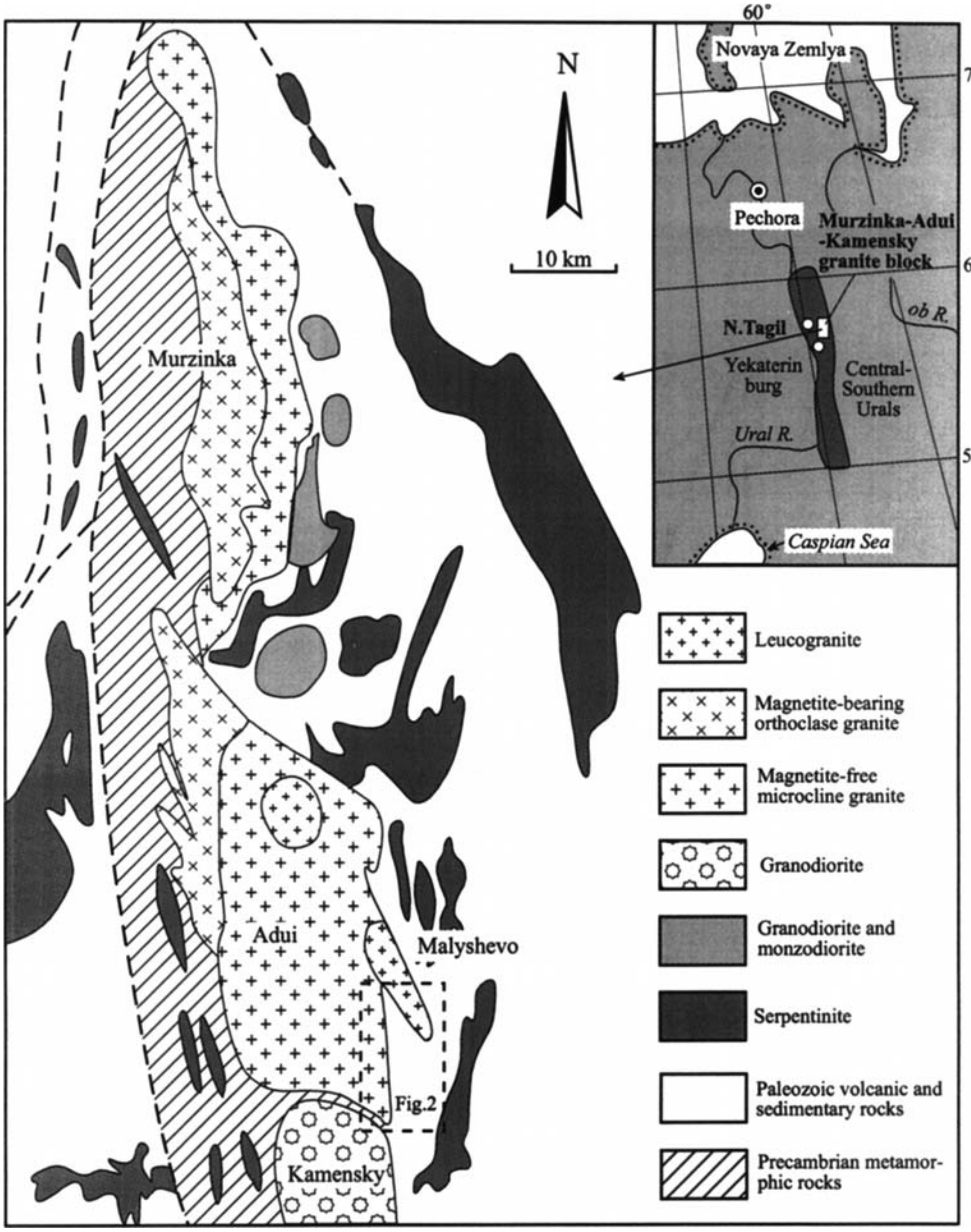

Fig. 1 Schematic geologic maps of the Murzinka–Adui–Kamensky granite intrusions (modified from Levin et al. 2000), located in the active continental margin of the Uralide orogen (Fershtater 1992). The N–S-trending Murzinka–Adui–Kamensky granite block is hosted by Precambrian metamorphic rocks in the immediate west and Paleozoic volcanic rocks in the east, and is locally intruded by younger two-mica leucogranitic stocks

Characteristics of the rare metal and porphyry Mo deposits and sampling

The Lipovy Log rare metal deposit

The Lipovy Log deposit, discovered in 1952 and mined since 1986 (Levin et al. 2000), is located in the southern exocontact zone of the Adui granitic pluton (Fig. 2). The pegmatite suite consists of 20 pegmatite veins, striking N330–340°W and dipping 55–70°NE. The veins are commonly100–1,000 m long and 10–50 m thick. Host rocks are Precambrian amphibolite, amphibole schist, and carbonaceous chert with embedded lenses of serpentinite and diorite (Levin et al. 2000). All the veins exhibit zoning, characterized by a fine-grained quartz–albite zone, medium coarse-grained quartz–albite–microcline zone, and a muscovite–quartz–albite zone from the margin inwards (Levin et al. 2000).

Tantalite and columbite are the major Ta and Nb ore minerals. The white and light green beryls in the pegmatites at Lipovy Log occur as large coarse-grained crystals. The BeO reserve is about 1,000 t with average grade of 0.034%. The Ta_2O_5 reserve is 300 t and its grade varies from 0.0004 to 0.02% with a mean of 0.007%. The Nb_2O_5 reserve is about 530 t with a mean grade of 0.0125%. The Ta_2O_5: Nb_2O_5 = 1:1.8. The tantalum mineralization is concentrated in several ore shoots located in axial portions and hanging walls of veins. Although the Mo grade is not known, many large euhedral crystals of molybdenite, which range from 0.3 to 1.2 cm in diameter, can be observed in the central zone of the ore veins. We chose five samples of molybdenite for Re–Os dating.

The Shameika Mo porphyry deposit

The stockwork of quartz–molybdenite veinlets is temporally and spatially related to the Malyshevo leucogranitic stock (Figs. 2 and 3) and includes a lateral offset into amphibole schist. It was explored from 1989–1993, and has a reserve of 43,000 t Mo with grade of 0.08% (Seltmann et al. 2000). The length of the stockwork reaches 1,200 m and the width exposed at the surface is 200 m. The

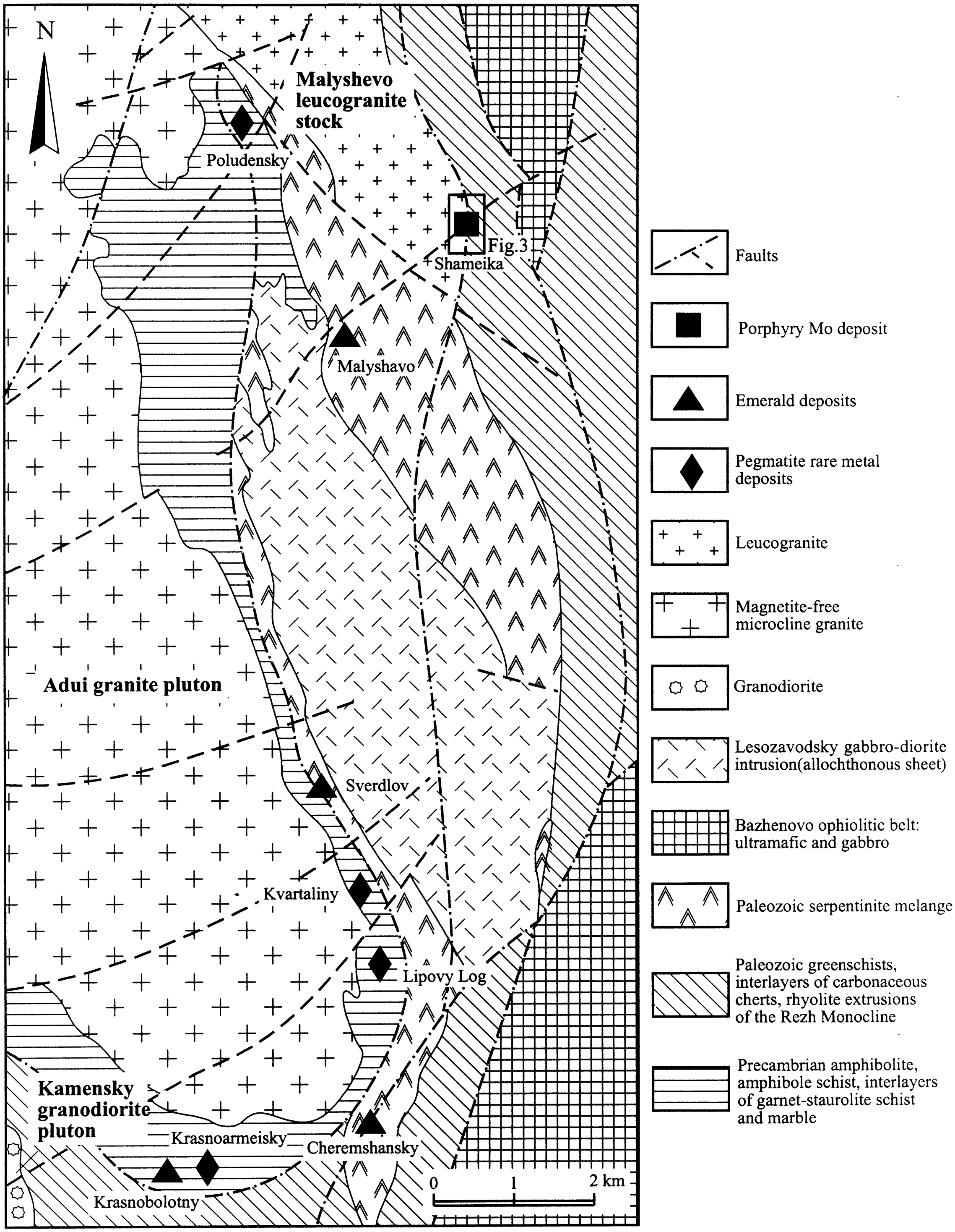

Fig. 2 Schematic geologic map of the southeastern margin of the Adui granite pluton and southern half of the Malyshevo leucogranite stock (modified from Levin et al. 2000). Locations of pegmatite rare metal, emerald, and porphyry Mo deposits are shown

lateral leucogranitic offset is hidden and occurs at a depth of 50–150 m. The host amphibole schist above the offset is transformed to a banded altered rock consisting of biotite, epidote, and calcite, cut by a dense network of granitic dikes. The stockwork of ore-bearing quartz veinlets can be traced to a depth of 220–280 m.

The stockwork Mo mineralization (dense network of ore-bearing quartz veins) is hosted both in the granitic rocks and in the exocontact hornfels zone. Around 75% of ores are hosted in the granitic rocks and 25% in the exocontact hornfels zone. The mineralization appears in a network of thin molybdenite- and pyrite-bearing fluorite–quartz veinlets. Both types of host rocks are strongly altered. Granite hosting the ore vein system is pink-colored due to an increase K-feldspar and albite, and quartz depletion relative to the primary granite. Amphibole and chlorite schists, diabase, granitic porphyry, and trachyte dikes in the exocontact zone are replaced by epidote–calcite biotite-altered rocks.

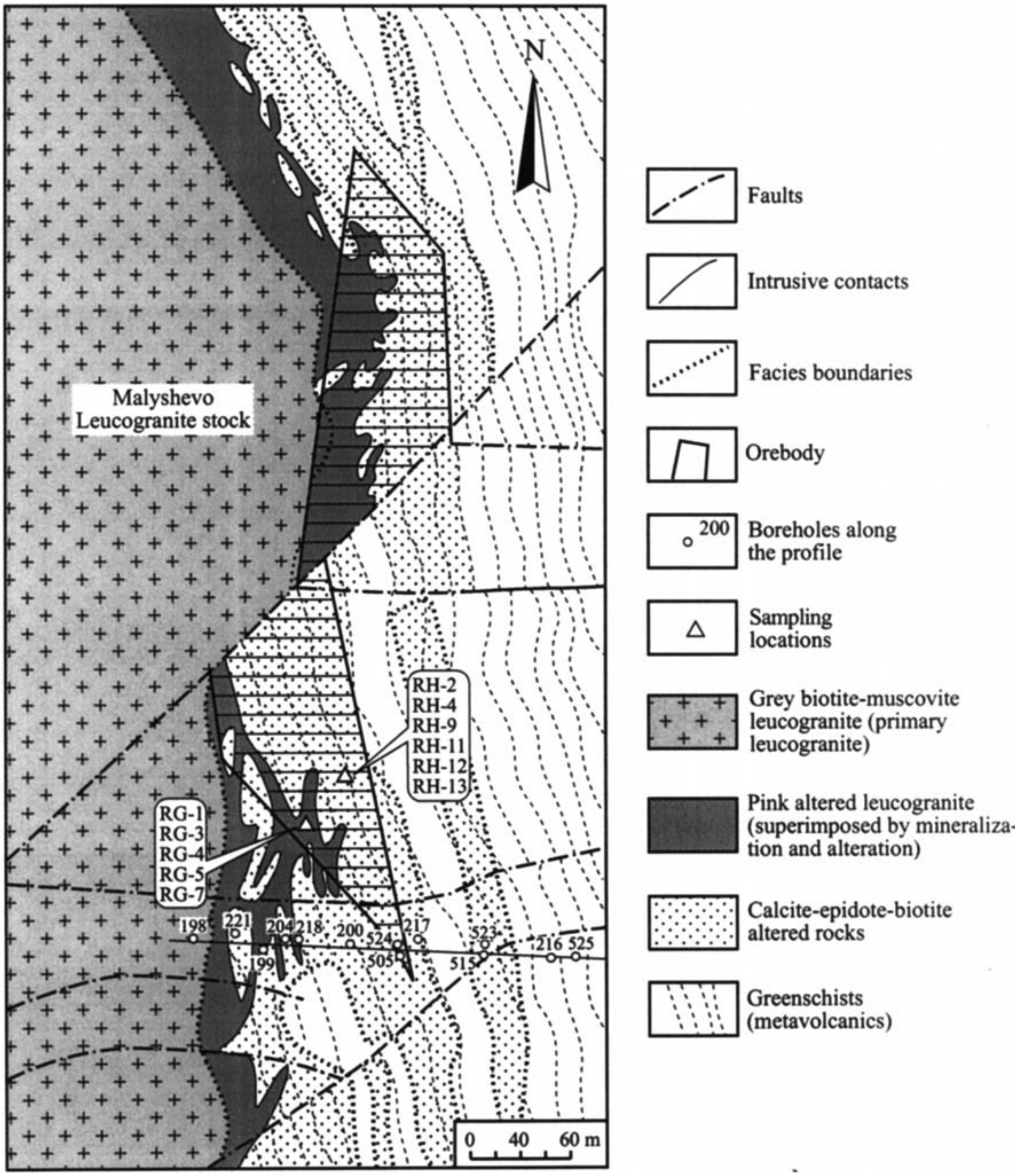

Fig. 3 Geologic map of the Shameika porphyry Mo deposit and molybdenite sample locations for Re–Os dating (modified from Seltmann et al. 2000). Samples include the stockwork quartz molybdenite hosted by leucogranite and molybdenite aggregates hosted in altered rock within the hornfels

Fine-grained molybdenite commonly occurs as banded aggregates of parallel flakes in the ore veins hosted by both granitic stock and hornfels. Both molybdenite and pyrite are concentrated near the margins within quartz veinlets. Eleven samples of molybdenite were taken for Re–Os dating, five (RG-series) hosted in the leucogranite, and six (RH-series) hosted in the exocontact hornfels zone (Fig. 3).

Re–Os isotope analysis

Re–Os isotope analyses were made in the Re–Os Laboratory, National Research Center of Geoanalysis, Chinese Academy of Geological Sciences. Du et al. (1995, 2001), Shirey and Walker (1995), Stein et al. (1998), Markey et al. (1998), and Mao et al. (1999) have described the chemical separation procedure. It is briefly described here.

Enriched ^{190}Os and ^{185}Re were obtained from the Oak Ridge National Laboratory. A Carius tube (a thick-walled borosilicate glass ampoule) digestion was used. The weighed sample was loaded in a Carius tube through a thin-neck long funnel. The mixed ^{190}Os and ^{185}Re spike solutions and 2 ml of 12 M HCl and 6 ml of 15 M HNO_3 were loaded while the bottom part of the tube was frozen at –80 to –50 °C in an ethanol–liquid nitrogen slush; the top was sealed using an oxygen–propane torch. The tube was then placed in a stainless-steel jacket and heated for 10 h at 230 °C. Upon cooling, the bottom part of the tube was kept frozen, the neck of the tube was broken, and the contents of the tube were poured into a distillation flask and the residue was washed out with 40 ml of water.

Os was distilled twice. In the first distillation step, OsO_4 was distilled at 105–110 °C for 50 min and trapped in 10 ml of water.

Table 1 Re–Os data for molybdenites from the Lipovy Log rare metal deposit and the Shameika porphyry Mo deposit, Urals, Russia. Decay constant: $\lambda(^{187}Re) = 1.666\times10^{-11}$/year (Smoliar et al. 1996). Uncertainties are absolute at 2σ with error on Re and ^{187}Os concentrations and the uncertainty in the ^{187}Re decay constant in parentheses. Locations of samples: RG-1, RG-3, RG-5, RG-6, and RG-7 are from the quartz molybdenite stockwork in the Malyshevo leucogranite stock, host to the Shameika porphyry Mo deposit; RH-2, RH-4, RH-9, RH-11, RH-12, and RH-13 are from molybdenites hosted in the hornfels surrounding the stock, and also constitute part of the Shameika porphyry Mo deposit; RP-1 to RP-5 represent pegmatite-hosted molybdenite from the Lipovy Log rare metal deposit

Sample	Weight (g)	Common Os (ng/g)	Re (μg/g)	^{187}Re (μg/g)	^{187}Os (ng/g)	Model ages (Ma)
RG-1	0.20024	0.017 (17)	8.76 (3)	5.51 (2)	25.74 (13)	271.7 (3.2)
RG-3	0.20304	0.007 (19)	16.59 (5)	10.43 (3)	48.33 (18)	273.2 (3.0)
RG-5	0.20013	0.000 (24)	13.90 (8)	8.74 (5)	40.49 (14)	272.4 (3.3)
RG-6	0.20012	0.011 (18)	5.95 (4)	3.74 (20)	17.85 (13)	273.9 (3.8)
RG-7	0.20328	0.000 (36)	8.42 (8)	5.29 (50)	25.00 (22)	274.2 (4.4)
RH-2	0.10132	0.051 (56)	36.94 (2)	23.22 (13)	110.14 (30)	283.8 (3.4)
RH-4	0.20005	0.000 (37)	12.72 (9)	8.00 (50)	37.67 (21)	281.3 (3.8)
RH-9	0.20098	0.050 (48)	9.92 (3)	6.24 (20)	28.62 (27)	273.8 (3.9)
RH-11	0.20052	0.093 (10)	2.17 (1)	1.36 (4)	6.552 (56)	282.8 (3.8)
RH-12	0.20112	0.000 (15)	9.08 (2)	5.71 (1)	27.04 (13)	282.5 (3.2)
RH-13	0.20028	0.059 (20)	11.59 (7)	7.28 (4)	34.83 (35)	285.4 (4.4)
RP-1	0.05122	0.269 (50)	23.76 (20)	14.94 (12)	64.89 (16)	258.6 (3.4)
RP-2	0.05136	0.00 (16)	22.75 (13)	14.30 (8)	63.4 (1.0)	263.9 (5.1)
RP-3	0.05119	0.035 (55)	29.35 (17)	18.45 (11)	82.43 (82)	266.3 (4.0)
RP-4	0.05128	0.121 (61)	11.87 (4)	7.460 (20)	33.04 (27)	262.0 (3.5)
RP-5	0.05065	0.00 (11)	12.42 (8)	7.810 (50)	34.81 (46)	264.0 (4.6)

The residual Re-bearing solution was saved in a 50-ml beaker for Re separation. The water trap solution plus 40 ml of water were distilled a second time. The OsO_4 was distilled for 1 h and trapped in 10 ml of water, which was used for ICPMS (TJA PQ ExCell) determination of the Os isotope ratio.

The Re-bearing solution was evaporated to dryness, and 1 ml of water was added twice with heating to near-dryness in between. An aliquot of 10 ml of 20% NaOH was added to the residue followed by Re extraction with 10 ml of acetone in a 120-ml Teflon separation funnel. The water phase was then discarded and the acetone phase washed with 2 ml of 20% NaOH. The acetone phase was transferred to a 100-ml beaker that contained 2 ml of water. After evaporation to dryness, the Re was picked up in 1 ml of water, which was used for the ICPMS determination of the Re isotope ratio. Cation-exchange resin was used to remove Na if the salinity of the Re-bearing solution was more than 1 mg/ml (Du et al. 1995).

Average blanks for the total Carius tube procedure, as described above, were ca. 10 pg Re and ca. 1 pg Os. The analytical reliability was tested by repeated analyses of molybdenite standard HLP-5 from a carbonatite vein-type molybdenum–lead deposit in the Jinduicheng–Huanglongpu area of Shaanxi Province, China. Seventeen samples were analyzed over a period of 6 months. The uncertainty in each individual age determination was about 1.4% including the uncertainty of the decay constant of ^{187}Re, uncertainty in isotope ratio measurement, and spike calibrations. The average Re–Os age for HLP-5 is 221.3 ± 0.3 Ma (95% confidence limit). Median age and mean absolute deviation were 221.34 ± 0.12 Ma. The average Re concentration was 283.71 ± 1.54 μg/g. The average Os concentration was 657.95 ± 4.74 ng/g. The AIRIE Group at Colorado State University (USA) also uses the same material as an in-house standard. They produced a median age of 221.30 ± 0.24 Ma on 19 analyses run over a period of 18 months (Markey et al. 1998). The decay constant used for ^{187}Re of 1.666×10^{-11}/year has an absolute uncertainty of ± 0.017(1.0%) (Smoliar et al. 1996).

Results

The Re–Os analytical results of 16 molybdenite samples from the Lipovy Log rare metal deposit and the Shameika Mo deposit are listed in Table 1. Five samples from the Lipoy Log rare metal deposit defined an isochron age of 262.0 ± 7.3 Ma (2σ) with an initial ^{187}Os of 0.4 ± 1.2 (MSWD = 1.6) and a correlation coefficient of 0.9994 (Fig. 4a). Model ages for the ore samples range from 259–266 Ma (Table 1).

Molybdenites associated with the stockwork deposit hosted by the Malyshevo leucogranitic stock were divided into two groups based on their geological host. One group was hosted by the hornfels in the Shameika porphyry molybdenum deposit and the other in the Malyshevo leucogranitic stock. Both groups yielded similar isochron and model ages. Five stock-hosted molybdenites yielded an isochron age of 272.7 ± 4.5 Ma with an initial ^{187}Os of 0.76 ± 0.50 (MSWD = 0.30) and a correlation coefficient of 0.99997 (Fig. 4b). Their model ages range from 272 to 274 Ma (Table 1). Six samples hosted in hornfels yielded an isochron age of 282.0 ± 5.7 Ma with an initial ^{187}Os of 0.11 ± 0.34 (MSWD = 2.8) and a correlation coefficient of 0.99993 (Fig. 4c). Their model ages varied from 274 to 285 Ma.

Discussion and conclusions

The Late Paleozoic Uralide orogen is a linear collision belt formed by convergence and accretion of outboard island arcs with the East European Craton, and includes considerable obduction of oceanic crust onto the East European Craton (Brown et al. 1997). The oceanic crust along the main suture defines internal Sm–Nd isochrons of 397 ± 20 and 396 ± 33 Ma (Edwards and Wasserburg 1985). In the past 10 years, several granitoids in the central–southern Urals have been dated. Bea et al. (1997), Fershtater et al. (1997), and Sazonov et al. (2000) summarize the intrusive history as older tonalites, trondhjemites, and granodiorites of 315–320 Ma intruded by younger granodiorites, adamellites, and granites dated at 275–290 Ma. Our molybdenite Re–Os ages are consistent with the ages for younger granitoids and related lode gold deposits dated at 280–230 Ma (Sazonov et al. 2000).

The Adui two-mica granite intrusion associated with pegmatite rare metal and emerald deposits (including Lipovy Log) is intruded by the Malyshevo two-mica leucogranite stock associated with the Shameika porphyry Mo deposit (Fig. 2). However, the molybdenite Re–Os isochron age for the former is slightly younger than the latter. This is possibly due to pegmatite-type mineralization outlasting the porphyry type (Stein and Cathles 1997).

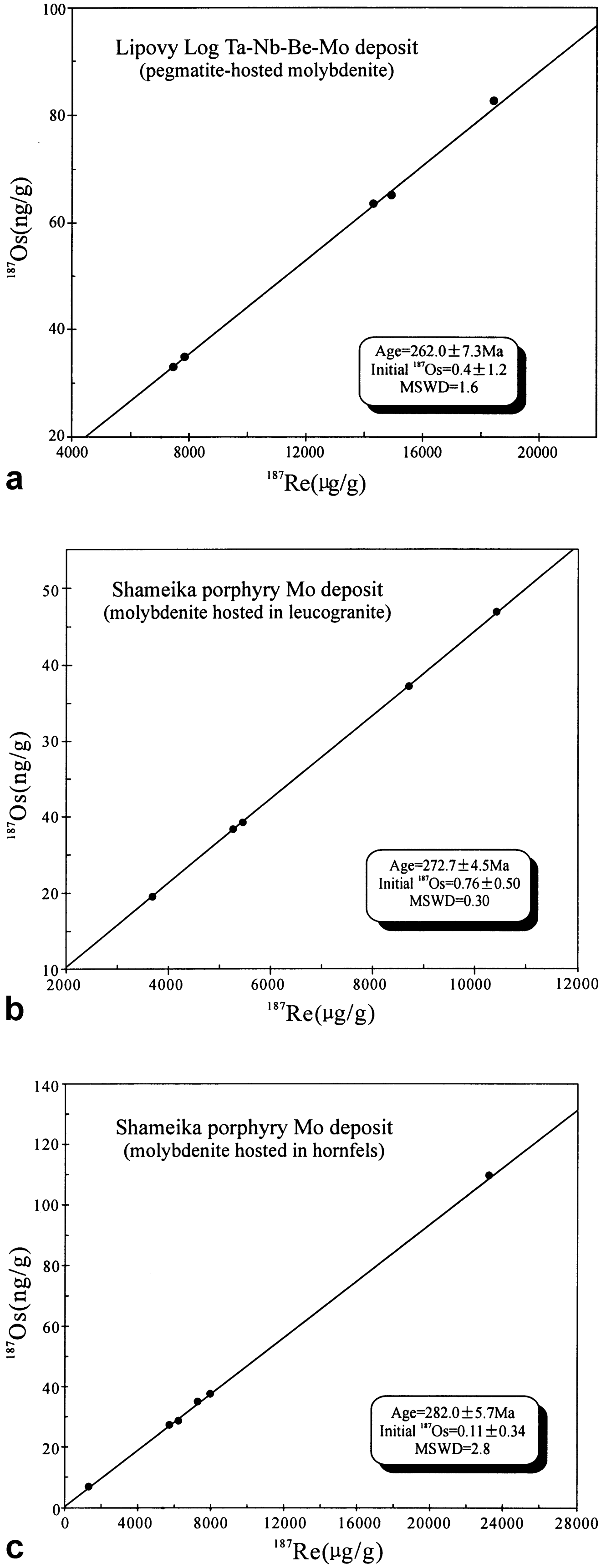

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Fig. 4 Re–Os isochron plots for molybdenite samples from **a** the Lipovy Log pegmatite rare metal deposit, and the Shameika porphyry Mo deposit: **b** leucogranite hosted and **c** hornfel hosted. ISOPLOT software of Ludwig (1999) was used to calculate the isochron ages

Rhenium contents in molybdenites vary greatly (Fleischer 1960; Terada et al. 1971). Mao et al. (1999) suggested that the rhenium content in molybdenites could reflect the sources of the deposits with Re content decreasing from mantle to I type to S type granite-related deposits. Stein et al (2001) also suggested that deposits with a mantle component to their derivation have significantly higher Re contents than those deposits that are crustally derived. The Re data of the molybdenites from the Lipovy Log pegmatite rare metal deposit and the Shameika porphyry Mo deposit (Table 1) could suggest that the Adui two-mica granite intrusion contains more mantle components than the Shameika two-mica leucogranite stock.

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