Isotopic Re-Os age of molybdenite from the Szklarska Poręba Huta Quarry (Karkonosze, SW Poland)

Wojciech MAYER, Robert A. CREASER, Ksenia MOCHNACKA, Teresa OBERC-DZIEDZIC and Adam PIECKZA

New Re/Os isotopic data for molybdenite from the Szklarska Poręba Huta Quarry provide ages of 307 ± 2 Ma and 309 ± 2 Ma, respectively. The quarry is dominated by the porphyritic (“central”) and equigranular (“ridge”) varieties of the Karkonosze granite. Ore mineralisation hosted in aplogranite includes an assemblage of sulphides, sulphosalts, oxides and various rare phases. The molybdenite ages obtained are consistent with a previously published isotopic age of leucogranite (aplogranite?) from the same quarry and are only slightly older than a recently published, refined 206Pb/238U age of untreated zircons from the Szklarska Poręba Huta porphyritic granite. The age of the molybdenite corresponds moderately well to the younger stage of post-magmatic, pneumatolitic/hydrothermal activity of the Karkonosze granite (about 312 Ma).


INTRODUCTION

The Variscan Karkonosze granite intrusion is located in southwestern Poland and in northeastern Bohemia. It belongs to a system of European Variscan granitoid plutons known from Poland, the Czech Republic, Germany, France, England, Spain and Portugal and elsewhere (see e.g., Seltmann and Faragher, 1994). The Polish members of this granitoid province are generally related to various stages of the Variscan orogeny although their geotectonic affinity is still disputed (e.g., Wilamowski, 1998; Kennan et al., 1999; Obere-Dziedzic et al., 1999, 2010; Mazur et al., 2007; Mierzejewski, 2007).

As in other Variscan granitoids (see e.g., Seltmann and Faragher, 1994), the Karkonosze intrusion and its metamorphic envelope are well-known hosts of diverse, primary ore mineralisation resulted from the combined effect of the thermal energy transfer from the pluton and a related, hydrothermal solution circulation system. General data on ore mineralisation in the Karkonosze granite and its metamorphic envelope can be found in Berg (1913), Petrascheck (1933, 1937), Gajda (1960a), Kozłowski (1978), Mochnacka et al. (1995), Mochnacka (2000), Mochnacka and Banaś (2000), Michniewicz (2003) and Mikułski (2007) (and references therein).

A well-known site of hydrothermal ore mineralisation including molybdenite is the granite quarry in Szklarska Poręba Huta (Fig. 1). As molybdenite is a perfect material for Re-Os isotopic age determination due to relatively high contents of Re and to the origin of practically all Os from the decay of Re, the authors used MoS2 specimens for age determination of part of the ore mineralisation from that site. It supplements existing age determinations of Karkonosze granite-related mineralisation.

GEOLOGICAL SETTING

The Karkonosze-Izera Massif (KIM) is the largest structure in the Western Sudetes. It comprises two main elements: the
Variscan Karkonosze granite intrusion and its Neo-proterozoic-Paleozoic metamorphic cover. The latter shows remarkable diversity in stratigraphy and metamorphic history, which enable distinction of four consecutive structural units: Izera-Kowary, Ještěd, South Karkonosze and Leszczyńiec, arranged as a stack of nappes formed in the Late Devonian and re-arranged in the early Carboniferous (for details see Mazur and Aleksandrowski, 2001). During the Variscan orogeny the nappe structure was intruded by the Karkonosze granite which resulted in the formation of an extensive contact aureole (Mierzejewski and Obere-Dziedzic, 1990).

The Karkonosze granite is a complex intrusion comprising three petrographic varieties: central (porphyritic), ridge (equigranular) and granophyric (fine-grained), of roughly similar chemical compositions (corresponding to monzonites and granodiorites) but different structures, accessory mineral assemblages, and the frequency of schlieren and enclaves (for details see Borkowska, 1966). Various aspects of the Karkonosze granite were discussed by e.g., Cloos (1925), Borkowska (1966), Klomínský (1969), Mierzejewski and Obere-Dziedzic (1990), Wilamowski (1998), Mierzejewski (2003, 2007), Žák and Klomínský (2007), Słaby and Martin (2008) and others.

Isotopic data (see Duthou et al., 1991; Mierzejewski et al., 1994) as well as geochemical modelling (Słaby and Martin, 2008) preclude a pure, crustal source of magma and suggest rather its origin from the mixing of crustal and mantle magmas (Mierzejewski et al., 1994; Mierzejewski, 2007), which resulted in the formation of porphyritic granite and subsequent fractional crystallisation leading to the equigranular variety (Słaby and Martin, 2008).
ORE MINERALISATION IN THE SZKLARSKA PORĘBA HUTA QUARRY

In the Szklarska Poręba Huta Quarry both the porphyritic (“central”) and the equigranular (“ridge”) granite varieties can be found. Both enclose common, bright (aplitic) and dark (biotitic) schlieren and dark, ellipsoidal, fine-crystalline enclaves, and both are cut by thin aplite veins. The porphyritic granite contains coarsely crystalline, pink K-feldspar accompanied by white plagioclase, grey quartz, and biotite with accessory zircon and apatite. A characteristic feature is the presence of large phenocrysts of pink K-feldspar rimmed by plagioclase (see Kryza et al., 2012). Aplogranite, which accompanies the porphyritic granite, appears as a whitish, generally finely crystalline mass of grey quartz, whitish feldspars including plagioclases, and biotite. It encloses small (about 5 cm across), irregular, pegmatitic aggregates composed of euhedral/subhedral, white feldspars and grey quartz accompanied by biotite and pyrite. Field data and isotopic age determinations (Mikulski et al., 2004) indicate that the aplogranite is younger than the porphyritic granite (see Table 2).

The Szklarska Poręba Huta Quarry is a well-known site of ore mineralisation described by many authors (see Berg, 1923; Gajda, 1960a, b; Karwowski et al., 1973; Kozłowski et al., 1975; Olszyński et al., 1976; Kozłowski et al., 2002; Pieczka and Gółębiowska, 2002; Kozłowski and Sachanbirsło, 2007; Mikulski and Stein, 2007). A diverse ore mineral assemblage identified by these authors includes: Fe-wolframite, scheelite, cassiterite, native Bi, bismuthinite, molybdenite accompanied by arsenopyrite, pyrrhotite, chalcopyrite, pyrite, tetrahedrite, sphalerite, galena, marcasite, melanikovite, chalcocite, native Ag, Ti-magnetite, magnetite, wolframite, stolzite, emplectite, nussellitite, rutile, monazite, zircon, fergusonite, niobite, gadolinite, hingganite, thorite, titanite and a variety of secondary minerals.

We found ore mineralisation in bright, fine-crystalline aplogranite. Ore minerals form disseminated structures or, less commonly, larger aggregates, up to 2 mm across, accompanying coarsely crystalline, drusy quartz-feldspar intergrowths. Under the microscope we identified: pyrite, pyrrhotite, sphalerite and chalcopyrite accompanied by molybdenite, rutile, wolframite, scheelite, magnetite, cassiterite, marcasite, uranothorite? and trace amounts of native Bi, bismuthinite, chalcocite and ilmenite. At the present stage of observations, a detailed ore mineral succession cannot be established due to the small number of samples although at least two stages of this mineralisation are suggested.

Molybdenite was found in several samples as individual, disseminated crystals accompanied coarsely crystalline, drusy quartz-feldspar aggregates (Fig. 2). Molybdenite crystals show typical optical properties. Its chemical composition indicates trace admixtures of tungsten (0.01 and 0.07 wt.%).

Pyrrhotite usually forms anhedral crystals and aggregates. Some pyrrhotite grains resemble pseudomorphs after an unidentified flaky mineral. Pyrrhotite does not contain significant admixtures of trace elements.

Chalcopyrite forms intergrowths with pyrrhotite or individual crystals. The chemical composition of the chalcopyrite does not include remarkable trace elements.

Marcasite forms aggregates of elongated crystals. Their chemical composition reveals Mn (0.03 wt.%) and Ti (0.04 wt.%).

Pyrite was observed as disseminated crystals, locally accompanying magnetite aggregates.

Wolframite and scheelite form spotty aggregates composed of anhedral crystals. Their intercrystal spaces are filled with chalcopyrite, bismuthinite and native Bi. The chemical composition of the wolframite shows increased amounts of Mn (6.8 wt.%) whereas in scheelite Mn contents are low (0.02 wt.%).

Magnetite forms aggregates of anhedral crystals, which fill spaces between large crystals of rock-forming minerals. Lamellar intergrowths of ilmenite are common. Locally, magnetite aggregates are rimmed by ilmenite overgrowths. Some ilmenite crystals host minute cassiterite inclusions as well as uranothorite crystals. Magnetite-ilmenite intergrowths are usually surrounded by disseminated pyrite accumulations.

Ilmenite contains high amounts of MnO (up to 10 wt.%) and also TiO₂ (51.2–51.4 wt.%), FeO (2.0–3.0 wt.%) and V₂O₅ (0.2–0.3 wt.%).

The X-ray powder pattern enabled us to identify xenotime and monazite accompanied by ilmenite, pyrite and unidentified uranium minerals.

AGE DETERMINATIONS

AVAILABLE DATA

The age determinations of the Karkonosze granite are listed in Table 2. A wide range of results obtained with various methods of isotopic age studies give age limits of Karkonosze intrusion formation between 328 ± 12 Ma (Pin et al., 1987) and 292 Ma (Przewlocki et al., 1962) (see Table 2). The age of the porphyritic granite variety, which hosts our molybdenite crystals, was determined by several authors, giving ages between 328 ± 12 Ma (Pin et al., 1987) and 296 Ma (younger age provided by Depciuch and Lis, 1971). However, Kryza et al. (2012) showed that the young ages reported for the porphyritic granite (297 and 301 Ma) may be an effect of Pb loss.

There are few isotopic ages of ore minerals from the Karkonosze granite. Kucha et al. (1986) provided a U/Th/Pb age of disseminated, Th-bearing uraninite (bröggerite) collected from a core from the Jakuszyce IG 1 well at 299.8 Ma. Mikulski et al. (2004) determined, using the CHIME method (U, Th, Pb), the ages of monazite and xenotime in aplogranite from the Szklarska Poręba Huta Quarry at 271 ± 20 Ma and interpreted this age as the formation time of the aplogranite and of pneumatolitic/hydrothermal mineralisation. Mikulski and Stein (2007) provided Re/Os isotopic ages of molybdenite from the Karkonosze granite samples collected in the Lomnica Górna (326 ± 1 Ma) and the Michalowice (315 ± 1 Ma) quarries. Recently, Mikulski and Stein (2011) provided two Re/Os ages of
vein-type and disseminated molybdenite from the Szklarska Poręba Huta Quarry at 310 ± 1 Ma and 323 ± 1 Ma, respectively.

GENERAL REMARKS

Molybdenite is naturally enriched in rhenium (Re) and contains insignificant amounts of Os, meaning that effectively all Os is derived from the decay of Re. To measure the abundance of Re and Os in molybdenite samples by isotope dilution, a mixed double spike solution was used containing isotopically enriched $^{185}$Re together with isotopically enriched $^{188}$Os and $^{190}$Os (Selby and Creaser, 2004).

The $^{185}$Re abundance in the tracer solution is calibrated directly against a gravimetric Re standard solution made from 99.999% Re metal and shows a reproducibility of better than ±0.20% 1σ (n = 6). The Os abundance in the tracer solution is calibrated directly against a gravimetric Os standard solution of known isotopic (Selby and Creaser, 2004) composition. The abundance of $^{187}$Os in molybdenite is calculated by measuring the Os abundance after equilibrating $^{187}$Os in molybdenite and the double $^{188}$Os and $^{190}$Os in the tracer solution. In this way, the isotopic analysis of Os can be corrected for instrumental fractionation during analysis, and potential “common” Os in the molybdenite quantified.

MATERIAL

For age determinations three samples were selected, labeled Mo-1, Mo-2 and Mo-3. All contained exposed grains of molybdenite in altered granite from the Szklarska Poręba Huta Quarry.

METHODS

Microprobe analyses of the molybdenite and of other ore minerals were carried on at the Joint-Institute Analytical Complex for Minerals and Synthetic Substances, Faculty of Geology, University of Warsaw under standard analytical conditions (see e.g., Mochnacka et al., 2008).

Re/Os isotopic age determinations were carried out at the Geochronology and Radiogenic Isotopic Analyses Laboratory, Geospec Consultants LTD., Edmonton, Canada.

The molybdenite was separated by full mineral separation procedures of crushing and milling, followed by magnetic and gravity concentration techniques (see Selby and Creaser, 2004).

The Carius-tube method was used for the dissolution of molybdenite and equilibration of sample, tracer Re and Os. Molybdenite samples were dissolved and equilibrated with a known amount of tracer in reverse aqua regia (2:1 16N HNO$_3$).
and 12N HCl, 3 ml) at 240°C for 24 h then cooled and refrigerated prior to Os and Re separation. Extraction of OsO₄ from the acid-sample mix was achieved using modified solvent extraction and microdistillation techniques. Mo was removed by solvent extraction from the acid-sample mixture after Os separation. Rhenium was then purified by HNO₃ + HCl-based anion exchange chromatography using standard techniques. Total procedural blanks for Re and Os were less than 2 picograms and 0.5 picograms, respectively. These procedural blanks are insignificant in comparison to the Re and Os concentrations in the molybdenite analysed here. The purified Re and Os separates were analysed by Negative Thermal Ion Mass Spectrometry (N-TIMS), and the abundances of ¹⁸⁷Re and ¹⁸⁷Os were calculated. A trial analysis established the Re abundance of the molybdenite concentrate at ~0.13 ppm, followed by the full Re-Os analyses. A second full Re-Os analysis was completed several weeks later than the first. The results of these analyses are presented below in Table 1.

The Chinese molybdenite powder HLP-5, used as an in-house “control” in the molybdenite laboratory, AIRIE, Colorado State University, was used as an external control of sample absolute age and reproducibility for this work. For this “control sample” using the Carrius-tube technique with mixed-double spike described here, we obtained an average Re-Os age of 220.0 ± 1.0 Ma (2σ). This age is nominally younger than the long-term average age of 220.52 ± 0.24 Ma (2σ) reported by Selby and Creaser (2004) using the “Normal Addition” method for Os.

## RESULTS AND DISCUSSION

The ore mineral assemblage found in aplogranite samples from the Szklarska Poręba Huta Quarry does not differ from that previously described from that site (see references above) neither in the index of minerals nor in their structures and textures. However, our molybdenite specimens represent the disseminated variety, not molybdenite hosted in quartz veins (see e.g., Kozlowski et al., 1975; Mikulski and Stein, 2011).

Our Re/Os isotopic age determinations revealed two consistent values for molybdenite disseminated in the Szklarska Poręba Huta aplogranite: 307 ± 2 Ma and 309 ± 2 Ma (Table 1). These values correspond best to leucogranite (aplogranite?) from the same quarry (310 ± 5 Ma; Mierzejewski et al., 1994). Simultaneously, our results are only slightly older than a recently published, refined ²⁰⁶Pb/²³⁸U age of untreated zircons from the Szklarska Poręba Huta porphyritic granite (306 ± 4 Ma; Kryza et al., 2012), and are consistent also with previously determined ages of equigranular granite (309 ± 3 Ma, Duthou et al., 1991 and 310 ± 14 Ma, Pin et al., 1987) and a porphyritic granite enclave from Malý Staw (309 ± 17 Ma, Mierzejewski et al., 1994). In general, our results are consistent with the younger magmatic event in the Sudetes distinguished by Mazur et al. (2007). It suggests pene-contemporaneous crystallisation of disseminated molybdenite and granite rock-forming minerals in, at least, a part of the intrusion.

Considering the age determinations of the in-granite ore mineralisation, our molybdenite ages are consistent with the younger age (310 ± 1 Ma) of two different generations of molybdenite published by Mikulski and Stein (2011) for samples from the Szklarska Poręba Huta Quarry. This mineralisation may be related to the younger stage of post-magmatic, pneumatolitic/hydrothermal activity distinguished by these authors (ca. 312 Ma, Mikulski and Stein, 2007). However, our molybdenite represents the disseminated type for which Mikulski and Stein (2011) determined a much older age (323 ± 1 Ma). Such time relationships may suggest diverse, long-lasting activity of pneumatolitic and hydrothermal systems of the Karkonosze granite, extending at least from 326 ± 1 Ma to 307 ± 2 Ma. This interpretation is supported by the multi-pulse character of the intrusion (Mierzewski, 2007), which renewed the thermal capacity of the pluton and, thus, extended the driving force of the surrounding hydrothermal system. Robb (2005) proposed the lifetime of hydrothermal fluid circulation to be about 10⁴ to 10⁶ years for small intrusions (1–2 km wide) and Misra (2000) estimated a much shorter cooling time of “reasonably sized” intrusions (<10 km) to be some 10⁴ years. Obviously, as the Karkonosze intrusion is much larger, the hypothetical lifetime of its hydrothermal system was much longer.

## CONCLUSIONS

1. Molybdenite from the Szklarska Poręba Huta Quarry disseminated in aplogranite was dated at 307 ± 2 Ma and 309 ± 2 Ma with the Re-Os isotopic method.
Table 2

List of isotope ages revealed by various methods applied to the Karkonosze granitoids (Polish part of the Karkonosze intrusion) and to related ore mineralisation

<table>
<thead>
<tr>
<th>Rock/locality</th>
<th>Method</th>
<th>Granite age [Ma]</th>
<th>References</th>
<th>Mineralisation age [Ma]</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Karkonosze granite, Szklarska Poręba</td>
<td>Rb/Sr K/Ar</td>
<td>292</td>
<td>Przewłocki et al. (1962)</td>
<td></td>
<td></td>
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<tr>
<td>Aplogranite, Szklarska Poręba Huta</td>
<td>U. Th, Pb CHIME xenotime</td>
<td>ca. 294</td>
<td>Mikulski et al. (2004)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aplites</td>
<td>K/Ar biotite</td>
<td>294–304</td>
<td>Depciuch and Lis (1971)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equicrystalline granite</td>
<td>K/Ar biotite</td>
<td>294–306</td>
<td>Depciuch and Lis (1971)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porphyritic, medium-crystalline granite</td>
<td>K/Ar biotite</td>
<td>296–307</td>
<td>Depciuch and Lis (1971)</td>
<td></td>
<td></td>
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<tr>
<td>Karkonosze granite, Borów</td>
<td>K/Ar whole rock</td>
<td>299 ± 27</td>
<td>Borucki (1966)</td>
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<td></td>
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<tr>
<td>Karkonosze granite, Jakszyce</td>
<td>U/Pb microprobe</td>
<td>299.8 bröggerite</td>
<td>Kucha et al. (1986)</td>
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<tr>
<td>Equigranular granite</td>
<td>U/Pb SHRIMP zircon</td>
<td>302 ± 6</td>
<td>Kusiak et al. (2008)</td>
<td></td>
<td></td>
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<tr>
<td>Granophytic granite</td>
<td>K/Ar biotites</td>
<td>302–305</td>
<td>Depciuch and Lis (1971)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porphyritic, coarse crystalline granite</td>
<td>K/Ar biotites</td>
<td>303</td>
<td>Depciuch and Lis (1971)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microgranular enclave in equigranular granite</td>
<td>Pb/Pb, U/Pb SHRIMP zircon</td>
<td>304 ± 3</td>
<td>Kusiak et al. (2009)</td>
<td></td>
<td></td>
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<tr>
<td>Porphyritic monzogranite</td>
<td>Pb/Pb evaporation, U/Pb, zircon</td>
<td>304 ± 14</td>
<td>Kröner et al. (1994)</td>
<td></td>
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<tr>
<td>Porphyritic granite, Szklarska Poręba Huta</td>
<td>U/Pb SIMS, untreated zircons</td>
<td>306 ± 4</td>
<td>Kryza et al. (2012)</td>
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<tr>
<td>Aplogranite, Szklarska Poręba Huta</td>
<td>Re/Os</td>
<td>307 ± 2 and 309 ± 2 molybdenite</td>
<td>this paper</td>
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<td>“Ridge”, equigranular granite</td>
<td>Rb/Sr whole rock isochrone</td>
<td>309 ± 3</td>
<td>Duthou et al. (1991)</td>
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<tr>
<td>Porphyritic granite enclave Mal Staw</td>
<td>Rb/Sr whole rock</td>
<td>309 ± 17</td>
<td>Mierzejewski et al. (1994)</td>
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<tr>
<td>Aplogranite, Szklarska Poręba Huta</td>
<td>Re/Os</td>
<td>310 ± 1 molybdenite</td>
<td>Mikulski and Stein (2011)</td>
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<td>Leucogranite, Szklarska Poręba Huta</td>
<td>Rb/Sr whole rock</td>
<td>310 ± 5</td>
<td>Mierzejewski et al. (1994)</td>
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<tr>
<td>Ridge, equigranular</td>
<td>Rb/Sr whole-rock isochron</td>
<td>310 ± 14</td>
<td>Pin et al. (1987)</td>
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<tr>
<td>Izera village granite</td>
<td>K/Ar whole rock</td>
<td>310 ± 28</td>
<td>Borucki (1966)</td>
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<tr>
<td>Microgranodiorite Karpacz–Janowice Wielkie dyke swarm</td>
<td>U/Pb SHRIMP zircon</td>
<td>313 ± 3–318 ± 3</td>
<td>Awdankiewicz et al. (2010)</td>
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<tr>
<td>Porphyritic granite from NE part of intrusion</td>
<td>U/Pb SHRIMP zircon</td>
<td>314 ± 3–318 ± 4</td>
<td>Machowiak and Armstrong (2007)</td>
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<tr>
<td>Equigranular granite</td>
<td>U/Pb SHRIMP zircon</td>
<td>314 ± 5</td>
<td>Kusiak et al. (2008)</td>
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<tr>
<td>Michałowice granite</td>
<td>Re/Os</td>
<td>315 ± 1 molybdenite</td>
<td>Mikulski and Stein (2007)</td>
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<tr>
<td>Equigranular granite</td>
<td>Ar/Ar muscovite</td>
<td>315 ± 2</td>
<td>Marheine et al. (2002)</td>
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<td>Porphyritic granite (Liberec type)</td>
<td>Ar/Ar biotite</td>
<td>320 ± 2</td>
<td>Marheine et al. (2002)</td>
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### REFERENCES


