

Re-Os ages for molybdenites from the Saga I and Sagåsen larvikite quarries, Oslo Rift, south Norway

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Abstract

Here we present molybdenite to constrain the ages of two nepheline syenite pegmatites in larvikite quarries (Saga I and Sagåsen quarries) in the Larvik Plutonic Complex of the Oslo Rift, Norway. We discuss three dates acquired from the Saga I molybdenite, and three dates acquired from the Sagåsen molybdenite and report ages of 287 ± 1 and 289 ± 1 Ma, respectively. The molybdenite samples are hosted in analcime and spreustein (hydrothermally-altered nepheline), a common feature in the region. We interpret the molybdenite dates as the time of hydrothermal alteration of ~290 Ma nepheline syenite pegmatites.

Introduction

It was not until well into the 20th century that it became possible to obtain absolute ages for rocks and minerals. The U-Pb dating technique was first demonstrated by Boltwood (1907) using quantitative Pb and U concentrations in minerals obtained from published literature. Holmes (1911) made the first Pb and U analysis specifically designed for age determination purposes, using a set of 17 mineral samples (13 different species) from the syenite pegmatites in the Larvik Plutonic Complex (LPC). His pioneering work revealed an age of about 370 Ma. The U-Pb method became the prime tool for age determination of minerals and rocks. Several other radiometric dating techniques, however, have been established over the years. The rhenium-osmium (Re-Os) geochronometer is a novel tool for dating sulfides, and its first success was with the mineral molybdenite (Stein *et al.* 2001). Here we use for the first time Re-Os dating of molybdenite from LPC nepheline syenite pegmatites.

Sample Descriptions

The syenite pegmatites and their diversity of minerals from the LPC became famous through the classic monograph by Brøgger (1890), updated by Larsen (2011; 2013). The mineral characteristics of the pegmatites span from miaskitic to mildly agpaitic.

Practically all the pegmatites in the LPC have suffered some degree of alteration during multiple events of late-stage, hydrothermal-fluid interactions. Primary (magmatic) minerals, especially nepheline, sodalite and K-feldspar have been altered by hydrothermal fluids resulting in the formation of zeolites and Al-hydroxides. Primary leucophanite and meliphanite have been altered into a plethora of secondary, hydrous Be-minerals. Most of the sulphides have formed from the hydrothermal fluids,

and the crystallization of molybdenite was discussed already by Brøgger (1890, p. 5). He concluded that the mineral was formed late, slightly before the zeolite sequence.

The dated samples were collected by A.O. Larsen from fresh quarry workings in the Saga I and Sagåsen larvikite quarries, Auen area, Porsgrunn community, Telemark county, Norway. Additional details on these two quarries and their histories can be found in Larsen (2011, p. 54-57). The locations for the Saga I and Sagåsen samples are N59.04366 at E9.83056 and N59.04393 at E9.82876, respectively (Fig. 1).

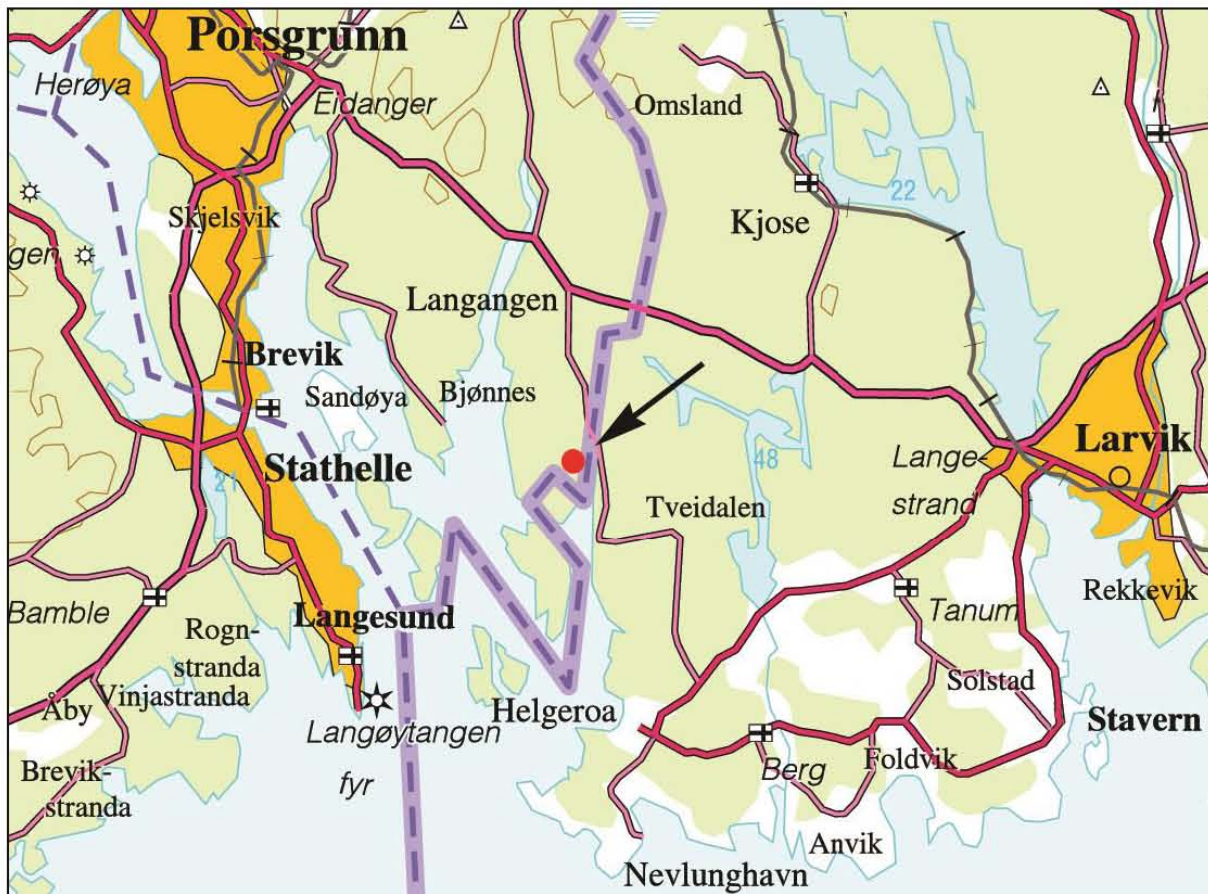


Fig. 1. Map showing the location of the Saga I and Sagåsen quarries (red dot). The violet line indicates the border between Telemark county (left) and Vestfold county (right). Scale: 1 cm \approx 2 km.

Both molybdenites are hosted in analcime and spreustein, a hydrothermal alteration product of nepheline (and/or sodalite) primarily composed of finely fibrous natrolite with minor amounts of boehmite/diaspore (Larsen 1981). Accessory minerals include green, needle-shaped, second generation aegirine. The molybdenite analyzed in this study is shown *in situ* in the collected samples (Fig. 2, before).

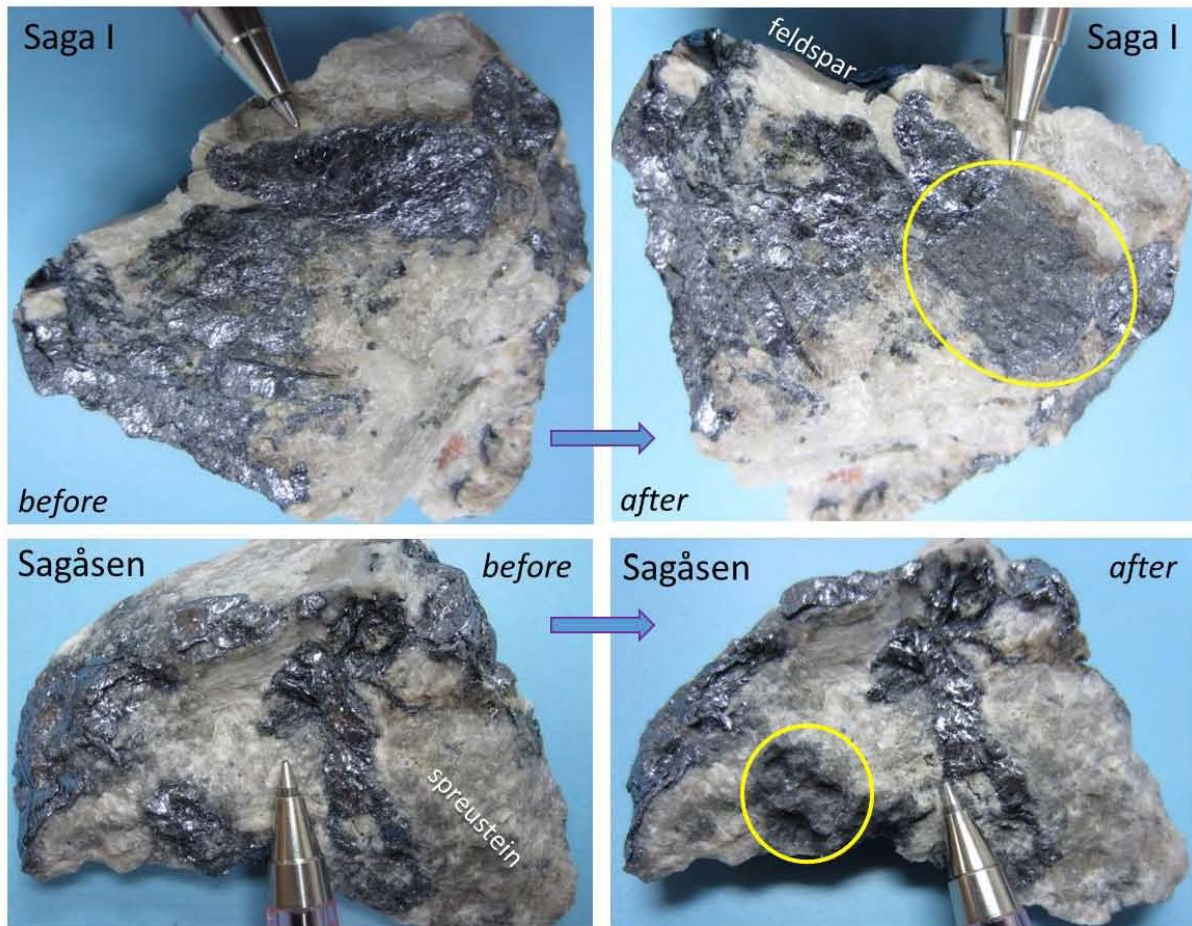


Fig. 2. Molybdenite-rich samples from hydrothermally-altered nepheline syenite pegmatite in the Larvik Plutonic Complex, Oslo Rift, south Norway. Before drilling for mineral separate and after drilling views are shown. Molybdenite separates were drilled from a single region in both samples, as outlined in the yellow circles. Pen tip for scale.

Methods

Re (rhenium) and Os (osmium) are highly chalcophile and siderophile elements. Successful Re-Os dating of molybdenite is a recently developed methodology based on the beta decay of $^{187}\text{Re} \rightarrow ^{187}\text{Os}$ (Stein *et al.* 2001) and the discovery that Re and Os can be measured as negative ions using TIMS (Creaser *et al.* 1991). The single mineral dating of molybdenite is based on the fact that initial (or common) Os is rare in this mineral. The Os budget in molybdenite is overwhelmingly radiogenic daughter (^{187}Os), accumulated through time.

Originally aimed at dating molybdenite-bearing assemblages in the ore-forming environment, the method immediately found application for dating other magmatic and metamorphic assemblages where molybdenite was present as an accessory mineral (*e.g.* Stein and Bingen 2002). Subsequently, the Re-Os chronometer in molybdenite found widespread use for reconstruction of shear zone and terrane histories (*e.g.* Stein *et al.* 2004; Zimmerman *et al.* 2008). The Re-Os clock in molybdenite is robust through granulite facies conditions (Bingen and Stein 2003). Rather than closure temperature molybdenite's fallibility lies in its chemical sensitivity to oxidation, and its distaste for Os which can create spatial decoupling of ^{187}Re parent and ^{187}Os daughter, particularly in older deformed

molybdenites (Stein *et al.* 2003; Stein 2014). The decoupling issue is easily resolved with smart sampling, for example, removing and analyzing whole crystals for Re-Os isotopic analyses even if those crystals are sub-milligram size (Stein 2006).

A small hand-held drill was used to separate molybdenite from its host rock. The textural and mineralogic context of the molybdenite is carefully documented at the hand specimen scale. During the separation process, we make a visual estimate of any quartz, feldspar, or other silicate that dilutes the molybdenite separate. Silicate contamination does not affect Re-Os dating of molybdenite, as silicates do not take Re and Os into their structure. Any silicate dilution of the molybdenite separate simply lowers the measured Re and Os concentrations proportionately without disturbing the radiometric clock.

A weighed quantity of the molybdenite separate is combined with a mixed Re-double Os spike (^{185}Re - ^{188}Os - ^{190}Os) pioneered by the AIRIE Program (Markey *et al.* 2003). Use of a double Os spike permits precise determination of common Os and corrects for mass fractionation. The sample-spike dissolution-equilibration takes place in a sealed Carius tube, heated at 250°C for 12 hours. Re is subsequently separated and purified using anion exchange chromatography. Os is separated by a two-step solvent extraction followed by micro-distillation. Re-Os isotopic ratios are measured using a Triton TIMS machine at the AIRIE Program, Colorado State University. Samples are archived as part of the molybdenite collection at AIRIE.

Results

Re and Os concentration data and calculated ages are presented in Table 1. All data are blank corrected and reported at two-sigma uncertainty. These data were acquired from a drilled molybdenite powder extracted from each sample (Fig. 2, after). Three separate Re-Os dates were acquired for each of the two samples, based on two different mineral separates acquired from each sample (see footnotes, Table 1).

Re concentrations are extremely low for these molybdenites, falling at the low ppb level. Correspondingly, the radiogenic ^{187}Os concentrations are low, to the point where blank corrections become important. Analytical blanks are run side-by-side with each sample, but knowledge of the true analytical blank in a given analysis of a sample is never known. For nearly all molybdenites, blank corrections are irrelevant (though we make them). In this study, however, careful examination of the data in Table 1 shows how sensitive sample calculations are to the blank concentrations and/or the certainty on a blank determination. We report all the data acquired for these two samples, but blank issues allow us to place less emphasis on the two ages that are slightly older (MD-1573 and MD-1574), as noted in the Table footnotes. Accordingly, we are most confident in the four boxed ages in the data table. These four ages suggest that the molybdenite from Saga I is nominally younger than the Sagåsen molybdenite.

Discussion

This study clearly illustrates the utility of the Re-Os chronometer in molybdenite, even at Re concentrations in the low ppb range. Knowledge of Re and Os blanks is critical, however, and the blank corrections for each sample must be carefully considered. Also critical is a common Os

component of essentially zero, especially for analyses where the radiogenic ^{187}Os count is very low. Both of the molybdenite samples in this study fit the criterion for a high ^{187}Os /common Os situation. Therefore, the discussion for the slight variation in ages can be focused on blank issues, not issues of common Os and guesses on the initial $^{187}\text{Os}/^{188}\text{Os}$ during molybdenite crystallization. These criteria place the most confidence in the boxed ages. Beyond this, the two ages for molybdenite separates registering essentially zero common Os are tied to AIRIE Runs MD-1564 (Saga I = 287 ± 1 Ma) and MD-1591 (Sagåsen = 289 ± 1 Ma).

Analytically speaking, the model ages for the two analyses of Saga I do not analytically overlap whereas the two ages for Sagåsen highly overlap (see probability values, Fig. 3). When comparing Re-Os ages to Re-Os ages, only the analytical error should be used in determining a weighted average, and not the larger multiplicative error added from the ^{187}Re decay constant uncertainty. When comparing a Re-Os age to an age based on another isotopic clock (*e.g.* U-Pb), however, the larger full uncertainty (analytical + ^{187}Re decay constant uncertainties) must be used.

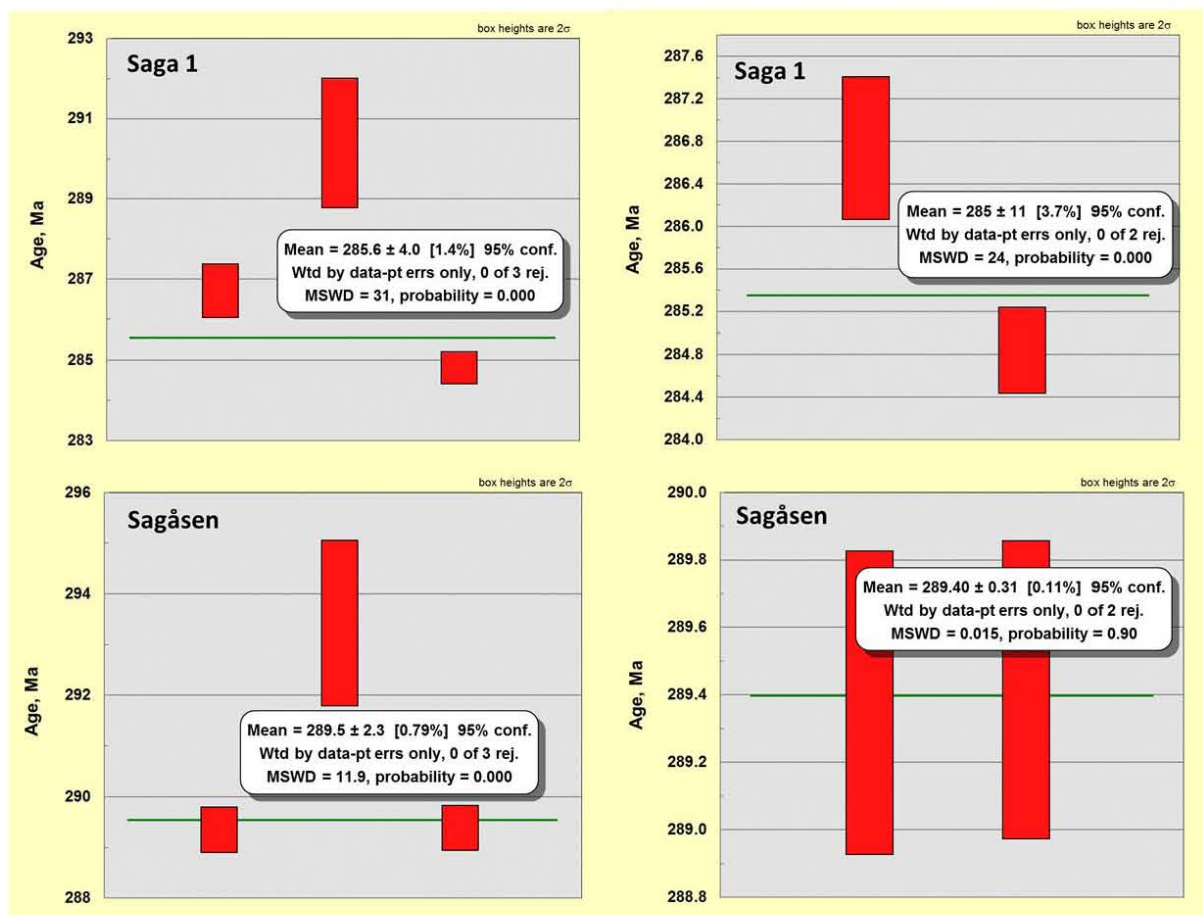


Fig. 3. Weighted mean Re-Os ages for the Saga 1 and Sagåsen molybdenite samples. Reproducibility cannot be tied to mineral separation, but is a reality in working with young, low Re samples. The variability in ages is tied to blank corrections. Higher blanks, and or a larger uncertainty in a blank Re and/or Os concentration directly impacts the uncertainty on calculated Re-Os ages.

It is important to not become lost in the analytical analysis of ages and over-interpret the nominal difference that could be drawn between the molybdenite ages for these two samples. While the particular molybdenite we analyzed from Saga I may continue to fall slightly younger, should we analyze both molybdenites ten times, a geologic perspective puts these ages into context.

The present Re-Os dating of molybdenite is likely dating a “period” of hydrothermal alteration in these pegmatites. There are probably multiple generations of alteration represented by the late-stage minerals at these localities, not just one alteration event.

Conclusions

Using the Re-Os chronometer to date hydrothermal molybdenites at the Saga I and Sagåsen larvikite quarries, we conclude that hydrothermal alteration events affecting nepheline syenite pegmatites in these samples are less than ~290 Ma. The Re-Os ages are 287 ± 1 Ma and 289 ± 1 Ma for the Saga I and Sagåsen molybdenites, respectively.

U-Pb dating on zircon and baddeleyite from larvikite and magmatic zircon from syenite pegmatite at the Tuften quarry in Tvedalen (about 1.8 km SE of Saga I and Sagåsen quarries) was reported by Dahlgren *et al.* (1996) and Dahlgren (1998). Larvikite and pegmatite showed identical ages (within the uncertainties): 293.2 ± 1.3 Ma and 294.3 ± 1.2 Ma, respectively. The slightly lower age found by Re-Os dating of the late-stage molybdenites is not easily interpreted and more study is needed on this topic.

Acknowledgements

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References

- Bingen, B. & Stein, H. (2003): Molybdenite Re-Os dating of biotite dehydration melting in the Rogaland high-temperature granulites, S. Norway. *Earth and Planetary Science Letters* **208**, 181-195.
- Boltwood, B.B. (1907): The ultimate disintegration products of the radioactive elements. Part II. The disintegration products of uranium. *American Journal of Science* **23**, 77-88.
- Brøgger, W.C. (1890): Die Mineralien der Syenitpegmatitgänge der süd-norwegischen Augit- und Nephelinsyenite. *Zeitschrift für Kristallographie und Mineralogie* **16**, 663 pp + 28 plates.
- Creaser, R.A., Papanastassiou, D.A. & Wasserburg, G.J. (1991): Negative thermal ion mass spectrometry of osmium, rhenium and iridium. *Geochimica et Cosmochimica Acta* **55**, 397-401.

- Dahlgren, S., Corfu, F. & Heaman, L.M. (1996): U-Pb isotopic time constraints, and Hf and Pb source characteristics of the Larvik plutonic complex, Oslo Paleorift. Geodynamic and geochemical implications for the rift evolution. *V.M. Goldschmidt Conference Abstracts. Ruprecht-Karls-Universität, Heidelberg. Germany* **1**, 120.
- Dahlgren, S., Corfu, F. & Heaman, L. (1998): Datering av plutoner og pegmatitter i Larvik pluton-kompleks, sydlige Oslo Graben, ved hjelp av U-Pb isotoper i zirkon og baddeleyitt. *Norsk Bergverksmuseum Skrift* **14**, 32-39 (in Norwegian).
- Holmes, A. (1911): The association of lead with uranium in rock-minerals, and its application to the measurement of geological time. *Proceedings of the Royal Society, London* **A85**, 248-256.
- Larsen, A.O. (1981): Boehmite from syenite pegmatites in the Oslo region, Norway. *The Mineralogical Record* **12**, 227-230.
- Larsen, A. O. (2011): *The Langesundsfjord: History, geology, pegmatites, minerals*. Bode Verlag GmbH., Salzhemmendorf, Germany. 240 pp.
- Larsen, A. O. (2013): Contributions to the mineralogy of the syenite pegmatites in the Larvik Plutonic Complex. *Norsk Bergverksmuseum Skrift* **50**, 101-109.
- Markey, R.J., Hannah, J.L., Morgan, J.W. & Stein, H.J. (2003): A double spike for osmium analysis of highly radiogenic samples. *Chemical Geology* **200**, 395-406.
- Stein, H.J. (2006): Low-rhenium molybdenite by metamorphism in northern Sweden: recognition, genesis, and global implications. *Lithos* **87**, 300-327.
- Stein, H.J. & Bingen, B. (2002): 1.05-1.01 Ga Sveconorwegian metamorphism and deformation of the supracrustal sequence at Sæsvatn, south Norway: Re-Os dating of Cu-Mo mineral occurrences. In Blundell, D., Neubauer F. & von Quadt, A. (eds.): *The Timing and Location of Major Ore Deposits in an Evolving Orogen. Geological Society, London, Special Publications* **204**, 319-335.
- Stein, H.J., Markey, R.J., Morgan, J.W., Hannah, J.L. & Scherstén, A. (2001): The remarkable Re-Os chronometer in molybdenite: how and why it works. *Terra Nova* **13**, 479-486.
- Stein, H.J., Scherstén, A., Hannah, J.L. & Markey, R. (2003): Sub-grain scale decoupling of Re and ¹⁸⁷Os and assessment of laser ablation ICP-MS spot dating in molybdenite. *Geochimica et Cosmochimica Acta* **67**, 3673-3686.
- Stein, H.J., Hannah, J.L., Zimmerman, A., Markey, R., Sarkar, S.C. & Pal, A.B. (2004): A 2.5 Ga porphyry Cu-Mo-Au deposit at Malanjhand, central India: implications for Late Archean continental assembly. *Precambrian Research* **134**, 189-226.
- Zimmerman, A., Stein, H.J., Hannah, J.L., Kozelj, D., Bogdanov, K. & Berza, T. (2008): Tectonic configuration of the Apusini-Banat-Timok-Srednogorie belt, Balkans-South Carpathians, constrained by high precision Re-Os molybdenite ages. *Mineralium Deposita* **43**, 1-21.

Table 1. Re-Os data for molybdenite samples from the Saga I and Sagåsen larvikite quarries, Porsgrunn, Norway.

AIRI E Run #	Quarry	Re, ppm	Re err, abs (ppm)	Re err, percen t	¹⁸⁷ Os , ppb	¹⁸⁷ Os err, abs (ppb)	¹⁸⁷ Os err, perce nt	Comm on OsC, ppb	OsC err, abs (ppb)	OsC err, perc ent	Age, Ma	Sam ple wt, gra ms
MD- 1564	Saga I	0.01 399	0.0000 3	0.19	0.04 209	0.0000 6	0.14	0.0000 0	0.000 3	39	286.7 ± 1.1	0.06 55
MD- 1574	Saga I (new separate)	0.00 848	0.0000 1	0.10	0.02 584	0.0001 4	0.54	0.0003 0	0.000 09	31	290.4 ± 1.9	0.11 53
MD- 1590	Saga I (same sep. as MD-1574)	0.01 002	0.0000 0	0.038	0.02 996	0.0000 4	0.14	0.0004 3	0.000 09	22	284.9 ± 1.0	0.19 82
MD- 1565	Sagåsen	0.01 376	0.0000 1	0.07	0.04 180	0.0000 6	0.14	0.0013	0.000 3	22	289.4 ± 1.0	0.06 73
MD- 1573	Sagåsen (new separate)	0.01 708	0.0000 2	0.11	0.05 262	0.0002 9	0.54	0.0001	0.000 1	121	293.4 ± 1.9	0.10 16
MD- 1591	Sagåsen (same sep. as MD-1573)	0.01 796	0.0000 1	0.063	0.05 456	0.0000 8	0.14	0.0000 1	0.000 09	1268	289.4 ± 1.0	0.20 30

Re-Os data were acquired using a double Os spike and Carius tube dissolution for sample-spike equilibration; sample weights ranged from 66 to 203 milligrams.

Uncertainties reported at two-sigma; uncertainties on reported Re-Os ages include propagation of all analytical uncertainties and the uncertainty in the ¹⁸⁷Re decay constant.

For runs MD-1564 and MD-1565, Re blanks are 3.46 ± 0.07 pg, Os blanks = 0.676 ± 0.017 pg with a ¹⁸⁷Os/¹⁸⁸Os = 0.130 ± 0.003 .

For runs MD-1573 and MD-1574, Re blanks are 0.95 ± 0.32 pg, Os blanks = 1.188 ± 0.008 pg with a ¹⁸⁷Os/¹⁸⁸Os = 0.200 ± 0.001 .

For runs MD-1590 and MD-1591, Re blanks are 0.80 ± 0.03 pg, Os blanks = 0.710 ± 0.019 pg with a ¹⁸⁷Os/¹⁸⁸Os = 0.350 ± 0.005 .

First mineral separate for Saga I (MD-1564) estimated at 80% molybdenite; second mineral separate used in MD-1574 and MD-1590 estimated at 95% molybdenite.

First mineral separate for Sagåsen (MD-1565) estimated at 95% molybdenite; second mineral separate (MD-1573, MD-1591) was 100% pure molybdenite.

Assumed initial ¹⁸⁷Os/¹⁸⁸Os for age calculation is 0.2; common Os measured is insignificant relative to determined ¹⁸⁷Os in each sample, and does not affect the age calculation.

Runs MD-1573 and MD-1574 also have a higher Os blank which adds to the uncertainty on the calculated Os concentrations for these two runs; if Os blank is in fact anomalously high, this will push the age older.

Runs MD-1573 and MD-1574 are associated with a less well determined Re blank which propagates into the uncertainty calculated for the age.