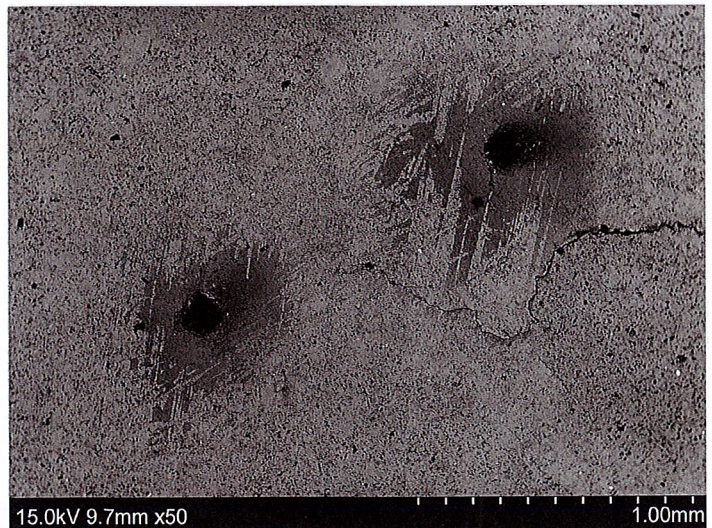


IN SITU RE-OS DATING OF MOLYBDENITE USING LA-ICP-MS/MS

Analytical protocol and standardization



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Abstract

Dating with the Re-Os isotopic system provides several advantages compared to conventional chronometers such as Rb-Sr. Because of the sidero- and chalcophilic nature of Re and Os, those can be found as trace elements in sulfides, meaning that ages can be obtained for sulfide deposit, giving valuable information of ore genesis. To ensure the quality of the analytical measurements needed in isotopic dating, a reference material with known concentrations of Re and Os is necessary. The aim of this study is to develop a method to produce a homogenous tablet of the sulfide molybdenite, and validate its use as a reference material for calibration of in situ Re-Os dating using LA-ICP-MS/MS. Molybdenite from Kingsgate, Australia, was used as a test material, molybdenite from Moly Hill, Canada, as the reference material for the tablet, and molybdenite from Ytterby, Sweden, as a validation of the produced tablet. The molybdenite was milled by hand with ethanol in an agate mortar and pressed into a tablet in a tablet die set by applying 2.5 t (0.19×10^6 kPa) for 2 min. Molybdenite proved to be hard to mill due to its layered structure and milling in a high power planetary ball mill was therefore unsuccessful in producing fine material. The optimum pressure and corresponding time depended on several factors, such as the tablet die set and material, and will affect for example numbers of cracks in the tablet. The tablet was analyzed with LA-ICP-MS/MS, an analytical method that was chosen because it provides the opportunity to target specific ions, created after a reaction with a reaction gas, in this case CH₄. This is a tool used to chemically separate the parent and daughter isotopes and overcome the isobaric overlap. Isotopes of Re and Os, as well as potential elements in inclusion, was measured. Despite signs of inclusions in the final tablets, the Re and Os signals seemed unaffected by this. Ratios for $^{187}\text{Re}/^{187}\text{Os}$ was calculated for the tablet of molybdenite from Moly Hill, and for Ytterby molybdenite. The literature Re-Os age for Moly Hill, 2646 Ma, was used to obtain a corresponding $^{187}\text{Re}/^{187}\text{Os}$ ratio, which in turn could be used to calculate a correction factor. This was applied to the Ytterby molybdenite to obtain corrected ratios, then calculating an age of 1823 ± 28 Ma, which overlaps the literature age for Ytterby, 1795 ± 2 Ma. The results validate the quality of the tablet produced of molybdenite from Moly Hill and confirms that it can be used for calibration of in situ Re-Os dating with LA-ICP-MS/MS, even if several improvements of the methods can be done in the future, both in the milling process and the analytical process.

Keywords: Re-Os dating, Re-Os chronometer, isotopic dating, in situ dating, LA-ICP-MS/MS, reference material, molybdenite, reaction gas, methane, microgeochemistry

Sammanfattning

Att datera med det isotopiska systemet Re-Os har flera fördelar jämfört med konventionella kronometrar som Rb-Sr. Eftersom både Re och Os är sidero- och chalkofila kan de finnas som spårämnen i sulfider, vilket kan användas för att datera sulfidfyndigheter och därmed ge värdefull information om malmers ursprung. Ett referensmaterial med kända koncentrationer av Re och Os krävs för att försäkra kvalitén på de analytiska mätningar som görs vid datering med isotoper. Syftet med denna studie är att utveckla en metod för att tillverka en homogen pellets av sulfiden molybdenit och validera dess användning som referensmaterial vid kalibrering av in situ Re-Os datering med hjälp av LA-ICP-MS/MS. Molybdenit från Kingsgate, Australien, användes som ett testmaterial, molybdenit från Moly Hill, Kanada, som referensmaterialet i pelletsen och molybdenit från Ytterby, Sverige, som validering av den tillverkade pelletsen. Molybdeniten maldes för hand i en agatmortel med etanol och pressades till en pellets i ett 'tablet die set' genom att lägga på ett tryck motsvarande 2.5 t (0.19×10^6 kPa) i 2 min. Molybdenit visade sig vara svårt att mala på grund av dess skiktade struktur och att mala i en 'high power planetary ball mill' skapade därför inte fina partiklar. Det optimala trycket och tiden för pressning beror på flera saker, så som 'tablet die set' och material, och påverkar till exempel antalet sprickor. Pelletsen analyserades med LA-ICP-MS/MS, en analytisk metod som valdes eftersom den erhåller möjligheten att välja ut specifika joner, skapade efter en reaktion med en reaktionsgas, i detta fallet CH₄. Detta används för att kemiskt separera moder- och dotterisotoper och på så sätt förbigå det isobariska överlappet. Isotoper av Re och Os mättes, liksom potentiella grundämnen i inklusioner. Trots indikation av inklusioner i den slutgiltiga pelletsen var signalerna för Re och Os opåverkade av detta. ¹⁸⁷Re/¹⁸⁷Os-kvoterna beräknades för pellets av molybdenit från Moly Hill och molybdeniten från Ytterby. Litteratüråldern från Re-Os datering för Moly Hill, 2646 Ma, användes för att erhålla ett ¹⁸⁷Re/¹⁸⁷Os-ratio, som i sin tur kunde användas för att beräkna en korrektionsfaktor. Faktorn användes för att erhålla korrigerade ration för molybdeniten från Ytterby och åldern 1823 ± 28 Ma beräknades, vilket överlappar litteratüråldern 1795 ± 2 Ma. Detta validerar kvalitén på den tillverkade pelletsen av molybdenit från Moly Hill och bekräftar att den kan användas för kalibrering av in situ Re-Os datering med LA-ICP-MS/MS, även om flertalet förbättringar av metoden kan göras i framtiden, både i malningsprocessen och i den analytiska processen.

Nyckelord: Re-Os datering, Re-Os kronometer, isotopisk datering, in situ datering, LA-ICP-MS/MS, referensmaterial, molybdenit, reaktionsgas, metan, mikrogeokemi

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1. Introduction

The applications of laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) have been increasing over the last decades as a result of the significant improvements of accuracy, precision and detection limits. One area of use is dating rocks by measuring concentrations of parent and daughter nuclei in radioactive, isotopic pairs. In the rhenium-osmium (Re–Os) isotopic system, ^{187}Re decays by β -decay to ^{187}Os (Naldrett & Libby, 1948) with the half-life of ^{187}Re that is approximately 10 times the age of the Earth (H. J. Stein, Markey, Morgan, Hannah, & Scherstén, 2001).

The Re-Os chronometer have interesting fields of application and several differences compared to other chronometers, and it is therefore of importance to continue the development of methods using this isotopic system. According to Stein et al. (2001), compared to chronometers such as Rb-Sr and K-Ar, the Re-Os chronometer is remarkably robust, not susceptible to chemical and thermal disturbance, therefore surviving both heavy deformation and high-grade thermal metamorphism. This means that the Re-Os age will be the actual age of the rock's formation, whereas Rb-Sr is favorable to use when dating for example hydrothermal events, if such as occurred. An important consequence of this, is that chronometers like Rb-Sr should not be used as a base in determination of accuracy in Re-Os dating, often done in the past. Another important contribution of Re-Os dating, pointed out by Suzuki, Qi-Lu, Shimizu, & Masuda in 1993, is the fact that it could be used to date sulfide minerals in ore deposits. Applying conventional geochronometers, like Rb-Sr, directly on sulfide minerals is normally unsuccessful. This is because the parent isotope is lithophile, and therefore occurs in too low concentrations to be useful. The age of the wall rock is normally used to estimate an age for the ore deposit, but those did not necessarily form at the same time, as in the case of a deposit origin from a later fluid infiltration. Obtaining an age directly from the ore minerals is important to provide information on ore genesis.

In 2003, H. Stein, Scherstén, Hannah, & Markey presented results of a decoupling between Re and ^{187}Os in molybdenite. A study by Selby & Creaser (2004) made similar conclusions, also finding that the degree of decoupling appeared to increase as a function of increasing grain size and age. This can give severe problems when using Re-Os dating, such as poor accuracy and irreproducible ages, and is one of the toughest challenges of the in situ Re-Os dating. The key to overcome this, according to (Selby & Creaser, 2004; H. J. Stein et al., 2001) is to use large sample sizes. Another difficulty is the careful sample preparation needed when using dilution

methods (H. J. Stein et al., 2001; Suzuki et al., 1993). Those two problems make the Re-Os isotope system complicated to use. Yet, to use in situ Re-Os dating would be a faster way to obtain correct ages and provide a tool to understand zonation.

Reference materials are standards with known concentrations, used to guarantee precision in analyses, and provides a way to prove the quality of results. Producing adequate reference materials for dating of rocks are still an area in need of progress (Garbe-Schönberg & Müller, 2014; Markey et al., 2007). In situ microanalysis with LA-ICP-MS of minerals typically requires small spot sizes, <20–50 μm , to obtain sufficient spatial resolution, which means that the reference material need to be sufficiently homogenized (Garbe-Schönberg & Müller, 2014) and preferably lack inclusions. Producing a reference material of a nano-particulate powder by pressing it to a powder tablet is a method successfully used by Garbe-Schönberg and Müller (2014). Since there are no NIST-certified (National Institute of Standards and Technology) molybdenite standard available for Re-Os (H. J. Stein et al., 2001), and the fact that producing such reference could to some extent solve current problems with Re-Os dating and assure quality of measurements, this is indeed an area in need of progress.

1.1 The properties of molybdenite

Molybdenite is a metallic mineral with the chemical formula MoS_2 and is the major ore mineral for mining of the metal molybdenum. Typical environmental settings are high temperature hydrothermal veins and disseminated porphyry deposits. The hardness is 1-1.5 on Mohs scale of hardness, a scale between 1 and 10, meaning that molybdenite is a very soft mineral. The crystal structure is a sheet-like, three-layered structure, with sulfur atoms at top and bottom with molybdenum atoms in between. Strong bonds connect the molybdenum and sulfur atoms, but the bonds connecting the sulfur atoms between every third layer are weaker, resulting in a perfect cleavage (Barthelmy, 2012; Mindat.org, Hudson Institute of Mineralogy, n.d.). Because Mo, Re and Os all are both sidero- and chalcophilic (White, 2013), Re can occur as trace element in relatively high amounts in molybdenite (Fleischer, 1959) and therefore also ^{187}Os . It is assumed that the ^{187}Os from common Os in molybdenite are insignificant compared to the naturally accumulated radiogenic ^{187}Os (Markey et al., 2007; H. J. Stein et al., 2001); all radiogenic daughter can be thought to be derived from the parent isotope.

To be able to continue the development with the in situ Re-Os dating, well-studied and dated molybdenite could be used as reference materials.

1.2 Aim

The aim of this study is to develop a method to produce a tablet of molybdenite, and validate its use as a reference material for calibration of in situ Re-Os dating using LA-ICP-MS/MS.

2. Methods

2.1 Materials

To make sure that the concentration of radiogenic Os is sufficiently high to be measured in the final tablet, a high concentration of Re in the molybdenite is vital. The factors controlling the concentration of Os are the age and the starting concentration of Re when the mineral formed. An old molybdenite with a low Re content may have had the time to produce enough radiogenic Os, even if the starting concentration was low, and can therefore be an appropriate molybdenite for this study. If the mineral is younger, the starting concentration of Re is more important to make the molybdenite appropriate, since the radioactive Re won't have had much time to decay to Os. Data of both age and Re concentrations for different molybdenites were therefore studied, where the age was an indicator for potential high Os contents, whereas the Re content was primarily considered; despite an old age, a molybdenite with no Re will have no radiogenic Os. By studying literature, appropriate molybdenite (see Moly Hill molybdenite below) to use for the tablet was found.

2.1.1 Kingsgate molybdenite

The Kingsgate Mine is situated in the Kingsgate mineral field, 20 km east of Glen Innes in the New England district of northeastern New South Wales, Australia, and is the second largest producer of molybdenum in Australia (Partington, Mustard, Little, & Bowden, 2007). The mineralization is mostly found in pegmatite-like, coarse-grained quartz-rich pipes, several meters in diameter, in a late-orogenic leucogranitoid, dated to 243-246 Ma according to Geoscience Australia (2012). The main ore minerals include molybdenite, native bismuth, and bismuthinite, but also native gold and silver, wolframite, pyrrhotite, pyrite, chalcopyrite, arsenopyrite, galena, and cassiterite are minerals of interest (Hess, 1924; Kleeman, 1988; Orlandi et al., 2011; Partington et al., 2007).

In this study, an available sample of molybdenite from the Kingsgate mineral field was used as a test material to be able to develop the final method, but tablets of Kingsgate molybdenite was also analyzed and evaluated with the same methods as the final tablet of molybdenite from Moly Hill.

2.1.2 Moly Hill molybdenite

The Moly Hill Mine is situated a few kilometers southeast of La Motte, in southeastern Québec, Canada (Sabina, 2003). The mine is located in the Preissac pluton, which is one of several in the late Archean Preissac-Lacorne batholith, which consists of comagmatic pegmatites, quartz veins and biotite-muscovite-bearing monzogranite (Mulja, Williams-Jones, Wood, & Boily, 1995). The plutons in the area are thought to have formed from melting of lower crustal sedimentary rocks during continental collision and compression as a part of the Abitibi Greenstone Belt (Taner, Williams-Jones, & Wood, 1998).

Material from Moly Hill is appropriate to use for production of tablet in this study because it is older than several other molybdenite deposits, which is normally hosted by Mesozoic and younger intrusions in back-arc or subduction related tectonic environments (Taner et al., 1998), and therefore have potential of higher Os-content. Furthermore, the plutons are dated with several isotopic systems, such as Sm-Nd, U-Pb and Re-Os, which is a requirement in this study to be able to verify the tablets usability. Ducharme, Stevenson, & Machado, (1997) dated the Preissac pluton to 2681–2660 Ma, obtained by Sm–Nd data and U–Pb monazite and titanite ages from a biotite–muscovite monzogranitic phase. Suzuki, Qi-Lu, Shimizu, & Masuda (1993) presented an isotope-dilution ICP-MS molybdenite Re-Os age of 2680 ± 90 Ma. However, Košler et al. (2003) recalculated this Re-Os age with the often used decay constant for ^{187}Re by Smoliar, Walker, & Morgan (1996) to 2766–2526 Ma, which overlaps the range of the study by Ducharme, Stevenson, & Machado (1997). As mentioned earlier, Sm-Nd and U-Pb ages are obtained from wall rock and do not necessarily apply to the deposit of interest. Therefore, the Re-Os age for Moly Hill (Preissac pluton) will be used in this study, in particular, the mean from the recalculations by Košler et al. (2003); 2646 Ma. This age is required to be able to calculate a correction factor, to use for age determinations of other materials.

2.1.3 Ytterby molybdenite

Due to the mineralogical similarities and spatial closeness (10 km) Romer & Smeds (1994) suggests that the Ytterby pegmatite most probably belongs to the same pegmatite swarm as the Gruvdalen pegmatite, located north-east of Stockholm, Sweden. They are both NYF-type (niobium-yttrium-fluorine) pegmatites, found in granitic and granodioritic intrusions, with an early orogenic origin, in felsic metavolcanic rocks. Typical minerals occurring in this type of pegmatite includes K-feldspar, albite, quartz, beryl, schörl, fluorite, muscovite, columbite and minor amounts of biotite and garnet. Romer & Smeds (1994) reports U-Pb columbite ages of the Gruvdalen pegmatite to 1795 ± 2 Ma and claims that this age also applies for Ytterby.

No tablet will be produced of the Ytterby molybdenite in this study but analysis with LA-ICP-MS/MS will be conducted directly on a sample of Ytterby molybdenite. The calculated age, based on the measurements combined with the correction factor obtained from the Moly Hill tablet calculations, will be compared with the literature age for this material. Consequently, Ytterby will serve as a verification of the tablets produced of the molybdenite from Moly Hill. The sample of molybdenite from Ytterby used in this study was a part of a 5 x 5 cm big crystal found in pegmatite according to I. Dahlgren (personal communication, 17th of May 2017).

Note that all three material locations are associated with pegmatites.

2.2 SEM of materials

Sample preparation was performed using Struers' cold mounting EpoFix kit. Parts of the molybdenite crystals from Moly Hill, core and rim, and Kingsgate were mounted, polished, carbon coated with a Bal-Tec CED 030 Carbon Evaporator and studied in a Hitachi S-3400N Scanning Electron Microscope (SEM). An already mounted crystal from Ytterby was studied as well. The homogeneity of the materials was evaluated and potential inclusions identified. Backscatter electron (BSE) images were taken to visualize the result.

2.3 Milling and pressing

2.3.1 Pre-test

Because the experimental setup for pressing the tablet in this study, for practical reasons, is different than the one used by Garbe-Schönberg and Müller (2014), a test was conducted to verify the functionality of the equipment, e.g. the hydraulic press and the tablet die set. This was done by pressing a tablet of a nano powder of pyroxenite by applying 8.5 t (0.63×10^6 kPa) for 1 min with a 10-t hydraulic press, which was then evaluated regarding cracks and pressed surface by using a stereomicroscope together with an external light source (Leica MZ12 and Leica CLS 150). The properties of the pressed powder are similar to the ones used by Garbe-Schönberg and Müller. The tablets produced by Garbe-Schönberg and Müller were pressed by applying 10 t (0.74×10^6 kPa) but due to malfunction of the hydraulic press, this could not be tested. In the produced pre-test tablet, no extensive cracks were visible and the surface was well pressed; the experimental set up was therefore considered to be valid for further testing.

2.3.2 Development of the method

The milling of molybdenite started with pre-separation of the material with a grater before milling it by hand together with ethanol in an agate mortar. Three different methods were then tested. The first method is the method most similar to the one performed by Garbe-Schönberg

and Müller in 2014. Approximately 0.5 g material was grinded in a high power planetary ball mill (Fritsch Pulverisette 7 classic line) in 45 ml silicon nitride vials, together with 20 g of agate grinding balls with a diameter of 5 mm and 10 ml of ultra-pure water. The grinding was done for a total of 153 min in cycles of 3 min of grinding at 800 rpm and 1 min of cooling in between the grinding cycles. The temperature was measured during the cooling period with a handheld digital infrared thermometer (Dibotech DT8500 IR-thermometer). The suspension was then subsequently extracted with a pipette to a petri dish of glass, which then was put in a freezer. When the suspension was frozen, the sample was freeze-dried for 24 hours in a VirTis BenchTop K Freeze Dryer. Finally, the sample were re-homogenized by hand in an agate mortar before pressing a tablet in a tablet die set of a diameter of 13 mm by applying 5 t (0.37×10^6 kPa) for 1 min with a 20-t hydraulic press.

Instead of using a high power planetary ball mill, the other method tested was a milling-by-hand method only. Approximately 0.5 g of the sample was continuously milled for 1 hour by hand in an agate mortar with ethanol before extracted with a pipette to a test tube of plastic. The top of the tablet die set was used as a lid to the test tube and thread sealing tape was used between the test tube and the top of the tablet die set to make the test tube completely sealed. The test tube was then put upside down in a laboratory bench centrifuge (MSE Centaur 2) and centrifuged for 20 min at a speed of approximately 1500 rpm. By placing the test tube upside down, the milled molybdenite grains in suspension were spun down on the tablet die set top, the coarsest furthest down and finer upwards. The test tube was left upside down for 24 h to obtain a higher degree of sedimentation of finer particles. The lid was then separated from the test tube and put together with the rest of the tablet die set before pressing the tablet by applying 5 t (0.37×10^6 kPa) for 1 min with a 20-t hydraulic press.

The last method tested was also a milling-by-hand method. Approximately 0.5 g of the sample was continuously milled for 1 hour by hand in an agate mortar with ethanol. At the end of this period, no further ethanol was poured on the sample and the milling continued until all ethanol had evaporated and the sample was completely dry. A few minutes of dry-milling was done before the sample was put in the tablet die set. To make as much material as possible go into the tablet die set, it was filled fully and manually pre-pressed with the top of the tablet die set. This was done twice and the tablet die set was then finally filled a third time. To evaluate the most suitable pressure regarding the number and lengths of cracks in the final tablet, a series of pressing tablets, produced with the method above, was conducted. Each test was done with a 20-t hydraulic press and the sample was under pressure for only a few seconds up to 3 minutes.

The tablets in the test series were pressed by applying 0.5, 2, 2.5, 3, 4, and 5 t (0.037, 0.15, 0.18, 0.22, 0.30, and 0.37×10^6 kPa).

The tablets from the different methods were evaluated regarding particle size and cracks by using a stereomicroscope together with an external light source (Leica MZ12 and Leica CLS 150).

After evaluation of the different methods, the last described milling-by-hand method was used to produce tablets of a crystal of the Moly Hill molybdenite (Fig. 1), with a milling time of 2 h and pressed by applying 2.5 t (0.19×10^6 kPa) for 2 minutes.



Figure 1. Molybdenite crystal in quartz from Moly Hill Mine, approximately 1.5 x 1 cm big, and a few mm thick. This crystal in particular was used for the tablet.

2.4 Mounting for LA-ICP-MS/MS

To be able to easily place the produced tablet in the LA-ICP-MS, three different methods were tested to encapsulate the tablet in some type of holder. The first method used a sealing layer of super glue, Loctite 454, between a tablet of pyroxenite and epoxy. This was done by covering a piece of glass with parafilm and then placing the tablet on the surface. The tablet was covered by super glue and the earlier mentioned procedure of making an epoxy mount were done before studied in SEM to see if any of the glues (epoxy or Loctite) penetrated the tablet. The second method tried was to press powder of molybdenite, surrounded by milled cellulose, in the tablet die set to make a permanent cup for the tablet. The third method, the one used for the tablets that were to be further analyzed, started with cutting off the edges of the tablets. The central pieces were then attached with Loctite or carbon tape to a glass, sized for a sample holder for the LA-ICP-MS.

Two pieces from tablets made by the Kingsgate molybdenite were chosen to be further analyzed and were therefore mounted. Those two tablets were produced with the centrifuge method. One of those was pressed by applying 2.5 t (0.18×10^6 kPa), the other one by applying 5 t (0.37×10^6 kPa). Two pieces from tablets made by the Moly Hill molybdenite were also mounted for further analysis.

2.5 LA-ICP-MS/MS analysis

The tablets were analyzed by using laser ablation induced coupled plasma mass spectrometry (LA-ICP-MS), in particular, an ESI 213NWR (TwoVol2) laser ablation system connected to an ICP-MS Agilent 8800 QQQ, which can be used as a ICP-tandem mass spectrometer or ICP-MS/MS. This instrument is equipped with two quadrupoles with a reaction cell in between (a so-called ORS³, octopole reaction system). The first quadrupole (Q1) allows selected mass/charge ratios (m/z ratio) to enter the reaction cell, where separation of analytes and interferences with the same mass can result from interaction with the reactive gases. The reaction gas is chosen to make an as effective reaction as possible, forming a reaction product with a new mass. The analyte will now have another m/z ratio, it will be “mass-shifted”, compared to the interference ions and this allows the second quadrupole (Q2) to make a separation of those before further analyzation. If an ion of interest does not react with the reaction gas, it can be measured by setting both quadrupoles to the same mass, the so called “on-mass mode” (Bolea-Fernandez, Balcaen, Resano, & Vanhaecke, 2017; Zack & Hogmalm, 2016).

The optimum use of the reaction cell is obtained when the reaction gas strongly reacts with the daughter isotope and not at all with the parent isotope, overcoming the isobaric overlap. This makes a complete chemical separation of the two different elements possible, which can be targeted and measured individual. In the case of the Rb-Sr isotope system, different reaction gases have been demonstrated to react effectively with Sr, but without affecting Rb (Hogmalm, Zack, Karlsson, Sjöqvist, & Garbe-Schönberg, 2017). So far, no such optimum and effective set up have been developed for the Re-Os system, however, an ongoing study shows that CH₄ is a promising reaction gas, where 96.5% Re shows no mass-shift, whereas 98.5% Os do. The most common mass-shift, 83.2%, occurred when Os reacted with CH₂⁺ (Dahlgren, 2017). The aim of the study is based on the findings of the extensive investigation of reactions between cations and CH₄, performed by Shayesteh, Lavrov, Koyanagi, & Bohme (2009). In Figure 2 it can be seen that the reaction between CH₄ and Re is almost non-existing and the reaction with Os is almost complete. According to this knowledge, the reaction cell was in this study filled

with the reaction gas CH₄, and the settings for Q2 was set to +14 from the ions of interest (Table 1). Note that even though Re to some extent reacts with CH₄ and the reaction between CH₄ and Os not is complete, no specific adjustments of the signals need to be done in this study; when calculating the concentration of ¹⁸⁷Re and the correction factor for the Re-Os ratios, this will be included.

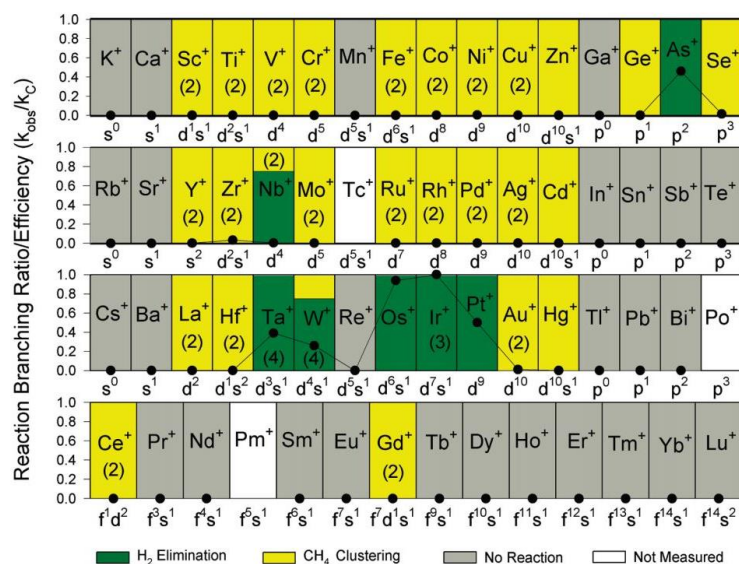


Figure 2. The periodic variations observed in the reaction efficiency (k/k_c), for the reactions of cations with CH₄ (Shayesteh et al., 2009).

Analysis with LA-ICP-MS/MS on completed tablets of material from Kingsgate and Moly Hill was done for characterization and evaluation, and direct on molybdenite from Ytterby to obtain values for verification. Furthermore, a standard called AI-3, with Re given as 11.90 ± 0.34 ppm and Os as 22.15 ± 0.77 ppm was also ablated. For spot documentation (Table 2). The analyzed isotopes, on-mass and mass-shifted, and corresponding dwell time can be found in Table 1. Pb and Bi was selected for analysis due to the knowledge about inclusions in the molybdenites, obtained from the study of materials in SEM, and W that, according to Fleischer (1959), also can be associated with Re. Experimental conditions are provided in Table 3.

Table 1. Quadrupoles settings for Q1 and Q2 and dwell times for selected elements.

	Q1 (m/z)	Q2 (m/z)	Dwell times (in ms)
Mo	95	95	3
W	182	182	10
Re	185	185	200
Re	185	199	200
Os	187	201	200
Os	189	203	200
Pb	208	208	10
Bi	209	209	10

Table 2. Spot documentation for analysis with LA-ICP-MS/MS.

Spot documentation
2 × AI-3 standard
5 × Moly Hill tablet 1
5 × Moly Hill tablet 2
2 × AI-3 standard
4 × Ytterby molybdenite
2 × Kingsgate tablet
2 × AI-3 standard
5 × Moly Hill tablet 1
5 × Moly Hill tablet 2
2 × AI-3 standard

Table 3. Laser and ICP-MS parameters.

Laser	
Spot size	110 µm
Fluence	3.257 J/cm ²
Frequency	10 Hz
He flow rate	650 mL/min
N ₂	9 mL/min
ICP	
<i>Plasma</i>	
RF Power	1350 W
RF Matching	1.50 V
Sample Depth	3.5 mm
Carrier Gas (Ar)	0.66 L/min
Option Gas	0.00%
Nebulizer Pump	0.00 rps
S/C Temp	2 °C
Gas Switch	Makeup Gas
Makeup/Dilution Gas	0.00 L/min
<i>Lenses</i>	
Extract 1	-29.0 V
Extract 2	-250.0 V
Omega Bias	-150 V
Omega Lens	11.0 V
Q1 Entrance	-4 V
Q1 Exit	-13 V
Cell Focus	2.0 V
Cell Entrance	-130 V
Cell Exit	-120 V

Deflect	0.0 V
Plate Bias	-80 V

Q1

Q1 Mass Gain	133
Q1 Mass Offset	127
Q1 Axis Gain	1.0005
Q1 Axis Offset	0.07
Q1 Bias	2.0 V
Q1 Prefilter Bias	-3.0 V
Q1 Postfilter Bias	-2.0 V

Cell

Use Gas	Yes
He Flow	On
He Flow Rate	11.7 mL/min
H2 Flow	Off
H2 Flow Rate	0 mL/min
3rd Gas Flow Off	Off
3rd Gas Flow Rate	0 %
4th Gas Flow	On
4th Gas Flow Rate (CH ₄)	7 % ~ 0,05 mL/min
OctP Bias	-4.0 V
OctP RF	200 V
Energy Discrimination	-20.0 V

Q2

Mass Gain	128
Mass Offset	128
Axis Gain	1.0002
Axis Offset	-0.04
QP Bias	-24.0 V

Torch Axis

Torch H	0.0 mm
Torch V	-0.3 mm

EM

Discriminator	3.0 mV
Analog HV	1975 V
Pulse HV	1297 V

Wait Time Offset

Wait Time Offset	0 msec
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2.6 Data analysis

The data was processed using the software program GLITTER and was then exported to Excel.

To be able to obtain ages with the Re-Os isotope system, the $^{187}\text{Re}/^{187}\text{Os}$ ratio is needed. Because the amount of ^{185}Re (and not ^{187}Re) was measured and the amount of ^{187}Re was required for further calculations, the on-mass ^{185}Re was multiplied with the relative abundance factor for ^{187}Re and ^{185}Re . The relative abundance factor for these two rhenium isotopes is the ratio of natural abundance (in atomic percent) of ^{187}Re (62.60%) over ^{185}Re (37.40%) (Winter, n.d.-b). Concentration of mass-shifted ^{187}Re (+14) was obtained with the same procedure; by multiplying the mass-shifted ^{185}Re with the relative abundance factor. The mass-shifted ^{187}Os (+14), which in fact is a signal including the mass-shifted ^{187}Re , could then be calculated by subtracting the mass-shifted ^{187}Re from the apparent mass-shifted ^{187}Os . As mentioned before, the majority of the Os is reacting with the CH_4 and the mass-shifted ^{187}Os can in this first step be regarded as all ^{187}Os . A $^{187}\text{Re}/^{187}\text{Os}$ ratio could be obtained with previous calculations for each measured spot for Kingsgate, Moly Hill and Ytterby. Average of the ratios, standard deviation and precision (standard deviation divided by average) for each material was then calculated.

With the literature age of Moly Hill, 2646 Ma (Košler et al., 2003), the corresponding $^{187}\text{Re}/^{187}\text{Os}$ ratio was found by using the inversion of equation 1, which is a rewriting of the Re-Os isochron. Accordingly to Selby, Creaser, Stein, Markey, & Hannah, (2007), the most widely used decay constant for ^{187}Re is $1.666 \times 10^{-11} \text{ a}^{-1}$. This is based on cross calibration of Re-Os and Pb-Pb chronometers for different groups of iron meteorites, a work by Smoliar, Walker, & Morgan in 1996. The correction factor was calculated by dividing the actual average of the $^{187}\text{Re}/^{187}\text{Os}$ ratio for Moly Hill with the same ratio corresponding to the age. This factor was then used to correct the $^{187}\text{Re}/^{187}\text{Os}$ ratio for Ytterby and an age could be obtained by using equation 2, also a rewriting of the Re-Os isochron, and an age error by multiplying the age with the precision.

$$\frac{^{187}\text{Os}}{^{187}\text{Re}} = (e^{\lambda t} - 1) \quad (1)$$

$$T = \frac{\ln \left[\left(\frac{{}^{187}\text{Os}}{{}^{187}\text{Re}} \right) + 1 \right]}{\lambda} \quad (2)$$

Variations for the ten (in the first round) respectively four different spots for the Moly Hill tablet and Ytterby molybdenite (uncorrected and corrected) were displayed in a diagram with the average, absolute value and standard deviation. No correction for instrumental drift was made in this study.

To be able to evaluate whether possible inclusions affect the signal for Re and Os, a typical ablation pattern for a spot from the Moly Hill tablet was plotted as intensity in counts per second versus time in seconds. The intensity was plotted logarithmically. The signals included in this plot were ${}^{187}\text{Re}$, ${}^{187}\text{Os}$, Pb and Bi.

A ${}^{187}\text{Re}/{}^{187}\text{Os}$ ratio was calculated for the AI-3 standard by multiplying the Re and Os concentrations with the natural abundances for ${}^{187}\text{Re}$ (62.6%) and ${}^{187}\text{Os}$ (1.96%) (Winter, n.d.-a) and divided those numbers with each other.

2.7 SEM of tablets

After the analysis with LA-ICP-MS/MS, the tablets of molybdenite from Kingsgate and Moly Hill were studied in SEM to evaluate laser spots and homogeneity of the tablets.

3. Results

3.1 SEM of materials

3.2.1 Kingsgate molybdenite

In general, the molybdenite from Kingsgate appears rather homogenous (Fig. 3), but two elongated inclusions are identified, both which are approximately 500 x 100 μm . The majority of the inclusions consist of bismuthinite, however, native bismuth and bismuth telluride are also recognized (Fig. 4 & 5).

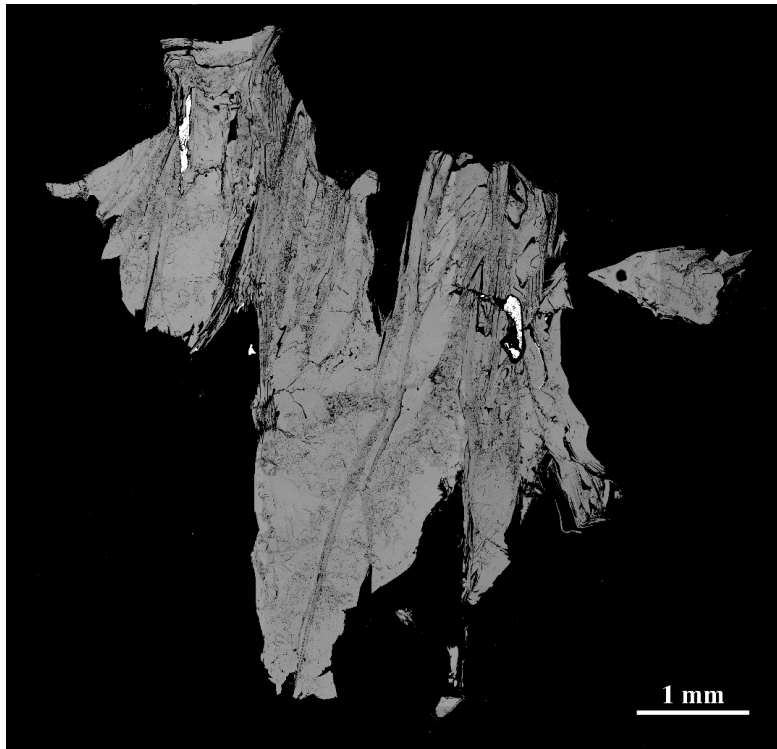


Figure 3. BSE image from SEM of molybdenite (gray) from Kingsgate, Australia. Note the two big inclusions (white).

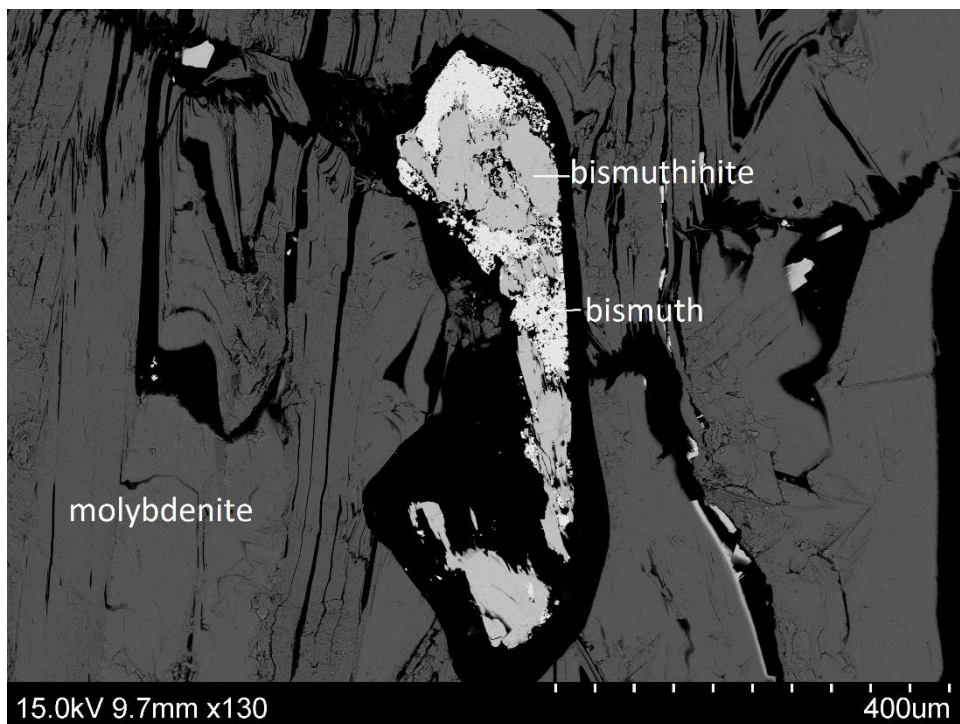


Figure 4. BSE image from SEM of molybdenite from Kingsgate, Australia, with inclusion of bismuthinite and native bismuth

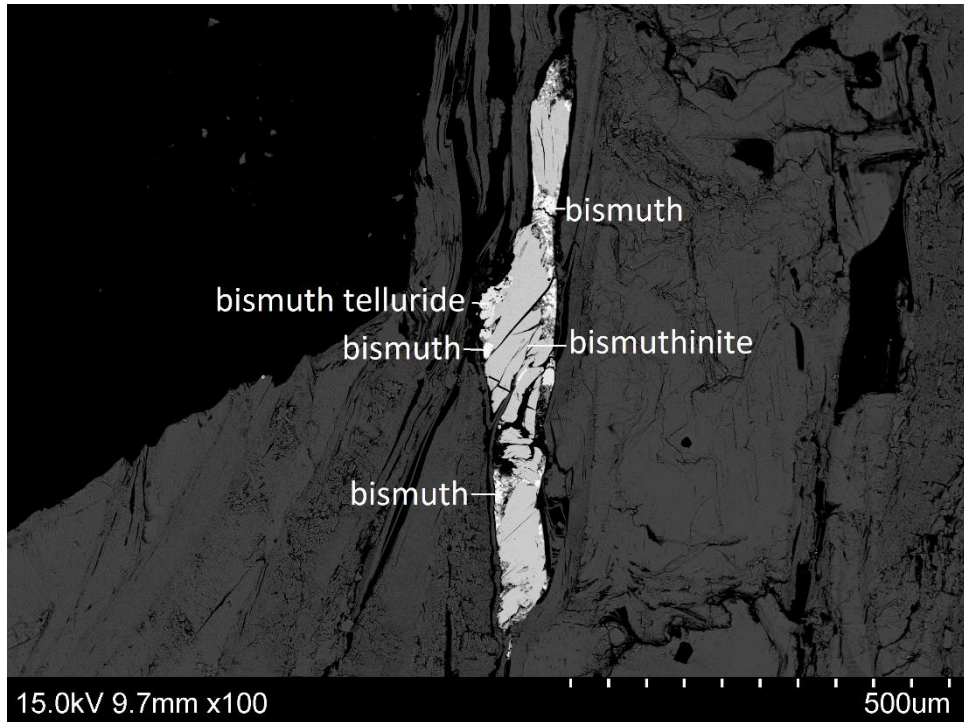


Figure 5. BSE image from SEM of molybdenite from Kingsgate, Australia, with inclusion of bismuthinite, native bismuth and bismuth telluride.

3.2.2 Moly Hill molybdenite

The Moly Hill molybdenite mostly displays areas of homogeneous molybdenite (Fig. 6), both the rim and core of the crystal. A few inclusions of native bismuth are found, the biggest one visible in Figure 7. Only one inclusion of galena is found (Fig. 8).

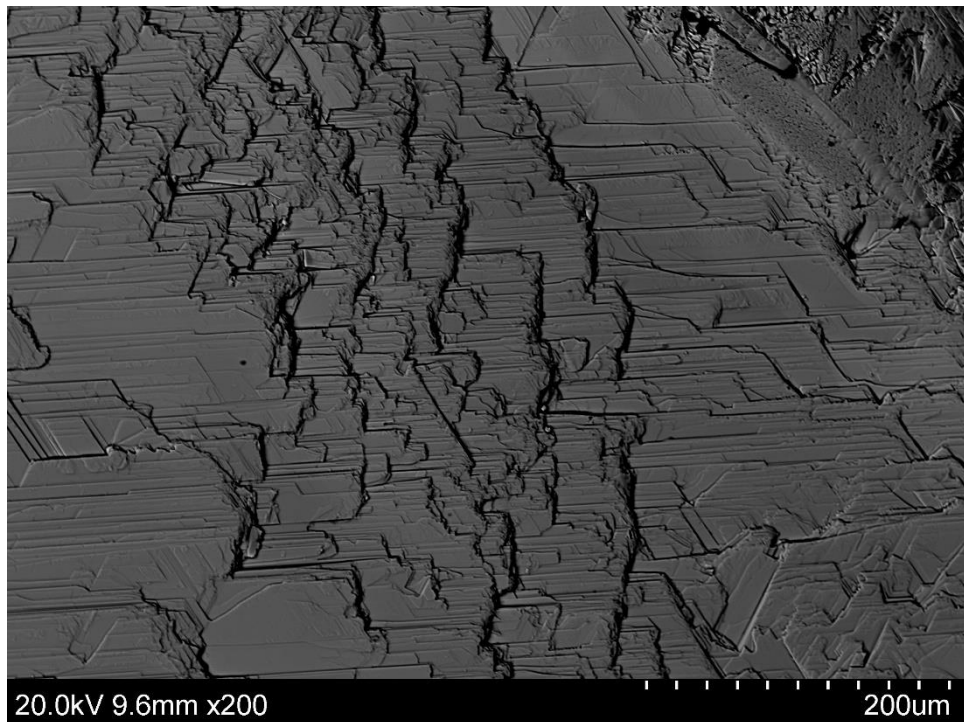


Figure 6. BSE image from SEM of an area of homogeneous molybdenite from Moly Hill, Canada, rim of crystal.

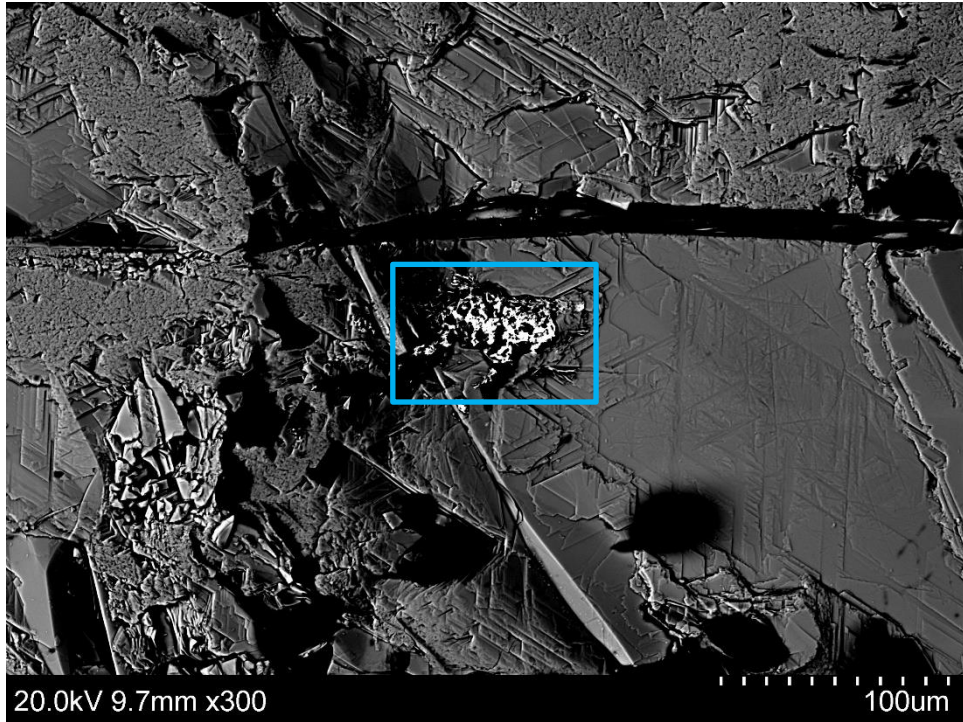


Figure 7. BSE image from SEM of molybdenite from Moly Hill, Canada, with inclusion of native bismuth, marked with blue square, approximately $50 \times 30 \mu\text{m}$. The area is located at the core of the crystal.

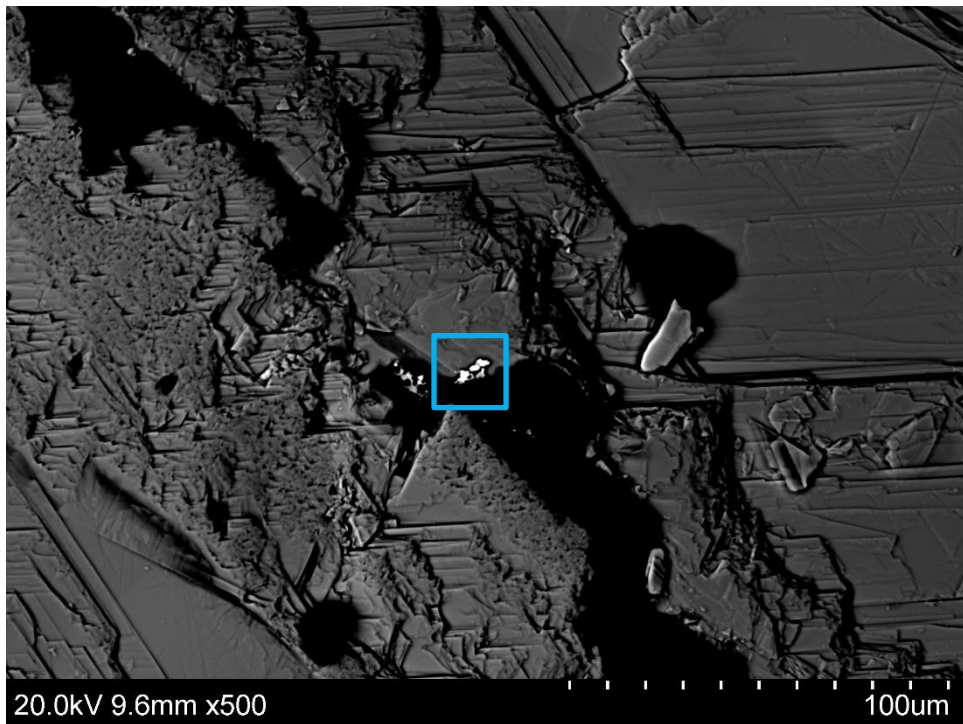


Figure 8. BSE image from SEM of molybdenite from Moly Hill, Canada, with inclusion of galena, marked with blue square, approximately $10 \times 5 \mu\text{m}$. The area is located at the rim of the crystal.

3.2.3 Ytterby molybdenite

The study in SEM of the Ytterby molybdenite also gives the result of a generally homogenous molybdenite (Fig. 9). However, areas with what appears to be inclusions, just a few microns wide, are found (Fig. 10). Because of the small size, no spectrum could be obtained for those inclusions and the chemistry is therefore unknown.

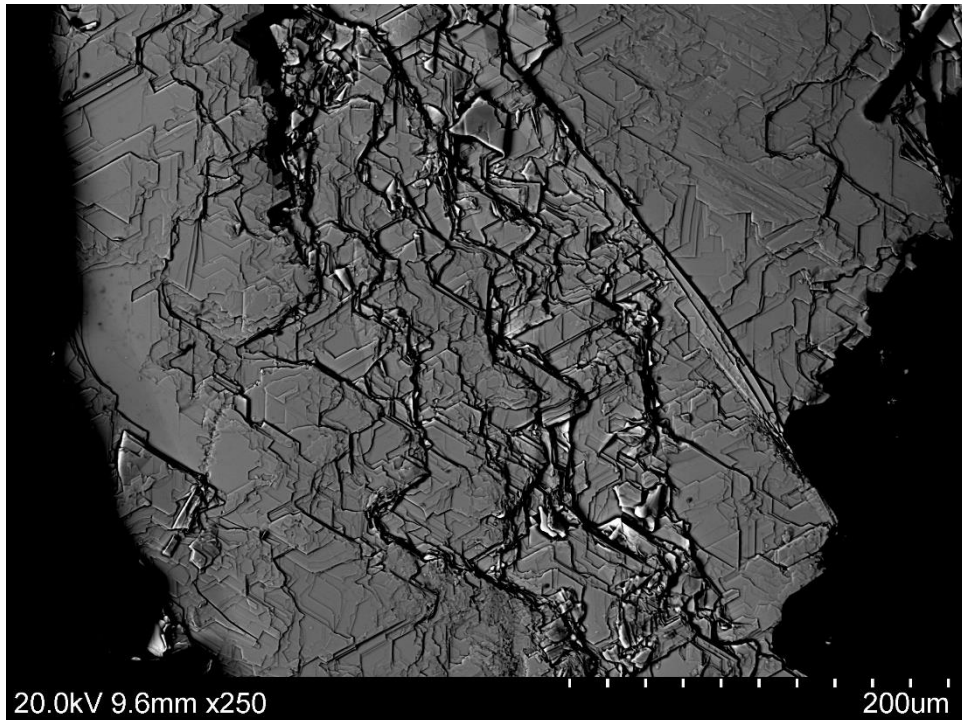


Figure 9. BSE image from SEM of an area of homogenous molybdenite from Ytterby, Sweden.

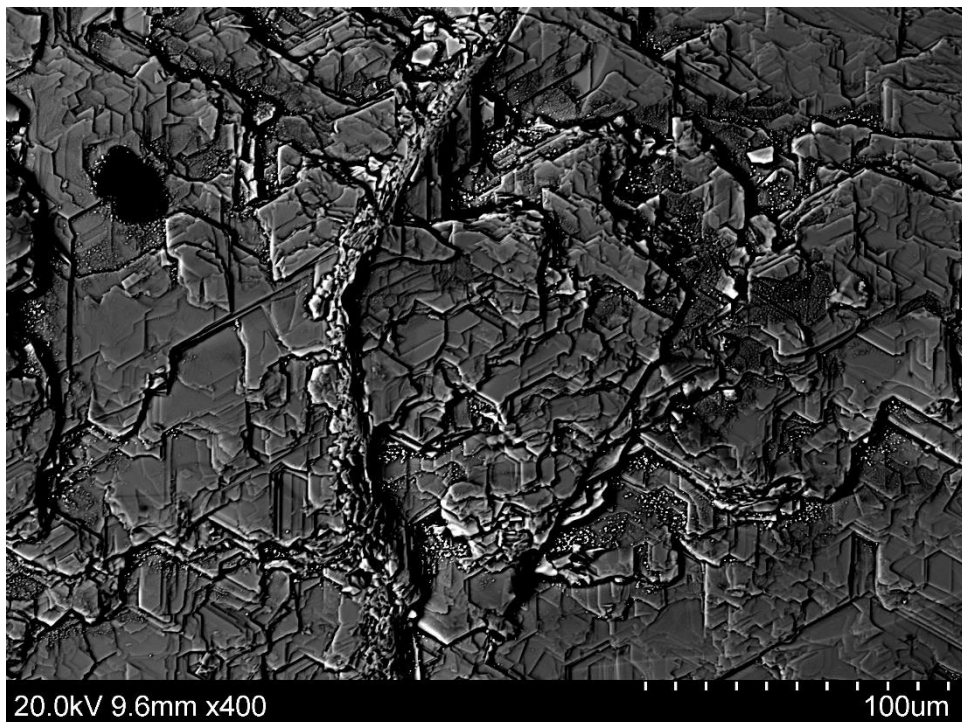


Figure 10. BSE image from SEM of molybdenite from Ytterby, Sweden. Note the apparent inclusions, just a few microns wide, however of unknown chemistry.

3.2 Milling and pressing

The optimum pressure, according to the conducted pressure test, is obtained by applying 2.5 t (0.18×10^6 kPa). At pressures higher than this, the cracks forming in the tablet are too many and extended to use the tablet for laser analysis. At lower pressures, the pressed surface is regarded to be too small for laser analysis. No specific optimum time for pressing is found, however, the tablet should be under pressure for at least 1 minute. Shorter pressing time than this gives a smaller pressed surface. No advantages are gained while pressing for a longer time. The cracks seem to vary only with pressure and not with time.

The milling in the Pulverisette results in grains in a flaky form, which are not getting smaller than approximately 0.5×0.5 cm, independent on increased time of milling. The temperature after the cooling intervals is approximately 30-33°C. After freeze drying the material, it reaggregates. The same happens when milling in pure water, however, not when milling in ethanol. When milling by hand in the agate mortar with ethanol, the molybdenite smears into finer layers and finally smaller particles.

The tablets produced have a diameter of 13 mm and a thickness of 1-2 mm. Some of the tablets exhibit a slightly concave form. The outer parts of the tablets are brittle and to some extent fall apart while handling the tablet. Most of the final tablets have some cracks, extending from the edges towards the center of the tablet, but not as many that laser spots cannot be easily placed between them. The absolute center of the tablets is free from cracks. Sizes of the grains in the tablets were less than 20 μm in diameter.

3.3 Mounting for LA-ICP-MS/MS

The tablet of pyroxenite mounted in Loctite and epoxy displays no signs of penetration of any of the two different glues while studied in SEM (Fig. 11). No major interaction between the glues seem to occur, however, a tendency of mixing appears in the proximate zone of contact, seen by different nuances of gray in SEM. Note that glue appear both above and below the tablet.

The test of pressing material in cellulose results in unevenly distributed particles of cellulose throughout the entire tablet.

Attaching the tablets to glass with both carbon tape and Loctite exhibits no obvious results of disturbing the tablet and provides an adequate approach of mounting before analysis with LA-ICP-MS/MS.

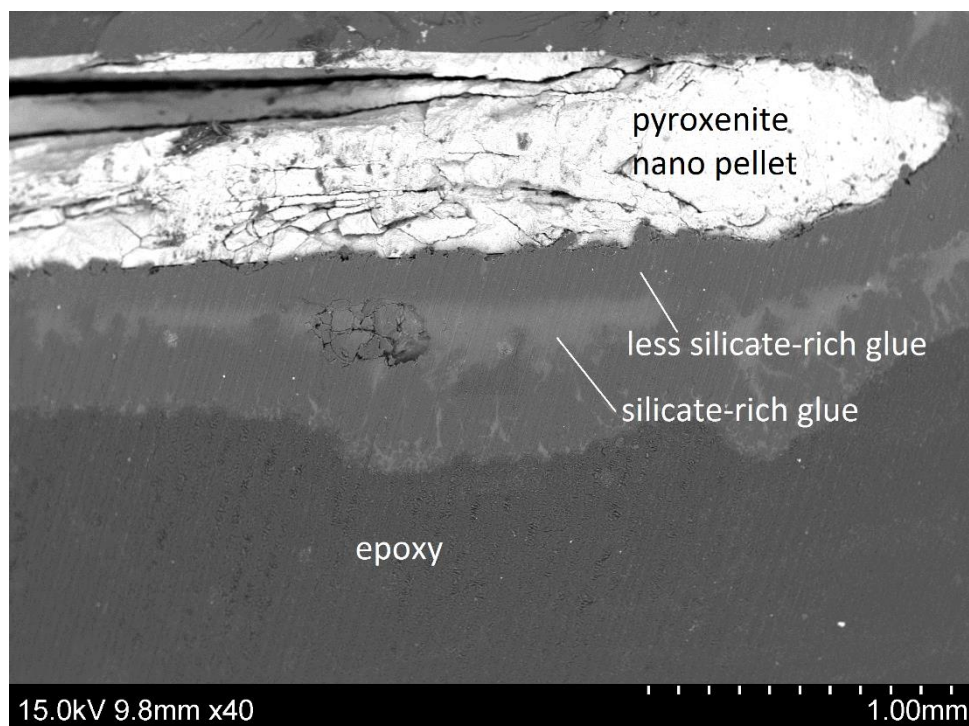


Figure 11. BSE image from SEM showing pyroxenite tablet made from nano powder, surrounded by Loctite and epoxy. Note that the tablet has not been penetrated by any of the glues.

3.4 LA-ICP-MS/MS analysis

Inconsiderably low amounts of both Re and Os were measured in the tablets made of molybdenite from Kingsgate and this material will therefore be excluded from the following presentation of results.

An instrumental drift was seen in the later part of the analyzing schedule; therefore, values only for the first analyzing round of Moly Hill tablets are processed further.

The relative abundance factor $^{187}\text{Re}/^{185}\text{Re}$ obtained from the calculations was 1.67. Average $^{187}\text{Re}/^{187}\text{Os}$, standard deviation and precision for Moly Hill and Ytterby are seen in Table 4 and the variation of the different spots together with average and standard deviation is seen in Figure 12 and 13. The $^{187}\text{Re}/^{187}\text{Os}$ corresponding to the literature age of Moly Hill was 22.19, giving a correction factor of 1.61. Corrected average and standard deviation for Ytterby are seen in Table 4, as well as the subsequent calculated age and age error. The age range for Ytterby in this study is 1795-1851 Ma. Figure 14 displays the results from the corrected values for Ytterby, showing variations of $^{187}\text{Re}/^{187}\text{Os}$ from the four different spots together with the average and the standard deviation. Figure 15 shows the uncorrected and corrected values together, in the same type of plot as found in Figure 12, 13 and 14. Note that the precision is the same for the

uncorrected and corrected values, as well as the relationship between the absolute values and the averages for the ratios.

Table 4. Average $^{187}\text{Re}/^{187}\text{Os}$, standard deviation and precision for Moly Hill and Ytterby (uncorrected and corrected) and calculated age and age error for Ytterby.

	Average $^{187}\text{Re}/^{187}\text{Os}$	Standard deviation	Corrected average $^{187}\text{Re}/^{187}\text{Os}$	Corrected standard deviation	Precision (%)	Calculated age (Ma)	Calculate age error (\pm Ma)
Moly Hill	35.77	0.66	-	-	1.84	-	-
Ytterby	52.28	0.80	32.43	0.50	1.54	1823	28

A typical ablation pattern for a spot from the Moly Hill tablet is found in Figure 16 and 17. The result is plotted as intensity in counts per second versus time in seconds. Note that the intensity is plotted logarithmically and that the actual ablation starts after approximately 28 seconds. Not all background data is plotted. The signals included in Figure 16 are ^{187}Re , ^{187}Os , Pb and Bi and the first two have a stable signal during the ablation, whereas the latter two are seen to vary irregularly. Figure 17 displays the same relationship, except that the signals for ^{187}Re and ^{187}Os are replaced by the $^{187}\text{Re}/^{187}\text{Os}$ ratio.

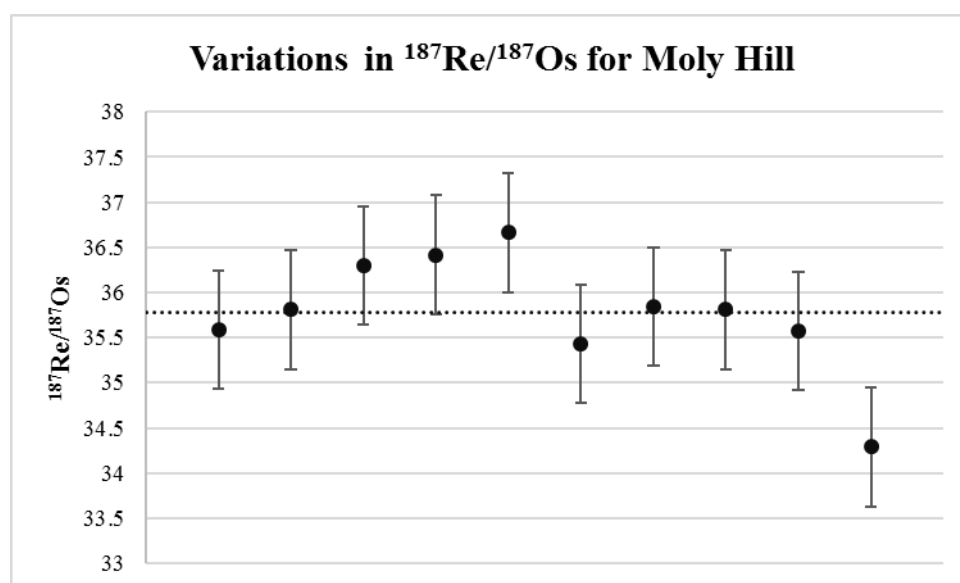


Figure 12. Variations in $^{187}\text{Re}/^{187}\text{Os}$ for the ten different spots for the Moly Hill tablet together with average (dashed line) and standard deviation.

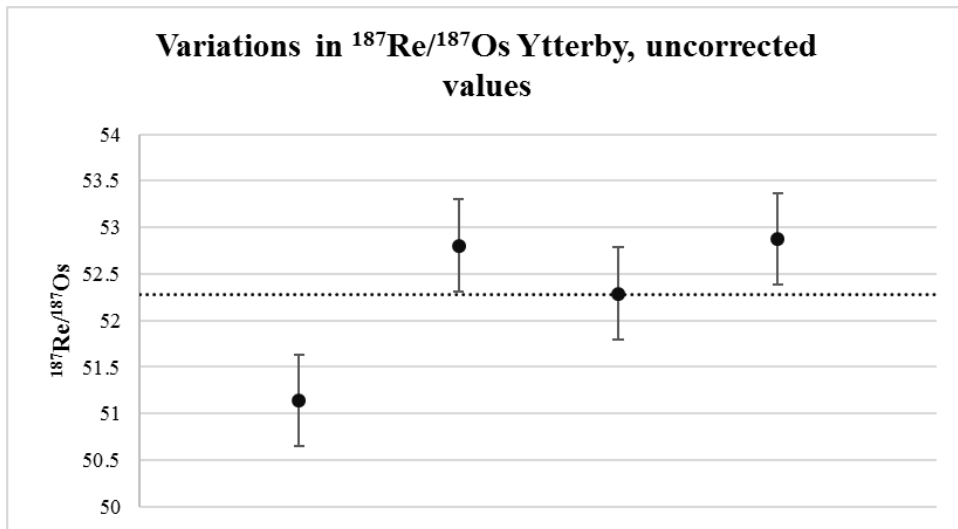


Figure 13. Variations in $^{187}\text{Re}/^{187}\text{Os}$ for the four different spots for the Ytterby molybdenite together with average (dashed line) and standard deviation, all uncorrected.

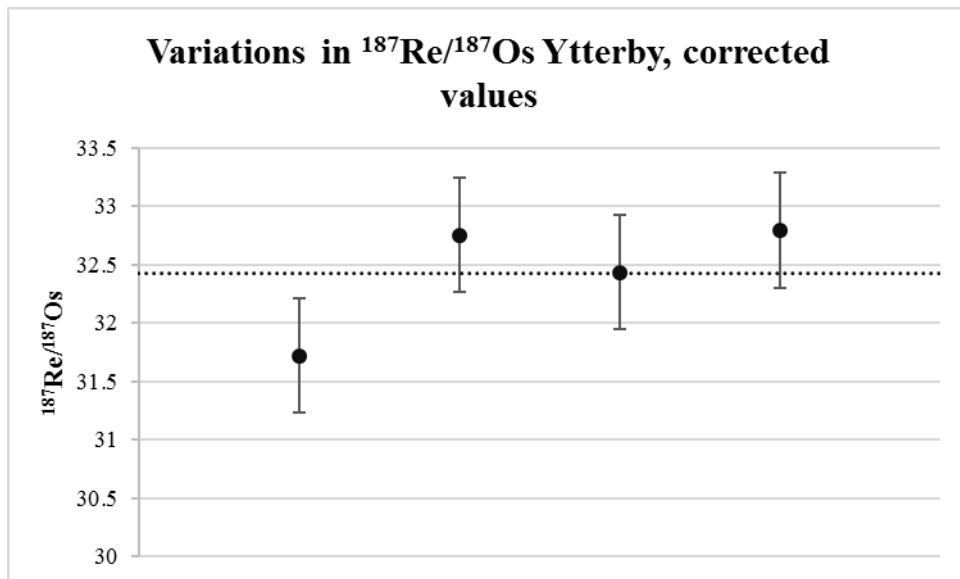


Figure 14. Variations in $^{187}\text{Re}/^{187}\text{Os}$ for the four different spots for the Ytterby molybdenite together with average (dashed line) and standard deviation, all corrected.

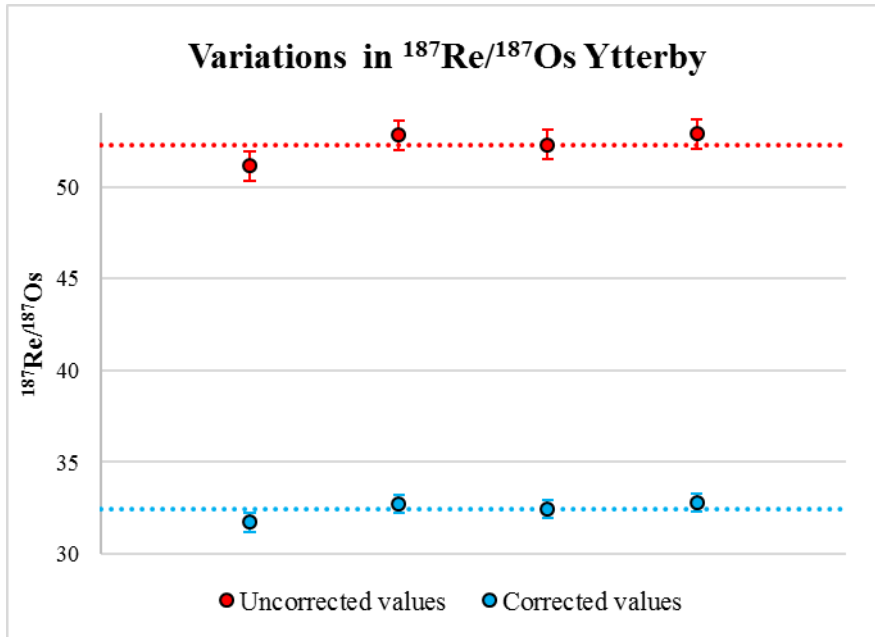


Figure 15. Variations in $^{187}\text{Re}/^{187}\text{Os}$ for the four different spots for the Ytterby molybdenite together with average (dashed line) and standard deviation, uncorrected and corrected. Note that the relation between the values and the average will be the same for both uncorrected and corrected.

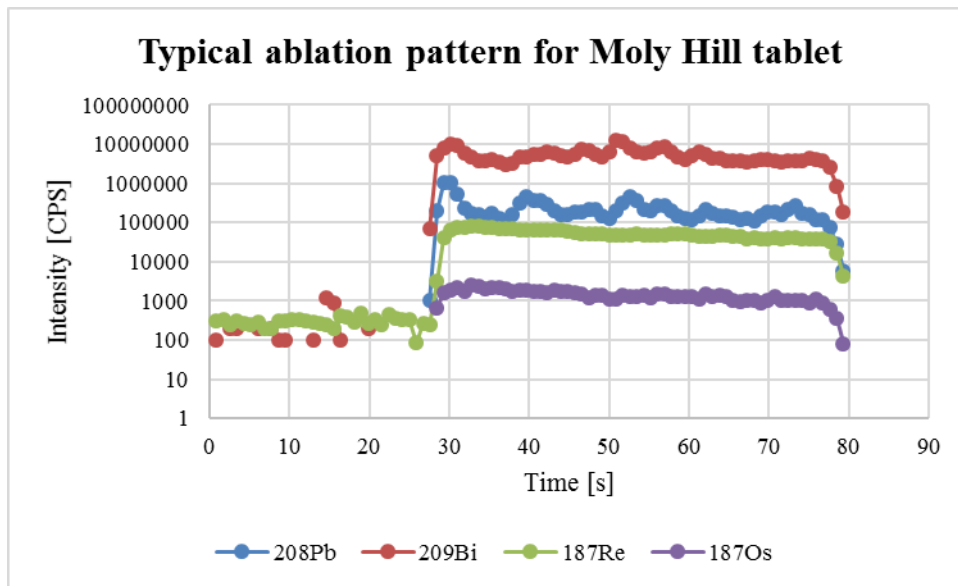


Figure 16. Typical ablation pattern for Moly Hill tablet, intensity in counts per second versus time in seconds. Note that the intensity is plotted logarithmically and that not all background data is plotted. Also note that the signals for ^{187}Re and ^{187}Os are stable whereas the signals for Pb and Bi are not.

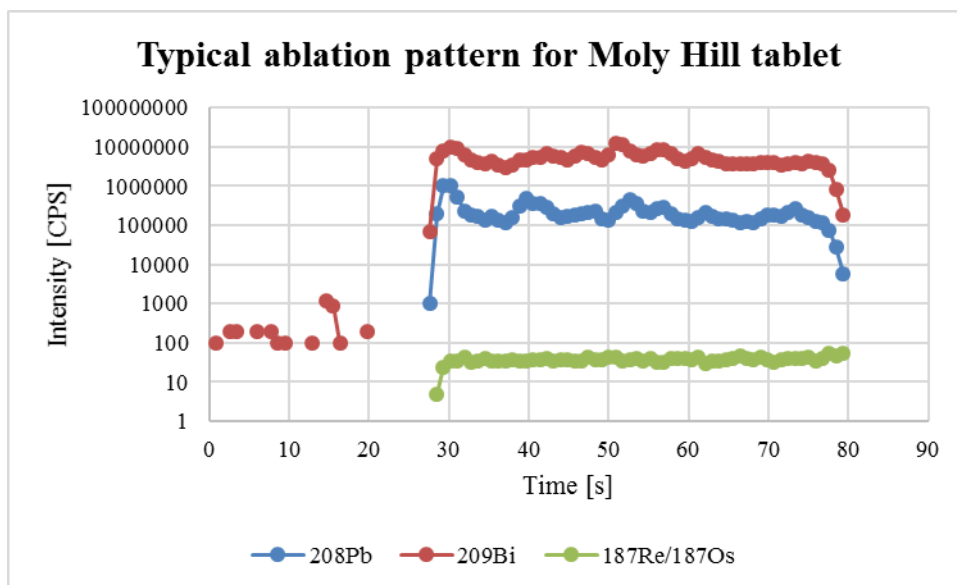


Figure 17. Typical ablation pattern for Moly Hill tablet, intensity in counts per second versus time in seconds. Note that the intensity is plotted logarithmically and that not all background data is plotted. Also note that the signal for $^{187}\text{Re}/^{187}\text{Os}$ is stable whereas the signals for Pb and Bi are not.

The ^{187}Re and ^{187}Os concentrations in the AI-3 standard is 7.45 and 0.43 ppm and the corresponding ratio 17.16. This is compared with the ratio obtained from the actual ablation of the standard which gave an average ratio of 18.46. Note that no correction for the reaction with CH_4 is done in this calculation, meaning that this is not dealt with as in the case for the corrected ratios for Ytterby.

3.5 SEM of tablets

3.5.1. Kingsgate molybdenite

The tablet pressed by applying 5 t (0.37×10^6 kPa) from material of the Kingsgate molybdenite shows a low degree of destruction by the laser outside the actual area of the laser spots (Fig. 18). A considerable number of inclusions, only a few micrometers wide, can be seen scattered across the tablet (Fig. 18 & 19). Furthermore, heterogeneities are seen as areas in the tablet with more or fewer inclusions or unevenly distribution of the sizes of the inclusions (Fig. 19).

Compared to the tablet pressed by applying 5 (0.37×10^6 kPa), the tablet pressed by applying 2.5 t (0.18×10^6 kPa) shows a higher degree of destruction of the laser (Fig. 20). The amount of inclusions may be fewer but the sizes of them are bigger (Fig. 21). Variation of sizes of the inclusions can also be seen but the areas of heterogeneities found in the 5-t tablet are missing its equivalent in the 2.5-t tablet.

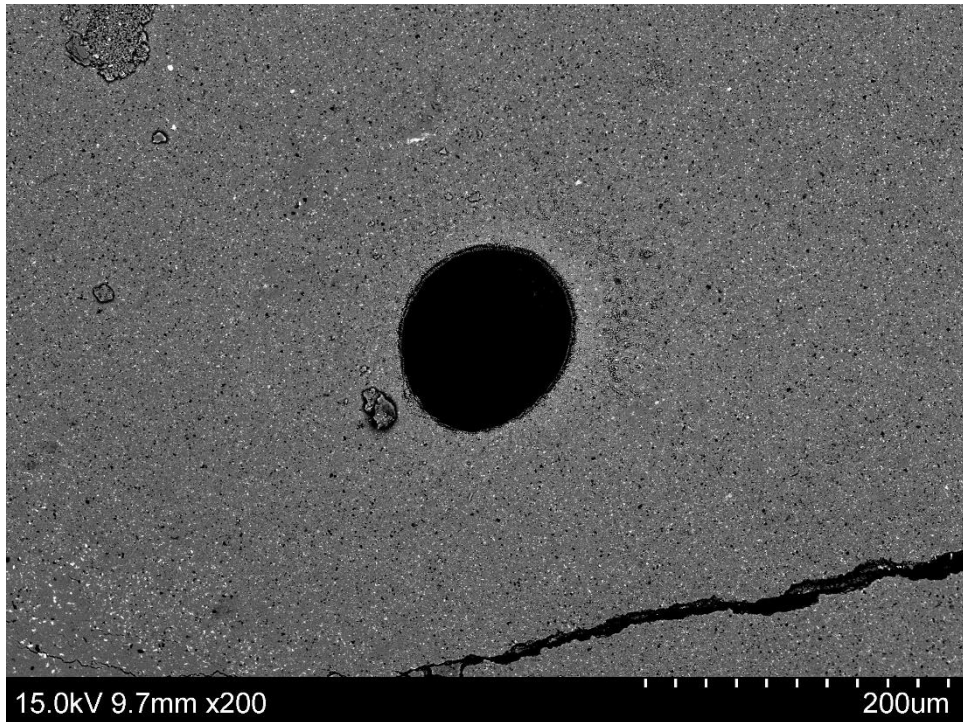


Figure 18. Laser spot, 110 μm wide, with a distinct circumference, in a tablet pressed by applying 5 t (0.37×10^6 kPa), made of molybdenite from Kingsgate, Australia.

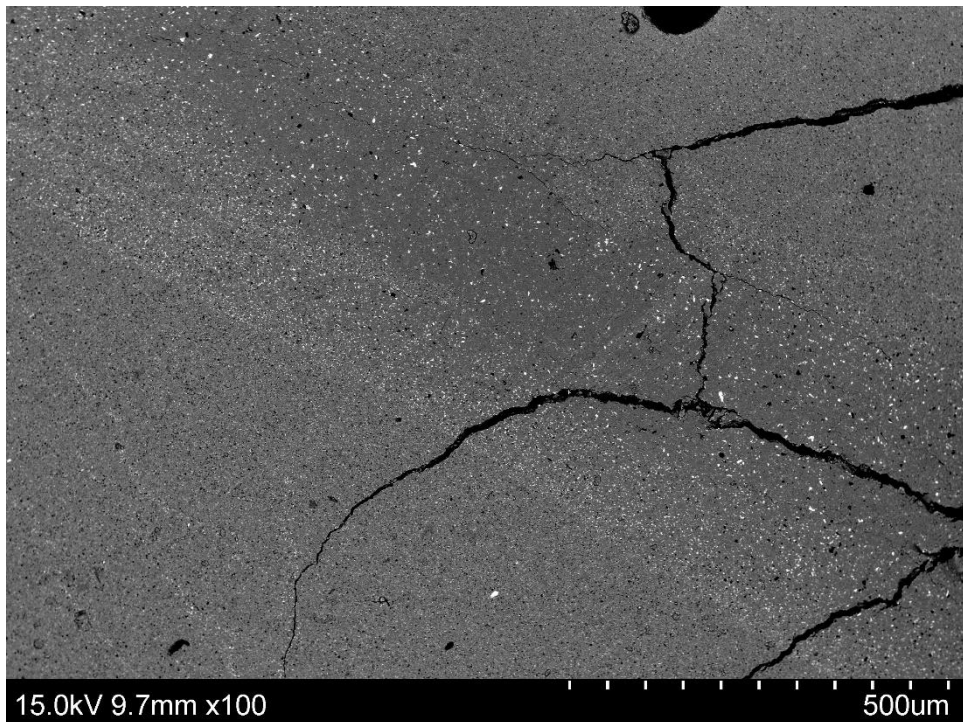


Figure 19. Area of heterogeneities due to amount and sizes of inclusions of mostly bismuthinite and bismuth in a tablet pressed by applying 5 t (0.37×10^6 kPa), made of molybdenite from Kingsgate, Australia.

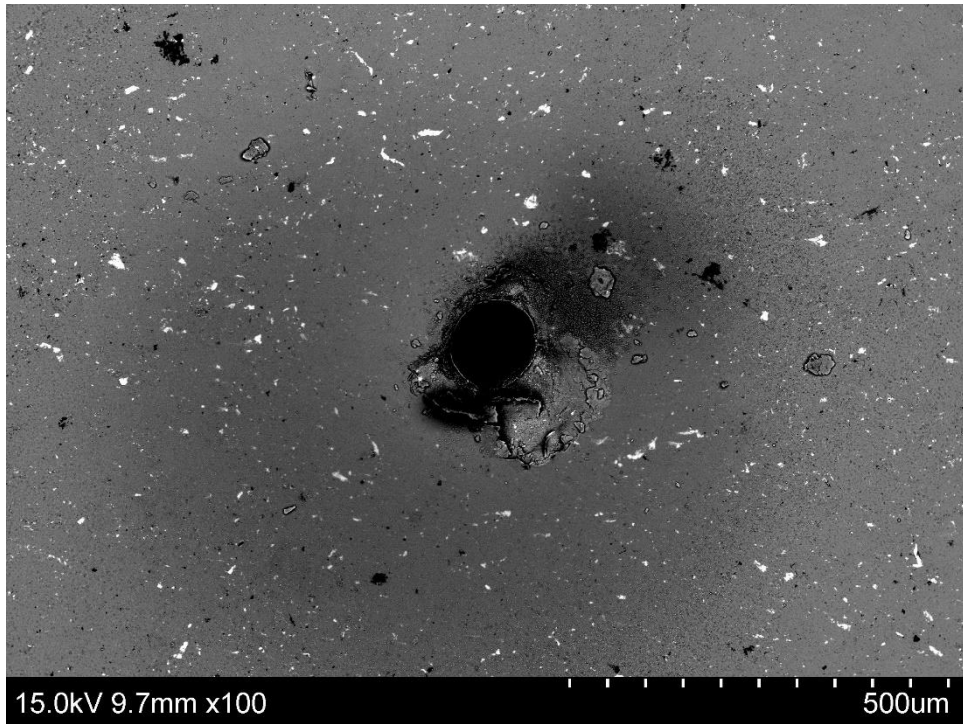


Figure 20. Laser spot, 110 μm wide, in a tablet pressed by applying 2.5 t (0.18×10^6 kPa), made of molybdenite from Kingsgate, Australia. Note the indistinct circumference of the crater at the surface of the spot.

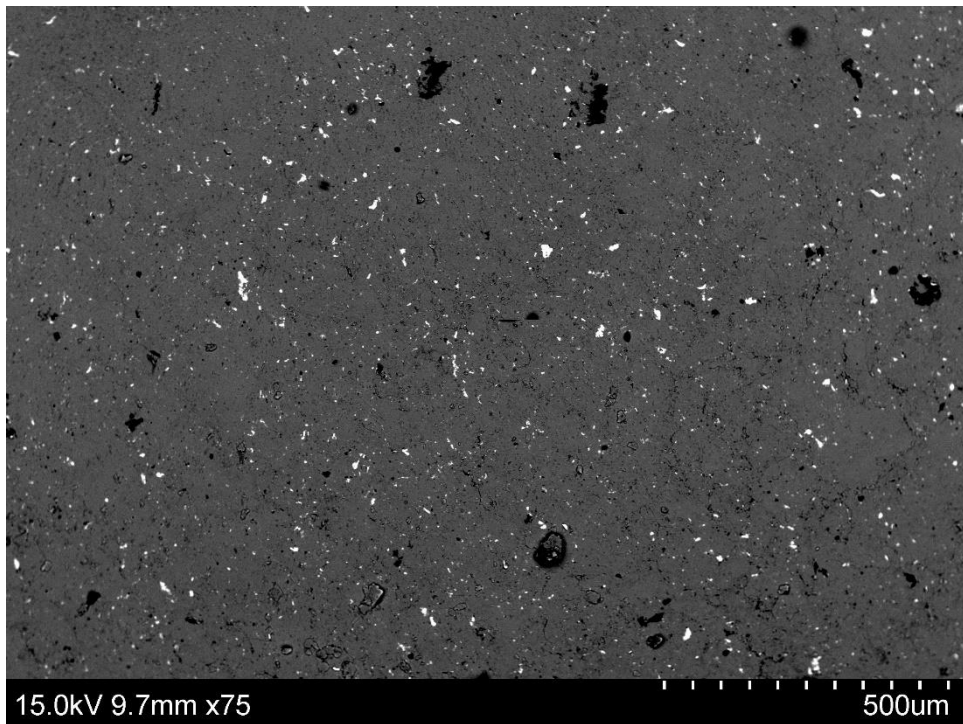


Figure 21. Inclusions of mostly bismuthinite and native bismuth in a tablet pressed by applying 2.5 t (0.18×10^6 kPa), made of molybdenite from Kingsgate, Australia.

3.5.2 Moly Hill molybdenite

Most of the laser spots in the Moly Hill tablets are well delimited (Fig. 22) even though some exceptions exist (Fig. 23). The surface of the tablets appears to be more porous compared to the tablets made of molybdenite from Kingsgate. A few inclusions of mostly native bismuth are identified (Fig. 24), the largest one found is approximately 10 x 15 μm .

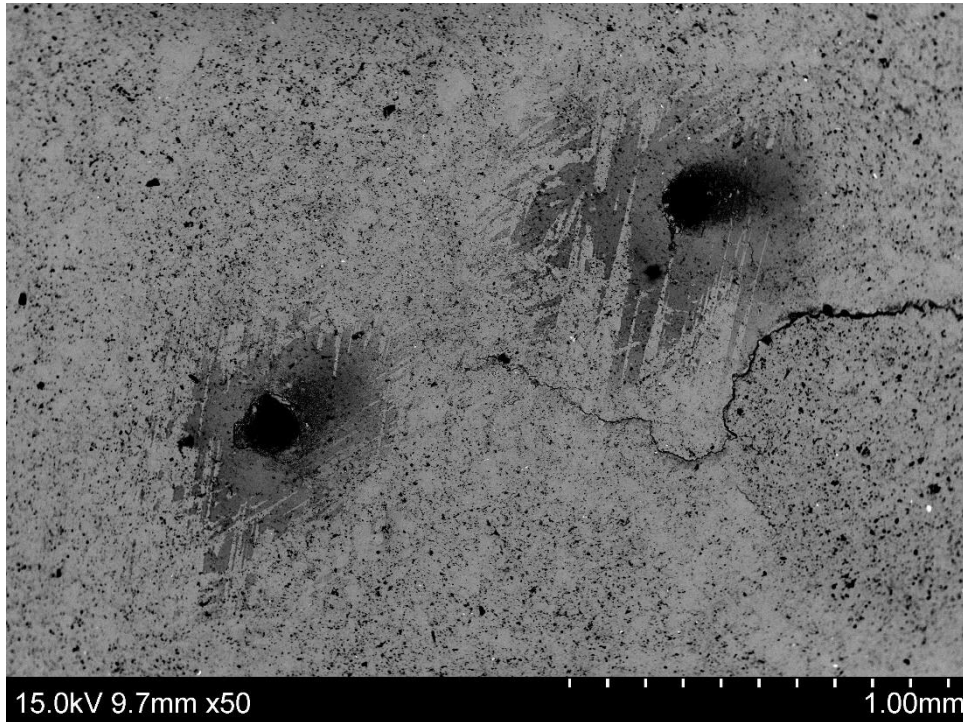


Figure 22. Laser spots, 110 μm wide, in a tablet pressed by applying 2.5 t (0.18×10^6 kPa), made of molybdenite from Moly Hill, Canada.

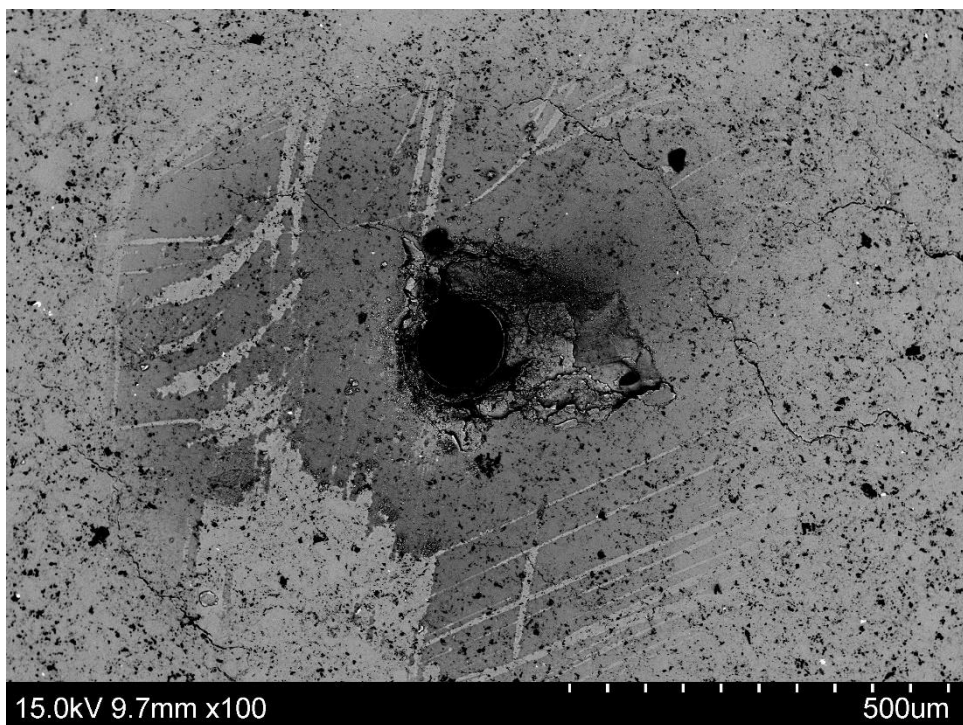


Figure 23. Laser spots, 110 μm wide, in a tablet pressed by applying 2.5 t (0.18×10^6 kPa), made of molybdenite from Moly Hill, Canada.

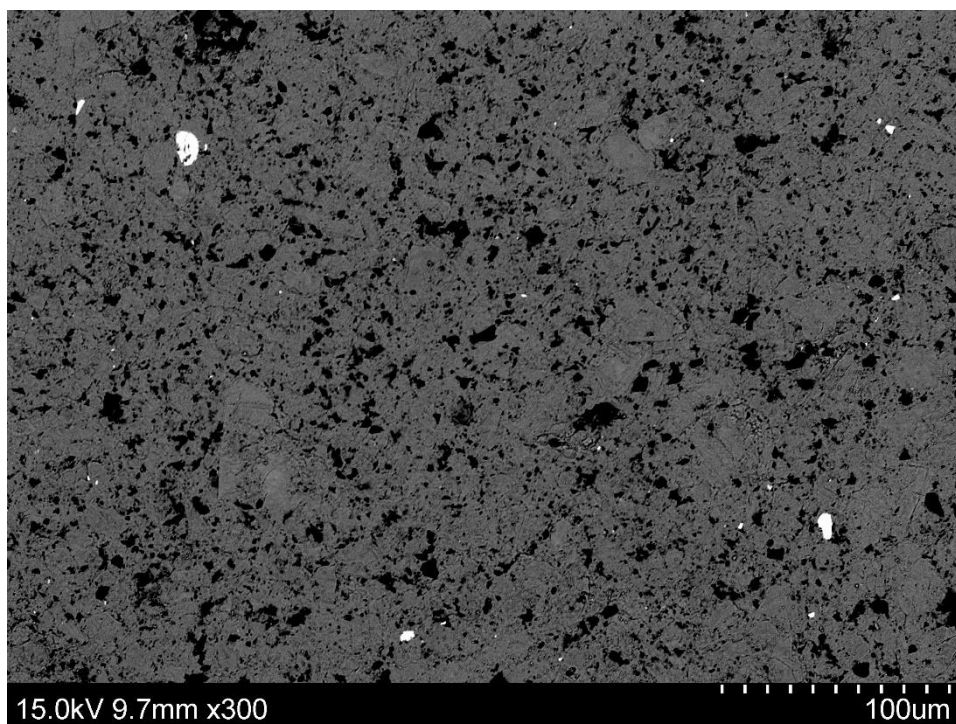


Figure 24. Inclusions of mostly native bismuth in a tablet made of molybdenite from Moly Hill, Canada.

4. Discussion

4.1 Milling and pressing

The method used by Garbe-Schönberg and Müller in 2014, and which was thought to be a guideline for the process of development in this study, was mostly unsuccessful. This is a consequence of the special properties of molybdenite, in particular the layered crystal structure, which prevented the mineral of breaking into smaller particles while milling in the Pulverisette, instead dividing into flakes. The best way to further separate the molybdenite flakes was instead to smear them by hand in the agate mortar, this is how the final method was chosen. An advantage of this method compared to Garbe-Schönberg and Müllers method from 2014 is that smaller amounts of sample can be handled, and at the same time give a smaller loss of material than if milled in the Pulverisette. No visible result was obtained while dry-milling relatively large particles by hand, therefore a pre-separation with the grater was conducted, before continuing with wet-milling. Ethanol was chosen instead of pure water, because the molybdenite reaggregated while suspended in water, but not in ethanol. This was also one of the reasons why freeze drying was not a part of the final method; before freeze drying, it is favorable if the material is frozen in pure water, and because this made the material aggregate, this step was neglected. Another reason to skip the freeze drying was that the result of this was

even more lumping of material, not the brittle powder obtained in Garbe-Schönberg and Müller's experiment in 2014.

The pressure used while producing the tablets seem to have an influence on the laser spots. This can be evaluated at looking at the two tablets made of molybdenite from Kingsgate. They were created by using the same method except for pressure. Laser spots in the tablet produced with higher pressure were distinct and did not affect the material surrounding the spots (Fig. 18), whereas the laser spots in the tablet produced with lower pressure were irregular and destructive to material outside the actual ablating area (Fig. 20). Higher pressure tablets are more compact and therefore more resistant against the energy from the laser while lower pressure ones are more porous in structure and more easily destroyed. According to this, a higher pressure would be preferred but should be balanced with the number of cracks that the pressure creates, which seems to be fewer with lower pressures.

The properties of the tablets could have been improved in several ways. Firstly, and maybe most importantly, a smaller grain size of the particles making up the tablet, would result in a more homogenous tablet with smaller inclusions and even more stable and correct Re and Os values. In future production of tablets, a method for objectively evaluating the size of the particles should be developed, to ensure the quality of the tablets to the user. Garbe-Schönberg and Müller completed a grain size analysis by laser diffraction. Secondly, the used tablet die set indicates minor, but still critical malfunctions, which probably affected the tablets. While pressing, small amounts of material could slip out from the edges of the tablet die set. This could explain the concave form of the tablets, as well as the variations of pressed surface of the tablets. With a properly functioning and maybe a more suitable tablet die set, those negative effects might have been avoided, instead obtaining flat surfaces and completely pressed tablets that would be less fragile. A hypothesis is that the optimum pressure and corresponding time also would be different with another tablet die set and that the number of cracks and their extent might be reduced with less fragile areas of the tablet as a result of better and flatter pressed surfaces. The size of the tablet is the equal to other reference material tablets, but with the properties of the produced tablets and the expense of the material, smaller tablets would maybe be an alternative when refining the method in the future. However, the size of the tablets is regarded appropriate in this study because 110 μm laser spots are big in these contexts and a lot of material will be used during ablation, requiring big tablets.

4.2 Mounting for LA-ICP-MS/MS

Even if the test with encapsulating the pyroxenite tablet was successful with regard to minimum penetration of glue in the tablet, a similar test must be conducted on a tablet of molybdenite to be able to validate this method. Pyroxenite and molybdenite have too distinct physical properties to ensure that the results would be the same.

Glue above the tablet will require polishing to reach the surface of the tablet, and polishing will contaminate the sample by polishing powder entering pores of the tablet, as well as destroy the structure of the surface. Another option could be sawing, but this would also destroy the surface of the sample because the precision of the sawing needed would be unattainable. A method where no glue relocates to the surface above the tablet - the surface of the tablet that are used for analyzing - must be developed if mounting in epoxy should be an appropriate option.

Even though cellulose will have no concentrations of Re or Os, particles of cellulose in the tablet will interrupt the homogeneity and the results from this method is therefore regarded unsuccessful.

Because of the scarcity and expense of appropriate reference materials for tablet production, it would be desirable to re-mill and reuse the material after ablation of the whole surface. This requires that the tablet not have been contaminated during the mounting process. This could possibly be true for tablets attached with carbon tape to glass and is therefore considered the so far most suitable method. Due to the dubiety whether Loctite penetrates the tablet or not, this method is needed to be examined further.

4.3 Materials and LA-ICP-MS/MS

The tablet made of molybdenite from Kingsgate was recognized to host a great amount of relatively small inclusions. This can be explained by a combination of two theories. Firstly, the starting material (e.g. the material before milling), appeared to have inclusions of significant size (Fig. 3), consequently leading to corresponding inclusions in the milled material, however, reduced in size by milling. Secondly, both Kingsgate tablets analyzed were produced with the centrifugation method. As mentioned earlier, centrifugation leads to a sorting of fractions. In the case that the material of the inclusions tends to be milled in certain sizes, meaning that some fractions will be enriched in inclusions, this could explain why the surface of the tablet exhibits this considerable number of inclusions. A condition for this to be true is that a fraction enriched in inclusions must, by chance, be the one at the top of the tablet by the end of the centrifugation and remain there during pressing. Furthermore, the inhomogeneities in distribution of

inclusions seen in the Kingsgate tablets (Fig. 19), could also be explained with this sorting of fractions. If the tablet happens to be pressed at an angle compared to the orientation during centrifugation, fractions rich in inclusions could be visible as layers at the surface.

Another critical consequence of the centrifugation method is that not all fractions are included in the final tablet. This happens both while pipetting material before centrifugation leading to exclusion of coarser grains, and during centrifugation, where the smallest grains stay in suspension. If the concentrations of Re and Os are heterogenous in the molybdenite crystal and areas with different Re and Os tend to be milled in different sizes, this exclusion of material will lead to errors in measured concentrations and therefore also in age calculations.

As can be seen in Figure 12, the $^{187}\text{Re}/^{187}\text{Os}$ ratios for the first analyzing round of the Moly Hill tablet are differing and could be grouped in two. This might be explained by that the first five spots are ablated in one tablet, and the other five in another (two tablets from Moly Hill were ablated).

Ablated inclusions with Pb and Bi are represented by the irregular spikes in the ablation pattern (Fig. 16 & 17). Despite this, the intensities for the ^{187}Re and ^{187}Os signals are stable and indicate no relation with the spikes for Pb and Bi. This means that the inclusions encountered while ablating the tablet have no effect on neither the signals for Re and Os and therefore the dating, nor the general homogeneity of the tablet. However, spikes from inclusions, despite this result, are not desirable and if the material of the tablet could have been milled to finer particles before pressing, the influence of such inclusions could have been even smaller.

As mentioned earlier, the age of the Ytterby pegmatite provided by Romer & Smeds in 1994 was 1795 ± 2 Ma. In this study, molybdenite from Ytterby was dated to 1795-1851, an age which range overlaps the literature age, although with a minimal margin. This validates the quality of the tablet produced of molybdenite from Moly Hill and confirms that it can be used as reference material for calibration of in situ Re-Os dating with LA-ICP-MS/MS. However, improvements could be made to create a bigger overlap of ages.

Note that it is not known whether the composition of isotopes in the AI-3 standard is the same as natural abundance, which was assumed when calculating the $^{187}\text{Re}/^{187}\text{Os}$ ratio. What is known is the actual concentrations. This could be an explanation to why the obtained value from the analysis is 18.46, while the calculated one from the concentrations from the standard is 17.16. To decrease the differences between those numbers, the ^{187}Os composition of the standard need to be higher than the natural abundance, and/or the ^{187}Re need to be lower.

However, it is not known by the author of this study if this is possible. Another reason for the differing values could be sulfide fractionation, a process not explained further in this study. Furthermore, no correction for the reaction with CH₄ was done, which would give a higher ¹⁸⁷Os and therefore a more plausible result.

The analytical method in this study could be optimized regarding such as dwell time, spot size, measured isotopes, gas flow and laser parameters such as output energy and frequency. A correction for instrumental drift could have been done to improve the precision of the measurements. Without this, the precision is <2%, and with a better precision obtained from drift correction, the errors of the ages would decrease, providing a smaller age interval. Combining mentioned improvements, it is not unreasonable to acquire a precision of approximately 1% for 100 μm spots for in situ dating with the Re-Os isotope system.

The method used in this study could implicate dating of complex molybdenites and their associated deposits. The problem with decoupling between Re and Os, obtained when shooting with laser at a molybdenite crystal, could be overcome by the homogenization made possible by milling. So far, the method is promising, however, more analyses of tablets produced from well-researched materials need to be done, such as the Merlin deposit in Australia. This is the world's highest-grade Mo-Re deposit (Babo et al., 2017) and is therefore a potentially suitable reference material for calibration of in situ Re-Os dating with LA-ICP-MS/MS.

5. Conclusions

- Molybdenite is hard to mill due to its layered structure. Nano size was not reached, which has been obtained in other studies and would be preferred in this one as well. The best method so far is to mill by hand in an agate mortar with ethanol.
- The optimum pressure and corresponding time depend on several factors, such as the tablet die set and material, and will affect for example numbers of cracks in the tablet.
- Despite signs of inclusions in the final tablets, the Re and Os signals seemed unaffected by this.
- The range of age of the Ytterby molybdenite, measured and calculated in this study, overlaps the age obtained by Romer & Smeds (1994). This validates the quality of the tablet produced of molybdenite from Moly Hill and confirms that it can be used for calibration of in situ Re-Os dating with LA-ICP-MS/MS. This method is promising; however, it needs further development and improvements.

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