LETTER

First in situ Re-Os dating of molybdenite by LA-ICP-MS/MS

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Abstract

Conventional dating of molybdenite (^{187}Re-^{187}Os) provides one of few options for direct dating of sulfide mineralization. Unfortunately, in situ dating of molybdenite is considered unreliable due to intra-granular decoupling of ^{187}Re-^{187}Os. In this study, we developed a new analytical protocol for studies of micron- to grain scale ^{187}Re-^{187}Os systematics in molybdenite. Online chemical separation using ICP-MS/MS technology enables in situ dating by β-decay systems (e.g., Rb-Sr and K-Ca in micas) using laser ablation. Here, the methodology is extended to the ^{187}Re-^{187}Os system, another β-decay system that cannot be resolved by mass spectrometry. Several reaction gases were evaluated, and production of $OsCH_2$ by reaction with CH_4 was found to produce strong separation of Os from Re. However, in contrast to the e.g., ^{87}Rb-^{87}Sr system, 1–2% of the parent isotope Re also reacted to $ReCH_2$, leaving a significant interference. A mathematical correction of this remaining interference is possible, and ^{187}Re-^{187}Os (mass-shifted) can be measured accurately even for fairly extreme ratios. For laser ablation, standards were developed by pressing particulate pellets of conventionally dated molybdenite (Moly Hill and Merlin), because there are no appropriate reference materials available. Six natural molybdenite samples from a range of geological settings, containing > 10 ppm Re, were analyzed by 70 μm laser ablation spots, and ages were calibrated by analysis of molybdenite pellets. Contrary to our expectation, weighted average ages obtained were in agreement (within 1%) with conventional age determinations, with fairly good precision (from ~ 1 to 5% 2σ depending on Re concentration), suggesting limited or essentially nonexistent decoupling within crystals. Two important implications of this result are that decoupling Re-Os is not universal, and that our new analytical protocol is useful both for dating and for studies of decoupling. The benefit of in situ dating compared to conventional dating is, apart from lower cost and time consumption, the possibility of targeting smaller molybdenite crystals (≥ 100 μm) in thin sections and epoxy mounts. The youngest sample in the study is 920 Ma, but we see potential of dating significantly younger Re-rich molybdenite.

Keywords Molybdenite · In situ · Re-Os · ICP-MS/MS · CH_4

Introduction

The ^{187}Re-^{187}Os β-decay system habilitates direct dating of sulfide mineralization events, and is a critical tool for studies of ore–

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forming processes. Molybdenite (MoS_2) is the most attractive target for Re-Os dating due to high partitioning of Re, negligible "common" Os, and resistance to metamorphic resetting (Stein et al. 2001; Selby and Creaser 2004; Suzuki et al. 1993). However, dating of molybdenite is hindered by several analytical complications and is only performed in highly specialized labs. The main problem is that the mass difference between ^{187}Re and ^{187}Os cannot be resolved by mass spectrometry, and chemical separation of these isotopes is comparatively difficult. Additionally, decoupling of Re and Os within molybdenite crystals has been reported, especially in older and coarser grains, which means that extra care has been urged in sample preparation (Selby and Creaser 2004; Stein et al. 2003; Suzuki et al. 2000). In situ dating of molybdenite by Re-Os using laser ablation (LA) multicollector (MC), or quadrupole (Q) inductively coupled plasma mass spectrometry (ICP-MS) has been attempted on very old samples, but the correction for the overlap

of ^{187}Re on ^{187}Os is rather extreme, and matrix-matched standardization was unavailable (Košler et al. 2003).

With the introduction of ICP tandem mass spectrometry (MS/MS), it has become possible to control a range of isobaric interferences previously out of reach of quadrupole ICP-MS (Bolea-Fernandez et al. 2017). Several β-decay couples (^{87}Rb and ^{87}Sr, ^{40}K and ^{40}Ca) are able to separate during analysis with the help of a range of reaction gases, allowing in situ dating of Rb (and K)-rich minerals (Zack and Hogmalm 2016; Hogmalm et al. 2017). Effective separation is possible because the daughter isotope reacts with a reaction gas and is measured in the so-called mass-shift mode, while the parent isotope does not react and is measured on-mass. The same principle can potentially also be applied to the Re-Os system, since methane (CH_4) has been demonstrated to react efficiently with Os^+, forming $OsCH_2^+$ in a static reaction environment, while Re+ does not form $ReCH_2^+$ (Shayesteh et al. 2009). Post-ionization separation of Re and Os by reactions with CH_4 has been demonstrated in fourier-transform ion cyclotron resonance mass spectrometry (Irikura et al. 1994), but has, to our knowledge, not been applied analytically. In this study, CH_4 was evaluated with the goal of achieving high reactivity with Os and low reactivity with Re to improve in situ measurements of ^{187}Re/^{187}Os ratios in molybdenite.

In the absence of accessible Re-Os standards, homogeneous in both Re and Os, new reference material need to be developed to enable in situ Re-Os dating. Out of a compilation of 38 commonly used standards for in situ studies (Jochum and Stoll 2008), only the three synthetic sulfides report Re and Os contents above 1 ppm (Wohlgemuth-Ueberwasser et al. 2007). However, those standards are not available any more. To our knowledge, the only accessible standard is a synthetic Fe(Cu, Ni)S, labeled AI-3, that has sufficient Os and Re (Os 22.15 ± 0.77 ppm and Re 11.90 ± 0.34 ppm, respectively; personal communication Dany Savard), but exhibits substantial heterogeneity. In this study, pressed pellets of naturally occurring molybdenite crystals, previously dated by conventional Re-Os dating, were prepared for cross-calibration of isotopic ratios. A similar approach has been adopted for in situ Rb-Sr dating (Hogmalm et al. 2017), but molybdenite is a greasy and sticky material that is much more challenging to homogenize.

The strategy of the study was first to evaluate gas reaction, separation efficiency, corrections, and calibrations. Initial tests performed by solution analysis guided the development of the LA-ICP-MS/MS-based protocol. Analysis of pressed particulate pellets of natural molybdenite was used to assess the protocol with respect to detection limits and precision and accuracy of Re-Os ratios. Finally, the analytical protocol was tested on natural molybdenite crystals from a range of geological settings and ages.

Methods and materials

LA-ICP-MS/MS analysis

In situ analysis was performed using an ESI 213NWR (TwoVol2) laser ablation system connected to the ICP-MS Agilent 8800 QQQ, with CH_4 (≥ 99.9995 mol %; Air Liquide) connected to the oxygen mass flow controller. The basic set-up of the system has been described previously (Hogmalm et al. 2017; Zack and Hogmalm 2016), and optimization for Re-Os analysis was performed by line or spot analysis of NIST SRM 610, AI-3, and Moly Hill pressed pellet (see below). The protocol was developed and evaluated in two test sessions and three analytical runs. The first two analytical runs were focused on the analysis of pressed pellets with a 110 μm spot size to evaluate reproducibility within runs and between runs and to evaluate age precision and accuracy. In the third run, a range of molybdenite crystals were targeted using 70 μm spot size, in order to evaluate the protocol on natural materials.

The comparatively high detection limits associated with laser ablation analysis make it necessary to focus more on $OsCH_2$ production than minimization of $ReCH_2$ formation. The octopole bias controls acceleration of ions in the reaction cell; a weak negative voltage (-4 V) was found to provide an acceptable trade-off between $ReCH_2$ and $OsCH_2$ production. CH_4 flow-rate was optimized for maximum sensitivity of $OsCH_2$, with the trade-off of higher $ReCH_2$ production relative to $OsCH_2$. It was found that the conditions that provided maximum $OsCH_2$ sensitivity resulted in ~2% of Re reacting to $ReCH_2$. To gain sufficient signal and to lessen the effect of potential heterogeneities in Re and Os, relatively large spot sizes were used (> 70 μm), and for analysis of pellets, a fairly low energy (3.1 J/cm^2) and a frequency of 5 Hz were found to produce the most stable signal. Analytical conditions for 70 μm spot size analysis are presented in Electronic Appendix 1, and elements, masses, and integration times in Electronic Appendix 2.

Corrections and calibrations

Correction for ^{187}ReCH$_2$ formation, interfering on ^{187}OsCH$_2$, was performed by measuring the ^{185}ReCH$_2$ signal (I), recalculating to ^{187}ReCH$_2$ assuming natural abundance, and subtracting from the signal on mass 201 according to Eq. 1.

$$I^{187}OsCH_2 = I\left(^{187}ReCH_2 + {}^{187}OsCH_2\right) - I^{185}ReCH_2 \left(\frac{\%\text{Nat. abundance } 187Re}{\%\text{Nat. abundance } 185Re}\right)$$
(1)

The natural abundance ratio was corrected for the influence of instrument mass bias by measuring ^{187}ReCH$_2$/^{185}ReCH$_2$ in NIST SRM 610. This standard contains negligible amounts of Os, and thus ^{187}ReCH$_2$ can be measured without interference. Although a

minor issue for molybdenite, "common" Os was monitored by measuring $^{189}OsCH_2$ and was used for minor corrections of $^{187}OsCH_2$ assuming a natural abundance relation between the isotopes. Age intercomparisons between Moly Hill and Merlin pressed pellets were performed using the ^{187}Re decay constant ($\lambda^{187}Re$) of $1.666 \pm 0.005 \times 10^{-11}\ a^{-1}$ (Selby et al. 2007). For calculation of ages of the natural molybdenite, an average age calibration factor (($^{187}OsCH_2/^{185}ReCH_2$)/Age) was calculated from analysis of the Moly Hill and Merlin pressed pellets.

Materials

Molybdenite samples in this study came mainly from the mineral collection of the Swedish Museum of Natural History. The sample from Moly Hill was purchased from David K. Joyce Minerals, and the sample from Merlin deposit was provided by Chinova Resources Pty Ltd. Information about the samples is summarized in Table 1, and a more detailed description of samples and age constraints are provide in Electronic Appendix 3. Samples from Pielisjärvi (Fin), Mätäsvaara (Fin), Uddgruvan (Swe), Smögen (Swe), Baggetorp (Swe), Wigströmsgruvan (Swe), and Kingsgate (Aus) were also analyzed, but Re concentrations were too low (Re < 10 ppm) for the purpose of this study.

Production of pressed molybdenite pellets

Molybdenite separates from Moly Hill and Merlin were pulverized by hand with ethanol in an agate mortar for 2 h. The ethanol was continuously refilled during the milling process. At the end of this period, no further ethanol was poured on the sample, and the milling continued until all ethanol had evaporated. The molybdenite powder was poured in a tablet die set (13 mm) and pressed by applying 2.5 ton for 2 min. A Fritsch planetary ball mill was tested for pulverization, but failed to produce a fine grained powder of molybdenite. Inclusions of native bismuth, inherited from the starting material, in the Moly Hill pressed pellets are < 10 μm and evenly distributed over the surface of the pellet, indicating that grinding by hand was reasonably effective for this material (Fig. 1a). Grinding of the Merlin molybdenite separate produced a pellet with relatively large quartz inclusions, up to 100 μm in diameter, which also implies a coarser molybdenite particle size. The reason for the different behavior of the molybdenite materials is unclear. When pellets are produced by applying ~ 190 MPa (2.5 ton; 13 mm die) for 2 min, laser spots have well-defined walls and the material surrounding the crater is undeformed. Test runs revealed that too much pressure (> 300 MPa) fractured the material, and too little pressure (< 100 MPa) resulted in poor ablation characteristics.

Results and discussion

Laser ablation analysis

The Re concentration of Moly Hill and Merlin pellets were ~ 42 ppm and ~ 1239 ppm (calibrated by NIST SRM 610), respectively, and the standard deviation were 11% and 55%, respectively (n = 16). Homogenization of Moly Hill molybdenite reduced standard deviation of Re concentration from ~ 50% in the natural crystal to ~ 11% in the pressed pellet. The heterogeneous Re concentrations of Merlin pressed pellet suggest that the molybdenite powder was not homogenized before pelletizing and/or that mineral inclusions containing no Re are diluting the molybdenite signal. Inclusions and variations in Re intensity are clearly visible in the time resolved data from pellets, but importantly do not significantly influence $^{187}Re/^{187}Os$ ratios (Fig. 1b). Using Moly Hill pressed pellet for calibration, the resulting ages of Merlin pressed pellet were 1527 ± 15.3 Ma (run 1) and 1513 ± 7.7 Ma (run 2), in agreement with conventional Re-Os age of 1535 ± 6 Ma (Babo et al. 2017) (Fig. 2). After applying a linear drift correction, the weighted error (2σ) of the two runs was ~ 1% (n = 11) for the first run and ~ 0.5% (n = 22) for the second for both Moly Hill and Merlin (Fig. 2).

For dating of natural molybdenite crystals (run 3), areas on polished molybdenite, free from inclusions, e.g., galena, bismuthinite, quartz, fluorite, pyrite, and chalcopyrite were identified using SEM, and targeted for analysis. The weighted average ages for Lelång, Ytterby, Pitkyaranta, Knabengruver, Moly Hill crystals and for Moly Hill and Merlin pressed pellets are shown in Fig. 3 and data is presented in Electronic Appendix 4. Precision of calculated ages was between 1.2 and 5% (2σ) for all natural molybdenite, and weighted average ages are within 1% of published conventional ages. A rim-core-rim spot profile across a grain of Moly Hill molybdenite reveals no significant variation in spot Re-Os ages, indicating no grain-scale decoupling of Re and Os in this grain (Fig. 3).

Comparison with in situ dating without separation

Analysis of Re-Os doped NiS by LA-MC-ICP-MS demonstrated that it is possible to correct for a relatively large overlap of ^{187}Re on ^{187}Os (up to 93% of the total signal on mass 187), without the use of reaction cell technology (Pearson et al. 2002). In situ Re-Os ages of old and Re-rich molybdenite samples obtained by this method have single spot age precision better than 2% (1σ), with even larger ^{187}Re overlap (~ 97%) (Košler et al. 2003). LA-ICP-MS analysis in combination with aspiration of reference W isotopic solution for calibration has reported single spot age precision of ~ 10% (1σ) of the same material (Košler et al. 2003). The accuracy of ages obtained by these techniques is difficult to assess since

Table 1   Materials

Samples		Literature			This study		
		Geology	Age (Ma)	Ref.	Decay system	Age (Ma) 2σ	Re (ppm)
Merlin	Aus	Hydrothermal	1535 ± 6	Babo et al. 2017	Re-Os (Mo)	1521±11	800-3500
Molly hill	Can	Pegmatite	2750 ± 27	Birck et al. 1997	Re-Os (Mo)	2777±34	up to 108
Ytterby[1]	Swe	Pegmatite	1795±2	Romer and Smeds 1994	U-Pb (Col)	1809±23	up to 74
Lelång[2]	Swe	Aplite	917±38	Eliasson and Schöberg 1991	U-Pb (Zr)	919±46	up to 49
Pitkyaranta[3]	Rus	Hydrothermal	1795±8	Stein et al. 1996	Re-Os (Mo)	1807±26	43-317
Knaben[4]	Nor	Hydrothermal	~982-974	Bingen et al. 2006	Re-Os (Mo)	976±39	up to 54

GEO-NRM sample # 1=19670128, 2=19390500, 3= 18880225, 4=18870053

no proven homogenous molybdenite material has been analyzed in previous studies, and instead large age variations of molybdenite crystals were explained by natural variations (Košler et al. 2003; Stein et al. 2003; Selby and Creaser 2004). With our LA-ICP-QQQ-based protocol, separation between Re and Os in the methane-filled reaction cell allows for a reduction of the ^{187}Re interference to 25–30% for molybdenite with comparable age to previous studies. This is a major improvement, and based on our analysis of pressed pellets and natural crystals, we obtain similar or even better precision of ages than achieved by LA-MC-ICP-MS, and on a quadrupole-based system. The significant reduction in Re interference also allows dating of younger samples compared to prior studies, and we can demonstrate that our protocol works for samples as young as ~920 Ma. Theoretically, Re interference in 200 Ma old molybdenite should be ~80% compared to 99.7% for methods without separation, and Re-rich

molybdenite of this age could potentially be dated with reasonable precision using our protocol.

Decoupling of Re and Os in Molybdenite

The LA-ICP-MS/MS protocol provides a new tool that can be used to unravel post-crystallization modification of molybdenite Re-Os systematics, including intra-granular variations in ^{187}Os/^{187}Re ratios, Os exchange between molybdenite and surrounding sulfide minerals (Stein et al. 2003), and the potential resetting of molybdenite due to interactions with hydrothermal fluids (Suzuki et al. 2000). Previous in situ molybdenite studies have reported fairly extreme age variations of billions of years within single grains, to date interpreted to reflect decoupling of Re and Os. It has been concluded that the small quantity of material sampled by laser ablation is not sufficient to give representative ages of molybdenite (Selby
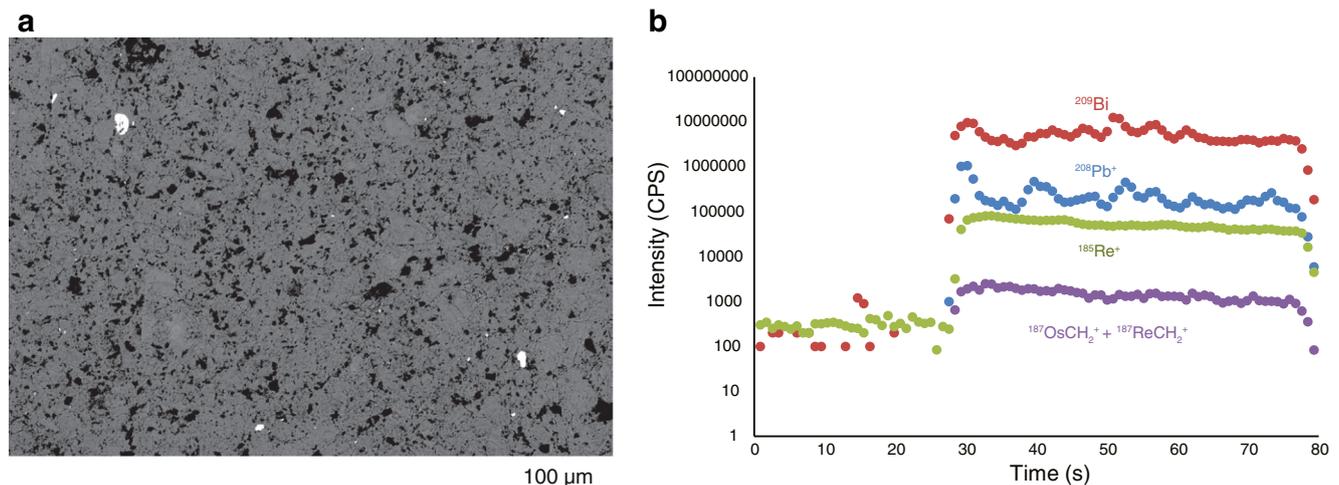
Fig. 1 Characteristics of pressed pellets of molybdenite powder produced by hand grinding in agate mortar. **a** Inclusions of native bismuth in Moly Hill pellet are evenly distributed in back-scatter electron images, indicating that the material was homogenized during hand grinding.
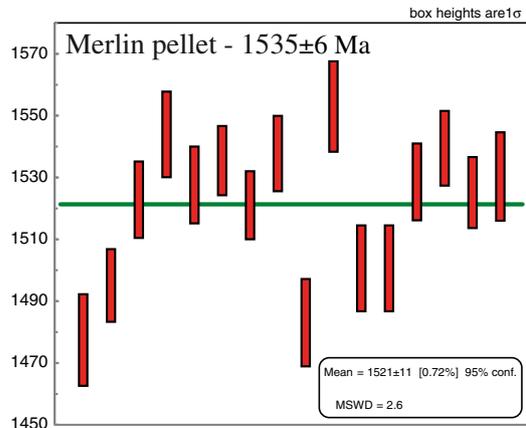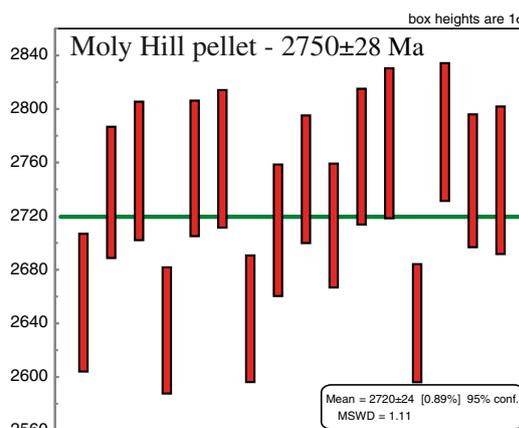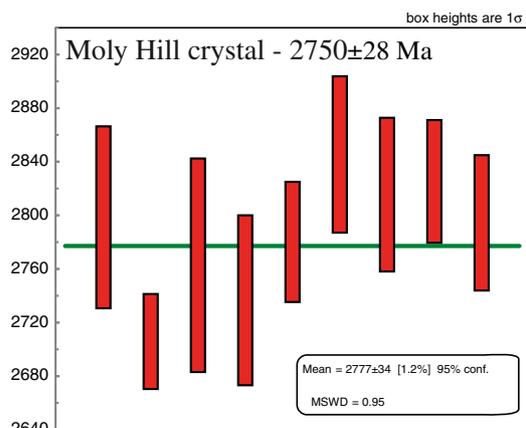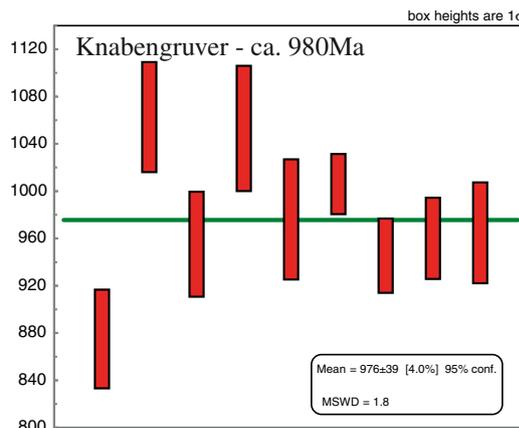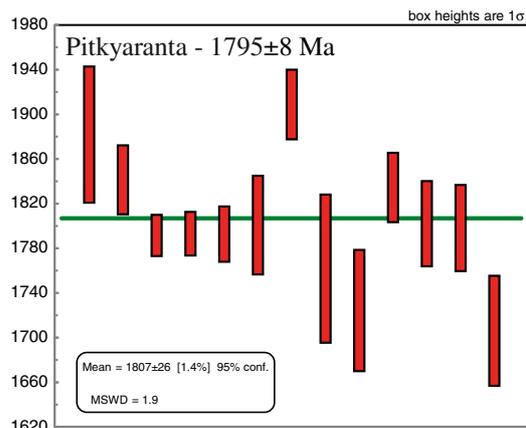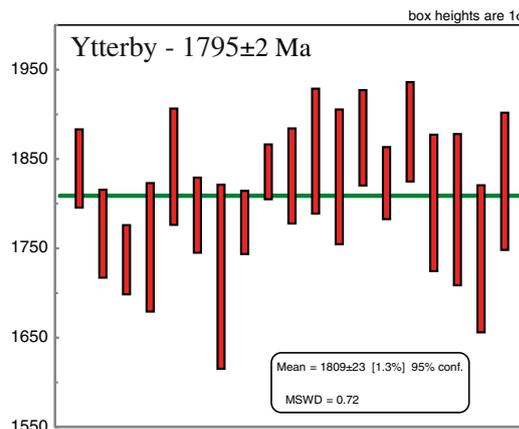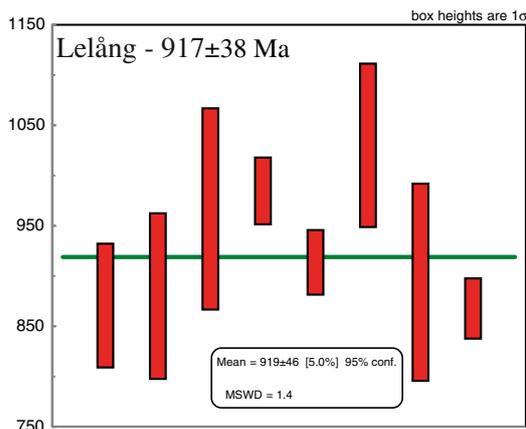
The small grain size of inclusions (< 10 μm) supports a significant reduction in molybdenite grain size during hand-grinding. **b** LA-ICP-MS/MS analysis of Moly Hill pellet shows that inclusions of native bismuth do not significantly influence Re/Os systematics
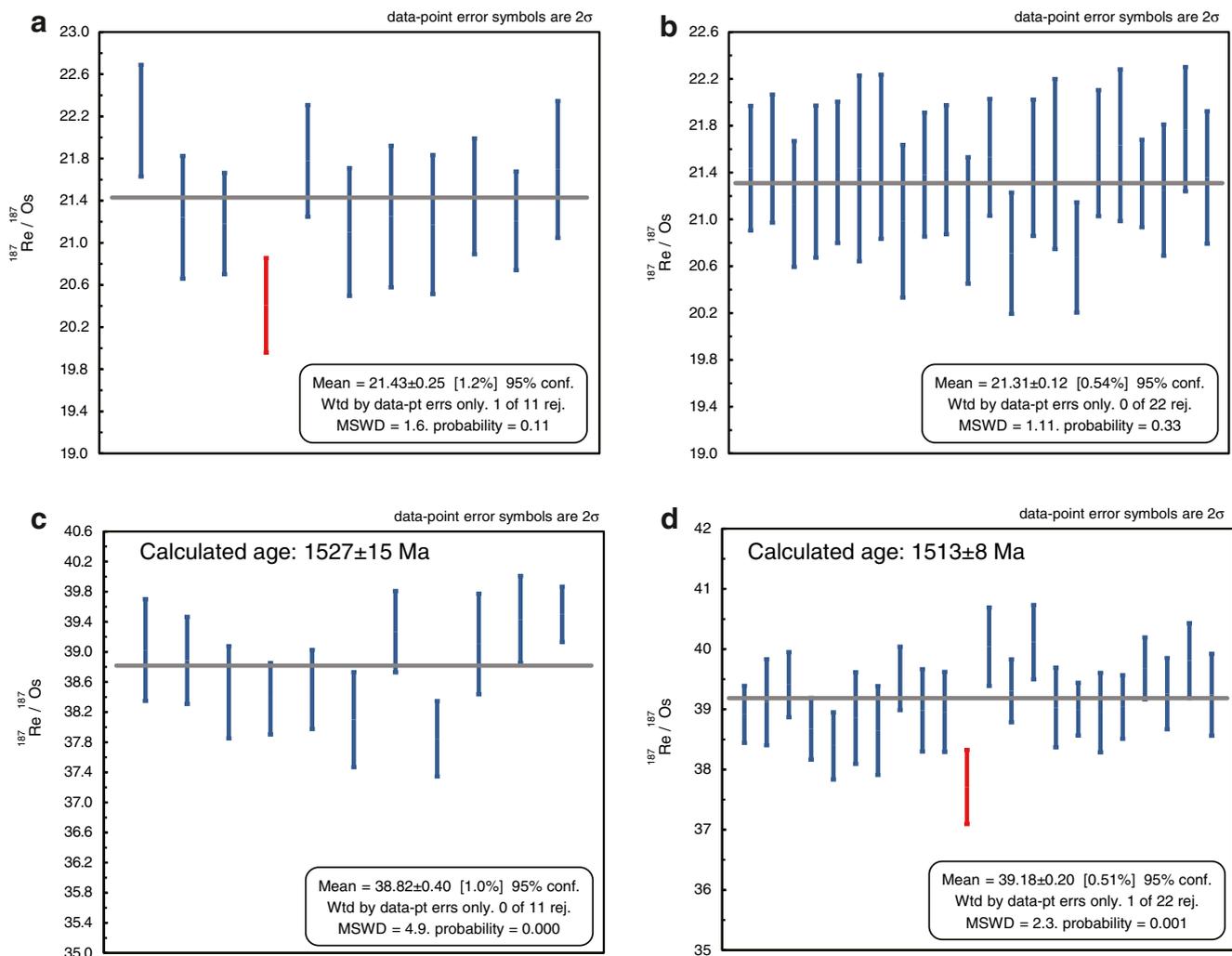
Fig. 2 Reproducibility tests of ^{187}Re/^{187}Os analysis of Moly Hill and Merlin pressed pellets. Data was collected in two analytical sessions a few weeks apart. Moly Hill was used as a standard for isotopic ratio and for drift correction, and Merlin as a quality control

and Creaser 2004; Stein et al. 2003). This view is also supported by conventional TIMS dating of micro samples of individual grains that also points to strong decoupling (Selby and Creaser 2004). The mechanism of intra-granular decoupling is still unclear, but proposed explanations are based on post-crystallization diffusion of ^{187}Os (Selby and Creaser 2004; Stein et al. 2003). It has, e.g., been suggested that ReS$_2$ inclusions or 3R polytype molybdenite (high Re content) formed during the crystallization of molybdenite would, over time, result in a chemical gradient for ^{187}Os that may homogenize during a thermal event. Decoupling could possibly also result from exsolution of Os-rich sulfides or diffusion of Os to crystal dislocations within the molybdenite during metamorphism (Stein et al. 2003; Selby and Creaser 2004). Interestingly, we have not found any evidence of this beyond the analytical precision in any of the six natural

molybdenite samples investigated. The agreement between in situ ages of natural crystals and conventional ages indicates no decoupling on the grain scale, despite large variations in Re concentrations within some crystals. Additionally, we have not found any support for micron scale decoupling, since the small volume sampled with 70 μm spots results in stable analytical signals and a meaningful age, even when inclusions (e.g., bismuthinite) are unintentionally included in the analyzed spot. No Re-spikes were detected by time-resolved analysis in this study, which would be expected if ReS$_2$ inclusions are a common feature in molybdenite. The discrepancy between our findings and conclusions from previous in situ studies utilizing LA-MC-ICP-MS is not clear at the moment. Most troubling is that reported decoupling in Moly Hill molybdenite (Košler et al. 2003) could not be reproduced in the present study (Fig. 4). The studies were not performed on the same

crystal, so it is possible that some molybdenite crystals in the Moly Hill quarry have been affected by alteration, resulting in the decoupling of Re and Os. Therefore, a more detailed study of the molybdenite of this site would be required for a conclusive answer. Reported bulk Re concentrations of other molybdenite samples previously dated by LA-MC-ICP-MS are ~ 10 ppm (Setting Net Lake deposit, Canada), ~ 14 ppm (Aittojärvi prospect, Finland), and ~ 4 ppm (South Mountain Batholith, Canada) (Selby and Creaser 2004). At these comparatively low concentrations, it would be difficult to evaluate intergranular decoupling with the LA-ICP-MS/MS. Bulk Re concentrations of Aittojärvi prospect molybdenite is likely to be sufficient for LA-ICP-MS/MS dating by focusing on the Re-rich parts of the molybdenite. However, strong zoning of Re (variations in Re intensity) reported by Stein et al. (2003) for Aittojärvi propect indicates that it would be impossible to get accurate Re/Os ratios in low Re areas of the crystals using our protocol for LA-ICP-MS/MS. Regardless, our study clearly demonstrates that decoupling of Re and Os is not a universal feature of molybdenite, since our molybdenite samples cover a range of geological settings. However, this does not completely rule out decoupling as a process, but instead suggests that the topic should be reevaluated by new techniques, e.g., nano-scale thermal ionization mass spectrometry (Barra et al. 2017) and LA-ICP-MS/MS. Targeting metamorphosed molybdenite crystals with chemical and isotopic mapping

should help to constrain further the mechanism of resetting and closure temperature of the Re-Os isotopic system for this mineral.

Conclusions

In situ dating of molybdenite by LA-ICP-MS/MS is possible by partial separation of Os from Re utilizing CH_4 as a reaction gas. The ^{187}Re signal interfering on ^{187}Os is, e.g., reduced from 96.7 to 28.1% for 2000 Ma molybdenite, which is sufficient to allow reliable isotopic measurements. The current limitations of the protocol are the requirement of Re concentration > 10 ppm for > 900 Ma molybdenite, and for younger samples, a correspondingly higher Re concentration is required. The natural molybdenite crystals analyzed using our new protocol show no evidence of disturbances or decoupling of the Re/Os system on either the grain or the micrometer scale. Therefore, the common assumption that ALL molybdenite crystals have decoupled Re and Os on the micron scale is incorrect. The fact that all six molybdenite samples analyzed in this study gave precise and accurate ages suggest that molybdenite in many cases can be dated by in situ analysis. We cannot yet explain the discrepancy between our results and previous in situ studies, but we now have an analytical technique and protocol to address reliably the prevalence of Re-Os decoupling in molybdenite in more complex geological settings. A major advantage of in situ LA-ICP-MS/MS dating is direct analysis of molybdenite in thin-sections and epoxy mounts, which allows analysis of sub-millimeter grains in a microtextural context.
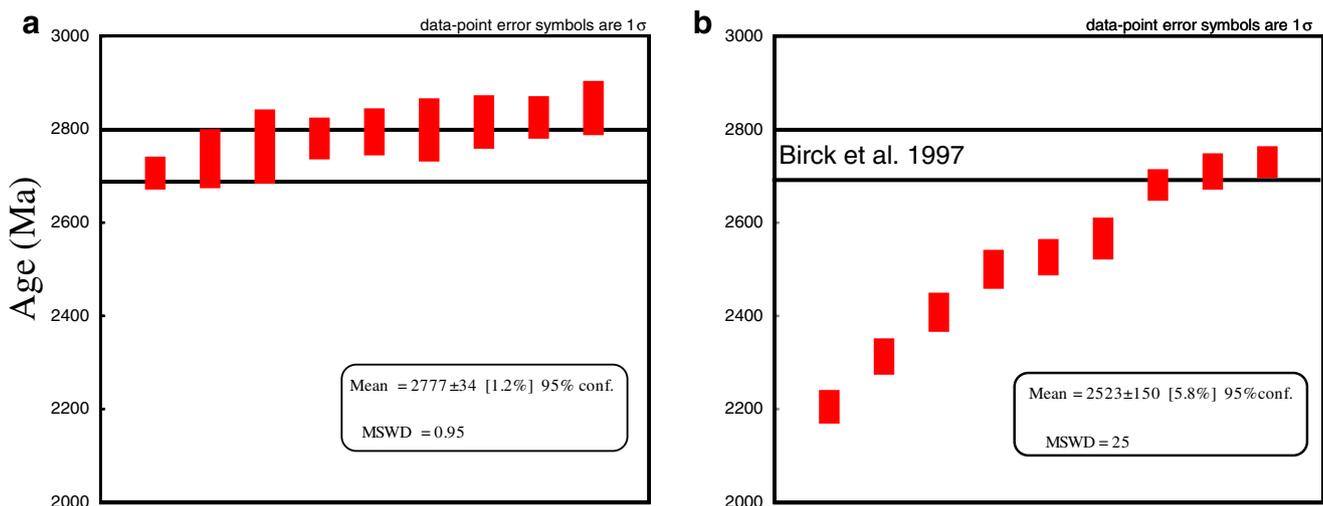
Fig. 4 Moly Hill molybdenite in situ age data by LA-ICP-MS/MS agree with conventional Re-Os dating (**a**) in contrast to LA-MC-ICP-MS analysis (Košler et al. 2003) that display large variations in ages for individual spots (**b**). Different crystals were analyzed, so it is possible that intragranular decoupling is present in some of the molybdenite crystals in the Moly Hill quarry

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