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LASER-ABLATION ICP–MS MEASUREMENTS OF Re/Os IN MOLYBDENITE AND IMPLICATIONS FOR Re–Os GEOCHRONOLOGY

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Abstract

Laser-ablation quadrupole ICP–MS analyses of molybdenite samples from Preissac, Quebec, and Mokrsko, Bělčice and Kašperské Hory gold deposits in the Bohemian Massif, Czech Republic, for Re and radiogenic ^{187}Os suggest the presence of strong zoning in Re and in ^{187}Os/^{187}Re values within grains. The zoning patterns indicate decoupling of daughter ^{187}Os from parent ^{187}Re after molybdenite crystallization. Whereas Re is not homogeneously distributed in the molybdenite grains studied, the lack of correlation between the calculated ^{187}Os/^{187}Re value and the Re content also reflects the mobility of ^{187}Os within individual grains of molybdenite. Such decoupling of Re and Os could affect the accuracy of Re–Os ages if disturbed portions of molybdenite are sampled for dating by conventional isotope-dilution N–TIMS or ICP–MS techniques. The results re-emphasize the critical need for homogenization of quantities of molybdenite sufficiently large to capture the bulk Os/Re of the sample to be dated by these methods. Laser-ablation sampling, when used with a multicollector magnetic-sector ICP–MS instrument, is able to produce Re–Os ages with a precision better than 2% ($1\sigma_m$) from single spots in certain old and Re-rich molybdenite grains, but would be difficult to use as a dating tool given the extreme ^{187}Os/^{187}Re heterogeneity seen in individual grains.

Keywords: laser-ablation ICP–MS, molybdenite, Re–Os, age dating, element decoupling.

Sommaire

Les analyses d'échantillons de molybdénite pour le Re et l'isotope radiogénique ^{187}Os par la technique ICP–MS à quadrupole avec ablation au laser (échantillons prélevés à Preissac, Québec, et les gisements d'or à Mokrsko, Bělčice et Kašperské Hory, dans le massif bohémien, en République Tchèque), montrent la présence d'un forte zonation intragranulaire en Re et en valeurs du rapport ^{187}Os/^{187}Re. Une telle zonation indique un découplage de l'isotope engendré ^{187}Os du parent ^{187}Re après la cristallisation de la molybdénite. Tandis que le Re n'est pas réparti de façon homogène dans les cristaux de molybdénite, le manque de corrélation entre la valeur ^{187}Os/^{187}Re calculée et la teneur en Re illustre aussi la mobilité de l'isotope ^{187}Os à l'intérieur des grains. Un tel découplage de Re et Os pourrait bien diminuer la justesse des ages Re–Os si des portions altérées des échantillons sont prises pour datation par méthodes conventionnelles N–TIMS avec dilution des isotopes ou bien par ICP–MS. Les résultats soulignent le besoin essentiel d'une homogénisation de quantités de molybdénite suffisamment grandes pour évaluer le rapport Os/Re global de l'échantillon à dater par ces méthodes. Un échantillonnage par ablation au laser, utilisé de concert avec un instrument ICP–MS multicollecteur à secteurs magnétiques, peut fournir des âges Re–Os avec une précision supérieure à 2% ($1\sigma_m$) dans le cas de prélèvements à des sites ponctuels dans certains échantillons de molybdénite assez vieux et relativement riches en Re. Par contre, il semble difficile de se servir de cette technique de datation vue l'hétérogénéité extrême en valeurs de ^{187}Os/^{187}Re des grains individuels.

(Traduit par la Rédaction)

Mots-clés: ablation au laser, ICP–MS, molybdénite, Re–Os, datation, découplage d'éléments.

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INTRODUCTION

Defining the precise age of mineralization within an ore-forming system is essential to understanding genetic processes and in locating economic deposits. Sulfide deposits commonly lack minerals typically used in geochronology, such as zircon and monazite (U–Th–Pb system). In addition, most sulfide minerals themselves do not contain high concentrations of elements used for radiogenic isotope dating, or have low initial parent–daughter isotope ratios. Thus, sulfide ores are difficult to date directly. The most commonly used technique for direct dating of sulfide deposits is Re–Os geochronology, which is based on radioactive decay of ^{187}Re to radiogenic ^{187}Os. The Re–Os isotopic system is particularly powerful where the age of Re-bearing mineral phases can be related to discrete episodes of hydrothermal activity. The mineral most widely used for Re–Os dating is molybdenite (MoS_2) because it contains low ppm to percent concentrations of Re and only ppt amounts of initial, non-radiogenic Os. Molybdenite is also a common accessory phase in many sulfide deposits as well as in many differentiated granites (*e.g.,* Stein *et al.* 2001, and references therein). Owing to the trivial contents of non-radiogenic Os in molybdenite, its age (T) can be derived from the simple equation $T = l/\lambda * \ln[(^{187}Os/^{187}Re) +1]$, where λ corresponds to the ^{187}Re decay constant ($1.666 * 10^{-11}$ yr^{-1}; Smoliar *et al.* 1996).

The spatial distribution of Re within molybdenite grains has been previously studied with electron-microbeam techniques (McCandless *et al.* 1993, and references therein). The low to sub-ppm concentrations of radiogenic ^{187}Os in most natural samples of molybdenite, however, precluded its quantification by the electron microprobe, making assessment of potential Re and Os decoupling (see below) difficult. Laser-ablation inductively coupled plasma – mass spectrometry (ICP–MS) possesses the spatial resolution required to assess mobility of Re and ^{187}Os on a fine scale within mineral grains. We have therefore used this method to study Re and ^{187}Os distributions in molybdenite from localities where the assemblages have been dated by negative-thermal ionization mass spectrometry (N–TIMS) and ICP–MS isotope-dilution techniques. The implications of post-crystallization inhomogeneities in Re and ^{187}Os in molybdenite on Re–Os isotopic dating are discussed. Multicollector (MC) magnetic sector ICP–MS measurements of Re and Os in molybdenite were also carried out to assess the improvement in precision over quadrupole measurements, with a view toward the development of *in situ* Re–Os dating. Preliminary results of this study were presented by Košler *et al.* (2000).

BACKGROUND INFORMATION

The potential of the Re–Os molybdenite geochronometer has been recognized for over forty years (Herr *et al.* 1961, Hirt *et al.* 1963), but dating attempts in the past generally produced erroneous ages. The conventional approach of isotope-dilution N–TIMS and ICP–MS techniques of Re–Os dating requires a complicated procedure of sample preparation, involving chemical separation to prevent the isobaric interference of ^{187}Re on ^{187}Os. Difficulties also arise during the measurements by mass spectrometry because both Re and Os are difficult to ionize by the positive-ion TIMS that is used for most geological applications. As a result, very few laboratories worldwide run Re–Os analyses of molybdenite routinely.

An important issue in Re–Os geochronology is whether Re, Os or both are inhomogeneously distributed and decoupled in molybdenite grains as a result of disturbance to the Re–Os system by thermal or aqueous alteration events following molybdenite crystallization (McCandless *et al.* 1993, Stein *et al.* 1997b, 1998b). The experimental data of Brenan *et al.* (2000) suggest that the closure temperature for Os in sulfides is low (~300°C for pyrrhotite), allowing diffusion of the metal during even low-grade metamorphic events. Also, the layered structure of molybdenite makes the mineral particularly susceptible to infiltration of hydrothermal fluid along cleavage planes, which may be widened during deformation, enhancing permeability. Such fluids could leach and transport Re and Os from their original sites in the mineral. Mobility and decoupling of Re and Os within a molybdenite grain, so-called closed-system disturbance, could cause inaccurate Re–Os isotopic ages if only a portion of a disturbed grain is analyzed, though analysis of the whole grain might produce an accurate age (Stein *et al.* 1998b). Alternatively, if the analyzed grain behaved as an open system during an alteration event, preferentially losing (or gaining) Re or Os, erroneous ages may be derived despite analysis of the entire grain or multiple grains.

DECOUPLING OF Re AND Os IN MOLYBDENITE

Discrepancies between Re–Os ages of molybdenite as obtained by N–TIMS and ICP–MS isotope dilution and those obtained by other chronometers, along with the scatter of some Re–Os ages beyond that expected from analytical procedures (*e.g.,* Luck & Allègre 1982, Ishihara *et al.* 1989, Suzuki *et al.* 1996, 2001, McCandless *et al.* 1993) suggest that the Re–Os isotopic system in molybdenite may be disturbed following crystallization. This observation has been contradicted by other studies that imply a robustness to the Re–Os molybdenite chronometer (Frei *et al.* 1998, Stein *et al.* 1998a, Raith & Stein 2000, Selby & Creaser 2001). The effect of alteration on the selective loss of Re from molybdenite has been studied both experimentally (Suzuki *et al.* 2000) and on naturally altered samples (McCandless *et al.* 1993) using electron-microbeam techniques, infrared spectroscopy and X-ray diffraction. Authors of both studies concluded that even at low temperatures (*ca.* 150–180°C), hydrothermal alteration can induce Re loss from molybdenite. Xiong & Wood (1999) presented experimental data suggesting that Re would be particularly well mobilized in molybdenite by high-temperature, saline and sulfide-poor hydrothermal solutions. In addition, Suzuki *et al*. (2000) have shown that radiogenic ^{187}Os may be leached preferentially relative to Re from molybdenite, resulting in low apparent Re–Os ages. Loss of Re or Os (or both) in response to the hydrothermal alteration is not associated with any structural changes to molybdenite, and neither can it be correlated with changes in its near-infrared transparency (Suzuki *et al*. 2000).

Molybdenite forms two natural polytypes, 2*H* and 3*R*, that differ in the way Mo–S layers are stacked above one another (Wickman & Smith 1970, Newberry 1979a, b). Newberry (1979b) suggested that enhanced substitution of Re^{4+} for Mo^{4+} increases the presence of the otherwise less common polytype 3*R*, and that its conversion to the more common 2*H* structure is associated with Re loss from molybdenite. Whereas this proposal has not been confirmed by later studies, McCandless *et al.* (1993) suggested that the presence of Re in molybdenite results in the formation of point defects and screw-dislocation growth because of the smaller ionic size of Re^{4+} (0.63 Å) relative to Mo^{4+} (0.65 Å). Such point defects would be more prone to bond breaking and preferential Re loss during alteration. Although it has been documented that Re^{4+} can substitute for the octahedrally coordinated Mo^{4+}, there are no crystal-chemical obstacles for the octahedrally coordinated Os^{4+} (0.63 Å; Liu & Bassett 1986) to occupy the same position in the molybdenite structure. However, owing to the low abundance of Os, it is not clear which sites, if any, in the molybdenite structure are occupied by Os^{4+}. The weak bonding of radiogenic ^{187}Os in the molybdenite structure may contribute to the decoupling of Re and Os, as evidenced during alteration experiments of molybdenite (Suzuki *et al*. 2000). Alternatively, if the radiogenic $^{187}Os^{4+}$ establishes bonds with sulfur, it is likely to form the cubic mineral erlichmanite, OsS_2 (Snetsinger 1971) and hence, during the alteration, the osmium may be decoupled from Re present elsewhere in the molybdenite structure.

SAMPLES

We have studied four samples of natural molybdenite from four localities that have been previously analyzed for Re and Os isotopes by isotope dilution N–TIMS or ICP–MS techniques.

The molybdenite sample from the Preissac pluton in the late Archean Abitibi Subprovince of Quebec, Canada comes from one of the numerous molybdenite-bearing pegmatite veins at Moly Hill. Molybdenite occurs as large grains up to several centimeters across, some of which are euhedral, and are enclosed in quartz. The first attempts to date the molybdenite samples from the Preissac pluton yielded unrealistically old Re–Os ages of 5819 ± 228 and 6215 ± 183 Ma [Luck & Allègre 1982; ages recalculated using $\lambda(^{187}Re) = 1.666{*}10^{-11}$]. Another Re–Os study of this sample that used a different sampling strategy and a chemical technique of separation gave an age of *ca.* 2750 Ma (Birck *et al*. 1997). Suzuki *et al*. (1993) obtained isotope-dilution ICP–MS molybdenite Re–Os ages within the range of 2766–2526 Ma for samples from the same pluton. This range overlaps with U–Pb titanite and monazite ages from the Preissac monzogranite and aplite (2681–2660 Ma; Ducharme *et al*. 1997). Average Re and ^{187}Os concentrations reported by Suzuki *et al*. (1993) for the Preissac molybdenite are 30 and 0.849 ppm, respectively. The sample used in this study was part of a single grain of molybdenite.

The molybdenite sample from Bělčice comes from a quartz vein in an abandoned gold mine located in the southern part of the Bohemian Massif, Czech Republic. The quartz veins in Bělčice are hosted by a late Variscan granodiorite that is part of the Central Bohemian Plutonic Complex. U–Pb and Pb–Pb zircon dating of this complex define ages within the range of 356–336 Ma (Holub *et al*. 1997, Dörr *et al*. 1998). Molybdenite occurs as grains up to 2 mm enclosed in quartz. The molybdenite used in this study is taken from a mineral separate; another portion of molybdenite separated from this sample yielded an isotope-dilution N–TIMS Re–Os age of 338.5 ± 1.3 Ma (Zachariáš & Stein 2001).

The molybdenite sample from the Mokrsko gold deposit, central Czech Republic, comes from a quartz vein hosted by upper Proterozoic lower-amphibolite-grade metasedimentary and metavolcanic rocks, adjacent to a late Variscan tonalite intrusion. The intrusion has been dated at 349 ± 12 Ma using Pb–Pb evaporation of zircon (Holub *et al*. 1997). The molybdenite forms up to 2 mm grains enclosed in quartz and yielded a conventional isotope-dilution N–TIMS Re–Os age of 342.9 ± 1.4 Ma (Zachariáš & Stein 2001). The sample used in this study was part of a single grain of molybdenite enclosed in quartz.

A fourth sample of molybdenite came from the Kašperské Hory gold deposit, located along a regional shear-zone in the high-grade metasedimentary rocks of the Moldanubian Zone in the southern Bohemian Massif, Czech Republic. Molybdenite occurs as irregular grains up to 2 mm in size in a quartz vein and commonly contains inclusions of gold. The molybdenite used in this study is present as small grains and veinlets hosted in quartz. Molybdenite separated from quartz at the same outcrop yielded a conventional isotope-dilution N–TIMS Re–Os age of 345.3 ± 1.9 Ma and averaged 35 ppm of Re and 0.128 ppm of ^{187}Os (Stein *et al.* 1997a). The Re–Os age of this molybdenite sample is distinctly higher than the $^{40}Ar/^{39}Ar$ cooling age for muscovite from this suite of quartz veins (*ca.* 325–331 Ma; Ďurišová *et al*. 1997) and a Re–Os age of 309.5 ± 3.4 Ma for another sample of molybdenite from the same locality (Stein *et al*. 1997a). The differences in the molybdenite Re–Os ages from the Kašperské Hory gold deposit have been interpreted to reflect multiple periods of hydrothermal mineralization (Stein *et al*. 1997a).

ANALYTICAL TECHNIQUES

Instrumentation

Prior to analysis for Re and Os isotopes, the polytype abundance in the molybdenite samples was studied using a Rigaku Ru–200 automated X-ray powder diffractometer at Memorial University. The method followed the technique described in Frondel & Wickman (1970): small flakes were scraped off the molybdenite surface and sprinkled onto a double-sided tape attached to a glass slide to prevent preferred orientation of the sample. The rotating anode was operated at 40 kV and 180 mA, and the samples were exposed to Cu$K\alpha$ radiation. The data were acquired over the interval 26°–60° 2θ in steps corresponding to 0.03° 2θ, with an acquisition time of 1.2 second per step.

For laser-ablation ICP–MS analysis, the molybdenite samples were mounted in epoxy-filled grain-mount blocks and polished to obtain even surfaces. For this experiment, we utilized a VG PlasmaQuad 2+ "S" ICP–MS instrument coupled to an in-house-built 266 nm Nd YAG laser at Memorial University of Newfoundland. The ICP–MS instrument is equipped with a fast-switching quadrupole mass filter and a single Galileo-type electron multiplier. In laser-ablation mode, with a laser-repetition rate of 10 Hz, energy of 0.5 mJ/pulse, a focused 60 μm laser spot and ablation in He gas, the instrument has a sensitivity of at least 1–5 × 10^4 cps/ppm for each monoisotopic element greater than mass 85.

The sample-introduction system was modified to enable simultaneous nebulization of a 15 ppb natural W tracer solution and laser ablation of the solid sample. The tracer solution was aspirated to the plasma in an argon–helium mixture as a carrier gas through an MCN–100 Cetac micro-concentric nebulizer, Scott-type double-pass spray chamber and a T-piece tube attached to the back end of the plasma torch. A helium gas line carrying the ablated sample from the laser cell to the plasma was attached to the T-piece tube at the back end of the ICP torch.

The laser was set up to produce energy of 0.2–0.5 mJ/pulse (measured just before the beam entered the objective of the microscope) at a repetition rate of 10 Hz with the laser beam focused 100–200 μm above the surface of the sample. The 50 cm^3 sample cell was mounted on the microscope *via* a computer-driven mo-

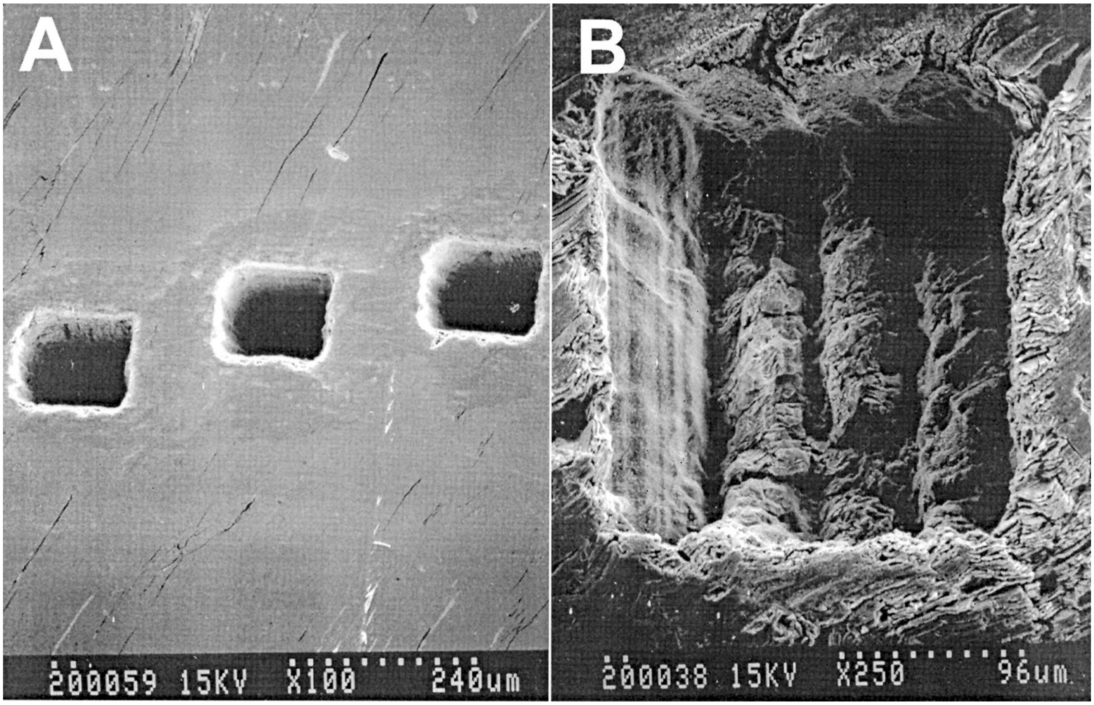

FIG. 1. A. SEM image of the laser-ablation rasters in the Preissac molybdenite. B. Close-up view of a laser raster in molybdenite.

torized stage. During the ablation, the stage was moved beneath the stationary laser beam to produce a square laser pit (200 × 200 μm) in the sample (Fig. 1). Where necessary, a smaller raster pit (*e.g.*, 100 × 100 μm) was produced by masking the laser beam and using a higher energy, >0.5 mJ per pulse, to provide sufficient count-rates for precise measurement. The estimated depth of each pit ranged from *ca.* 50 to 80 μm depending on the area of the raster, total power of the laser and ablation time. Previous studies have demonstrated that both laser-beam defocus (Jackson *et al.* 1996) and rastering (Campbell & Humayun 1999) result in a more efficient removal of material from the ablation site and substantially reduce time-dependent inter-element fractionation.

The typical data-acquisition procedure consisted of a 60-second measurement of the gas background and aspirated solution just before the start of ablation (Fig. 2). During ablation, Re, Os and W signals from molybdenite, along with the continuous ^{186}W and ^{184}W signals from the aspirated solution, were acquired for another 180 seconds. The data were acquired in time-resolved peak-jumping – pulse-counting mode with one point measured per peak for masses 183 (W – flyback), 184 (W), 185 (Re), 186 (W), 187 (Re + Os), 189 (Os)

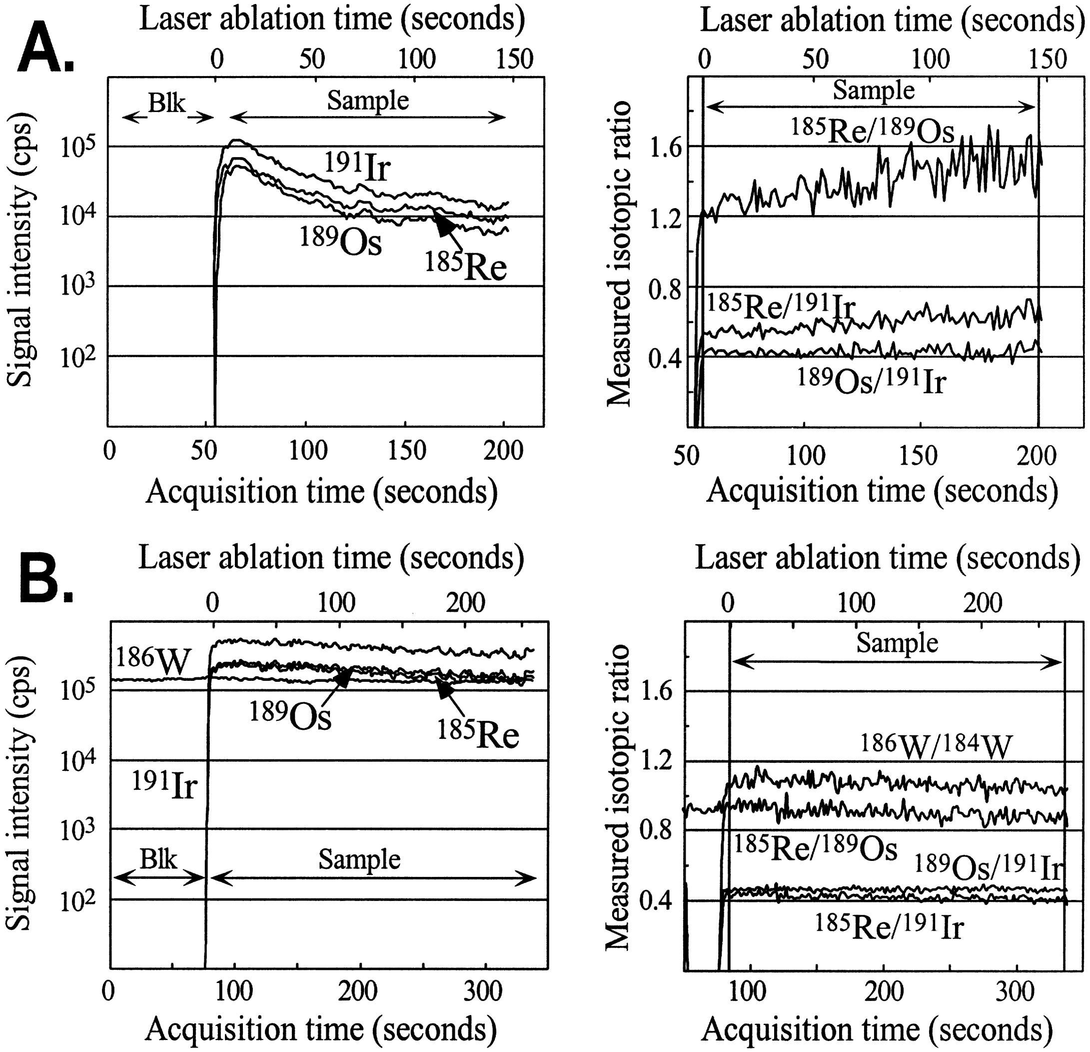

FIG. 2. A. Isotopic signals of Re, Os and Ir and the corresponding isotopic ratios obtained from a single laser-ablation pit in the NiS standard. B. Isotopic signals of Re, Os, Ir and W and the corresponding isotopic ratios obtained from a laser-ablation raster in the NiS standard.

and 191 (Os). Quadrupole settling time was 1 ms, and the dwell time was 8.3 ms on each mass. During 240 seconds of measurement, *ca.* 3000 data-acquisition cycles (sweeps) were collected.

Additional analyses of the Preissac molybdenite were carried out using a 193 nm ArF Excimer laser (LambdaPhysik Compex 102) coupled to the Micromass Isoprobe multicollector magnetic sector ICP–MS (MC ICP–MS) instrument at GEOTOP – UQAM in Montreal. All analyses were obtained from a raster area of 200 × 200 μm using laser energy of 0.12 mJ/pulse, a repetition rate of 15 Hz, a spot size of *ca.* 100 μm and He as a carrier gas. Total ablation time was 100 seconds, corresponding to 50 scans of two seconds integration each. The Faraday detector array was set to collect masses 183 (W), 184 (W), 185 (Re), 186 (W), 187 (Re + Os), 188 (Os) and 189 (Os). Before the start of ablation, a 60-second gas blank ("on-peak zero") measurement was conducted. Subsequent to the start of ablation, two half-mass-unit baseline measurements were obtained within the mass range 182.5 to 189.5, bracketing the masses used for data acquisition. Unlike the quadrupole ICP–MS measurements, no tracer solution was aspirated to the plasma source of the MC ICP–MS during ablation of sample material because of concerns that residual W in the instrument would compromise measurements of Hf isotopes being made for other studies.

Data reduction

Raw data from the quadrupole ICP–MS were corrected for dead time of the electron multiplier (20 ns) and processed offline using a Microsoft Excel® spreadsheet program to integrate signals from each sequential set of 10 sweeps. The ^{187}(Re + Os) and ^{185}Re counts were corrected for gas background before a correction for instrument mass-bias that utilized a power law and measurements of W isotopic tracer solution (^{186}W/^{184}W = 0.9279 ± 0.0034; Rosman & Taylor 1999) that was simultaneously aspirated to the plasma. The measurements by MC ICP–MS utilised the signal of W present in the molybdenite but, as in the case of the quadrupole ICP–MS data, the correction of ^{187}(Re + Os)/^{185}Re isotopic ratios for instrument mass-bias utilized the power law and natural isotopic composition of W. During this study, the mass bias per a.m.u. calculated from the measurements of ^{186}W/^{184}W values was up to 0.9 and 1.2% for the quadrupole and MC ICP–MS, respectively. The ^{187}Os/^{187}Re values were calculated after subtracting the appropriate amount of ^{187}Re, determined using a ^{187}Re/^{185}Re value of 1.6738 ± 0.0010 (Rosman & Taylor

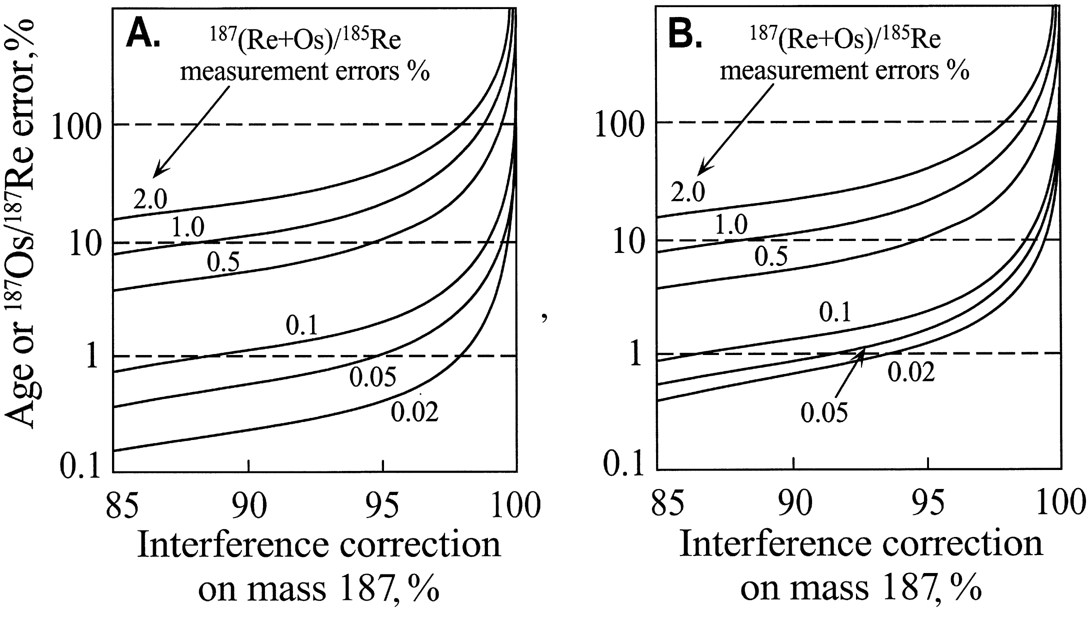

FIG. 3. A. Errors on the calculated ^{187}Os/^{187}Re values (or age) for various corrections for the isobaric interference on mass 187 and for different precisions on measured ^{187}(Re + Os)/^{185}Re values as expected from the counting statistics. B. Calculated error curves as in A, but taking into account the uncertainty on the natural ^{187}Re/^{185}Re isotopic composition (*ca.* 0.06%, 1 σ). Actual errors on the age would be somewhat larger than shown because the error in the decay constant and error associated with the mass-bias correction are not included in the calculation.

1999) from the total peak-intensity at mass 187. These corrections were very large, ranging from 95–97% in the Preissac sample to *ca.* 98–99% in the Bohemian Massif samples. However, using well-characterized Os-isotope reference materials, Pearson *et al.* (2002) demonstrated that this approach can yield accurate and precise corrections of up to at least 93% for ^{187}Re on ^{187}Os.

Because of the large isobaric interference of ^{187}Re on ^{187}Os, this correction was a major source of uncertainty in the calculated ^{187}Os/^{187}Re values and the corresponding Re–Os molybdenite ages. Figure 3 illustrates how the isobaric correction affects the overall error of the ^{187}Os/^{187}Re measurements. We have assumed that the error in the calculated ^{187}Os/^{187}Re values is mostly controlled by the error in the measured ^{187}(Re + Os)/^{185}Re values, and the extent of the isobaric ^{187}Re interference on ^{187}Os is inversely proportional to the age of molybdenite. As an example, if the Re isobaric interference on mass 187 is 95%, *i.e.*, 5% of the peak intensity at mass 187 is ^{187}Os, and if the uncertainty on the natural isotopic composition of Re is not considered in the error calculation, the ratio ^{187}(Re+Os)/^{185}Re would need to be measured with a precision of 0.05% or better to produce a final age uncertainty of <1%. Correspondingly, should the uncertainty on the natural Re isotopic composition be considered, a measurement precision of 0.02% or better would be required to achieve the age uncertainty of <1% (Figs. 3A, B). Because the quadrupole ICP–MS is not capable of such precise ^{187}(Re + Os)/^{185}Re measurements, we use the term "apparent age" for lower-precision data as a measure of the calculated ^{187}Os/^{187}Re values.

All errors in this study are quoted at the one sigma confidence level and were derived from analytical uncertainties on the measured values of the ratios ^{187}(Re + Os)/^{185}Re and ^{186}W/^{184}W. Uncertainties in the natural isotopic composition of Re and W do not contribute significantly to the overall error of the quadrupole ICP–MS age data, and hence they were omitted from the error calculation. They would, however, significantly magnify the errors on the more precise MC ICP–MS measurements (*cf.* Figs. 3A, B). The error calculation also does not take into account the uncertainty in the ^{187}Re decay constant.

Re/Os fractionation during laser sampling and analysis

Pairs of elements may become fractionated during laser sampling and analysis. Time-dependent inter-element fractionation is induced at the ablation site. It occurs as a result of preferential condensation of more refractory elements onto the walls of an ablation pit progressively deepened during laser sampling (Eggins *et al.* 1998). Thus fractionation between refractory–volatile element pairs occurs most rapidly during drilling of narrow, deep pits with large areas of exposed wall relative to the total ablation-volume. Laser sampling by rastering (rather than spot analysis) effectively suppresses the time-dependent fractionation by limiting the rate of exposure of ablated material to steep walls. A second kind of inter-element fractionation may occur in the argon plasma source as a result of space-charge effects on elements of different masses or incomplete vaporization and ionization of ablated particles (Guillong & Günther 2002).

In order to explore whether laser sampling and analysis of sulfides produced significant fractionation between Re and Os in this study, we have synthesized and analyzed a NiS reference material and compared measured and known ratios of Re, Os and Ir. Iridium was added to the NiS because it has a mass similar to W, and thus can be used for instrument mass-bias correction of Re and Os isotopic ratios (*e.g.*, Pearson *et al.* 2002). Preparation of the NiS standard followed a procedure similar to that of the NiS fire-assay method outlined in Jackson *et al.* (1990). Briefly, pure nickel metal, sulfur, borax, silica and sodium carbonate were mixed in a clay crucible. The mixture was doped with small amounts of a solution containing Os and Ir; Re was added as ReS_2 powder in an amount exceeding the target concentration in the NiS bead by a factor of 100. This was done to compensate for weak partitioning of Re into the NiS (Frimpong *et al.* 1995). The mixture was then heated for 90 minutes at 1100°C and formed a NiS bead containing a portion of the added elements, topped by a layer of silicate glass. In order to achieve the maximum homogeneity of NiS, the entire clay crucible and its contents were quenched by immersing in cold water.

Sample homogeneity of the NiS was subsequently tested by multiple laser-ablation analyses and was found to be better than 5% (RSD) for individual elements. Study of the NiS bead by back-scattered electron imaging and electron-microprobe analysis (courtesy of L.J. Cabri) revealed the presence of small grains (<10 μm) of heazlewoodite (Ni_3S_2) and godlevskite (Ni_7S_6). These inclusions are considerably smaller than the diameter of the laser beam, and may contribute to the minor heterogeneity seen in the laser-ablation measurements. The concentrations of Re, Os and Ir in the NiS bead, as determined by solution ICP–MS, are 63, 131 and 185 ppm, respectively, corresponding to 3, 65 and 93% recovery for the three elements added to the experimental charge.

The effect of laser sampling in single spot and raster modes on fractionation of Re, Os and Ir is best demonstrated by comparing the isotopic signals plotted in Figures 2A and B. Measured ^{185}Re/^{189}Os and ^{185}Re/^{191}Ir values acquired from single laser-spot analysis display laser-induced fractionation, *i.e.*, there is an increase in the values when plotted against ablation time (number of laser shots applied). Corresponding ^{185}Re/^{189}Os, ^{185}Re/^{191}Ir and ^{189}Os/^{191}Ir values acquired in raster mode do not show any significant increase with ablation time, suggesting that rastering the laser beam over a small area of sample surface suppressed laser-induced fractionation of elements almost completely. Accordingly, no fractionation correction was applied to the ^{187}(Re + Os)/^{185}Re values measured by laser-beam rastering of the molybdenite samples studied. Element fractionation in the ICP source of the mass spectrometer also did not appear to be a significant problem in this study. Guillong & Günther (2002) reported that element ratios in NIST 612 silicate glass, sampled by rastering, were significantly different from the known values, requiring large corrections. However, in this study, accurate ^{185}Re/^{189}Os values were obtained for the NiS reference material after correction of the measured ratios for the instrument mass-bias.

Single laser-spot and laser-raster analyses (Figs. 2A, 2B) were acquired using different conditions of instrument tuning and, unlike the single laser-spot analysis, the laser-raster analysis was performed with the simultaneous aspiration of W tracer solution to the source of ICP–MS. We therefore attribute different measured isotopic ratios of Re, Os and Ir in Figures 2A and 2B to different instrument mass-bias conditions during the two analyses. Given the high intensity of the ^{186}W signal from the aspirated tracer solution (Fig. 2B), and the low natural isotopic abundance of ^{186}Os in the NiS (*ca.* 1.58% of the total Os), the contribution of ^{186}Os from the ablated NiS sample to the measured intensity of the 186 mass peak is trivial. Rather, the shift in measured ^{186}W/^{184}W values from *ca.* 0.9 to 1.1 at the start of laser ablation in Figure 2B suggests that a matrix-induced space-charge effect accounts for a significant part of the mass bias.

A problem that remains to be addressed quantitatively is whether the different ionization potentials of Re (7.88 eV), Os (8.7 eV) and W (7.98 eV) significantly affect the ionization efficiencies of those elements in the ICP and hence the accuracy of the derived Os/Re values. Three lines of evidence, however, suggest that this effect is small relative to the other errors considered above. First, after correction for instrument mass-bias using measurements of the W tracer solution, we were able to arrive at the expected ^{185}Re/^{189}Os value of 1.14 for the NiS reference material (*cf.* Fig. 2B). Second, the range of calculated apparent ages for each of the samples studied overlaps with the previously established isotope-dilution N–TIMS ages. Third, the results of Pearson *et al.* (2002) demonstrated that differential ionization of Re and Os leads to an inability to derive accurate Os-isotope ratios for known reference materials by laser-ablation ICP–MS.

Mo-dimer interferences

The very large quantities of Mo introduced to the ICP during ablation of molybdenite could produce Mo-dimers (Mo_2) that would interfere with analytes of interest at masses 184 (W), 186 (W) and 187 (Re + Os). We have evaluated this possibility by monitoring the size of the potentially largest dimer, $^{98}Mo_2$, at mass 196, during ablation of the Preissac molybdenite. For ablations at four separate spots, only small signals of about 10–30 cps were observed. Even if these tiny signals are indeed produced by $^{98}Mo_2$ (trivial amounts of Pt in the molybdenite would be another possible cause, as peaks of broadly similar size to that at mass 196 were observed at masses 194 and 195), the maximum contribution of ^{92}Mo–^{95}Mo dimer to the intensity of the peak at 187 mass would be insignificant (less than 3‰), *i.e.,* well within the errors of our measurements. The corresponding contributions to signal intensities at masses 184 and 186 would be even smaller.

RESULTS

The X-ray-diffraction analyses suggest that all molybdenite samples studied correspond to the more common 2*H* type; no diffraction peaks indicating the presence of even small amounts of the 3*R* polytype were identified in the samples.

Re and Os isotopic data from quadrupole ICP–MS and MC ICP–MS for molybdenite samples from Preissac, Bělčice, Mokrsko and Kašperské Hory are given in Table 1 and Figures 4, 5 and 6. Calculated ^{187}Os/^{187}Re values for the individual laser-ablation rasters in each sample of molybdenite have a greater range than analytical error at 1σ for the quadrupole ICP–MS measurements. At 2σ, the range in ^{187}Os/^{187}Re is greater than analytical error for the Mokrsko and Kašperské Hory samples, and for the measurements on the Preissac samples performed by MC ICP–MS. The range of apparent ages based on the calculated ^{187}Os/^{187}Re values for each sample overlap the Re–Os age obtained by conventional isotope-dilution N–TIMS and ICP–MS methods (Figs. 4A, 5A). There is, however, no systematic bias of our laser-ablation ICP–MS data toward higher or lower values of apparent age compared to the isotope-dilution N–TIMS and ICP–MS ages. The calculated ages for the Preissac and Bělčice samples tend to be lower than the conventional isotope-dilution ages, whereas most of the apparent ages for the Mokrsko and Kašperské Hory samples are significantly higher than their corresponding isotope-dilution N–TIMS ages.

When the abundance of Re (represented by the intensity of the interference-free ^{185}Re signal) is plotted against the calculated age, there appears to be no systematic variation in age as a function of Re content (Figs. 4B, 5B). This is true for all of the samples studied. The lack of correlation between low Re-content and high Re–Os ages, consistent with Re loss, or between high Re content and low Re–Os apparent ages, consistent with Re gain, is noteworthy. It suggests that both Re and Os have been redistributed within the molybdenite grains following crystallization. The nature of our measurements and of the molybdenite samples does not allow us to assess whether Re, Os or both may have migrated out of the grains studied. In particular, we

TABLE 1. LASER-ABLATION ICP–MS DATA FOR MOLYBDENITE FROM MOKRSKO (M), BĚLČICE (B) AND KAŠPERSKÉ HORY (K), BOHEMIAN MASSIF, CZECH REPUBLIC, AND PREISSAC (P), ABITIBI SUBPROVINCE, QUEBEC

	Measured isotopic ratios[1]				Calculated isotopic ratios[2]				Apparent age	
Sample	$^{187}(\mathrm{Re+Os})/^{185}\mathrm{Re}$	±1σ	$^{186}\mathrm{W}/^{184}\mathrm{W}$	±1σ	$^{187}(\mathrm{Re+Os})/^{185}\mathrm{Re}$	±1σ	$^{187}\mathrm{Os}/^{187}\mathrm{Re}$	±1σ	Ma	±1σ
M1	1.6699	0.0025	0.9232	0.0010	1.6784	0.0031	0.0027	0.0017	164	110
M2	1.6872	0.0022	0.9298	0.0011	1.6836	0.0029	0.0058	0.0010	350	105
M3	1.6880	0.0022	0.9301	0.0011	1.6840	0.0030	0.0061	0.0009	363	107
M4	1.6813	0.0019	0.9253	0.0010	1.6860	0.0027	0.0073	0.0019	436	96
M5	1.6852	0.0017	0.9262	0.0011	1.6883	0.0026	0.0087	0.0013	517	93
M6	1.6906	0.0017	0.9291	0.0010	1.6883	0.0025	0.0087	0.0009	519	89
M7	1.6918	0.0017	0.9296	0.0011	1.6886	0.0026	0.0089	0.0008	529	92
M8	1.6827	0.0021	0.9244	0.0011	1.6891	0.0029	0.0091	0.0022	545	105
M9	1.6879	0.0020	0.9266	0.0010	1.6903	0.0027	0.0099	0.0014	588	96
M10	1.6891	0.0020	0.9268	0.0011	1.6911	0.0028	0.0103	0.0013	617	101
B1	1.6767	0.0030	0.9294	0.0009	1.6739	0.0034	0.0001	0.0001	4	122
B2	1.6801	0.0027	0.9298	0.0009	1.6766	0.0032	0.0016	0.0007	99	115
B3	1.6849	0.0026	0.9315	0.0010	1.6784	0.0031	0.0027	0.0006	163	112
B4	1.6838	0.0036	0.9298	0.0015	1.6802	0.0045	0.0038	0.0014	230	161
B5	1.6833	0.0029	0.9279	0.0012	1.6832	0.0037	0.0056	0.0017	336	131
B6	1.6809	0.0037	0.9266	0.0011	1.6832	0.0042	0.0056	0.0030	338	149
B7	1.6885	0.0043	0.9283	0.0014	1.6878	0.0049	0.0084	0.0024	499	175
K1	1.7051	0.0037	0.9402	0.0025	1.6828	0.0059	0.0054	0.0006	322	210
K2	1.7012	0.0036	0.9372	0.0018	1.6843	0.0049	0.0063	0.0008	376	175
K3	1.7077	0.0029	0.9360	0.0013	1.6929	0.0037	0.0114	0.0010	680	132
K4	1.7032	0.0031	0.9329	0.0013	1.6939	0.0039	0.0120	0.0013	718	138
K5	1.7113	0.0028	0.9355	0.0015	1.6974	0.0040	0.0141	0.0011	840	140
K6	1.7113	0.0032	0.9341	0.0014	1.6999	0.0042	0.0156	0.0013	927	147
K7	1.7140	0.0024	0.9336	0.0013	1.7035	0.0035	0.0177	0.0011	1055	122

	Measured isotopic ratios[1]				Calculated isotopic ratios[2]				Apparent age	
Sample	$^{187}(\mathrm{Re+Os})/^{185}\mathrm{Re}$	±1σ	$^{186}\mathrm{W}/^{184}\mathrm{W}$	±1σ	$^{187}(\mathrm{Re+Os})/^{185}\mathrm{Re}$	±1σ	$^{187}\mathrm{Os}/^{187}\mathrm{Re}$	±1σ	Ma	±1σ
P1	1.7555	0.0034	0.9408	0.0021	1.7313	0.0052	0.0344	0.0014	2028	180
P2	1.7597	0.0038	0.9442	0.0024	1.7293	0.0058	0.0331	0.0015	1957	203
P3	1.7417	0.0045	0.9400	0.0023	1.7192	0.0063	0.0271	0.0018	1607	218
P4	1.7478	0.0053	0.9363	0.0023	1.7320	0.0068	0.0348	0.0025	2051	236
P5	1.7555	0.0054	0.9399	0.0026	1.7330	0.0073	0.0354	0.0024	2087	252
P6	1.7502	0.0050	0.9396	0.0023	1.7283	0.0066	0.0326	0.0021	1924	228
P7	1.7565	0.0068	0.9381	0.0023	1.7373	0.0080	0.0380	0.0031	2237	276
P8	1.7344	0.0074	0.9352	0.0023	1.7208	0.0086	0.0281	0.0035	1663	300
P9	1.7518	0.0062	0.9336	0.0030	1.7411	0.0083	0.0402	0.0032	2367	287
P10	1.7440	0.0090	0.9259	0.0031	1.7476	0.0108	0.0441	0.0058	2589	370
P11	1.7640	0.0082	0.9350	0.0029	1.7505	0.0098	0.0458	0.0042	2689	337
P12	1.7471	0.0072	0.9316	0.0028	1.7400	0.0090	0.0396	0.0039	2329	309
P13	1.7427	0.0066	0.9305	0.0030	1.7378	0.0086	0.0382	0.0036	2251	297
P14	1.7374	0.0125	0.9232	0.0033	1.7461	0.0139	0.0432	0.0085	2538	477
P15	1.7365	0.0100	0.9271	0.0026	1.7379	0.0111	0.0383	0.0064	2255	384
P16	1.7551	0.0061	0.9331	0.0033	1.7452	0.0087	0.0427	0.0032	2508	301
P17	1.7388	0.0055	0.9314	0.0025	1.7322	0.0072	0.0349	0.0029	2059	249
P18	1.7373	0.0069	0.9327	0.0028	1.7283	0.0086	0.0326	0.0035	1923	300
P19	1.7353	0.0055	0.9327	0.0025	1.7262	0.0073	0.0313	0.0028	1851	253
P20	1.77765	0.00019	0.94993	0.00056	1.73642	0.00105	0.03741	0.000865	2205	36
P21	1.77976	0.00073	0.94935	0.00048	1.73954	0.00113	0.03928	0.000901	2313	39
P22	1.77682	0.00025	0.94627	0.00065	1.74232	0.00122	0.04094	0.000943	2408	42
P23	1.77934	0.00045	0.94616	0.00062	1.74499	0.00122	0.04253	0.000942	2500	42
P24	1.77746	0.00037	0.94475	0.00058	1.74575	0.00113	0.04299	0.000904	2526	39
P25	1.77646	0.00025	0.94360	0.00069	1.74690	0.00130	0.04367	0.000981	2566	45
P26	1.77691	0.00023	0.94204	0.00052	1.75024	0.00100	0.04567	0.000844	2681	34
P27	1.77995	0.00034	0.94319	0.00058	1.75110	0.00113	0.04618	0.000903	2710	39
P28	1.77629	0.00041	0.94093	0.00048	1.75169	0.00099	0.04654	0.000839	2730	34

Analyses of the Preissac molybdenite P20–P28 were made using MC ICP–MS at GEOTOP, UQAM. 1: Measured isotopic ratios corrected for dead time of the electron multiplier and gas blank (quadrupole ICP–MS data). 2: Calculated isotopic ratios corrected for instrument mass-bias and isobaric interference of ^{187}Re on ^{187}Os. All errors are expressed as $1\sigma_m$ absolute.

cannot reconstruct a bulk age for a single grain of molybdenite because our samples consist of fragments of crystals. Also, our molybdenite samples are hosted by quartz rather than minerals such as sulfides, which may have concentrated any Re or Os lost from the molybdenite.

The scale of inhomogeneities in the Re content in the Mokrsko molybdenite is illustrated by a linear raster of the laser across part of the grain studied (Fig. 7). This analysis revealed variations of up to an order of magnitude in the ^{185}Re signal on a scale of less than 50 μm. Even though these variations are large, they would not correspond to differences in Re–Os ages between different individual grains, provided that: (1) the variations result from the growth zoning, and Re and Os were not decoupled during post-crystallization movement within the molybdenite grain, or that the sampling strategy was sufficient to average out any within-crystal inhomogeneity caused by elemental decoupling, and (2) both elements remained entirely within each individual fragment of molybdenite after crystallization or were not decoupled from each other when leached from a grain. Given that the scale of element decoupling is large enough to be detected by ranges in apparent age using laser-ablation ICP–MS analysis, and is non-systematic, we discuss whether either of these two criteria are commonly met and the possible implications for Re–Os geochronology of molybdenite.

IMPLICATIONS FOR RE–OS DATING OF MOLYBDENITE

Experimental studies of the alteration of molybdenite have resulted in Re and Os leaching (Suzuki *et al.* 2000) and reported disturbance of the Re–Os system (Luck & Allègre 1982, McCandless *et al.* 1993, Suzuki *et al.* 2001). Those studies suggest that dating bulk samples of molybdenite may produce inaccurate ages if significant portions of the grains have been disturbed. In our study, variations in ^{187}Os/^{187}Re values are observed between different molybdenite grains within mineral separates from the same locality (*e.g.*, Bělčice sample), as well as within individual grains (*e.g.*, Preissac and Mokrsko samples), and reflect the presence of inhomogeneities on the scale of a few hundred μm or less. The lack of three-dimensional information on the ^{187}Os/^{187}Re variations in the molybdenite samples studied does not allow us to determine the minimum size of sample that, if analyzed by conventional bulk techniques, would produce an accurate Re–Os age. However, the large scatter of apparent ages obtained from the grains studied suggests that the size of a molybdenite sample needed for accurate Re–Os dating exceeds the total volume sampled by the laser in each molybdenite grain (*ca.* 0.02 mg per laser raster, and up to 28 laser rasters per sample). In a similar LA–ICP–MS study, Stein *et al.* (2001) and Stein *et al.* (in press) also demonstrated spatial decoupling of Re and ^{187}Os on a scale greater than the laser spot, utilizing one of their in-house molybdenite standards. Thus, for the Preissac molybdenite, a sample of *ca.* 0.5 mg would be too small to yield an accurate Re–Os age. In reality, up to several mg of molybdenite would have to be concentrated and homogenized in order to develop a confidence that the resulting Re–Os age will be representative of the event that led to molybdenite crystallization. This poses a significant challenge to the derivation of accurate ages of molybdenite formation through Re–Os geochronology.

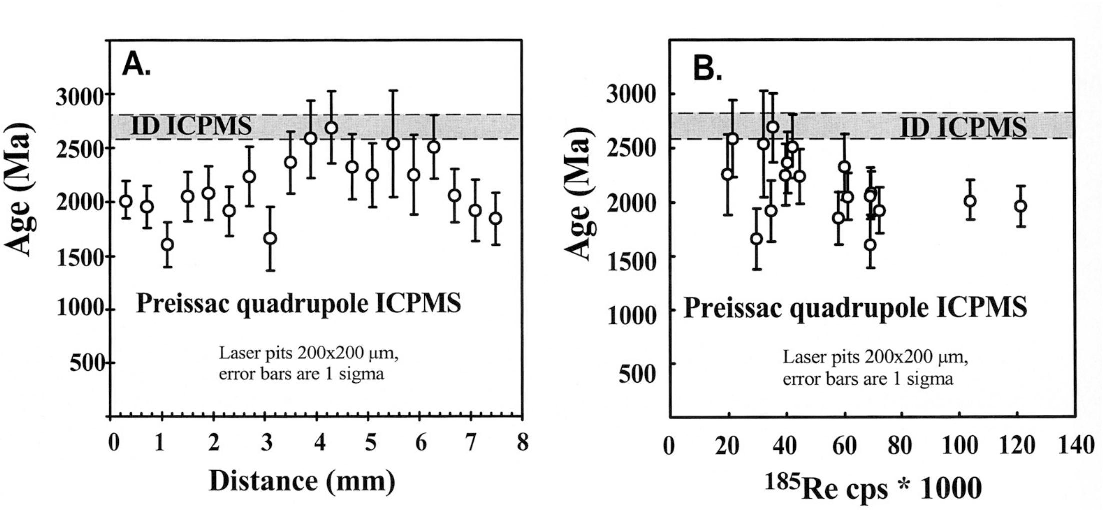

FIG. 4. A. Laser-ablation profile across part of the Preissac molybdenite grain (quadrupole ICP–MS data). B. Plot of the ^{185}Re signal intensity (in pulse counts per second) *versus* the calculated Re–Os age for the same data as plotted in Figure 4A. Shaded area corresponds to age obtained by conventional isotope-dilution ICP–MS analysis (Suzuki *et al.* 1993).

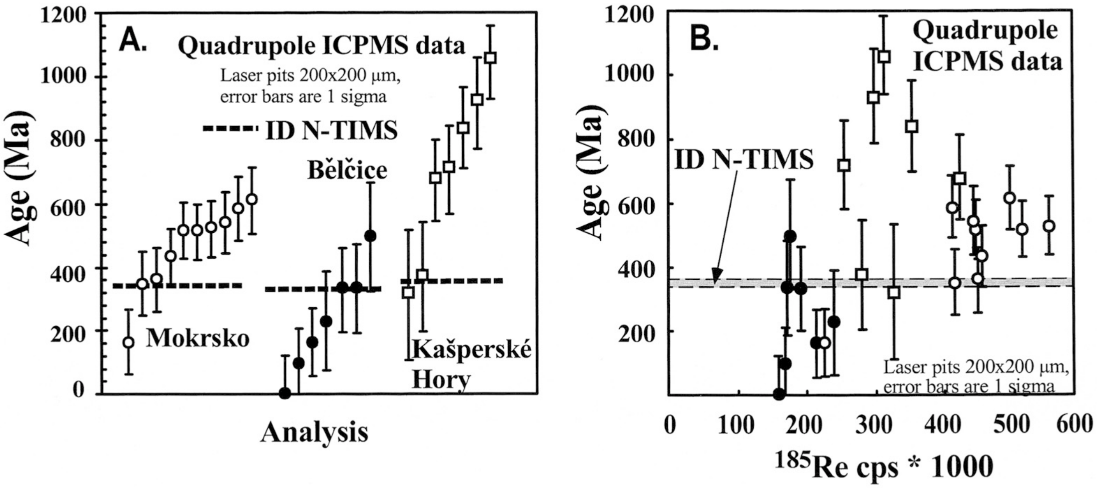

FIG. 5. A. Laser-ablation quadrupole ICP–MS analyses for three samples of molybdenite from the Bohemian Massif, plotted in the order of increasing apparent age. B. Plot of the intensity of the ^{185}Re signal (in pulse counts per second) *versus* the calculated Re–Os age for the same data as plotted in Figure 5A. Dashed lines and shaded area correspond to ages obtained by conventional isotope-dilution TIMS analysis (Stein *et al.* 1997a, Zachariáš & Stein 2001).

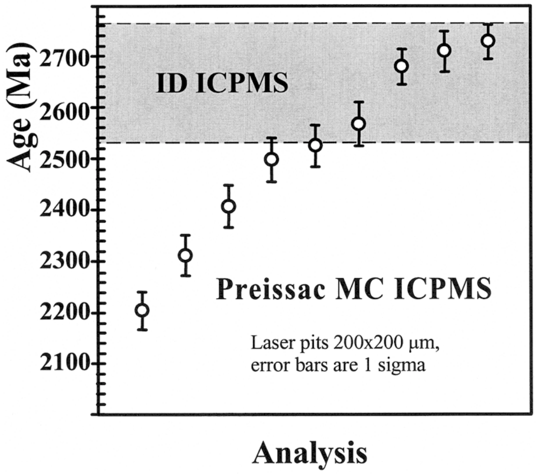

FIG. 6. Results of laser-ablation multicollector magnetic sector ICP–MS analyses for the Preissac molybdenite grain plotted in the order of increasing apparent age. Laser pits were randomly distributed within the molybdenite grain studied. Shaded area corresponds to age obtained by conventional isotope-dilution ICP–MS analysis (Suzuki *et al.* 1993).

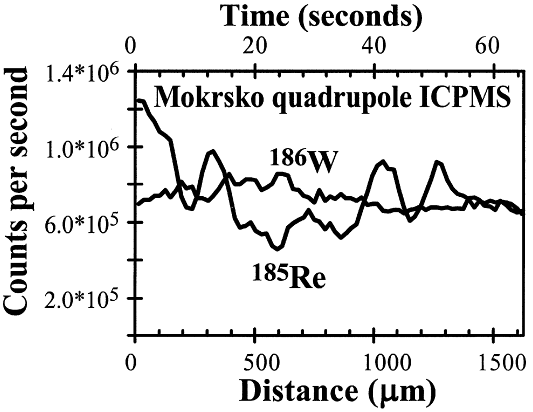

FIG. 7. A portion of a time-resolved laser-ablation raster across the Mokrsko molybdenite showing variation in the Re content. Isotopic signal due to ^{186}W present in the molybdenite is plotted for comparison. Laser-raster speed for this analysis was 25 μm/s, and the data were acquired without the simultaneous aspiration of the W tracer solution to the ICP.

Stein *et al.* (1998b) first recognized and defined this problem and developed a “whole-rock” approach of molybdenite sampling, which is designed to capture the bulk ^{187}Os/^{187}Re value of the system of interest by sampling over size scales much larger than those of the Re–Os heterogeneities. Thus, entire, individual crystals of molybdenite may be sampled in cases where Re and Os have not been lost from individual grains during secondary processes, whereas multi-crystal aggregates, or even extremely well-homogenized mine-mill concentrates (Stein *et al.* 1997b), are used to naturally overcome problems with Re–Os mobility. In this way, Re–Os molybdenite geochronology is fundamentally different than the most accurate method of dating, U–Pb zircon geochronology, which is based on identifying and dating only pristine portions of crystals, or making corrections for secondary alteration (*i.e.,* lead loss using discordia relationships). This is not to say that Re–Os molybdenite geochronology cannot provide accurate information about age in particular situations, as this potential has been clearly demonstrated (Stein *et al.* 2001), only that it should be applied with due caution. In particular, fine-scale differences in age, as might be expected in ore systems formed in multiple events, could be masked by the "whole-rock" approach of molybdenite sampling. On the other hand, heterogeneous Re–Os populations of molybdenite ages produced by secondary processes might be mistaken for distinct ore-forming events.

Laser-ablation MC ICP–MS analyses

Laser-ablation sampling provides a spatial resolution that is capable of documenting the presence of discrete ages of sulfide mineralization in an ore system. However, when coupled to the quadrupole ICP–MS instrument, it does not yield geologically useful refinements of individual ^{187}Os/^{187}Re values and subsequent age-determinations. As an alternative, we have tested the precision of laser-ablation Re–Os analyses of molybdenite with a multicollector magnetic sector ICP–MS, using the Preissac molybdenite sample. Although we have used a different wavelength of laser (193 nm excimer) for the MC ICP–MS analyses compared to that of the quadrupole ICP–MS system (266 nm Nd YAG), we have tried to match other conditions of ablation to those of the quadrupole system used elsewhere in this study as closely as possible (ablation in He gas, similar energy, raster size, and repetition rate). Simultaneous nebulization of the W tracer solution to the plasma during laser ablation was not carried out for the MC ICP–MS measurements. Thus, natural W in the molybdenite itself was used to make mass-bias corrections. The data suggest that a substantial improvement in precision of individual laser-ablation determinations of ^{187}Os/^{187}Re can be achieved using the MC ICP–MS instrument. Despite the error magnification that stems from correction of the large isobaric interference on mass 187, the precision of calculated ages for the Preissac sample improved from 9.0–16.1% for quadrupole ICP–MS measurements to 1.2–1.8% for MC ICP–MS measurements ($1\sigma_m$). Although the measurement would be less precise for younger and Re-poor samples of molybdenite, the error could be further reduced by aspiration of a W tracer solution to the plasma during ablation, providing larger signals for the W-based mass-bias correction.

A more serious problem to the applicability of laser sampling for Re–Os geochronology of molybdenite is the extreme, micrometer-scale variations in ^{187}Os/^{187}Re that are apparently typical of this mineral (Košler *et al.* 2000, Stein *et al.* 2001, this study), at least some of them as a result of secondary mobilization of Re and Os. The particular advantage of laser sampling in altered minerals is the ability to target particular regions that preserve primary chemical characteristics, but in the case of molybdenite, it would be difficult to know *a priori* which regions preserve primary information about age or where such regions have been intersected. Laser sampling could have a useful role in Re–Os geochronology of molybdenite either as direct dating tool in its own right when coupled to a MC ICP–MS instrument, or as a reconnaissance tool for identifying appropriate grains for more precise isotope-dilution analyses, if some grains preserve primary, homogeneous ^{187}Os/^{187}Re values. The results of this study suggest, however, that such grains are not common.

CONCLUSIONS

Laser-ablation ICP–MS measurements define the presence of inhomogeneities in the ratio ^{187}Os/^{187}Re in molybdenite that are outside experimental errors, and large-scale variations in Re-contents, up to a factor of 10 over length scales of only 50 μm. Hence there is widespread, non-systematic Re–Os decoupling within molybdenite on a scale far greater than that of volumes sampled (up to 0.5 mg) by laser ICP–MS analyses. Samples significantly larger than this thus are required for precise dating studies by isotope-dilution N–TIMS and ICP–MS methods (Stein *et al.* 1998b, 2001). The results emphasize the difficulty in designing a sampling strategy to meet the competing goals of homogenization of ^{187}Os/^{187}Re variations produced by secondary processes, and at the same time preserving primary differences in ^{187}Os/^{187}Re (age) within the sample population. Laser-ablation MC ICP–MS is, for some old and Re-rich samples of molybdenite, capable of providing *in situ* Re–Os ages with a geologically useful precision on very small volumes in single grains. Thus, in principle, laser sampling could be used for Re–Os geochronology if some samples of molybdenite preserve primary, homogeneous distributions of ^{187}Os/^{187}Re; unfortunately, such grains would seem to be rare.

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