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Macroscale NTIMS and microscale LA-MC-ICP-MS Re-Os isotopic analysis of molybdenite: Testing spatial restrictions for reliable Re-Os age determinations, and implications for the decoupling of Re and Os within molybdenite

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Abstract—We present a detailed study of Re-Os age determinations for eight natural molybdenite samples of like polytype (2H), spanning a range of age, natural grain size and deposit type. The focus of the study is to critically evaluate the effects of sampling, sample preparation and aliquant size on the accuracy and reproducibility of Re-Os ages for these molybdenite samples. We find that for some molybdenite samples, analysis of small sample aliquants (<20 mg) may not yield accurate or reproducible Re-Os ages, whereas analysis of larger aliquants from the same mineral separate do yield reproducible Re-Os dates. Such an observation is best explained if Re and ^{187}Os are internally decoupled within molybdenite grains. This finding is supported from spot analyses by laser ablation MC-ICP-MS analyses presented here and is consistent with previously published observations. The degree of decoupling between Re and ^{187}Os appears to increase both as a function of increasing grain size, and increasing age of molybdenite. From detailed dating of individual molybdenite mineral separates, we provide approximate minimum aliquant amounts required for reproducible Re-Os age dating, as a function of molybdenite age and grain size. Geologically younger, naturally fine-grained molybdenite samples appear to show little Re and ^{187}Os decoupling, and reproducible ages can be determined from some samples with as little as 1 mg of aliquant. Geologically old, and coarse-grained molybdenite samples may require as much as 40 mg of aliquant from a much larger mineral separate to overcome Re and ^{187}Os decoupling. The mechanism(s) of Re and ^{187}Os decoupling within molybdenite is not constrained by this results of this study, but the observation that the degree of decoupling increases with grain size (distance) and age (time/geologic history) may suggest primary diffusive control. Assuming that Re and ^{187}Os decoupling in molybdenite results primarily from diffusion of ^{187}Os , apparent diffusion coefficients are calculated ($D = x^2/t$). Estimates of D for Os made in this way range from 2.8×10^{-26} to 2.1×10^{-21} m²/s, which are broadly similar to experimentally derived diffusion coefficients for Os in Fe-sulfide minerals and for Re in molybdenite at temperatures <500°C. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

Molybdenite is naturally enriched in rhenium (Re) and contains little or no common osmium (Os) (Morgan et al., 1968; Markey et al., 1998; Selby and Creaser, 2001a), meaning that essentially all ^{187}Os is radiogenic, derived from the decay of ^{187}Re (Stein et al., 1998a). As such, this mineral is ideally suited for geochronology using the ^{187}Re - ^{187}Os isotope system. Since the first applications of Re-Os isotopic dating to molybdenite (Hirt et al., 1963; Herr et al., 1967; Luck and Allègre, 1982), the technique has become an important tool for determining the timing and duration of sulfide mineralization in ore deposit systems (McCandless et al., 1993; Suzuki et al., 1996; Stein et al., 1997, 1998b; Watanabe et al., 1999; Raith and Stein, 2000; Watanabe and Stein, 2000; Selby and Creaser, 2001a,b; Selby et al., 2002, 2004; Mao et al., 2003), and in some cases for metamorphic processes (Stein and Bingen, 2002; Bingen and Stein, 2003). Many studies find that the Re-Os molybdenite system is remarkably robust, not being disturbed by younger hydrothermal, metamorphic and/or tectonic events (e.g., Raith and Stein, 2000; Watanabe and Stein, 2000; Selby and Creaser, 2001a,b; Selby et al., 2001a,b, 2002;

Zachariás et al., 2001a,b; Stein et al. 2002, 2003; Stein and Bingen, 2002; Bingen and Stein, 2003).

In contrast, other studies conclude that the Re-Os systematics of molybdenite are easily disturbed (Luck and Allègre, 1982; McCandless et al., 1993; Suzuki et al., 2000; Suzuki et al., 2001). Molybdenite dates older than the Earth have been obtained (Luck and Allègre, 1982) and analyses of molybdenite crystal fragments have yielded Re-Os dates that differ by up to 20% from the true age of the molybdenite (Stein et al., 1998a, 2001). In some cases, irreproducible Re-Os molybdenite dates obtained using microwave digestion and ICP-MS techniques (Suzuki et al., 1992) from a single deposit (Lobash) have been interpreted to indicate that Re-Os systematics in molybdenite are easily disturbed after formation (Suzuki et al., 2000). However, Stein et al. (2001) subsequently obtained precise and reproducible Re-Os dates for molybdenite from the Lobash deposit, using their sampling protocol (analyzing an aliquant of a very fine-grained mineral separate of several hundred grams), and analytical methods (Carius tube and NTIMS). As demonstrated by Stein et al. (2001) and, in this study, sample preparation is critically important to obtain accurate and reproducible Re-Os molybdenite ages. To further investigate the Re-Os systematics of molybdenite, and to reconcile conflicting conclusions regarding the reliability of molybdenite Re-Os geochronology, we present here a detailed study of eight natural molybdenite samples of variable age, paragenesis and grain-

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Table 1. Characteristics of molybdenite samples used in this study.

Sample no.	Natural grain size	Mineralization characteristics ^a
HLP-5	~0.13–0.2 mm ¹	Mo-Pb-U carbonatite vein hosted, Huanglongpu deposit, China ~1 m × 500 m calcite-quartz-molybdenite veins ²
2706.SWB	<2 mm	Porphyry Mo, Endako deposit, British Columbia, Canada Laminated quartz-molybdenite veins ³
Sc13L	3–5 mm to 1 cm	W-Sn-U-Cu-Mo-Bi-Fe Long Lake deposit, Nova Scotia, Canada Pegmatitic K-feldspar-quartz ⁴
Sc15W	3–5 mm to 1 cm	W-Sn-U-Cu-Mo-Bi-Fe Walker deposit, Nova Scotia, Canada Pegmatitic K-feldspar-quartz ⁴
Sc20W	1–1.5 cm	W-Sn-U-Cu-Mo-Bi-Fe Walker deposit, Nova Scotia, Canada Pegmatitic K-feldspar-quartz ⁴
A996B	mm clots and rosettes Up to 1 cm	Mo prospect, Aittojärvi, Kuhmo-Suomussalmi Greenstone belt, east-central Finland Molybdenite is developed in aplitic zones of tonalitic gneiss ⁵
KQ78-84A	~1 mm	Porphyry-style Cu-Mo, Clark Lake, Chibougamau, Quebec, Canada Late-stage quartz-pyrite-molybdenite veins ⁶
76FR-77	~1 mm	Porphyry Mo, Setting Net Lake, Favourable Greenstone belt, Ontario, Canada Quartz-feldspar-biotite-molybdenite veins ⁷

^a References are as follows: ¹Du Andao (personal communication 2001); ²Stein et al. (1997); ³Selby et al. (2000); ⁴O'Reilly (1988); ⁵Stein et al. (2003); ⁶Pilote et al. (1995); ⁷Corfu and Ayres (1991).

size, with identical polytype (2H) using NTIMS and Laser Ablation (LA)-MC-ICP-MS protocols. This study has a specific emphasis on effects associated with analysis aliquant size and sample preparation, demonstrating the critical importance of these factors in obtaining accurate and reproducible Re-Os molybdenite dates. Although advances in Re and Os analytical and mass spectrometry allow for precise isotopic measurements using Faraday collectors of submilligram quantities of molybdenite (Creaser et al., 1991; Völkening et al., 1991; Shirey and Walker, 1995; Cohen and Waters, 1996; Markey et al., 1998), we demonstrate that analysis of such small quantities of molybdenite may, in some cases, yield erroneous Re-Os dates.

Knowledge of the mobility of Re and/or Os in molybdenite and other Fe-sulfide minerals by diffusion is limited (Brenan et al., 1998, 2000). We use the Re-Os data from molybdenite obtained from NTIMS and LA-MC-ICP-MS protocols to provide approximations for diffusion coefficients of Re and Os in molybdenite. These “apparent” diffusion coefficients compare favorably with the few determinations made from laboratory experiments in sulfide minerals.

2. SAMPLE PREPARATION AND ANALYTICAL METHOD

The details of physical characteristics, paragenesis and location for each molybdenite sample used in this study are presented below and Table 1. Molybdenite separates of samples 2706.SWB, SC15W, SC20W, and SC13L were prepared at the University of Alberta. Whole rock samples were ground in a porcelain disk mill, collecting the +44–210 μm (200–70 mesh) fraction. Molybdenite was then concentrated using heavy liquid techniques, and further purified by floatation using high purity water (MilliQ), magnetic separation, and/or removing impurities by hand under a microscope. For sample SC20W, three coarse-grained molybdenite grains were physically removed from the whole rock samples using tweezers. Molybdenite grain SC20W-B was cut into four semiequal pieces using a razor blade.

The full analytical procedure for Re-Os age determinations at the University of Alberta Radiogenic Isotope Facility is described by Selby and Creaser (2001a,b), and is only briefly noted here. Molybdenite samples were dissolved and equilibrated with a known amount of ¹⁸⁵Re and isotopically normal Os in inverse aqua regia (2:1 16 N HNO₃ and 12 N HCl, 3 mL) at 240°C for 24 h in a Carius-tube. Rhenium and Os were

isolated and purified by solvent extraction, microdistillation, and anion exchange chromatography, and analyzed by negative thermal ionization mass spectrometry on a Micromass Sector 54 mass spectrometer using Faraday collectors. Total procedural blanks for Re and Os <5 pg and <2 pg, respectively, with an ¹⁸⁷Os/¹⁸⁸Os blank composition of 0.24 ± 0.02 ($n = 6$). A blank correction was applied only to SC20W.

Rhenium and Os concentrations, and Re-Os molybdenite date uncertainties are presented at the 2σ level, which includes the uncertainties in Re and Os mass spectrometer measurement, spike and standard Re and Os isotopic compositions, and calibration uncertainties of ¹⁸⁵Re and ¹⁸⁷Os. Because a mixed ¹⁸⁵Re and Os tracer solution is used, uncertainties in weights of sample and tracer solution do not affect the calculated age, and are not considered. However, sample and tracer solution weight uncertainties are considered in determining the uncertainty in the Re and ¹⁸⁷Os concentrations. Uncertainty in the ¹⁸⁷Re decay constant (Smoliar et al., 1996) is also not considered. Weighted average ages are given at 95% confidence level, 2σ determined using Isoplot (Ludwig, 1998).

Laser ablation (LA) MC-ICP-MS analysis of molybdenite grains from mineral separates, were held in epoxy-filled mounts and analyzed using a 213 nm New Wave laser coupled to a Nu-Plasma MC-ICP-MS at the University of Alberta Radiogenic Isotope Facility. For all analyses element masses 185 (Re), 187 (¹⁸⁷Re + ¹⁸⁷Os), and 184 and 186 (W) were measured using Faraday collectors, with a 30 s background (“on-peak zero”) collected before each analysis. Spot analyses utilize a 100 μm diameter laser-beam, with a 10 Hz pulse rate, ablated into He gas. The ¹⁸⁴W/¹⁸⁶W ratio was measured either directly from W ablated in the molybdenite or from a 10 ppb natural W tracer solution aspirated simultaneously during sample ablation to enable correction for mass fractionation. For apparent age determinations, where $T = 1/\lambda \times \ln [(^{187}\text{Os}/^{187}\text{Re}) + 1]$, the ¹⁸⁷Os value was obtained as described by Kosler et al. (2003), subtracting the amount of ¹⁸⁷Re, determined using the intensity of ¹⁸⁵Re and the natural ¹⁸⁵Re/¹⁸⁷Re ratio of 1.67398 (Gramlich et al., 1973) from the total intensity of mass 187 (¹⁸⁷Re + ¹⁸⁷Os).

3. RESULTS

The Re-Os results for eight molybdenite samples (HLP-5, 2706.SWB, SC13L, SC15W, SC20W, A996B, KQ78-84A, and 76FR-77 are presented in Tables 2–7. Two of these samples (HLP-5, A996B) are used as in-house “control” samples at AIRIE, Colorado State University, and are also used at the University of Alberta Radiogenic Isotope Facility. The remaining samples were chosen to represent a wide range of natural grain-size (<1 to 15

Table 2. Re-Os isotopic data for the AIRIE-CSU molybdenite “control” sample HLP-5.

Sample No.	Sample wt. (mg)	¹⁸⁷ Re (ppm)	¹⁸⁷ Os (ppb)	Re-Os Age (Ma)
HLP-5-1 ^{ac}	1.5	166.4 ± 4.5	611.6 ± 16.4	220.2 ± 0.8
HLP-5-2 ^{ac}	2.1	167.8 ± 2.0	619.6 ± 12.0	221.2 ± 0.8
HLP-5-3 ^{ac}	1.0	160.6 ± 6.4	593.5 ± 23.7	221.3 ± 0.8
HLP-5-4 ^{ac}	0.9	150.6 ± 6.9	555.6 ± 25.3	221.1 ± 0.8
HLP-5-5 ^{ac}	1.7	163.3 ± 3.9	598.3 ± 14.2	219.6 ± 0.8
HLP-5-1-00 ^{bc}	1.9	173.1 ± 3.8	637.3 ± 13.8	220.6 ± 0.8
HLP-5-2-00 ^{bc}	1.5	170.4 ± 4.6	626.7 ± 16.7	220.4 ± 0.8
HLP-5-3-00 ^{bc}	2.3	166.6 ± 3.0	611.6 ± 10.9	219.9 ± 0.8
HLP-5-1-01	2.0	161.2 ± 3.2	593.2 ± 11.8	220.5 ± 0.8
HLP-5-2-01	5.3	164.5 ± 1.3	603.4 ± 4.7	219.8 ± 0.8
HLP-5-3-01	2.2	162.5 ± 3.0	598.2 ± 10.9	220.5 ± 0.8
HLP-5-4-01	5.2	169.4 ± 1.4	623.4 ± 4.9	220.5 ± 0.8
HLP-5-5-01	10.4	174.0 ± 0.8	640.8 ± 2.7	220.7 ± 0.8
HLP-5-6-01	15.5	172.4 ± 0.7	635.0 ± 2.0	220.6 ± 0.8
HLP-5-7-01	20.4	174.5 ± 0.6	643.0 ± 1.7	220.7 ± 0.8
HLP-5-8-01	24.8	175.1 ± 0.6	645.1 ± 1.5	220.7 ± 0.8
HLP-5-1-02	10.6	174.0 ± 0.8	640.7 ± 2.7	220.6 ± 0.8

mean: 220.52 ± 0.24 (0.11%, 95% conf., MSWD = 1.3, n = 17) see figure 1

Age calculated using the decay constant $\lambda^{187}\text{Re} = 1.666 \times 10^{-11}\text{yr}^{-1}$, without uncertainty (Smoliar et al., 1996).

^a Reported in Selby and Creaser (2001a); recalculated using the recalibrated ¹⁸⁵Re abundance in our tracer solution (Selby and Creaser, 2001b).

^b Reported in Selby and Creaser (2001b).

^c Re and Os concentrations and Re-Os age recalculated using uncertainties in Re and Os mass spectrometer measurements, spike and standard Re and Os isotopic compositions, and calibration uncertainties of ¹⁸⁵Re and ¹⁸⁷Os, previously not included in the calculations of Selby and Creaser (2001a,b).

mm), Re contents (<10 to 280 ppm) and age (Jurassic to Archean) (Table 1).

3.1. Results from Carius Tube and NTIMS Analyses

3.1.1. Fine-grained, young molybdenite I: AIRIE-CSU “control” sample HLP-5, Huanglongpu deposit, China

The sample originates from the Huanglongpu Mo-Pb-U carbonatite vein-type deposit in the Shaanxi Province, China (Stein et al., 1997). Our HLP-5 “control” sample is taken from a 2 kg aliquant of a molybdenite powder concentrate (~44 μm) obtained from the milling process at the deposit (Stein et al., 1997). All analyses of HLP-5 yield a weighted average Re-Os date of 220.52 ± 0.24 Ma (0.11%, MSWD = 1.3, n = 17; Fig. 1A, Table 2). This Re-Os date is identical to that reported by Markey et al. (1998; 221.0 ± 1.0 Ma, 0.4% 1σ, n = 19) analyzed at the AIRIE molybdenite laboratory, Colorado State University. The excellent interlaboratory agreement for HLP-5 is remarkable considering the analyses of Markey et al. (1998) were obtained by an earlier used analytical technique (alkaline fusion) and use significantly more sample (10–200 mg; average ~25 mg). The Re-Os dates are also in excellent agreement with two Carius tube analyses of HLP-5 obtained at AIRIE (219.8 ± 0.7 and 221.0 ± 0.8 Ma; H. J. Stein, personal communication, 2001; Fig. 1A). For this milled sample, there is no difference in the Re-Os dates obtained from sample amounts ranging between ~1 and ~25 mg (Fig. 1A; Table 1). For example, ≥10 mg aliquants yield a weighted average age of 220.66 ± 0.35 Ma, (MSWD = 0.02, n = 5) identical to the average weighted age obtained from <10 mg aliquants (220.46 ± 0.35 Ma, MSWD = 1.3, n = 12).

Selby and Creaser (2001a) previously noted that Re and ¹⁸⁷Os abundances for HLP-5 analyzed using 1 to 5 mg aliquants are lower and more variable (Table 2 and Figs. 1B,C) than those established at AIRIE using larger aliquants (Stein et al., 1997; Markey et al., 1998). Analyses using ≥10 mg yield more reproducible Re and ¹⁸⁷Os contents (HLP-5-5-01 to HLP-5-8-01, Table 2 and Figs. 1B,C), and these values are in better agreement with those of Stein et al. (1997) and Markey et al. (1998), and two Carius tube runs at AIRIE which gave ~280 ppm Re and ~652 ppb ¹⁸⁷Os (H. J. Stein, personal communication, 2001; Figs. 1B,C). The HLP-5 data determined here suggest that, even though this sample was obtained from the milling process from the Huanglongpu deposit, 1 to <10 mg aliquants are not homogeneous with respect to Re and ¹⁸⁷Os contents, but the concentration variability does not affect the determined age.

3.1.2. Fine-grained, young molybdenite II: sample 2706.SWB, Endako deposit, Canada

Molybdenite from the Endako deposit (Table 1) was isolated from a single vein sample of dimensions ~10 × 8 × 2 cm, yielding ~22 g of 44 to 210 μm mesh material. Previous Re-Os analyses of this sample (2706.SWB-1 to 5; Selby and Creaser, 2001a) used ~5 mg of sample and the isotopic data are shown in Table 3 recalculated using the recalibrated ¹⁸⁵Re abundance in our tracer solutions (Selby and Creaser, 2001b). The average Re-Os date for these analyses is 0.14% older than reported in Selby and Creaser (2001a) as a result of this recalibration. For this study, repeat Re-Os date determinations of 2706.SWB were undertaken using ~3, 5, and 10 mg sample aliquants of the same mineral separate. These analyses yield reproducible Re-Os dates all within 2σ analytical uncertainty of each other (Table 3). The weighted

Table 3. Re-Os isotopic data for molybdenite 2706.SWB from the Endako Porphyry Mo deposit, central British Columbia, Canada.^a

Sample No.	Sample wt. (mg)	¹⁸⁷ Re (ppm)	¹⁸⁷ Os (ppb)	Re-Os Date (Ma)
2706.SWB-1	5.0	17.05 ± 0.15	41.39 ± 0.34	145.5 ± 0.6
2706.SWB-2	4.5	19.17 ± 0.18	46.62 ± 0.42	145.8 ± 0.6
2706.SWB-3	4.2	19.23 ± 0.19	46.70 ± 0.47	145.6 ± 0.7
2706.SWB-4	4.5	19.07 ± 0.18	45.97 ± 0.43	144.5 ± 0.7
2706.SWB-5	5.7	19.51 ± 0.19	47.53 ± 0.35	146.0 ± 0.8
2706.SWB-6	4.7	19.14 ± 0.17	46.57 ± 0.41	145.9 ± 0.5
2706.SWB-7	10.3	18.91 ± 0.09	46.21 ± 0.19	146.5 ± 0.5
2706.SWB-8	5.2	19.21 ± 0.16	46.77 ± 0.37	145.9 ± 0.6
2706.SWB-9	10.2	19.55 ± 0.09	47.46 ± 0.21	145.5 ± 0.5
2706.SWB-10	2.9	18.60 ± 0.26	45.30 ± 0.62	146.0 ± 0.7

^a Age calculated using the decay constant $\lambda^{187}\text{Re} = 1.666 \times 10^{-11}\text{yr}^{-1}$ without uncertainty (Smoliar et al., 1996). 2706.SWB-1 through 5 recalculated from Selby and Creaser (2001a) using the new spike calibrations (Selby and Creaser, 2001b).

average age of all analyses is 145.76 ± 0.35 Ma (MSWD = 2.6, $n = 10$, Table 2). With the exception of 2706.SWB-1, all analyses yield highly similar Re and ¹⁸⁷Os contents (Table 3). Sample 2706.SWB-1 was not analyzed from the ~22 g mineral separate, but prepared by scraping ~5 mg of molybdenite directly from the mineral surface (Selby and Creaser, 2001a). Although 2706.SWB-1 gave an identical Re-Os date to all aliquant analyses from the pulverized sample, its Re and ¹⁸⁷Os concentrations deviate by ~11% from those for 2706.SWB-2 to 10 (Table 2).

3.1.3. Coarse-grained young molybdenite; samples SC13L, SC15W and SC20W, South Mountain Batholith, Canada

Molybdenite was isolated from two W-Sn-U-Cu-Mo-Bi-Fe deposits (Walker and Long Lake) of the New Ross pluton,

South Mountain Batholith, Nova Scotia, Canada (SC15W, SC20W, SC13L; Table 1). For Long Lake, SC13L ~7 g of molybdenite (44 to 210 μm) was isolated. For Walker, SC20W, three coarse-grained (1 to 1.5 cm diameter) molybdenite crystals were plucked from the rock using tweezers (Fig. 2), with the remaining molybdenite (~220 mg, 44 to 210 μm) separated as described above. In an identical sample from Walker, SC15W, ~2.5 g of molybdenite (44 to 210 μm) of very similar appearance to SC13L was isolated.

Two analyses of SC13L using ~10 mg of molybdenite yield irreproducible Re-Os dates (Table 3). However, five analyses using ~20 and 30 mg of molybdenite (SC13L-3 to SC13L-7) yield reproducible Re and ¹⁸⁷Os values, and Re-Os dates (Table 3), giving a weighted average of 371.0 ± 0.6 Ma (MSWD = 0.9, $n = 5$). This age is in good agreement with other isotopic age

Table 4. Re-Os isotopic data for molybdenite from the South Mountain Batholith, Nova Scotia, Canada.^a

Sample No.	Sample wt. (mg)	¹⁸⁷ Re (ppm)	¹⁸⁷ Os (ppb)	Re-Os Date (Ma)
Sc13L-1	10.0	4.213 ± 0.021	26.41 ± 0.12	375.0 ± 1.5
Sc13L-2	10.5	4.233 ± 0.021	26.03 ± 0.12	367.9 ± 1.5
Sc13L-3	21.1	4.209 ± 0.015	26.06 ± 0.07	370.5 ± 1.4
Sc13L-4	20.2	4.140 ± 0.015	25.65 ± 0.07	370.8 ± 1.4
Sc13L-5	20.2	4.248 ± 0.015	26.34 ± 0.07	371.1 ± 1.4
Sc13L-6	29.8	4.272 ± 0.014	26.45 ± 0.06	370.5 ± 1.4
Sc13L-7	30.1	4.227 ± 0.014	26.29 ± 0.06	372.1 ± 1.4
Sc15W-1	100.1	1.496 ± 0.005	9.297 ± 0.020	371.9 ± 1.6
Sc15W-2	49.6	1.496 ± 0.006	9.284 ± 0.030	371.4 ± 1.9
Sc15W-3	21.5	1.479 ± 0.006	9.144 ± 0.032	369.9 ± 1.8
Sc20W-1	10.9	0.447 ± 0.003	2.799 ± 0.016	374.6 ± 2.4
Sc20W-2	10.7	0.494 ± 0.004	2.950 ± 0.023	357.6 ± 3.5
Sc20W-3	21.4	0.466 ± 0.003	3.466 ± 0.023	444.4 ± 4.2
Sc20W-4	20.1	0.465 ± 0.003	2.961 ± 0.020	381.3 ± 3.6
Sc20W-5	29.4	0.497 ± 0.002	3.187 ± 0.015	383.8 ± 2.6
Sc20W-6	21.4	0.521 ± 0.003	3.167 ± 0.016	363.5 ± 2.5
Sc20W-7	49.10	0.336 ± 0.002	1.859 ± 0.008	330.9 ± 2.1
Sc20W-8	52.18	0.438 ± 0.002	1.931 ± 0.008	263.6 ± 1.7
Sc20W-A	5.0	0.381 ± 0.006	2.789 ± 0.047	437.9 ± 9.2
Sc20W-B1	29.2	0.365 ± 0.002	2.338 ± 0.011	383.5 ± 2.6
Sc20W-B2	20.9	0.348 ± 0.003	2.219 ± 0.019	381.2 ± 4.5
Sc20W-B3	17.8	0.260 ± 0.003	1.745 ± 0.017	401.7 ± 5.4
Sc20W-B4	24.1	0.393 ± 0.003	2.506 ± 0.017	381.4 ± 3.9
Sc20W-C	~32	0.413 ± 0.003	3.372 ± 0.023	488.5 ± 4.7

^a Age calculated using the decay constant $\lambda^{187}\text{Re} = 1.666 \times 10^{-11}\text{yr}^{-1}$ without uncertainty (Smoliar et al., 1996).

Table 5. Re-Os isotopic data for the AIRIE-CSU molybdenite “control” sample A996B.^a

Sample No.	Sample wt. (mg)	¹⁸⁷ Re (ppm)	¹⁸⁷ Os (ppb)	Re-Os Age (Ma)
A996B-1	1.5	13.50 ± 0.37	641.3 ± 17.5	2785.3 ± 9.1
A996B-2	2.0	16.79 ± 0.33	805.0 ± 15.9	2811.8 ± 9.1
A996B-3	3.2	14.00 ± 0.18	667.2 ± 8.5	2796.2 ± 8.9
A996B-4	9.9	13.77 ± 0.06	656.3 ± 2.8	2795.4 ± 8.8
A996B-5	10.6	14.04 ± 0.06	666.6 ± 2.8	2784.2 ± 8.7
A996B-6	40.2	13.77 ± 0.04	655.4 ± 1.3	2791.1 ± 9.7
A996B-7	39.8	14.19 ± 0.04	677.4 ± 1.4	2793.9 ± 9.8
A996B-8	40.5	13.68 ± 0.04	651.6 ± 1.3	2791.9 ± 9.8
A996B-9	50.4	14.32 ± 0.04	683.6 ± 1.3	2797.5 ± 9.9

^a Age calculated using the decay constant $\lambda^{187}\text{Re} = 1.666 \times 10^{-11}\text{yr}^{-1}$ without uncertainty (Smoliar et al., 1996).

constraints of greisen formation within the South Mountain Batholith (e.g., ⁴⁰Ar/³⁹Ar muscovite dates of 368.2 ± 6, 368.6 ± 6, 373.1 ± 6 Ma, Keppie et al., 1993).

For sample SC15W, a 20 mg aliquant yields a Re-Os date within analytical uncertainty of 50 and 100 mg analyses, yielding a mean age of 371.2 ± 2.5 Ma (MSWD = 1.4, n = 3; Table 3). Again this age is in good agreement with that of SC13L and the age constraints of greisen formation (Keppie et al., 1993, and references therein).

In contrast to the Re-Os age of SC15W, eight Re-Os dates from SC20W, also from the Walker deposit, range between 263.6 ± 1.7 and 444.4 ± 4.2 Ma (Table 3). Sample SC20W is from a K-feldspar-quartz pegmatite identical to SC15W, suggesting a similar genetic origin and formation time, however failed to yield a similar 371 Ma date, or any reproducible date using 10 to 50 mg aliquants (Table 3). In comparison to SC15W, SC20W has a factor of 3 to 5 less total Re (Table 3), is less abundant (~1% versus 5%), and is much coarser grained, typically 1 to 1.5 cm diameter crystals. Given that samples SC15W and SC20W originate from the same deposit, the inability to obtain reproducible Re-Os dates for SC20W, likely relates to one or more of its physical property differences such as grain size and/or low Re content (discussed below).

Hand picked molybdenite grains from SC20W (SC20W-A, C) (Fig. 2) yield Re-Os dates that are higher by 66 and 117 Ma in comparison to the 371 Ma Re-Os date of SC15W (Table 3). Further, grain SC20W-B (Fig. 2) that was divided into four semiequal pieces gave Re-Os dates that are higher by 10 to 30 Ma in comparison to the SC15W 371 Ma Re-Os date (Table 3). These grains do not exhibit euhedral hexagonal crystalline habit and therefore represent molybdenite grain fragments, rather than an entire crystal.

3.1.4. Coarse-grained ancient molybdenite; sample A996B, Aittojärvi prospect, Finland

Molybdenite was isolated during the separation of zircons from aplitic units at the Aittojärvi Mo prospect, east-central Finland by the Geological Survey of Finland (H. J. Stein, personal communication, 2001) (Table 1). An aliquant (~200 mg, 200 to 100 μm) of this sample was obtained for the analyses in this study (Table 5) from the AIRIE molybdenite laboratory, Colorado State University.

Re-Os dates obtained from 1.5 to 3.2 mg (n = 3) of sample range between 2785.3 ± 9.1 and 2811.8 ± 9.1 Ma, a difference of ~26 Ma. Using ~10 mg aliquants (n = 2), Re-Os dates are just reproducible within quoted uncertainties (2795.4 ± 8.7 and 2784.2 ± 8.7 Ma; Table 5). In contrast, four analyses using ~40–50 mg aliquants yield highly reproducible Re-Os dates of 2790.5 ± 9.7, 2793.9 ± 9.8, 2791.9 ± 9.8 Ma and 2797.5 ± 9.9 Ma (Table 5). The weighted average of all Re-Os dates is 2791.4 ± 6.4 Ma (MSWD = 3.2, n = 9), demonstrating that all, individual age determinations are within uncertainty of the weighted mean date. However, the reproducibility of Re-Os dates obtained from <15 mg is poorer than that aliquants of >40 mg (Fig. 3). The weighted average Re-Os dates for the <15 mg (A996B 1–5) and >40mg (A996B 6–9) data subsets are 2794 ± 14 Ma (2σ, MSWD = 6.1) and 2793.6 ± 4.8 Ma (2σ, MSWD = 0.3), respectively.

Re-Os dates for A996B conducted by AIRIE at Colorado State University yield a mean age of 2798 ± 3.4 (n = 11, Alkaline fusion) and 2809 ± 1.7 Ma (n = 15, Carius tube; Markey et al., 1999; Stein et al., 2001). Fifteen Re-Os dates for A996B, including two new analyses, recalculated based on improved spike composition determinations yields a mean age

Table 6. Re-Os isotopic data for molybdenite from the Clark Lake deposit, Quebec (KQ78-84A) and Setting Net Lake deposit (76FR-77), northwestern Ontario, Canada.^a

Sample No.	Sample wt. (mg)	¹⁸⁷ Re (ppm)	¹⁸⁷ Os (ppb)	Re-Os Age (Ma)
KQ78-84A-1	20.7	121.9 ± 0.412	5594.5 ± 14.5	2694.3 ± 9.5
KQ78-84A-2	41.6	122.3 ± 0.364	5617.8 ± 11.1	2695.2 ± 9.6
KQ78-84A-3	10.4	119.6 ± 0.569	5484.1 ± 23.0	2690.8 ± 9.6
KQ78-84A-4	5.5	116.1 ± 0.901	5312.8 ± 39.5	2685.1 ± 9.6
KQ78-84A-5	15.8	121.8 ± 0.464	5597.1 ± 17.2	2697.5 ± 9.6
76FR-77-3	39.6	9.878 ± 0.029	454.1 ± 0.913	2698.0 ± 9.5
76FR-77-4	19.8	9.870 ± 0.034	454.2 ± 1.223	2700.5 ± 9.7
76FR-77-5	9.8	9.921 ± 0.049	456.1 ± 2.059	2700.1 ± 10.0

^a Age calculated using the decay constant $\lambda^{187}\text{Re} = 1.666 \times 10^{-11}\text{yr}^{-1}$ without uncertainty (Smoliar et al., 1996).

Table 7. LA-MC-ICP-MS Re-Os isotopic data for spot analysis of molybdenite.

Sample No.	$^{187}\text{Os}/^{187}\text{Re}^a$	Apparent date ^b (Ma)
Sc13L—Long Lake, South Mountain Batholith		
Grain 2—perpendicular to cleavage		
1	0.00440	264 ± 57
2	0.00459	275 ± 64
3	0.00122	73 ± 47
4	0.00230	138 ± 56
5	0.00422	253 ± 57
6	0.00639	382 ± 34
8	0.03849	2267 ± 46
9	0.00289	173 ± 55
10	0.00082	49 ± 37
Grain 2—perpendicular to cleavage		
1	0.00655	392 ± 55
2	0.00637	381 ± 65
3	0.00500	300 ± 50
4	0.00127	76 ± 45
5	0.03031	1792 ± 26
7	0.00512	307 ± 68
76FR-77—Setting Net Lake deposit		
Grain 1—perpendicular to cleavage		
1	0.02873	1700 ± 47
2	0.02346	1392 ± 66
Grain 2—perpendicular to cleavage		
1	0.06326	3682 ± 20
Grain 3—perpendicular to cleavage		
1	0.03053	1805 ± 23
Grain 4—perpendicular to cleavage		
1	0.0426	2504 ± 11
Grain 5—perpendicular to cleavage		
1	0.0211	1253 ± 52
Grain 6—perpendicular to cleavage		
1	0.04246	2496 ± 16
A996B		
Grain 1—perpendicular to cleavage		
1	0.04890	2866 ± 29
Grain 2—perpendicular to cleavage		
1	0.03230	1908 ± 24
2	0.03238	1913 ± 46
Grain 3—perpendicular to cleavage		
1	0.05374	3142 ± 30
Grain 4—perpendicular to cleavage		
1	0.0409	2406 ± 13
2	0.05597	3269 ± 18
Grain 5—perpendicular to cleavage		
1	0.02672	1583 ± 14
2	0.03481	2054 ± 39

^a $^{187}\text{Os}/^{187}\text{Re}$ ratio was determined using the methodology of Kosler et al. (2003). See text for discussion.

^b Age calculated using the decay constant $\lambda^{187}\text{Re} = 1.666 \times 10^{-11}\text{yr}^{-1}$ without uncertainty (Smoliar et al., 1996).

of 2804 ± 4 Ma, with an individual uncertainty on each date of ~ 9 Ma (Markey et al., 2003). Recently, A996B has been analyzed at AIRIE using a double Os spike ($^{188}\text{Os} + ^{190}\text{Os}$), which allows for precise instrumental mass fractionation correction of Os isotope ratios, and assessment and correction for common Os (Markey et al., 2003). Molybdenite Os analysis at the University of Alberta uses the “normal addition” method, and thus all analyses are corrected for instrumental fractionation effects, but cannot be corrected for any common Os, if present. Analysis of A996B using the double spike method yields a mean age of 2797 ± 2 (1 SD, $n = 6$; Markey et al.,

2003), with an individual uncertainty on each date of ~ 9 Ma (Markey et al., 1998, 2003). Thus, all ages for A996B determined using the recalculated spike composition values and double Os spike are in agreement, within uncertainty, with the Re-Os dates obtained for this sample in this study.

3.1.5. Fine-grained ancient molybdenite; samples KQ78-84A and 76FR-77, Canada

Fine-grained (~ 1 mm) molybdenite from the Clark Lake, Chibougamau area, Quebec (Pilote et al., 1995) and Setting Net Lake, Favourable Lake greenstone belt, northwestern Ontario (Corfu and Ayres, 1991) porphyry Cu-Mo systems was isolated by froth flotation using a Denver Cell (adapted from Crozier, 1979) at the Geological Survey of Canada (Table 1). For Clark Lake, KQ78-84A, ~ 2 g of molybdenite of ~ 100 – 150 μm was isolated from a quartz-molybdenite-pyrite vein. For Setting Net Lake, 76FR-77 ~ 5 g of molybdenite of ~ 100 – 150 μm were isolated from a quartz-molybdenite vein.

For KQ78-84A, five analyses using ~ 5 mg to 40 mg yield Re-Os ages between 2685.1 ± 9.6 and 2697.5 ± 9.6 Ma (Table 6), giving a weighted average Re-Os date of 2692.6 ± 4.2 Ma (MSWD = 1.0). The single analysis using ~ 5 mg yielded the youngest individual age of 2685.1 ± 9.6 Ma, and has the lowest Re and ^{187}Os contents (Table 6). Removing this analysis from the data set yields an average weighted mean Re-Os date of 2694.4 ± 4.7 Ma (MSWD = 0.34). The highly reproducible Re-Os dates for KQ78-84A obtained using 10 to 40 mg aliquants are also shown for a similar age molybdenite, sample 76FR-77 (Table 6). The nominal Re-Os dates for 76FR-77 vary by only 2 Ma for a ~ 2700 Ma molybdenite using 10 to 40 mg aliquants (Table 6), and the three analyses yield an average weighted Re-Os date of 2699.5 ± 5.5 Ma (MSWD = 0.08).

3.2. Results from Laser Ablation MC-ICP-MS Analyses

Apparent Re-Os ages were obtained from 100 μm spot analyses by laser ablation (LA) MC-ICP-MS for samples SC13L, A996B, and 76FR-77 (Table 7). The grains analyzed were ~ 50 μm thick, yielding ~ 2 μg of molybdenite ablated. For SC13L, in contrast to the reproducible and accurate Re-Os age (371.0 ± 0.6 Ma) determined from using ≥ 20 mg aliquants and the carius tube and NTIMS protocol, Re-Os data obtained from 16 of 17 spot analyses from two grains ($\sim 3 \times 5$ mm) yield apparent ages that range between 49 ± 37 and 392 ± 55 Ma. One spot analysis gave an apparent age of 2267 ± 46 Ma (Table 7). Similarly, eight analyses of five grains, taken from the A996B mineral separate, gave spot ages ranging between 1583 ± 14 and 3269 ± 18 Ma (Table 7), a range of ~ 1600 Ma. Furthermore, Re-Os data from multiple spot analyses of a single grain yield apparent ages that differ by 5, 500 and 800 Ma (Table 7). Similarly, 7 spot analyses of grains, taken from the mineral separate of 76FR-77, yield apparent ages between 1253 ± 52 and 3682 ± 20 Ma, with two ages from one grain differing by ~ 300 Ma (Table 7). The discrepancy observed between the irreproducible spot ages and the reproducible ages obtained from using a large aliquant amount with the Carius tube and NTIMS protocol must relate to the physical location of Re and Os in the grain and is discussed below.

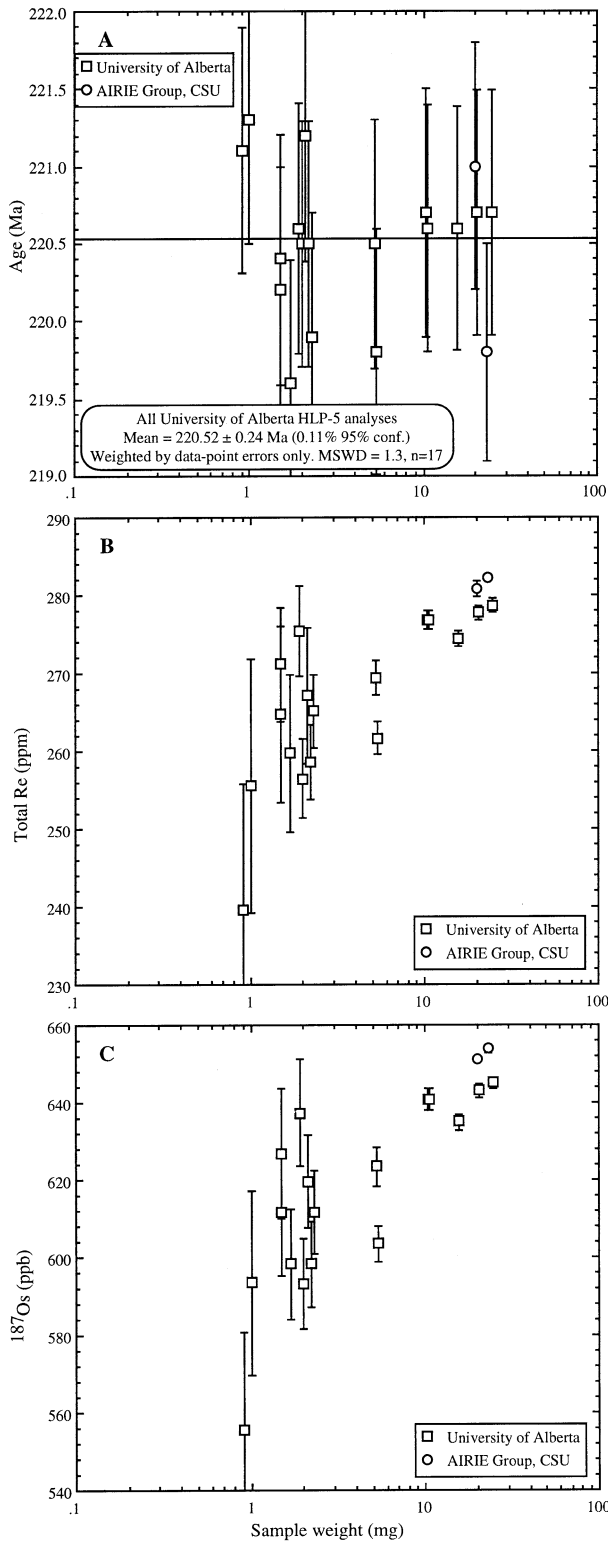


Fig. 1. Plots show sample weight (mg) used for analyses versus age (A), total Re (B), and ^{187}Os content (C), for sample AIRIE in-house molybdenite standard HLP-5. Data plotted from this study and two Carius tube analyses provided by AIRIE Group laboratory, Colorado State University (H. J. Stein, personal communication, 2001).

4. DISCUSSION

4.1. Relationship(s) between Grain Size, Aliquant Size and Re-Os Date Reproducibility

If Re and ^{187}Os were perfectly physically coupled within molybdenite, there would be no observable variation between aliquant size and the determined Re-Os age. However, as a primary observation, we find that for molybdenite with naturally coarse grain size ($>1\text{--}5\text{ mm}$), small aliquant sizes yield poorly reproducible Re-Os dates, whereas large aliquant sizes from the same mineral separate give reproducible Re-Os dates. The effect of the natural grain-size of molybdenite on the aliquant size needed to yield accurate and reproducible Re-Os dates is demonstrated here by the Re-Os ages obtained from Archean samples A996B, KQ78-84A, and 76FR-77 (Tables 5 and 6) and also by the data of Stein et al. (2001). For A996B, our Re-Os data show that to obtain reproducible Re-Os data for a sample of variable natural grain size ($\sim 0.5\text{--}5\text{ mm}$) of Archean age, $\geq 40\text{ mg}$ of molybdenite is necessary per analysis. However, to obtain reproducible Re-Os age data for naturally fine-grained ($\sim 1\text{ mm}$) Archean molybdenite, significantly less sample ($\geq 10\text{ mg}$) is required from a mineral separate (samples KQ78-84A and 76FR-77, Table 6). Similarly, for the Phanerozoic molybdenite examples, very fine-grained samples HLP-5 and 2706.SWB yield reproducible Re-Os dates with very small aliquant sizes ($<5\text{ mg}$). For some coarser-grained molybdenite ($\sim 5\text{ mm}$), such as the Phanerozoic South Mountain batholith samples SC13L and SC15W, we find $\sim 20\text{ mg}$ of sample from a mineral separate is required to obtain reproducible Re-Os ages. For these samples, results obtained from aliquant sizes of $\sim 10\text{ mg}$ deviate significantly from those of $\geq 20\text{ mg}$ (Table 5). Some extremely coarse-grained ($>1\text{ cm}$) Phanerozoic molybdenite failed to yield a reproducible age even with a 50 mg aliquant (SC20W). Such observations are not likely to result from geological processes effecting an open-system alteration on molybdenite after formation, because Jurassic sample 2706.SWB from the Endako batholith has been heavily overprinted by younger (Eocene) hydrothermal alteration and faulting, whereas the Devonian Walker pegmatite sample SC20W has not, and other samples from the same pegmatite did yield reproducible Re-Os ages comparable with ages determined from Ar-Ar geochronology. Thus, we conclude that the natural grain size of molybdenite is an important characteristic that influences the ability to obtain a reproducible Re-Os date.

This study builds on the observations and analytical tests of Stein et al. (1998a, 2001), that showed analysis of exposed single grains and/or grain fragments handpicked from rock samples yields inaccurate and nonreproducible Re-Os age data. A similar example from this study would be the single large grain fragments of SC20W from the Walker deposit, South Mountain batholith that yields inaccurate and nonreproducible dates. The Re-Os dates obtained from parts of large grains or grain fragments likely will not yield the true geological age or any significant age information for molybdenite and therefore should not be used to provide a Re-Os molybdenite date.

For many molybdenite samples, analysis of a sufficiently large aliquant can yield Re-Os dates in agreement with other geochronometers, such as South Mountain batholith samples SC13L and SC15W. This observation indicates that there can

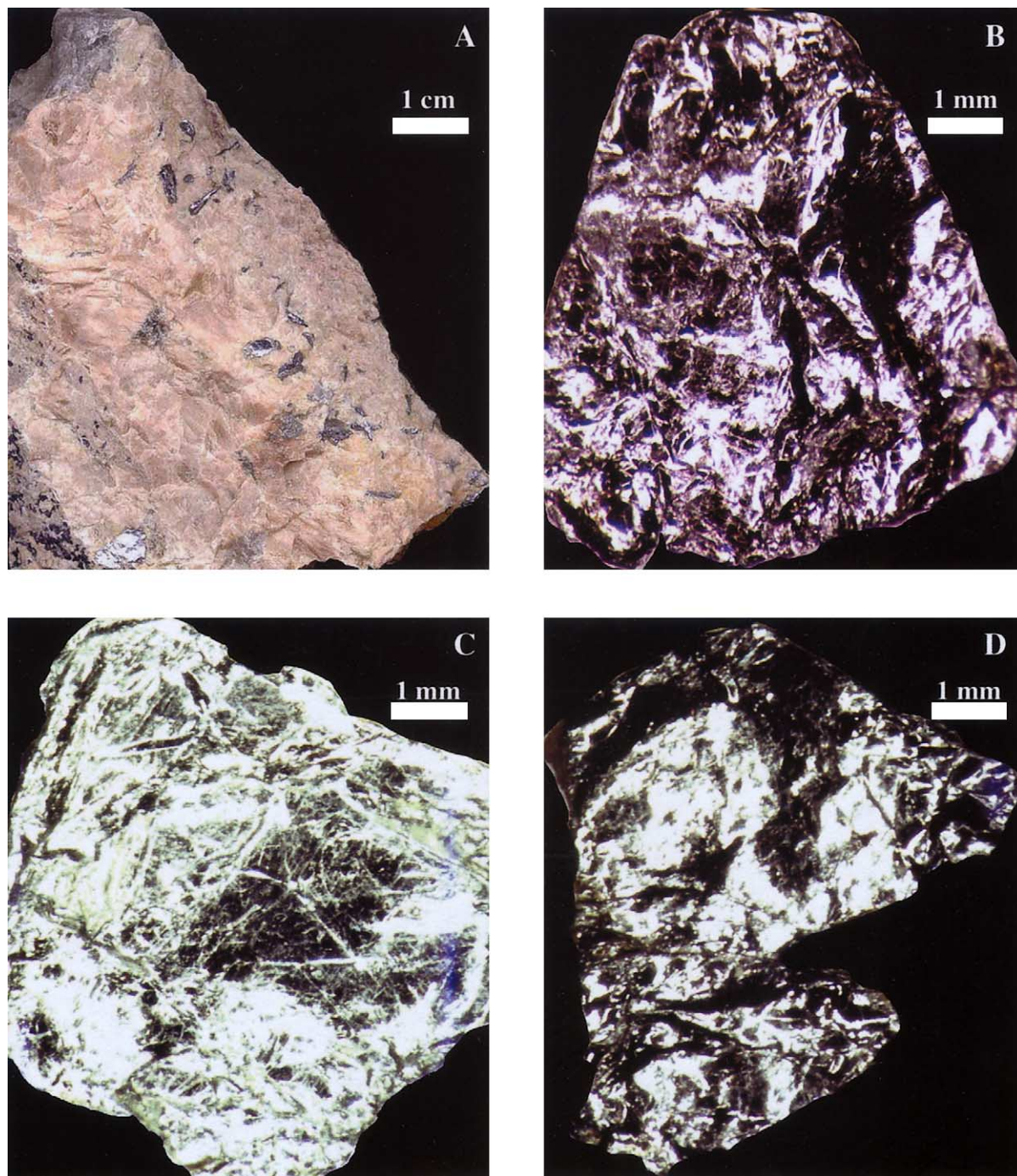


Fig. 2. Photomicrographs of molybdenite from sample SC20W South Mountain batholith, Nova Scotia. A: Molybdenite-bearing K-feldspar-quartz pegmatite from the Walker Deposit. Whole rock was crushed to isolate and homogenize the molybdenite. B, C, D: SC20W-A, SC20W-B, and SC20W-C are single molybdenite grains hand picked from SC20W. Molybdenite grains SC20W-A and SC20W-C were individually analyzed to determine a Re-Os date (Table 4). SC20W-B was divided into four semiequal pieces, with each piece analyzed for a Re-Os date (Table 4).

have been no net loss (or gain) of Re and/or ^{187}Os via any open system process, and that Re and/or ^{187}Os must have simply become physically redistributed or separated within molybdenite after formation. This separation of Re and ^{187}Os in molybdenite we term “decoupled,” a concept consistent with the conclusions of Stein et al. (2001, 2003) and of Kosler et al.

(2003). Additionally, the excellent agreement between the Re-Os molybdenite chronometer and the U-Pb chronometer argues against a general conclusion of open-system behavior of Re and/or Os in molybdenite (Stein et al., 2001; Selby and Creaser, 2003). Further, the contrast in the minimum aliquant requirements for obtaining accurate and reproducible ages for

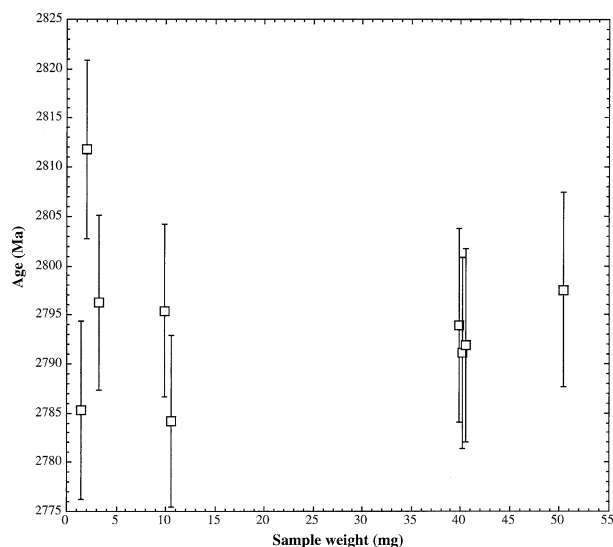


Fig. 3. Plot showing sample weight (mg) used for analyses versus age for sample A996B.

molybdenite of similar grain size, but of significant different age, may imply that the decoupling effect between Re and ^{187}Os is, in part, a function of time elapsed, and/or the geologic history since molybdenite formation (Stein et al., 2001).

4.2. Low-Re Bearing Molybdenite

Sample SC20W has a grain-size of ~ 1.5 cm and its geological relationship to SC15W suggests that it should return an age of ~ 371 Ma. However, analyses of 10 to 50 mg did not yield any reproducible Re-Os data (Table 3), and due to the small sample recovery (~ 220 mg) for SC20W very large sample aliquants could not be tested for this sample. In comparison to SC13L and SC15W, SC20W has a very low Re content (336 to 521 ppb) and because all ^{187}Os in molybdenite is radiogenic, has significantly less ^{187}Os than other south Mountain batholith samples. The coarse-grain size of this sample means that homogenizing the relatively small amounts of Re and ^{187}Os contained in a large crystal may be problematic. For example, a variation in Re content of 0.01 ppm for SC20W with 0.71 ppm Re equates to a deviation of 1.4%, but only 0.4% for a Re content of 2.38 ppm as in SC15W, and 0.1% for SC13L (6.73 ppm Re). The deviation in ^{187}Os concentration will not be the same for Re due to the decoupled nature of ^{187}Os from Re in molybdenite, and therefore may aid in magnifying the departure from the true Re-Os date. We cannot explain the disparity between the SC20W Re-Os irreproducible dates and the SC15W reproducible date by open-system disturbance to the Re-Os system by postore events, because the Walker deposit has not experienced such events. Also, the Re-Os date for SC15W from the same deposit gave an age in good agreement with that known from the South Mountain batholith. Also, many studies have demonstrated that the Re-Os molybdenite systematics are not disturbed by postore hydrothermal, magmatic, metamorphic and tectonic activity (Stein et al., 1998b; Selby and Creaser, 2001a; Selby et al., 2001, 2002; Stein and Bingen, 2002; Stein et al., 2003). Thus, we explain the disparity between the SC15W and

SC20W Re-Os ages as a function of the physical location of Re and Os in molybdenite (discussed below).

4.3. Decoupling of Re- ^{187}Os within Molybdenite

For some molybdenites, very small aliquants do not yield reproducible Re-Os dates whereas larger aliquants do yield reproducible Re-Os ages that are consistent with other geochronometers (e.g., SC13L, A996B; Fig. 3). This indicates that small-scale decoupling of ^{187}Os from Re has occurred, but at larger scale, neither Re nor ^{187}Os have been gained or lost from molybdenite by exchange with an external medium. To investigate the scale of Re- ^{187}Os decoupling in molybdenite we have carried out micron-scale (100 μm) LA-MC-ICP-MS spot analyses of Re and ^{187}Os from samples SC13L, 76FR-77 and A996B. All spot analyses yield apparent ages that are neither reproducible, nor reflect the true formation age of the sample, and further, for each sample, individual spot ages show a variation of tens to hundreds of m.y. (Table 7). These highly divergent Re-Os age given by LA-MC-ICP-MS spot analyses obtained from ~ 2 μg of molybdenite reinforce the observations made using the NTIMS protocol, which show that Re-Os dates become less reproducible as the aliquant size (mg) decreases (Tables 3, 4, and 5; Fig. 3). For these samples, the young and old apparent ages obtained from spot analyses indicate that at the 100 μm scale, there was very large deficiencies or excesses of ^{187}Os for the amount of ^{187}Re to give the true molybdenite formation age. Also, the highly divergent apparent ages obtained within and between different grains demonstrate the highly variable decoupled nature of Re and ^{187}Os at this scale (100 μm) in molybdenite.

Other evidence for this internal decoupling is shown by micron-scale LA-MC-ICP-MS analyses on molybdenite from the same locality as A996B, that yield spot Re-Os dates ranging from 0.5 to 4.0 Ga (Stein et al., 2001, 2003). These dates are in stark contrast to the reproducible ages obtained from NTIMS for A996B reported by Stein et al. (2001) and Markey et al. (1998, 2003), and also in this study. Such variability of LA-MC-ICP-MS spot ages for molybdenite is also reported by Kosler et al. (2003).

Using the NTIMS protocol we observe that in highly decoupled molybdenite, such as SC20W1-8, ^{187}Os shows considerably greater abundance variability than Re (Table 4). This supports the observations and conclusion of Stein et al. (2001, 2003) who proposed that ^{187}Os is mobile within the molybdenite crystal. The susceptibility of other sulfides to this mobility of ^{187}Os was demonstrated by the uptake of ^{187}Os in chalcopyrite bordering cogenetic molybdenite from the Pitkäranta Cu skarn deposit, Russia (Stein et al., 2003). Given highly contrasting Re and Os concentrations in the molybdenite and chalcopyrite, the loss of trace amounts of ^{187}Os from molybdenite into chalcopyrite means that the Re-Os molybdenite age is basically undisturbed, whereas the chalcopyrite Re-Os ages are impossibly old (Stein et al., 2003). For molybdenite that has experienced a complex geologic history, ^{187}Os has been suggested to accumulate in crystal defects in molybdenite as micron-scale areas of enrichment and depletion of ^{187}Os have been observed using LA-ICP-MS (Stein et al., 2003).

The specific mechanisms by which Re and ^{187}Os become

decoupled within molybdenite is not presently known, but several speculative possibilities are discussed below. One possibility is that Re forms a monosulfide impurity (likely ReS_2) in molybdenite (Newberry, 1979, and references therein), likely during formation. Pure Re sulfide has been discovered to be naturally occurring (Volborth, 1985; Korzhinsky et al., 1994). Such a phenomenon would potentially explain the variable distribution of Re observed in molybdenite, but would also require that in some cases, the ^{187}Os formed over time migrate away from the Re sulfide. Alternatively, elemental impurities (predominantly Re, but also W, Sn, Bi, Ti) in molybdenite can be associated with the occurrence of the 3R polytype (Ayres, 1974; Newberry, 1979). The 3R polytype is typically $\leq 1\%$ within the dominant 2H polytype in molybdenite with ≤ 300 ppm Re. However the 3R polytype becomes more abundant with Re contents > 300 ppm (Zelikman et al., 1970; Newberry, 1979, and references therein; Watanabe and Soeda, 1981). The minor abundance of the 3R polytype in molybdenite together with its association with Re may explain the Re heterogeneity observed within molybdenite, but again requires that ^{187}Os migrate from the 3R polytype locations after formation for molybdenite in which the Re-Os age data indicate decoupling has occurred.

Migration of ^{187}Os within molybdenite could occur by diffusion. Assuming that the decoupling of Re and ^{187}Os in molybdenite is primarily a consequence of mobility of ^{187}Os (Stein et al., 2003), our data from both LA-MC-ICP-MS and NTIMS protocols allow for an estimate of the diffusion coefficients (D) for Os in molybdenite, using the approximation

$$D = x^2/t$$

where x is diffusive lengthscale approximation in meters, and t is the duration in seconds. However, since the temperature-time history since molybdenite formation is not adequately known for any deposit studied here, this estimate of D can only be considered an approximation reflecting the integrated temperature-time history of any molybdenite sample; we refer to this as “apparent D.”

From the LA-MC-ICP-MS Re-Os data the scale of decoupling between Re and Os in molybdenite is at least $\sim 50 \mu\text{m}$, because $100 \mu\text{m}$ diameter sampling sites of the laser are clearly decoupled. Using $50 \mu\text{m}$ as an estimate of x , and the known ages for several samples, estimates of apparent D for ^{187}Os are $\sim 2.1 \times 10^{-25}$ and $\sim 2.8 \times 10^{-26} \text{ m}^2/\text{s}$ for South Mountain Batholith (using 371 Ma) and several Archean samples (using 2800 Ma), respectively. Further, from analysis of individual portions of single grains using the NTIMS protocol (SC20W) the diffusive lengthscale is at least $\sim 5 \text{ mm}$, which yields an apparent D for ^{187}Os of $\sim 2.1 \times 10^{-21}$. Similarly, from the irreproducible Re-Os dates of A996B (Table 5) obtained using small aliquants ($< 10 \text{ mg}$) of grains 100 to $200 \mu\text{m}$ in size an apparent D of 1.1×10^{-23} is estimated.

These apparent D values for Os in molybdenite are broadly similar to those of experimentally determined estimates of D for Os in some sulfide minerals (Brenan et al., 2000; J. M. Brenan, personal communication, 2003). For example, Os diffusion in pyrrhotite, extrapolated to 300°C is $6.9 \times 10^{-25} \text{ m}^2/\text{s}$ using the data of Brenan et al. (2000). For pyrite, D values for

Os in pyrite are $\sim 2.5 \times 10^{-23} \text{ m}^2/\text{s}$ at 500°C (Brenan et al., 2000). For molybdenite, the diffusion of Re at 400°C is found to be $\sim 4 \times 10^{-22} \text{ m}^2/\text{s}$ (J. M. Brenan, personal communication, 2003).

The similarity of diffusion coefficients for Os in Fe-sulfide minerals and Re in molybdenite to the apparent D values for Os determined here for molybdenite suggests that the primary control for Re-Os decoupling in molybdenite could be diffusion. Based on the variance in charge (^{+4}Re , ^{+5}Os) and ionic radii ($^{+4}\text{Re} \sim 0.63\text{\AA}$, $^{+5}\text{Os} \leq 0.63\text{\AA}$) of Re and Os as discussed in detail by Stein et al. (2003), some difference in diffusion coefficients for Re and Os within molybdenite should be expected. However, the large magnitude of age variations reported for laser ablation Re-Os studies of single molybdenite crystals (Stein et al., 2003; Kosler et al., 2003 this study), suggests that accumulation of either Re or ^{187}Os in specific parts of molybdenite crystals, a process that is not fully understood, but may relate to ^{187}Os preferentially accumulating in crystal dislocations and defects (Stein et al., 2003). It is also possible that diffusion of Re and/or Os may lead to the formation of Re and Os monosulfide minerals, both of which are known to occur (Volborth, 1985; Hart and Kinloch, 1989; Korzhinsky et al., 1994).

A substantial body of evidence now exists to show that Re and Os can become internally decoupled within molybdenite (Stein et al., 1998a, 2001, 2003; Kosler et al., 2003 this study). However, many NTIMS Re-Os ages obtained from molybdenite indicate that the Re-Os systematics in molybdenite are not disturbed post-formation (Stein et al., 1998b, 2000; Watanabe and Stein, 2000; Selby and Creaser, 2001a,b; Selby et al., 2001, 2002; Stein and Bingen, 2002). These findings contrast with some studies in which irreproducible or inaccurate Re-Os molybdenite ages are attributed to interaction of molybdenite with an external fluid after its formation—an open system process (McCandless et al., 1993; Suzuki et al., 2000, 2001). We suggest that these contradictory findings might relate to sample preparation protocol for molybdenite, specifically hand picking (McCandless et al., 1993; Suzuki et al., 2001) versus bulk isolation of molybdenite from whole rock (Stein et al., 1998a, 2001; Selby and Creaser, 2001; Selby et al., 2004; this study). Hand picking of small quantities of coarse molybdenite is shown here to result in irreproducible and inaccurate Re-Os ages. This effect has also been demonstrated for Archean molybdenite from the Lobash deposit, for which Suzuki et al. (2000) report a discordant data set (2224 to 3337 Ma, $n = 3$), whereas Stein et al. (2001) report reproducible ages of $\sim 2692 \text{ Ma}$ ($n = 3$).

5. CONCLUSIONS

The decoupled nature of Re and ^{187}Os in molybdenite samples (Stein et al., 2001) is of critical importance in obtaining accurate and reproducible Re-Os molybdenite dates. To overcome this decoupling, sampling, sample preparation and aliquant size are key factors for Re-Os molybdenite analysis. We find that the degree of Re- ^{187}Os decoupling within molybdenite increases with increasing natural grain size and age, and possibly with decreasing Re content. We empirically establish suitable aliquant amounts of molybdenite for reproducible analysis, taken from a larger mineral separate, of molybdenite from a variety of deposit ages and types. As such, it could be

expected that geologically young, naturally fine-grained molybdenites should have low degrees of Re-¹⁸⁷Os decoupling and reliable dates could be obtained using low milligram quantities of molybdenite. For naturally coarse-grained, ancient molybdenite, many tens of milligrams is required to overcome internal Re-¹⁸⁷Os decoupling. The specific mechanism by which Re and ¹⁸⁷Os become decoupled in molybdenite is not yet established, but may relate to diffusion; “apparent” diffusion coefficients for Os presented here are similar to those determined experimentally for Re in molybdenite and Os in Fe-sulfide minerals (Brenan et al., 2000; J. M. Brenan, personal communication, 2003). Further work is required to resolve both the nature and location of Re and ¹⁸⁷Os hosted by molybdenite. The decoupled nature of Re-¹⁸⁷Os in molybdenite suggests the LA-MC-ICP-MS technique cannot be applied to Re-Os molybdenite dating as ages calculated from ¹⁸⁵Re + ¹⁸⁷Os / ¹⁸⁵Re values on ≥100 μm spot analyses yield variable and erroneous ages (cf. Stein et al., 2001, 2003; Kosler et al., 2003; this study).

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