

The remarkable Re–Os chronometer in molybdenite: how and why it works

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ABSTRACT

The Re–Os (rhenium–osmium) chronometer applied to molybdenite (MoS_2) is now demonstrated to be remarkably robust, surviving intense deformation and high-grade thermal metamorphism. Successful dating of molybdenite is dependent on proper preparation of the mineral separate and analysis of a critical quantity of molybdenite, unique to each sample, such that recognized spatial decoupling of ^{187}Re parent and ^{187}Os daughter within individual molybdenite crystals is overcome. Highly precise, accurate and reproducible age results are derived through isotope dilution and negative thermal ion mass spectrometry (ID-NTIMS). Spatial decoupling of parent–daughter precludes use of the laser ablation ICP-MS microanalytical technique for Re–Os dating of molybdenite. The use of a reference or control sample is necessary to establish laboratory credibility and for interlaboratory comparisons. The Rb–Sr, K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ chronometers are susceptible to chemical and thermal disturbance, particularly in terranes that have experienced subsequent episodes of hydrothermal/magmatic activity,

and therefore should not be used as a basis for establishing accuracy in Re–Os dating of molybdenite, as has been done in the past. Re–Os ages for molybdenite are almost always in agreement with observed geological relationships and, when available, with zircon and titanite U–Pb ages. For terranes experiencing multiple episodes of metamorphism and deformation, molybdenite is not complicated by overgrowths as is common for some minerals used in U–Pb dating (e.g. zircon, monazite, xenotime), nor are Re and Os mobilized beyond the margins of individual crystals during solid-state recrystallization. Moreover, inheritance of older molybdenite cores, incorporation of common Os, and radiogenic Os loss are exceedingly rare, whereas inheritance, common Pb and Pb loss are common complications in U–Pb dating techniques. Therefore, molybdenite ages may serve as point-in-time markers for age comparisons.

Terra Nova, 13, 479–486, 2001

Introduction

In the last decade the Re–Os chronometer as applied to molybdenite (MoS_2) has met with renewed interest by many working groups. During this period a large number of highly erroneous molybdenite ages stemming from analytical error were blamed on the Re–Os chronometer. As a result, a long list of tests (e.g. infrared microscopy, back-scattering electron imagery, microprobe analysis, X-ray diffraction) was devised to establish the ‘suitability’ of a particular molybdenite sample for Re–Os dating (e.g. McCandless *et al.*, 1993). In addition, the inability to reproduce ages for a single molybdenite sample has been used to discredit the chronometer for molybdenite dating (e.g. Suzuki *et al.*, 2000, 2001). The lack of an NIST-certified molybdenite standard has also hampered progress in that there is no mechanism for a laboratory to check their analytical results against a known or accepted

value. In turn, this easily permits the conclusion that the Re–Os chronometer in molybdenite is fallible when erroneous or impossible age results are obtained in a laboratory. Based on our Re–Os dating of multiple (spatially discrete) molybdenite samples within a deposit or district, and our dating of molybdenite from more than 100 localities worldwide, we find that the Re–Os chronometer is robust under almost all geological conditions.

Molybdenite: a special case

Molybdenite (MoS_2) presents a special case for the Re–Os chronometer. It incorporates into its structure significant Re that is almost always well into the p.p.m. range and can be several per cent. In contrast, molybdenite incorporates essentially no Os upon crystallization so that all measured Os is daughter ^{187}Os , produced by the *in situ* decay of parent ^{187}Re . The ratio of Re to common Os in molybdenite is commonly $> 10^6$. Since there is essentially no initial or common Os to take into account, the age (t) can be calculated from the basic age equation, where λ is the ^{187}Re decay constant: $^{187}\text{Os} = ^{187}\text{Re} (e^{\lambda t} - 1)$. The most recently

determined decay constant for ^{187}Re is $1.666 \times 10^{-11} \text{ years}^{-1}$ (Smoliar *et al.*, 1996), which corresponds to a ^{187}Re half-life that is about 10 times the age of the earth. Because we calibrate against the same natural Re and Os standards used to determine the Smoliar *et al.* decay constant (Morgan *et al.*, 1995), we can take advantage of the reduced 0.31% uncertainty. The decay constant and its uncertainty in most isotopic systems is the primary source of analytical error and the primary limitation on accuracy for radioisotopic ages (Begemann *et al.*, 2001; Schmitz and Bowring, 2001). Our Re–Os ages have associated errors of 0.32–0.38%, with most of this derived from the uncertainty in the ^{187}Re decay constant.

Successful radiometric dating requires that the isotopic system has remained closed. That is, neither parent nor daughter have left or have been added to the system through alteration, metamorphism, fluid fluxing or any other processes acting on the mineral through geological time. Therefore, the parent measured today (^{187}Re) is essentially the same as was present when the mineral formed except for radioactive decay, and all of the radiogenic daughter (^{187}Os) was

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derived from the parent ^{187}Re isotope. Small amounts of ^{187}Os from common Os in molybdenite and from analytical blanks are insignificant compared with the extraordinarily high levels of naturally accumulated radiogenic ^{187}Os , even after a relatively short passing of geological time for high Re molybdenites.

Vanishingly small amounts of common Os in molybdenite and in analytical blanks are monitored, however, using ^{192}Os (the most abundant isotope of Os). We monitor and correct for common Os using an assumed initial ratio and a single isotope Os spike (^{190}Os), rather than spiking molybdenite with natural Os which does not permit a check on common Os. Our isotope dilution algorithm for determining radiogenic ^{187}Os corrects for an almost always insignificant amount of common ^{187}Os , using an assumed isotopic composition ($^{187}\text{Os}/^{188}\text{Os}$) for that common Os. In practical terms, the assumed $^{187}\text{Os}/^{188}\text{Os}$ does not significantly affect the calculated radiogenic ^{187}Os concentration because common Os, and particularly common ^{187}Os , is present in extremely low abundance relative to radiogenic ^{187}Os , and geologically reasonable initial $^{187}\text{Os}/^{188}\text{Os}$ ratios are far less than 10 (Fig. 1). The $^{187}\text{Os}/^{188}\text{Os}$ ratios measured in our blanks in the molybdenite laboratory are usually < 1 , but occasionally are

very radiogenic. The ^{187}Os concentrations in the blank, however, do not exceed 3 pg, and for Re they are less than 20 pg. We emphasize that common Os is very poorly determined during molybdenite analyses because in order to determine the total ^{187}Os with a high degree of precision we must grossly overspike with respect to ^{192}Os . This results in poorly determined $^{190}\text{Os}/^{192}\text{Os}$ with a very large error magnifier for the isotope dilution equation for common Os. This does not alter the fact, however, that measured common Os abundances are invariably near blank levels.

Factors controlling Re concentrations in molybdenite

Numerous early workers speculated that molybdenite from certain geological environments, forming at certain temperatures, and/or correlating with the 2H vs. 3R polytype could be related to measured Re concentrations (e.g. Paganelli, 1963; Giles and Schilling, 1972; Ayres, 1974). While we have observed craton-specific ranges for Re concentrations for certain deposit types, the wide variation in molybdenite Re concentrations in the porphyry–magmatic environment may be attributed to simple mass balance phenomena. For example, porphyry Cu–Mo deposits typically contain hundreds to thousands of

p.p.m. Re, whereas Climax-type porphyry Mo deposits are characterized by Re concentrations in the low to single digit p.p.m. range (AIRIE, published and unpublished data). Since essentially all of the Re budget will be taken up by molybdenite, the limited presence of molybdenite in a porphyry Cu–Mo system results in very high Re concentrations relative to Climax-type systems where the quantity of molybdenite is enormous, and the Re concentrations are volume-diluted. Although a few early workers noted the affinity for Re with Cu deposits or with Cu–Mo porphyry deposits (e.g. Giles and Schilling, 1972), limited explanation was offered. We propose a simple mass balance explanation for the large difference in Re concentrations observed in porphyry Cu–Mo deposits vs. porphyry Mo deposits.

In terranes where temporally distinct ore-forming events have been superimposed over a long geological history, Re concentrations in different molybdenite populations can be a key factor in fingerprinting spatially overlapping ore-forming events and, potentially, their relative economic importance. Moreover, we suggest that the Re concentration in molybdenite provides clues for the origin of a deposit (Stein *et al.*, 2001). For example, deposits that involve mantle underplating or metasomatism, or that involve melting of mafic or ultramafic rocks as part of their genesis, may be expected to have overall higher Re concentrations in associated molybdenites. In contrast, ore deposits whose origin is related to intermediate crustal rocks or organic-poor sedimentary sequences may be expected to have lower Re concentrations in associated molybdenites. As discussed earlier, the molybdenite volume variable must also be taken into consideration. The Re concentration in molybdenite provides evidence for, but not necessarily proof of, deposit genesis.

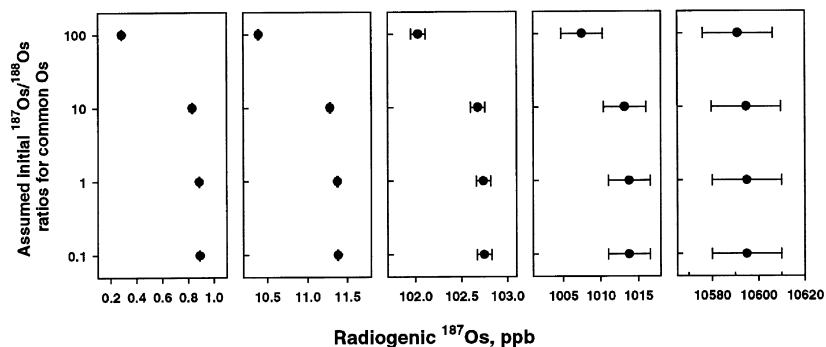


Fig. 1 The effect of varying the assumed initial $^{187}\text{Os}/^{188}\text{Os}$ ratio in the common Os on the calculated radiogenic ^{187}Os is shown for five molybdenites analysed at AIRIE. These five molybdenites have ^{187}Os concentrations, shown with their 2-sigma error bars that span more than four orders of magnitude. The assumed $^{187}\text{Os}/^{188}\text{Os}$ initial ratio is shown over three orders of magnitude and, except for geologically unreasonable ratios (> 10), has no effect on the calculated radiogenic ^{187}Os . The majority of molybdenites we have analysed have ^{187}Os greater than 20 p.p.b. Common Os abundances used in these calculations vary from 0.06 to 0.75 p.p.b., but it must be emphasized that these quantities are very poorly determined, as described in the text. It is significant that the higher quantities of calculated common Os can be tied to higher ^{187}Os samples, where more spike was required.

Sampling procedures, standards and analytical techniques

The reproducibility and accuracy of a molybdenite age is closely tied to grain size and the amount of sample analysed. Fine-grained, thoroughly homogenized samples are critical for accurate age results because Re and

Table 1 Comparison of Re–Os ages for different sample sizes of AIRIE in-house molybdenite standard A996D

AIRIE run	Sample weight (g)*	Re, p.p.m.	¹⁸⁷ Os, p.p.b.	Re–Os ages, Ma
CT-376	0.05613	17.369 (9)	513.7 (7)	2760 ± 10
CT-377	0.05903	17.269 (9)	510.9 (3)	2761 ± 9
CT-374	0.00524	16.624 (34)	535.5 (8)	3000 ± 11
CT-375	0.00392	17.515 (39)	520.4 (9)	2773 ± 10

*A sample size > 50 mg is required to safely overcome Re–¹⁸⁷Os decoupling at – 70 mesh in this sample. Illustration is for fine-grained (– 70 mesh) Aittojärvi molybdenite A996D (aplite granite), Finland. All ages were obtained by Carius tube digestion of molybdenite and all errors are 2σ absolute.

¹⁸⁷Os may become spatially decoupled in molybdenite. Naturally occurring fine-grained samples are therefore easiest to work with, as the mineral separation process automatically homogenizes the sample. Coarse-grained molybdenites, on the other hand, require extensive processing to create a finer grained homogeneous separate. The decoupling of Re and ¹⁸⁷Os was first intimated by experimenting with age reproducibility on fine-grained molybdenite separates and coarse-grained molybdenite crystal fragments from the same localities (Stein *et al.*, 1998a). Re–Os ages from single pieces of molybdenite crystals or a few coarse grains did not reproduce well, whereas fine-grained mineral separates reproduced well and gave geologically reasonable age results. Subsequently, we have documented Re–¹⁸⁷Os decoupling on the micro-metre scale in laser ablation (LA) ICP-MS traverses across molybdenite crystals from the same locality as our fine-grained molybdenite separate used as an in-house standard (A996B, tonalite–aplite host, Aittojärvi, Finland). The LA ICP-MS spot ages along traverses yield highly variable Re–Os ages of 0.5–4.0 Ga, which we suggest result from ¹⁸⁷Os mobility within the molybdenite structure. These results demonstrate that LA ICP-MS cannot be used as a dating tool for molybdenite, as has been advocated by some workers (e.g. Kosler *et al.*, 2000). For older molybdenites and particularly those that have experienced a complex geological history, we note that ¹⁸⁷Os may collect in crystal defects. We suggest that Re remains fixed in the Mo site, although significant variations in Re concentration are possible during crystal growth. The erroneous age results (0.5–4.0 Ga) using LA ICP-MS are a stark contrast to the highly reproducible Re–Os ages obtained by Carius tube dissolution and ID-NTIMS

analyses of our fine-grained A996B Aittojärvi in-house standard (weighted mean age, excluding uncertainty in ¹⁸⁷Re decay constant for each run, is 2809 ± 1.7 Ma, *n* = 15, MSWD = 0.062). However, the decoupling of Re and ¹⁸⁷Os in molybdenite can be captured if too small a sample size of the Aittojärvi fine-grained mineral separate is used (< 50 mg). Reproducibility is then compromised as illustrated in Table 1 for a younger molybdenite associated with Aittojärvi (A996D). The positive correlation between grain size and sample size needed for dating is further illustrated in our use of another in-house standard (HLP-5) that consists of a well-homogenized molybdenite powder from a mill in China (Stein *et al.*, 1997). In the case of a powder, smaller sample sizes (25 mg) yield highly reproducible results (Markey *et al.*, 1998). In fact, sample sizes for HLP-5 into the single mg range have yielded good results (Selby and Creaser, 2001).

To summarize, successful dating of molybdenite is dependent on a balance between amount of molybdenite, grain size of the molybdenite and the particular geological history experienced by that sample. For coarse-grained molybdenites, we used to chop crystals finely with a sharp razor blade, a tedious and time-consuming task. Now we use a diamond-tipped slow-speed mini-drill to create a powder from numerous random points on coarse-grained samples of molybdenite. This approach to mineral separation produces accurate and reproducible age results. It is especially useful on samples where the molybdenite occurs as fine grey wisps intergrown with quartz or other silicate. A drilled mixture of molybdenite + silicate dilutes the Re and precludes determination of its concentration in the pure molybdenite, but does not affect the age as silicates have insignificant Re and ¹⁸⁷Os relative to

molybdenite. As discussed earlier (Fig. 1), the contribution of common ¹⁸⁷Os from silicates or any other source can be estimated by monitoring the most abundant isotope of common Os (¹⁹²Os), and has proven insignificant. With proper sample preparation and sample size, we find that molybdenites provide geologically reliable and analytically reproducible ages using the Re–Os method.

Standards, replicating results, molybdenite isochrons

The ability of a laboratory to reproduce standard data is critical to establishing credibility in that laboratory and for interlaboratory comparison. We realized the need to establish in-house molybdenite control samples or in-house standards (e.g. Markey *et al.*, 1998) as there are no NIST-certified molybdenite standards available for Re–Os. These in-house standards are part of our routine analytical output to keep a constant monitor on our internal reproducibility. A demonstrated ability to replicate a control sample is necessary before attributing disparate replicates on geological samples to problems with the Re–Os chronometer. Recently, a discordant Re–Os data set for a *single* molybdenite sample from the Lobash Mo deposit in Russia (Fig. 2) led Suzuki *et al.* (2000) to claim that the Re–Os chronometer in molybdenite is disturbed. We compare their published Lobash data with our Re–Os results for Lobash molybdenite (Table 2). Our samples represent two geographically distinct localities from the granite-related Lobash vein and stockwork Mo deposit (Pokalov and Semenova, 1993). Our Re–Os ages, which include a replicate analysis for one sample by *two* different techniques, can be convincingly used to argue for the highly robust character of the Re–Os chronometer in moly-

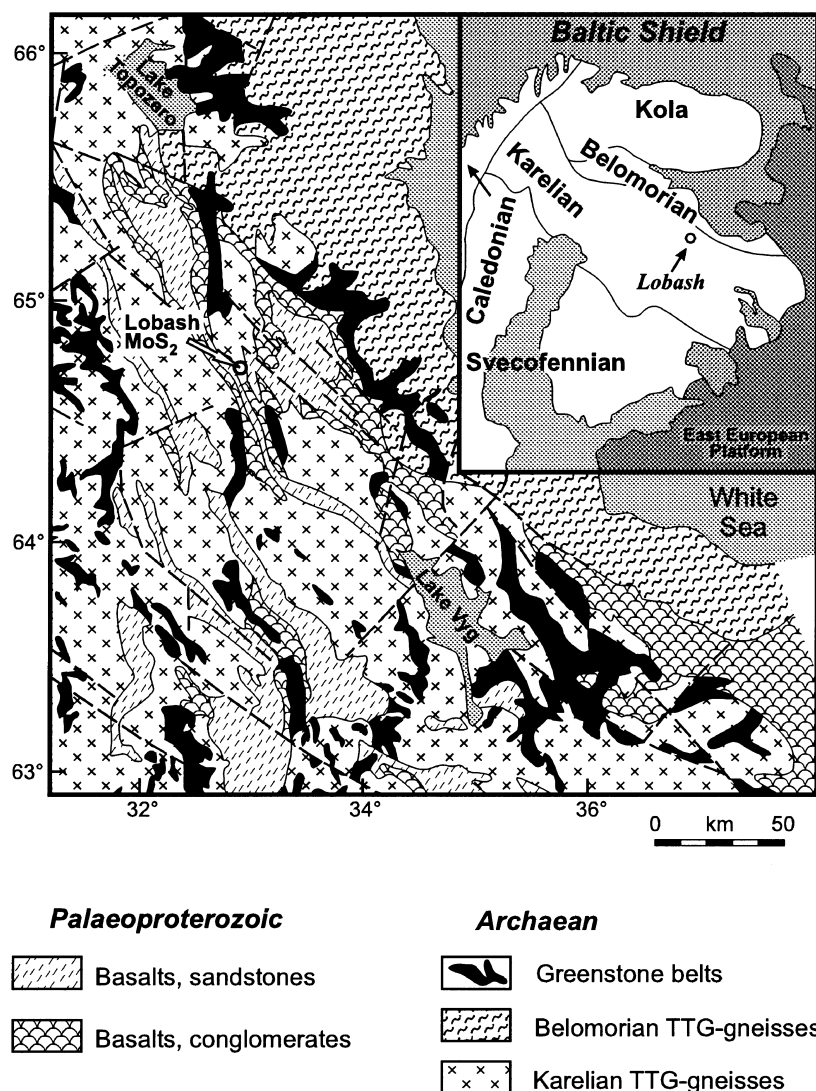


Fig. 2 Location of the Lobash molybdenite deposit (Pokalov and Semenova, 1993), Karelian granite–greenstone terrane, western Russia, Baltic Shield. Figure modified from Puchtel *et al.* (2001).

bdenite. Although we do not have accompanying U–Pb data for the intrusion affiliated with our analysed molybdenite samples, age estimates for intrusions in the Lobash area, based on U–Pb and Pb–Pb dating, range from about 2.6 to 2.8 Ga (Ovchinnikova *et al.*, 1995; Gorelov *et al.*, 1997; Puchtel *et al.*, 1998; Belyatsky *et al.*, 2000).

To illustrate the robustness of Re–Os results for molybdenite, correct treatment and plotting of the Re–Os isotopic data is essential (Fig. 3). The strongest measure of closed-system behaviour in a molybdenite sample suite is isochrony on a ^{187}Re – ^{187}Os

diagram (Stein *et al.*, 1998b), ideally based on different but genetically related molybdenite samples that comprise a linear regression with low uncertainty and low MSWD (Mean Squared Weighted Deviates, a measure of scatter). Molybdenite data should never be displayed on the more traditional $^{187}\text{Re}/^{188}\text{Os}$ – $^{187}\text{Os}/^{188}\text{Os}$ plot, as there is essentially no common Os (i.e. no ^{188}Os) in molybdenite, and any detected most likely originates from the analytical blank. On a ^{187}Re – ^{187}Os isochron plot, the ^{187}Os intercept (initial ^{187}Os) should be zero, as there is no common or initial ^{187}Os in molybdenite. If there is no excess

geological scatter and there is some spread in the data points, the uncertainty on a molybdenite isochron age should be less than the uncertainty on individual model ages for single molybdenite samples.

We have also determined that other sulphides (e.g. pyrite, tennantite, arsenopyrite, chalcopyrite) may have molybdenite-like Os isotopic compositions in that they may be dominated by radiogenic ^{187}Os (Stein *et al.*, 2000; Arne *et al.*, 2001). Such samples have been named LLHR (low-level, highly radiogenic), and should also be treated in ^{187}Re – ^{187}Os plotting space if meaningful age results are to be obtained (Stein *et al.*, 2000). In contrast to molybdenite (Fig. 1), however, the assumed initial $^{187}\text{Os}/^{188}\text{Os}$ for LLHR samples may have a small effect on the calculated age, as LLHR samples may contain measurable common Os. Data tables for LLHR samples should show the radiogenic ^{187}Os and common Os as two data entries.

Proterozoic and Archaean terranes provide the best scenario for detecting disturbances in the Re–Os chronometer in molybdenite because of their complex geological and tectonic histories that offer opportunities for open-system behaviour. For this reason, we have focused much of our early work in Proterozoic–Archaean terranes where we are most likely to uncover disturbances in Re–Os systematics if present. The chronometer is now shown to be extraordinarily robust and lacking disturbance, even through granulite facies metamorphism and intense deformation (e.g. Stein *et al.*, 1999; Raith and Stein, 2000; Bingen and Stein, 2001). Solid-state recrystallization of molybdenite in response to deformation does not result in loss of Re or Os. Both elements may be redistributed within the crystal, but both are preferentially retained in the molybdenite relative to surrounding silicate or aqueous phases. Trace amounts of ^{187}Os may be taken up by other adjacent sulphides, but we have found that the amount lost from the molybdenite is not detectable relative to the high ^{187}Os concentrations. Ages for adjacent low Re–Os sulphides, however, may be seriously disturbed, yielding impossibly old ages. We suggest that Re and Os are liberated only by complete chemical dissolution of the

Table 2 Comparison of Re–Os ages for molybdenite from the Lobash Mo deposit, western Russia

Suzuki <i>et al.</i> (2000)* Re–Os ages, Ma	This study† Re, p.p.m.	This study† ¹⁸⁷ Os, p.p.b.	AIRIE† Re–Os ages, Ma	This study Analytical Method
2582 ± 54	23.470 (8)	677 (1)	2694 ± 9	Carius Tube
2224 ± 60	39.967 (25)	1152 (3)	2692 ± 11	Alkaline Fusion
3337 ± 83	22.147 (16)	638 (2)	2691 ± 11	Alkaline Fusion

*Re–Os data by microwave digestion method as described in Suzuki *et al.* (1992). †All errors are 2σ absolute; decay constant uncertainty (± 0.31%, Smoliar *et al.*, 1996) included in AIRIE ages, but not in data reported by Suzuki *et al.* (2000).

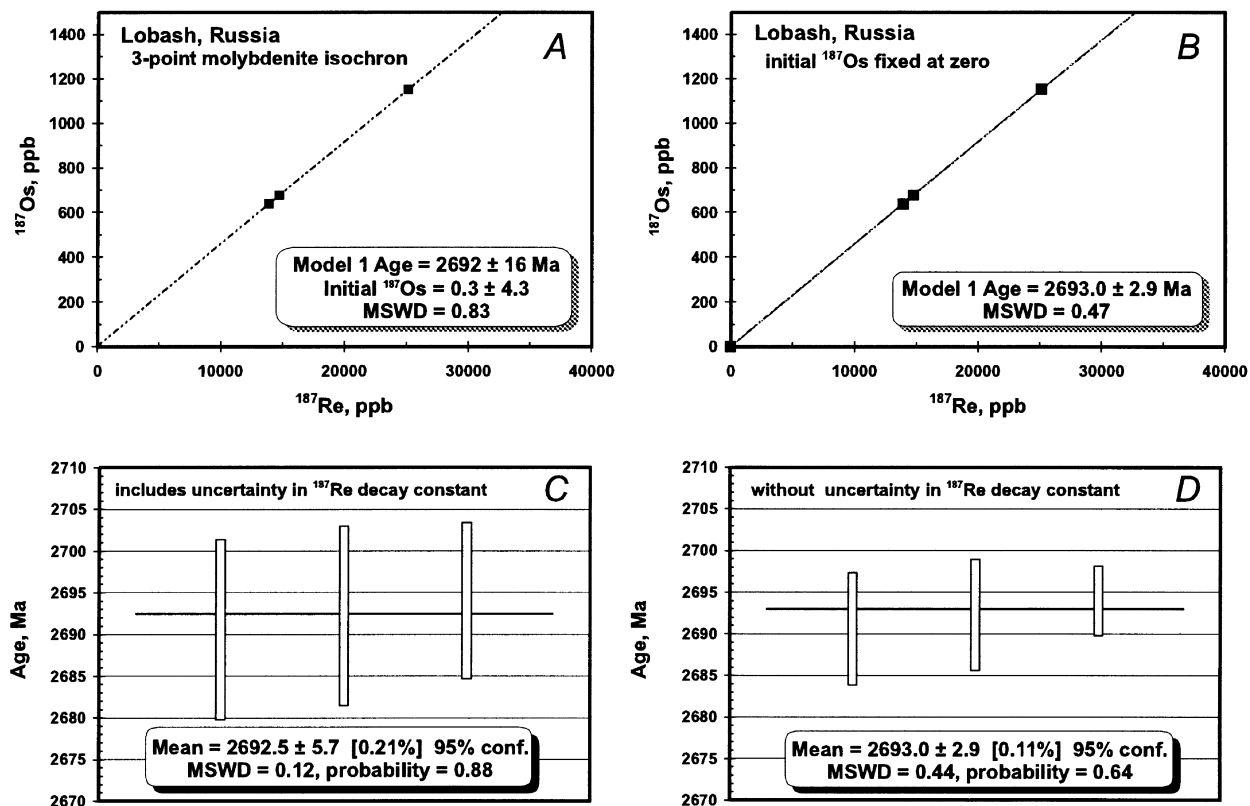


Fig. 3 Plotting possibilities for Re–Os data from molybdenites, using the Lobash results as an example. (A) An isochron plot utilizing ^{187}Re – ^{187}Os space, noting that molybdenites should never be plotted using the traditional $^{187}\text{Re}/^{188}\text{Os}$ – $^{187}\text{Os}/^{188}\text{Os}$ plot (Stein *et al.*, 2000). By regression of only three points, an isochronous data set is demonstrated with an intercept of 0.3 ± 4.3 for initial ^{187}Os , obtained on a very long projection to the lower left. The slight increase in the isochron age uncertainty, relative to the uncertainties for model ages (Table 2) is due to the limited number of data points and the fact that two points lie very close together on the line. This plot provides the most robust treatment of Re–Os isotopic data for molybdenites. (B) A four-point isochron plot derived by pinning the initial ^{187}Os at zero (implicit in individual model age calculations, and confirmed with isochron A). The origin essentially provides a fourth point on the isochron, thereby reducing the 2-sigma error significantly. The age remains the same. (C) Using the weighted average approach for individual model ages, each with their full analytical uncertainty, a weighted mean age derived from this method supports the ages obtained for isochrons A and B. (D) When two or more model ages from a single generation of molybdenite deposition or relative ages of several molybdenite samples are compared, removal of the uncertainty in the ^{187}Re decay constant, attached to each model age, provides a more correct treatment of the data. In effect, the uncertainty in the ^{187}Re decay constant only serves as an error magnification constant during comparison, as is evident in the decrease in age uncertainty and increase in MSWD from plot C to D. The decay constant uncertainty must be included when reporting a single Re–Os age or when comparing age data from other isotopic systems. The Isoplot plotting program was used (Ludwig, 1999).

molybdenite. The radiometric clock is set only by growth of entirely new molybdenite crystals.

In some cases the Re–Os chronometer in molybdenite may outperform

U–Pb in its ability to record and discern temporally close episodes of mineralization (Torrealdy *et al.*, 2000). For terranes with complex metamorphic and deformational his-

stories, the U–Pb system in commonly dated minerals may record overgrowths on inherited cores (e.g. Pidgeon *et al.*, 1996). This has the advantage of providing information

on original source material, subsequent events and their duration, and cooling histories (e.g. Hawkins and Bowring, 1999; Essex and Gromet, 2000; Graessner *et al.*, 2000; Hoskin and Black, 2000; Viskupic and Hodges, 2001). But the U–Pb system may also experience complications with high or excess common Pb and subsequent Pb loss (e.g. Zhang and Schäfer, 1996; Krohe and Wawrzenitz, 2000), although there are special cases where the U–Th–Pb systematics may be shielded from exchange and loss (e.g. Montel *et al.*, 2000). Inheritance, overgrowths, common Os or loss of radiogenic Os are exceedingly rare in molybdenite. It is unlikely that U–Pb dating of minerals such as monazite or xenotime will retain ages of older geological events since, in the presence of H₂O and CO₂ during any subsequent events, recrystallization is highly probable (e.g. Bingen and van Breemen, 1998; Corfu and Stone, 1998). Therefore, these minerals will take on younger ages regardless of their initial association, while molybdenite will preserve the true age of mineralization. Only under conditions of dry metamorphism will the U–Pb chronometer remain intact in minerals such as zircon, titanite and monazite, and at very high closure temperatures (e.g. Villa, 1998; Romer and Rötzler, 2001). Dry conditions are not normally the case in the ore-forming environment.

Chronometry in sulphide ore-forming environments

Igneous processes can be dated with many tools that include U–Th–Pb, Sm–Nd, Rb–Sr, K–Ar and ⁴⁰Ar/³⁹Ar. However, Re–Os is the only method to directly date sulphide (or oxide) mineralization (e.g. Stein *et al.*, 1998b, 2000; Morgan *et al.*, 2000), and the only chronometer in which the parent isotope substitutes directly for a major element in the sulphide structure. An argon-based chronometer (K–Ar and ⁴⁰Ar/³⁹Ar) is subject to thermal disturbance or resetting and the Rb–Sr chronometer is easily affected by chemical alteration (e.g. potassic alteration). In large ore-forming systems, where multiple, temporally close ore-forming events are common, use of an argon-based chronometer will generally record the passing of the last

event below the blocking temperature of the mineral analysed, usually a mica or feldspar. This leads to a diffuse spread in argon-based ages that are on the whole too young. In contrast, Re–Os ages will provide the correct age of ore formation, and can suggest or prove an association with a magmatic or metamorphic event dated by U–Pb (e.g. Stein *et al.*, 1999). An argon-based chronometer should not serve as a measure of accuracy for molybdenite Re–Os ages in the magmatic–hydrothermal environment, as has been done in the past (Ishihara *et al.*, 1989; McCandless and Ruiz, 1993; McCandless *et al.*, 1993; Santosh *et al.*, 1994). In particular, closely spaced magmatic–hydrothermal events in the porphyry setting will produce an array of argon-based ages that simply reflect a sequence of delayed isotopic closures, related to local thermal gradients. Similarly, argon-based ages in terranes that have been overprinted by dynamic metamorphism should not be used to describe primary mineralizing events. In the ore-forming environment, the Re–Os chronometer is sustained, while the ⁴⁰Ar/³⁹Ar, K–Ar and Rb–Sr chronometers may be moderately or seriously disturbed (Watanabe and Stein, 2000). A higher closure temperature for Re–Os in molybdenite relative to K–Ar has been suggested in the ore-forming environment (e.g. Suzuki and Masuda, 1993; Suzuki *et al.*, 1996).

Conclusions

The Re–Os chronometer in molybdenite is remarkably robust and is sustained through high-grade metamorphism and deformation. It exceeds the reliability of argon-based chronometers and the Rb–Sr chronometer in locking in the age of mineralization in multiply overprinted terranes. In conjunction with the U–Pb chronometer, Re–Os dating of molybdenite provides powerful age results that may be used to pinpoint events on the geological time scale. The proper preparation of the molybdenite mineral separate is key to producing geologically accurate ages, and the sample size must be large enough so that any spatial decoupling of Re and ¹⁸⁷Os is not captured. Coarser grained molybdenites (e.g. rosettes and large crystals) require larger sample amounts than

finer grained occurrences of molybdenite. For age determination, dilution of molybdenite Re and ¹⁸⁷Os concentrations by silicate minerals is permissible. When using Re concentration data to predict deposit genesis, any dilution of the analysed molybdenite by silicate phases must be taken into account. The LA ICP-MS method will not reliably produce meaningful age results on molybdenite because Re and ¹⁸⁷Os may be decoupled on the scale of the laser spot.

Acknowledgments

The molybdenite samples from Lobash were provided courtesy of Peter Sorjonen-Ward and Anatoly Larin. Discussions with Victor Melezhik and Igor Puchtel on Lobash, and with Bernard Bingen on U–Pb geochronology are much appreciated. Olavi Kouvo provided the Aittojärvi molybdenite mineral separates and Du Andao kindly provided the HLP-5 molybdenite powder, both used as in-house standards at AIRIE. We thank journal reviewers Bruce Schaefer, Bernard Peucker-Ehrenbrink and Gerhard Brüggemann for their constructive comments and suggestions. National Science Foundation awards EAR-9706185 and EAR-0087483 supported this work.

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Received 23 August 2001; revised version accepted 21 December 2001