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Subgrain-scale decoupling of Re and ^{187}Os and assessment of laser ablation ICP-MS spot dating in molybdenite

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Abstract—Reproducibility of Re-Os molybdenite ages depends on sample size and homogeneity, suggesting that Re and Os are decoupled within individual molybdenite crystals and do not remain spatially linked over time. In order to investigate the Re-Os systematics of molybdenite at the subgrain (micron) scale, we report LA-ICP-MS Re-Os ages for an Archean molybdenite crystal from Aittojärvi, Finland, analyzed in situ in a white aplite matrix. A related Aittojärvi molybdenite (A996D), in the form of a very fine-grained mineral separate, is used as one of our in-house NTIMS standards, and thus its age of 2760 ± 9 Ma is well established. Measurements of $(^{187}\text{Re} + ^{187}\text{Os})/^{185}\text{Re}$ on micron scale spots along 200 μm traverses across the crystal yield a wide range of ages demonstrating that, in this case, microsampling of molybdenite does not produce geologically meaningful ages. Experimentation with mineral separations and sample size over a 7-yr period predicted that this would be the outcome. We suggest that ^{187}Os is more likely to be the mobile species, based on its charge and ionic radius, and that ^{187}Os becomes decoupled from parent ^{187}Re with time on the micron and larger scale. Incompatible charge and ionic radius for Os ions formed during reduction of molybdenite-forming fluids may explain the widely observed absence of common (initial) Os in molybdenite. Geologically accurate ages for molybdenite can only be obtained for fully homogenized crystals (or crystal aggregates) so that any post-crystallization ^{187}Re - ^{187}Os decoupling is overcome.

A growing number of geologically accurate ID-NTIMS ^{187}Re - ^{187}Os ages for homogenized molybdenite suggest that postcrystallization mobility of radiogenic ^{187}Os must be limited to within the molybdenite mineral phase. We suggest that radiogenic ^{187}Os may be stored in micron scale dislocations, kink bands, and delamination cracks produced by deformation, and that the unusual structure and deformation response of molybdenite results in an increased chemical stability in this mineral. Migration of ^{187}Os into adjacent silicate phases is highly unlikely, but other contacting sulfides may take in Os. In an example from a Proterozoic skarn deposit at Pitkäranta (western Russia), we demonstrate minor loss of radiogenic ^{187}Os from molybdenite and a corresponding gain in adjacent chalcopyrite such that the molybdenite age is not perceptibly disturbed, whereas the resulting chalcopyrite ages are impossibly old. Therefore, it is inadvisable to perform Re-Os analytical work on any sulfide in contact or intimate association with molybdenite. In addition to large errors in the age, if the isochron method is employed, initial $^{187}\text{Os}/^{188}\text{Os}$ ratios could be erroneously high, leading to seriously errant genetic interpretations. Copyright © 2003 Elsevier Ltd

1. INTRODUCTION

Recently, use of microanalytical techniques such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), ion microprobe, and electron microprobe have received much attention as methods for analyzing micron scale domains, particularly in isotopically robust minerals such as zircon and monazite. Acquiring geologically accurate ages by spot analysis is particularly useful for dating orogenic events recorded in mineral overgrowths formed at different geologic times. The different methods carry strengths and weaknesses based on underlying assumptions and technical limitations. Successful dating by LA-ICP-MS requires that the dated domains fully retain parent and daughter isotopes at the micron scale. Using data from both LA-ICP-MS and isotope dilution-negative thermal ionization mass spectrometry (ID-NTIMS) studies, we demonstrate that for molybdenite the assumption of

closed ^{187}Re - ^{187}Os isotope systematics, fundamental for radiometric dating, is not met at the micron scale.

We first recognized postcrystallization decoupling of ^{187}Re - ^{187}Os when Re-Os ages from single fragments and thin layers of molybdenite crystals could not be reliably reproduced, giving erratic and inaccurate ages in both older and younger directions (Stein et al., 1998a). In contrast, a fine-grained mineral separate produced by homogenizing large molybdenite crystals or by utilizing naturally occurring fine-grained molybdenite yielded reproducible and geologically consistent age results. This led to the concept of a “whole molybdenite” sample, much like the “whole rock” concept, designed to overcome any parent-daughter decoupling through proper sample preparation procedures (Stein et al., 1998a, 2001). The Re-Os dating of molybdenite by ID-NTIMS using a “whole molybdenite” approach to mineral separation provides reliable ages that match geologic constraints and available U-Pb ages (e.g., Stein et al., 1997, 2001; Watanabe and Stein, 2000; Selby and Creaser, 2001a,b).

Molybdenite is stable over a wide range of geologic conditions and is found in a wide range of geologic environments. Its

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^{187}Re - ^{187}Os systematics have been shown to survive high-grade regional and contact metamorphism (Raith and Stein, 2000; Bingen and Stein, 2003), and ductile-brittle deformation (Stein and Bingen, 2002). The most robust way to date a geologic event accurately by molybdenite Re-Os geochronology is to analyze several discrete samples that are representative of that event. Alternatively, several different mineral separates can be made and analyzed from a single molybdenite-bearing sample or vein. In either case, isochronous behavior of the data in ^{187}Re - ^{187}Os space and a corresponding initial ^{187}Os of essentially zero (as determined by the isochron intersection with the y-axis) documents an isotopically closed system that preserves the primary age of molybdenite deposition (Stein et al., 1997, 1998b, 2000, 2001). Over 700 analyses in the AIRIE labs at CSU demonstrate that molybdenites, with rare exception, exhibit neither isotopic disturbances nor resetting (unpublished data and references above). The greatest possibility for complex (yet remarkably consistent) age results exists for molybdenites associated with large shear zones where several generations of molybdenite may form during temporally disparate movements on the shear zone (Hannah et al., 2002; Requia et al., in press). A thorough field understanding, careful petrography, and replicate analyses are essential, but further studies are needed to understand the development and preservation of multiple generations of molybdenite deposition in shear zones. In summary, ^{187}Re - ^{187}Os systematics in molybdenite remain intact within the mineral when it is subjected to deformation or recrystallization during metamorphism (Stein et al., 2001; Stein and Bingen, 2002), even at granulite facies (Bingen and Stein, 2003).

Spot dating by U-Pb methods has been successful for several minerals that record geologic events by renewed crystal growth, forming spatially and chemically discrete cores and overgrowths. In contrast, molybdenite overgrowths are exceedingly rare (we recognize three cases in about five hundred). New growth of molybdenite appears to result from chemical precipitation of MoS_2 as discrete new crystals, not as overgrowths. While epitaxial overgrowths may form and may be difficult to detect optically, in hundreds of analyses of molybdenites from discrete geologic settings, we have seen clear petrographic evidence for molybdenite overgrowths only three times. These three examples, all from relatively young, shallow plutons in long-lived batholithic systems, show erratic ages that are older than the hosting intrusion as determined by U-Pb (zircon or zircon rims). We suggest that, in these cases, sampling of variable amounts of older molybdenite core and younger overgrowth produces erratic age results in the older direction. Petrographic study is key to documentation of this phenomenon.

This study tests the qualitative "whole molybdenite" concept by spot dating a molybdenite crystal at the micron scale using LA-ICP-MS. The molybdenite crystal analyzed is from the same location as one of our well-characterized, fine-grained in-house molybdenite standards (A996D, Aittojärvi, Finland; Stein et al., 2001), and thus its ID-NTIMS Re-Os age of 2760 ± 9 Ma is very well constrained. In this paper, we provide a literature review of molybdenite crystal chemistry and behavior of constituent elements as a framework for understanding potential Re and Os mobility within molybdenite grains and exchange with adjacent minerals. In addition, we document

Re-Os interaction between molybdenite and adjacent chalcopyrite in a skarn deposit, based on ID-NTIMS analyses. There are now multiple lines of evidence to show that the Re-Os geochronometer in molybdenite is remarkably robust even under extreme temperature-pressure conditions, with exceedingly rare exchange (gain or loss) of either parent or daughter isotope with surrounding material. As suspected, however, ^{187}Os (and perhaps Re) is mobile within molybdenite grains such that parent and daughter isotopes are decoupled on the micron scale precluding spot dating by LA-ICP-MS. This advancement in our understanding of Re and Os behavior in molybdenite, coupled with a history of robust age results for molybdenite at AIRIE, and more recently University of Alberta, suggests that a decade of citations of unreliability in molybdenite dating is tied to analytical difficulties, and not to the Re-Os chronometer in molybdenite.

2. SPECIATION OF Mo, Re, W, AND Os IN MAGMATIC-HYDROTHERMAL SYSTEMS

Molybdenite (MoS_2) is now recognized as an important mineral for direct dating of many sulfide deposits using the ^{187}Re - ^{187}Os method (e.g., Stein et al., 1997; Selby and Creaser, 2001a), and thus a closer examination of the geochemical relationships between Mo, Re, and ^{187}Os is warranted. It has been known for decades that Re readily substitutes for Mo in molybdenite and that Re contents can be on the order of several hundred ppm or even into the percent range (e.g., Fleischer, 1959; Terada et al., 1971; Stein et al., 2001). In fact, a pure Re end member (ReS_2) has been described in the Kudriavoy volcano in Far East Russia, and this presumably rare mineral was initially mistaken for molybdenite (Korzinsky et al., 1994). In addition to this isostructural relationship between MoS_2 and ReS_2 , naturally occurring sulfides of Re have also been documented at the Stillwater complex in the form of pure Re_2S_3 (Volborth, 1985). Since tungstenite (WS_2) is isostructural with molybdenite, W readily substitutes for Mo in molybdenite as well (Fleischer, 1959; Smyth and McCormick, 1995 this study). In addition, W and Mo behave similarly in their partitioning between molten basaltic silicate and available Fe-S liquids, with Mo residing in the melt as MoO_2 , but ultimately taking on a more chalcophile-siderophile role relative to W (Lodders and Palme, 1991). In nature, this is manifested in significant differences in the mineral-forming behavior of W and Mo. Molybdenum most commonly forms sulfide (MoS_2), but also occurs as the molybdate wulfenite (PbMoO_4), whereas tungsten forms tungstates such as scheelite (CaWO_4) and wolframite ($(\text{Fe}, \text{Mn})\text{WO}_4$). Tungstenite (WS_2) is very rare (Hsu, 1977; Drbék, 1982). Even more rare, a disulfide of osmium, erlichmanite (OsS_2), has been documented at two platinum-metal localities (Snetsinger, 1971). The bonding of Os to S in cubic erlichmanite is structurally unlike the bonding of Mo or Re to S in hexagonal molybdenite and hence, substitution of Os in molybdenite is unlikely.

The behavior and speciation of Mo in the hydrothermal environment has been extensively studied and it has been suggested that Mo is present as ^{+6}Mo in the aqueous phase as one or more molybdate species (e.g., MoO_3 or $\text{MoO}_2(\text{OH})_2$; Candela and Holland, 1984). Previous workers noted the correlation of high Cl^- , F^- , and $(\text{CO}_3)^{-2}$ concentrations with Mo

enrichment in aqueous fluids associated with silicate melts (e.g., White et al., 1981). The partitioning of Mo between vapor and melt is also controlled by oxygen fugacity, however, as documented in giant Climax-type molybdenum deposits with distinctly positive $\delta^{34}\text{S}$ values in molybdenite that indicate the presence of $(\text{SO}_2)^{-2}$ in the magmatic-hydrothermal ore-forming environment (Stein and Hannah, 1985). With experimental confirmation of the strong control of oxygen fugacity rather than Cl^- , F^- , and $(\text{CO}_3)^{-2}$ complexes on the transport of Mo (Candela and Holland, 1984), it is suggested that F^- and $(\text{CO}_3)^{-2}$, manifested as fluorite and carbonate minerals, must be concentrated by the same processes that concentrate Mo, but are apparently not involved in the actual transport of Mo. After hydrothermal transport as molybdate species, crystallization of molybdenite (MoS_2) requires reduction of ^{+6}Mo to ^{+4}Mo .

The transport of W in the hydrothermal environment is also independent of chloride, fluoride, and carbonate complexes, common components in ore-forming environments. Like Mo, hydrothermal fluids transport W as tungstate species carrying ^{+6}W (e.g., H_2WO_4 , HWO_4^- , WO_4^{-2} , NaHWO_4 , NaWO_4^- ; Manning and Henderson, 1984; Wood and Samson, 2000). Economic W mineralization, however, unlike Mo, forms tungstate minerals (e.g., scheelite, CaWO_4) and therefore, does not include reduction of ^{+6}W in the aqueous complex to ^{+4}W with crystallization of scheelite.

The behavior of Re has been generally thought to follow closely that of Mo, particularly as molybdenite is the primary mineral host for Re (Wedepohl, 1978; Morgan, 1999a). Indeed, the geochemistry of Re does exhibit some similarities with Mo, but its transport suggests major differences. Clearly, Re is incorporated into the molybdenite structure as ^{+4}Re , in a comfortable cation substitution for ^{+4}Mo . It has been shown that Re dissolves in a silicate melt as the ReO_2 (^{+4}Re) and ReO_3 (^{+6}Re) species (Ertel et al., 2001). Relatively high Re contents (40 ppb) have been measured in magnetite (Fe_3O_4) from sulfide-poor extrusive magmatic suites, and the species present in the oxide host is suggested to be ^{+3}Re or ^{+4}Re (Righter et al., 1998). In strict analogy with Mo, it was originally proposed that Re is transported as a gas (HReO_4) in high temperature magmatic-hydrothermal fluids in its ^{+7}Re oxidation state (Bernard et al., 1990). Collectively, evidence has been presented for hydrothermal transport as ^{+7}Re , ^{+6}Re , ^{+4}Re , and ^{+3}Re .

More recent experimental studies, however, show that the ^{+4}Re oxidation state dominates in Cl-bearing hydrothermal fluids (Xiong and Wood, 1999, 2002). These experiments, run at 400 to 500°C, bracketed by the Co-CoO and MoO_2 - MoO_3 oxygen fugacity buffers, and constrained by the K-feldspar + muscovite + quartz pH buffer, show that Re solubility increases dramatically with increasing KCl. Thus, Re is most likely transported in the ^{+4}Re oxidation state as Cl-species in supercritical hydrothermal solutions. These results are in marked contrast to the established geochemical behavior of Mo, which is transported in the ^{+6}Mo oxidation state and as oxide species (Candela and Holland, 1984). In the presence of sulfide, however, Re is far less soluble. Xiong and Wood (2002) demonstrate that the solubility of ReS_2 is about two orders of magnitude less than ReO_2 , so that Re cannot be transported in a reducing, sulfur-bearing fluid. Oxidizing fluids must play a role in the transport of Re. The exact oxide species has not yet been determined, but we suggest that, like ^{+6}Mo ,

Re may exist at an oxidation state higher than $^{+4}$ before reduction and incorporation in molybdenite. This is in keeping with the suggestion of Xiong and Wood (2002) that deposition of Re is best accomplished by mixing of an oxidized Re-bearing fluid with a reduced sulfur-bearing fluid.

A recent experimental study of Re under subcritical conditions (100–200°C), as might characterize low temperature hydrothermal environments (e.g., sandstone and black shale-hosted mineralization), suggests that $\text{Re}(\text{OH})_4$ is the dominant aqueous species over a wide range of pH (~2.2–8.8), and that the perrhenate ion (ReO_4^-) is not important in the transport of Re, even under relatively oxidizing conditions (Xiong and Wood, 2001). Furthermore, Xiong and Wood (2001) demonstrate that Re concentrations in aqueous fluids in the sulfide stability field for ReS_2 are very low ($\sim 10^{-6}$ to 10^{-5}) at these subcritical conditions. These data strongly support the robust Re-Os isotope systematics in the sulfide-stable hydrothermal environment at subcritical temperatures, suggesting that post-mineralization effects on high-temperature mineralization are minimal, and that dating of low temperature sulfide deposits should not suffer from problems of Re mobility.

In contrast, under oxidizing conditions, Re is demonstrably mobile as oxide species. High vapor pressures of Re oxide species at shallow crustal levels have been demonstrated over a broad temperature range, even in the presence of sulfur (Bolshakov, 1969; Brookins, 1986). Although Re is highly concentrated as a sulfide in association with molybdenite (MoS_2), it is essentially absent from oxidized (secondary) molybdenum minerals such as ferrimolybdate ($\text{Fe}_2(\text{MoO}_4)_3 \cdot 7\text{H}_2\text{O}$), suggesting preferential migration as an oxidized species with the oxidation and breakdown of molybdenite (Morachevskii and Nechaeva, 1960). Thus, oxidation of molybdenite under near-surface weathering conditions can mobilize Re, but such situations are readily avoided during sampling.

Far fewer data are available on the speciation and solubility of Os. Nevertheless, like Re, it is known to be soluble under oxidizing conditions and fixed by organic material or sulfides under reducing conditions (Morgan, 1999b; Hannah and Scherstén, 2001). Xiong and Wood (2000) show that Os solubility increases rapidly with Cl concentration in supercritical hydrothermal fluids and is therefore most likely transported as a Cl complex. Their results also demonstrate marked increase in Os solubility with increasing oxygen fugacity.

3. OXIDATION STATES AND IONIC RADII FOR Mo, W, Re, AND Os

Comparison of ionic radii for different valence states of Mo and Re, with the possible valence state(s) for radiogenic ^{187}Os is critical to understanding ^{187}Re - ^{187}Os systematics and behavior in molybdenite. Similar data for W are also considered because we use W as one measure of compositional zoning in our LA-ICP-MS analysis of molybdenite. In the following discussion, all ionic radii are taken from the CRC Handbook (Lide, 2000) except those for ^{+6}Mo and ^{+6}W . The radius for ^{+6}Mo is not reported in the Handbook, so the Whittaker and Muntus (1970) value for ^{+6}Mo is used. Because different methods were used to establish the ionic radii, those reported in Whittaker and Muntus (1970) are, in general, significantly smaller than those reported in the CRC Handbook. For the

purposes of this paper, however, we are concerned with relative size differences between cations and not absolute values. Therefore, we also used the Whittaker and Muntus (1970) value for ^{6}W for comparison with ^{6}Mo .

In magmatic fluids (greater than 500°C), if we assume that Mo and W are transported as H_2MoO_4 and H_2WO_4 , molybdic and tungstic acid, respectively (Bernard et al., 1990), then Mo and W occur as ^{6}Mo and ^{6}W , with a corresponding ionic radius of 0.50 \AA for both species. Similarly, if we assume transport of Mo and W in a magmatic vapor phase as molybdate and tungstate species (Candela and Holland, 1984; Manning and Henderson, 1984; Wood and Samson, 2000), the Mo occurs as ^{6}Mo before reduction to ^{4}Mo necessary for inclusion in molybdenite (MoS_2), but the ^{6}W remains as ^{6}W , unreduced in scheelite (CaWO_4) and wolframite ($(\text{Fe}, \text{Mn})\text{WO}_4$). In low temperature geologic environments, oxidation states for Re range from ^{-1}Re to ^{+7}Re (Cotton and Wilkinson, 1972; Rouschias, 1974; Brookins, 1986). Of particular interest are the ionic radii for two common species of Re, with ^{+7}Re at 0.53 \AA and ^{+4}Re at 0.63 \AA . Not surprisingly, the ionic radius for ^{+4}Mo is 0.65 \AA , close to the 0.63 \AA for ^{+4}Re . Trace quantities of W are also accommodated since ^{+4}W has an ionic radius of 0.66 \AA , but unlike Re, W does not routinely occur at the ppm level in molybdenite. The lack of significant W in the MoS_2 lattice is likely the result of fractionation of W from Mo at the source and/or during subsequent mineral/melt partitioning, rather than during late stage magmatic fluid separation and molybdenite deposition (e.g., Candela and Bouton, 1990; Lodders and Palme, 1991).

Osmium has oxidation states ranging from ^0Os to ^{+8}Os , but in nature by far the dominant states are as ^{+3}Os and ^{+4}Os (Cotton and Wilkinson, 1972; Morgan, 1999b). The ionic radius of ^{+4}Os is 0.63 \AA , which at first consideration is charge and size compatible with the cation space in molybdenite. However, with the reduction of ore fluids (e.g., ^{+6}Mo and ^{+7}Mo are reduced to ^{+4}Mo), the ^{+4}Os in the fluid is most probably also reduced. Reduction potentials of Os species appear to be higher than Re and especially Mo species. Hence, a system capable of reducing Mo from the $+6$ or $+7$ oxidation state to $+4$ would be expected to reduce simultaneously ^{+3}Os or ^{+4}Os to lower oxidation states. Because lower oxidation states are associated with larger ionic radii, reduction of ^{+4}Os to a lower oxidation state, most likely ^{+3}Os or ^0Os , will not only yield an oversized Os cation relative to the available site in molybdenite, but also introduce a charge imbalance. We suggest that reduction of ^{+4}Os to larger, lesser-charged Os cations during the formation of sulfide may be the primary reason for the near complete absence of common (initial) Os in molybdenite. Several early workers (e.g., Hirt et al., 1963; Morgan et al., 1968) documented the absence of common Os in molybdenite, but no explanation was offered. If Os is present in the magmatic environment, other sulfide and oxide phases will serve as a sink for this element. It is this extreme incompatibility of Os in molybdenite during crystallization that creates a unique, single-mineral ^{187}Re - ^{187}Os chronometer.

As a final note, reduction of ore fluids in the magmatic-hydrothermal environment must provide the compatible ^{+4}Re for incorporation into the molybdenite structure. Since reduction potentials for Re species are generally higher than those of comparable Mo species, the preferred state of Re in hydrother-

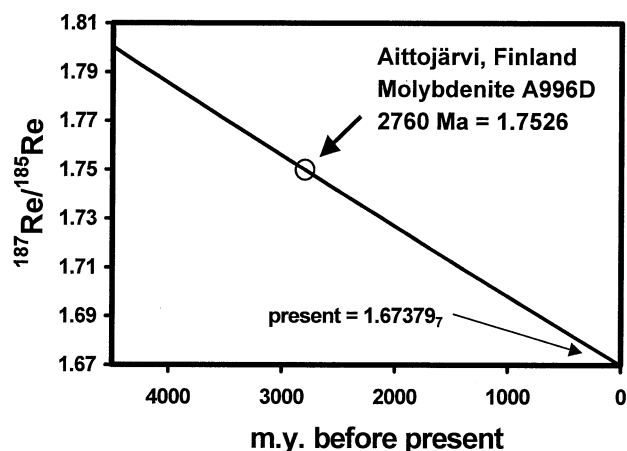


Fig. 1. The changing isotopic composition of Re from 4.5 Ga to present based on beta decay of ^{187}Re to ^{187}Os with passing time ($\lambda^{187}\text{Re} = 1.666 \times 10^{-11} \text{ yr}^{-1}$; Smoliar et al., 1996).

mal fluids should be ^{+6}Re or ^{+7}Re , so that reduction of the fluid and subsequent sulfide deposition results in the molybdenite-compatible ^{+4}Re ion. On the other hand, if Re is transported as a chloride or fluoride species in the ^{+4}Re state, it may be readily available to form sulfide without reduction. This latter scenario might allow ^{+4}Os to persist without reduction and remain a candidate for cation substitution in molybdenite. Because significant initial Os is never observed in molybdenite, it follows that both Re and Os are reduced sometime before their incorporation into (Re) and exclusion from (Os) molybdenite.

4. ^{187}Re - ^{187}Os GEOCHRONOMETER

Re has two isotopes, ^{185}Re and ^{187}Re . The ^{187}Re isotope decays to ^{187}Os by emission of a beta particle with a 2.3 keV maximum β^- energy (Morgan, 1999b). Any recoil effects are small or insignificant, given the low energy of the β^- decay. We use the decay constant of Smoliar et al. (1996; $1.666 \times 10^{-11} \text{ yr}^{-1}$). The decay of $^{187}\text{Re}^{+4}$ produces the smaller $^{187}\text{Os}^{+5}$ which, if reduced, will form $^{187}\text{Os}^{+4}$, a process of importance discussed in section 7 of this paper. It has been shown empirically through analysis of molybdenite that common Os does not enter the molybdenite structure to any significant degree during crystallization, thereby providing $^{187}\text{Os}/^{188}\text{Os}$ ratios in the tens or hundreds of thousands with time (Hirt et al., 1963; Morgan et al., 1968). This permits single sample ^{187}Re - ^{187}Os dating of molybdenite without correction for common ^{187}Os (illustrated in fig. 1 in Stein et al., 2001). Current state-of-the-art molybdenite dating yields single sample ^{187}Re - ^{187}Os ages with precisions $<0.4\%$, even on samples $<5 \text{ Ma}$ (Stein et al., 1997, 2001; Markey et al., 1998). With use of a double Os spike precisions are further reduced (Markey et al., in press). This precision is obtained by using the reduced $\pm 0.31\%$ uncertainty for the ^{187}Re decay constant which requires use of the same Os standard solutions as those used by Smoliar et al. (1996) in determining the $\lambda^{187}\text{Re}$ value and its uncertainty, or alternatively, close calibration with that standard.

Hirt et al. (1963) and Herr et al. (1967) made pioneering and

remarkably successful age determinations on molybdenite, realizing the potential offered by the Re-Os chronometer for this mineral. However, ^{187}Re - ^{187}Os age determinations on molybdenite yielding dates that were too old or that could not be reproduced (e.g., Luck and Allègre, 1982; McCandless et al., 1993; Suzuki et al., 2000, 2001) led some workers to conclude that the Re-Os chronometer in molybdenite is fallible. In a previous paper (Stein et al., 2001), we showed that precise and accurate ages could in fact be obtained from molybdenite from some of the same localities. We suggest that either failure to acquire a representative and homogeneous molybdenite separate and/or problems with sample-spike equilibration are responsible for the disparate age results. For example, in the alkaline fusion of spike and sample (Morgan and Walker, 1989), the method used for early molybdenite work, the oxidation and equilibration of Os spike and sample Os is not a trivial matter. Introduction of the Carius tube method for sample dissolution (Shirey and Walker, 1995) eliminated equilibration problems between spike and sample.

To achieve geologically accurate and precise Re-Os age results from molybdenite, we take the following approach: (1) the geologic and paragenetic relations must be carefully documented at the outcrop and thin section scale, as the resulting Re-Os geochronology must be integrated with field and petrographic observations for every sample, (2) the mineral separate is prepared using a diamond-tipped, slow-speed mini-drill to create a representative powder by drilling multiple discrete crystals representing a single generation of deposition, or for a fine-grained molybdenite sample, a standard separation procedure utilizing tens of milligrams may be employed; but, a few coarse pieces or single sheets of a molybdenite crystal are never used as they will likely capture inherent ^{187}Re - ^{187}Os decoupling as suggested by reproducibility experiments noted in Stein et al. (1998a), (3) either an age is replicated using a *second* mineral separate or, in the most robust approach, a ^{187}Re - ^{187}Os isochron is constructed from several related molybdenite samples (Stein et al., 2000, 2001), (4) Re-Os results are compared with other ages potentially associated with the event, using robust U-Pb ages for zircon, monazite, and sphene as the primary basis for comparison (argon-based chronometry for dating ore-forming events in complex and overprinting hydrothermal environments should be approached with caution), and (5) Re-Os results are interpreted and integrated with all available geologic and geochronologic constraints, keeping working models open to modification as needed.

With the growing interest in molybdenite dating and the lack of universal agreement in the chronometer's reliability, a better understanding of Re and Os behavior in molybdenite is urgently needed. We examined Re and Os mobility at the micron level by measuring ($^{187}\text{Re} + ^{187}\text{Os}$) and ^{185}Re in an in situ molybdenite in aplite from Aittojärvi, Finland. Three paragenetically distinct samples (A996B, A996C, and A996D) from this locality are well characterized by isotope dilution negative thermal ionization mass spectrometry (ID-NTIMS), as they serve as in-house standards at AIRIE. The fine-grained A996D Aittojärvi molybdenite is 2760 ± 9 Ma (Stein et al., 2001), as determined from a fine-grained mineral separate prepared from kilograms of bulk rock sample at the Geological Survey of Finland. The operating premise is that if neither Re nor ^{187}Os is mobile within the crystal after molybdenite formation, the

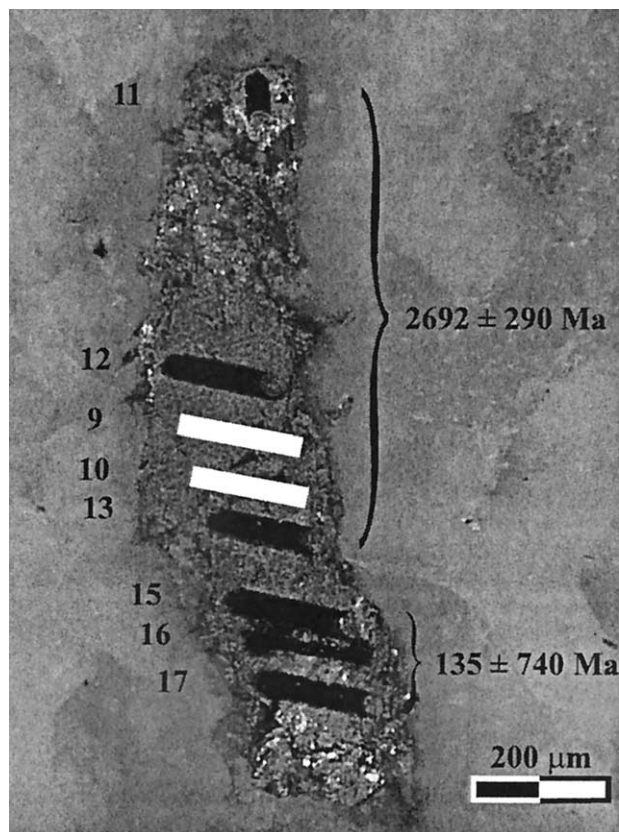


Fig. 2. Photograph of molybdenite crystal (grain) from Aittojärvi, Finland in situ in white aplite leucosome. Paths for eight scans are shown. The matrix minerals are quartz and feldspar. Sample represents the same setting and locality as one of our in-house standards from Aittojärvi (A996D; Stein et al., 2001). The grain was repolished after two initial experimental scans (9 and 10, shown as white bands). Scans are numerically labeled. Two weighted mean ages for sets of scans are indicated and discussed in the text.

$^{185}/^{187}$ mass ratio within any finite volume of molybdenite will be constant, reflecting the original Re isotopic composition, unique for the time of crystallization because of the fixed decay rate for ^{187}Re (Fig. 1). In other words, since decay of ^{187}Re produces ^{187}Os , no change in the $^{185}/^{187}$ mass ratio should be observed, and the ratio should exactly preserve the timing of isotopic closure defined by crystallization. We used laser ablation ICP-MS to measure ($^{187}\text{Re} + ^{187}\text{Os}$)/ ^{185}Re to assess Re and/or ^{187}Os mobility and we compare the known ID-NTIMS age with ages obtained for individual LA-ICP-MS scans and weighted mean LA-ICP-MS ages. This exercise provides a test of micron-scale ^{187}Re - ^{187}Os dating of molybdenite using the increasingly popular LA-ICP-MS method.

5. METHODS

An in situ molybdenite crystal from a sucrosic, near-white aplite interval (leucosome) in tonalitic gneiss at Aittojärvi, Finland was ground and polished (Fig. 2). The molybdenite was analyzed using a Cetac LSX200 UV laser coupled to a Hewlett Packard HP4500 ICP mass spectrometer (data acquisition parameters are given in Table 1). For each spot analysis, 40–270 s of background was collected before the ~ 30 μm diameter laser beam was activated with a 4 Hz pulse rate. In all our analyses, ^{184}W , ^{185}Re , and $^{187}\text{Re} + ^{187}\text{Os}$ were measured.

Table 1. LA-ICP-MS machine and data acquisition parameters.

Cetac LSX-200 266nm Nd:YAG laser	
Output energy	About 5 mJ at 266 nm
Pulse duration	6 ns
Repetition rate	1 to 4 Hz
Spot size	30 microns
Ablation cell	Metal cylinder with quartz window programmable X, Y, and Z stage control
Gas	Argon
Flow rate	1.41/min
Pit size/shape	Cylindrical with flat bottom, depth about one micron/shot
Line scans	Typically 1000 microns total length at 5 microns/sec
HP4500 (now Agilent) quadrupole ICP-MS	
Carrier gas	Argon, 1.4 l/min
Plasma gas	Argon, 15 l/min
Auxiliary gas	Argon, 0.45 l/min
RF power	1300 W
Detector mode	Electron multiplier (without overload protection)
Quadrupole settling time	2 ms
Analyzer vacuum	$<10^{-5}$ pascal
Data acquisition parameters	
<ul style="list-style-type: none"> • Time resolved mode, gas blank counted before and after sample runs • Peak hopping cycles, 0.16 sec counting time per peak; typically 200 sec acquisition time • Count rates for ^{187}Re typically 100 kcps • Raw data transferred to spreadsheet for reduction 	

Blank contributions varied from 0.01 to 0.25% for ^{184}W , 0.5 to 15.1% for ^{185}Re , and 0.4 to 13.9% for $^{187}\text{Re} + ^{187}\text{Os}$.

To check mass bias for the 187/185 mass ratio, Re solutions with concentrations of 0.1, 2, and 4 ppb were analyzed. These solutions are not known to contain any Os. The measured $(^{187}\text{Re} + ^{187}\text{Os})/^{185}\text{Re}$ ratios were compared to a modern $^{187}\text{Re}/^{185}\text{Re}$ of 1.67379 (Fig. 1), and a mass bias correction for each solution was calculated. The ^{185}Re signal intensity was plotted against the correction factor, resulting in a linear regression with a slope of $-4.387 \times 10^{-7} \pm 2.3 \times 10^{-7}$ and an intercept of 1.0262 ± 0.0047 . The correction does not account for differences in ionization efficiency between ^{187}Re and ^{187}Os , and resulting apparent molybdenite ages may therefore have an additional error, unknown and uncorrectable. Similarly, we have not accounted for potential fractionation effects induced in the plasma at the sample surface. Because no internal standard is available, the data were not converted into concentrations. Although these uncertainties limit the utility of this data set for other purposes, it is sufficient for estimating the magnitude of micron-scale heterogeneities. Most importantly, any Re-Os fractionation in the system will shift all apparent ages in the same direction. Uncorrected fractionation effects, therefore, cannot account for the enormous variability in apparent ages over small distances (as described below) unless the fractionation effects themselves are highly variable over very short times, in which case precise age determinations by this method would be impossible. We note that Pearson et al. (2002) find that mass fractionation coefficients for Re and Os remain constant over the range of operating conditions for LA-ICP-MS analyses with their facilities, so that extreme variations are unlikely.

Apparent ages may be calculated directly from measured $(^{187}\text{Re} + ^{187}\text{Os})/^{185}\text{Re}$ ratios. Determining ^{187}Os by subtraction from the normal Re isotopic composition introduces large and unnecessary uncertainties, and is not needed for age calculations. The apparent age for any given $(^{187}\text{Re} + ^{187}\text{Os})/^{185}\text{Re}$ mass ratio is given by

$$T = \ln \left[\frac{(^{187}\text{Re} + ^{187}\text{Os})/^{185}\text{Re}}{(^{187}\text{Re}/^{185}\text{Re})_{\text{today}}} \right] / \lambda$$

where T is the time before present in years, $(^{187}\text{Re}/^{185}\text{Re})_{\text{today}}$ was rounded off to 1.674 in the calculations, and λ is the decay constant for ^{187}Re ($1.666 \times 10^{-11} \text{ yr}^{-1}$; Smoliar et al., 1996). All reported apparent ages are based on blank-corrected $(^{187}\text{Re} + ^{187}\text{Os})/^{185}\text{Re}$ ratios.

For correct estimation of error, absolute values (atoms) must be used in the calculations. The use of relative errors of the absolute ratio will

grossly underestimate the true age error. For example, because the $^{187}\text{Re}/^{185}\text{Re}$ ratio exhibits only a small change from 4.5 Ga to present day (1.804 to 1.674; Fig. 1), a shift of 0.01 in the $(^{187}\text{Re} + ^{187}\text{Os})/^{185}\text{Re}$ mass ratio corresponds to ~ 360 million years. All reported errors are two-sigma standard deviations of the mean. No outlier rejections were allowed for any calculations. We reiterate that different ionization efficiencies for Re and ^{187}Os and our mass bias correction may cause inaccurate apparent ages since we are unable to correct for this. For the purpose of this study, however, apparent ages are not an issue as we seek only to examine and document heterogeneity of $(^{187}\text{Re} + ^{187}\text{Os})/^{185}\text{Re}$ within a molybdenite crystal of well-defined NTIMS age, and this is based on comparing relative ages.

Re-Os data for molybdenite and chalcopyrite samples reported in section 8 were acquired in 1996 by ID-NTIMS, with sample-spike equilibration achieved by alkaline fusion (Morgan and Walker, 1989). Os was separated by double distillation, and Re subsequently isolated using ion exchange. Details of the analytical method are given in Stein et al. (1998b). More recent analyses in the AIRIE labs use the Carius tube method (Shirey and Walker, 1995), in which sample and spike are dissolved and equilibrated by heating at 240°C overnight in reverse *aqua regia* in a thick-walled glass vessel. Analysis of aliquots of Aittojärvi molybdenite A996D (Stein et al., 2001) utilize the Carius tube dissolution and provide the ID-NTIMS age for the molybdenite analyzed by LA-ICP-MS in this study.

6. RESULTS

Eight scans across the polished Aittojärvi in situ molybdenite crystal (numbered 9–13 and 15–17; Fig. 2) show irregular signal intensity variations across the grain (e.g., counts of mass 185 per second; Fig. 3). Except for scan 11, all scans were parallel to subparallel and run from left to right across the elongation of the polished grain (Fig. 2). The rock chip was repolished after scans 9 and 10. The data for each scan are plotted with the starting point on the left in each diagram. We were unable to control crystallographic orientation of the grain as we were working with an in situ sample and therefore, the scans have unspecified angles relative to the c-axis.

Signal intensity was similar for the first five scans (9, 10, 11,

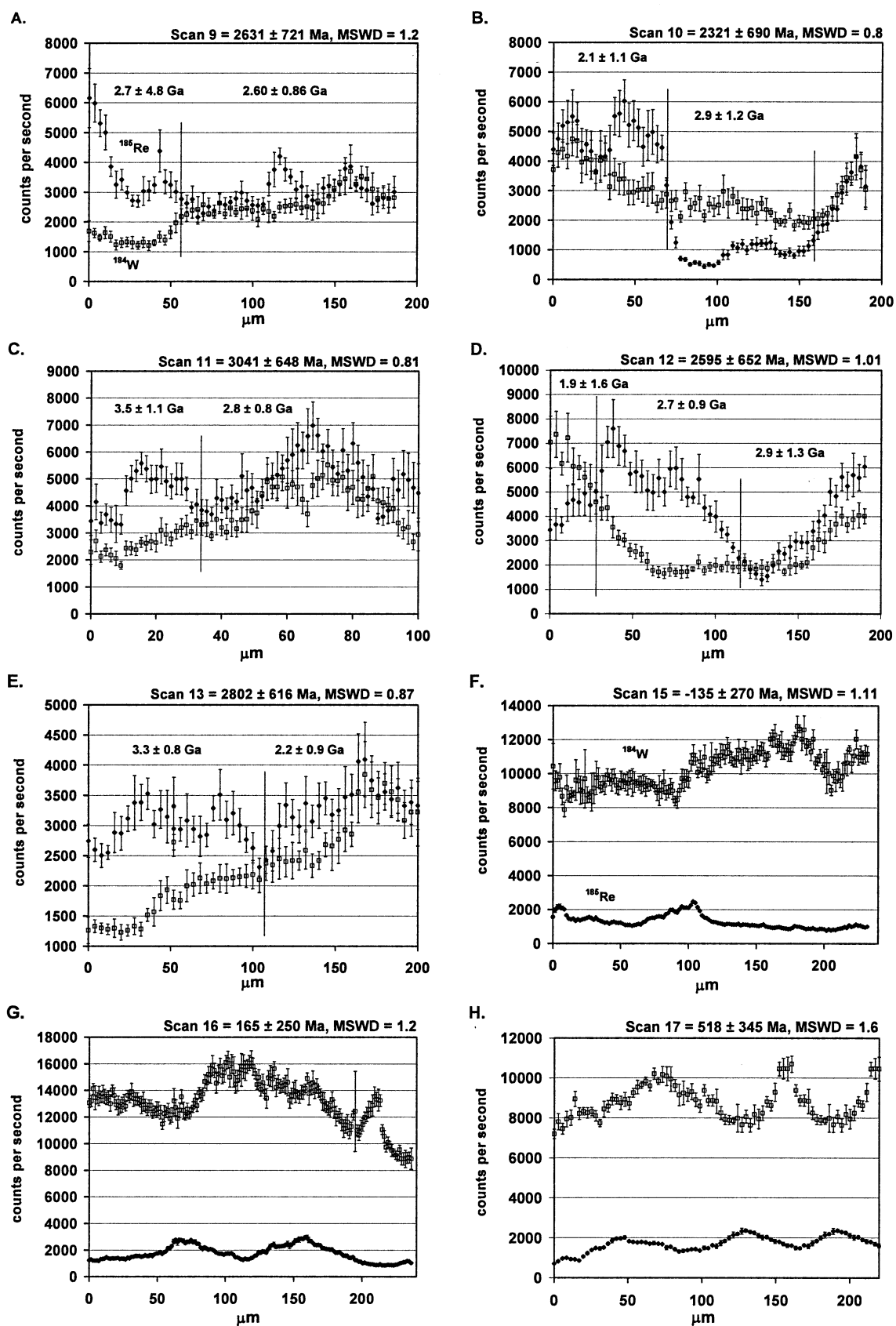


Fig. 3. Signal intensity for eight individual scans. Black diamonds are ^{185}Re and open squares are ^{184}W . Mean age for each scan is indicated at top. Ages for subsets within some scans are shown on individual diagrams above the section delineated by vertical lines.

12, 13), ranging between 450–7600 counts per second for ^{184}W and ^{185}Re , with Re showing both the lowest and highest signal intensities (Fig. 3). The last three scans (15, 16, 17) show considerably higher ^{184}W signal intensity, ranging between ~7200–16300 counts per second. The ^{185}Re -signal intensity remained within the range observed in the first five scans, but at the low end (<3000 cps). The $^{185}\text{Re}/^{184}\text{W}$ ratios are therefore systematically lower in the first five scans. In general, the right sides of the first five scans show similar ^{185}Re and ^{184}W intensity patterns, whereas the left sides of the scans show larger disparities between ^{185}Re and ^{184}W intensities, including abrupt changes and jumps. In the three last scans (15, 16, 17), ^{185}Re and ^{184}W intensities are roughly antithetic, as seen most clearly in scan 17 (Fig. 3H).

Simple plots of apparent age vs. distance along a scan are not meaningful. The errors on individual spot analysis are, in many cases, too high to see fine-scale variations. Calculating running averages to achieve greater precision smoothes out some heterogeneities and reduces resolution. Averages for whole scans or scan segments, however, reveal the extreme heterogeneity of the mass ratio over the molybdenite surface. Ages for individual scans range from an impossible future age of -135 ± 270 to a poorly defined Archean age of 3041 ± 648 Ma. The first five scans, with average blanks of less than 4%, vary between 2321 ± 690 and 3041 ± 648 Ma (Fig. 3A–E). Their weighted average of 2692 ± 290 Ma (MSWD = 0.64) is in two-sigma agreement with the 2760 ± 9 Ma ID-NTIMS age (Stein et al., 2001), but an uncertainty of greater than 10% for the LA-ICP-MS age is perhaps of little geologic value. To look for systematic and resolvable, within-scan age variations in the first five scans, ages were calculated for scan segments in which ^{185}Re and ^{184}W behavior were either correlated or not correlated. No trends toward higher or lower ages were noted for these two situations. Furthermore, no systematic trends between ^{185}Re signal intensity and age could be resolved beyond analytical error. The last three scans (15, 16, 17) yield drastically young apparent ages that vary between -135 ± 270 and 518 ± 345 Ma, with a weighted average of 135 ± 740 Ma (MSWD = 4.5). These three scans yield ages significantly different from the Aittojärvi A996D NTIMS reference age of 2760 ± 9 Ma (Stein et al., 2001).

As a check for heterogeneity and, more importantly, to establish a threshold for Re- ^{187}Os decoupling within single molybdenite crystals, Stein et al. (2001) compared ID-NTIMS analyses for large (~50 mg) and small (~5 mg) aliquots of ~70 mesh molybdenite from an Aittojärvi aplite leucosome (A996D; sample from same locality as that used for the LA-ICP-MS study). While an ideal comparison by NTIMS would use powdered aliquots microdrilled from the exact same sample used in the LA-ICP-MS study, the LA-ICP-MS sample analyzed is too small to microdrill using available tools. Two 50 mg aliquots of A996D yield identical ages of 2760 ± 10 and 2761 ± 9 Ma. In contrast, two 5 mg aliquots of A996D yield ages that differ from the true age by more than 8% (2773 ± 10 and 3000 ± 11 Ma). These results are representative of our experience with hundreds of molybdenite analyses: that is, the aliquot analyzed must be large enough to overcome postcrystallization decoupling of ^{187}Os from Re in molybdenite crystals. It is not possible to specify the sample size needed for a specific level of reproducibility, as this depends on grain size,

Re and Os concentrations, age, and the unknown degree of decoupling, heterogeneous in itself, and unique for any given sample. The LA-ICP-MS results clearly speak to heterogeneity and intense variability in degree of decoupling. In practice, for relatively coarse-grained samples, we achieve consistently reproducible age results by drilling an array of diverse spots to produce a separate of tens of mg. Alternatively, for relatively fine-grained samples, a mechanically-produced separate of >10 mg generally also produces robust and reproducible age results. We also have good success in drilling out small single grains in their entirety, particularly when hosted by silicate, thereby capturing all of the Re and ^{187}Os associated with the grain. In addition, wherever possible, we analyze multiple samples representative of a single depositional event, and employ the isochron approach to establish closed-system behavior and geologic accuracy (Stein et al., 1997, 2001).

7. DISCUSSION

The signal variations in ^{185}Re and ^{184}W are equivalent to unspecified Re and W concentration variations across the scans (Fig. 3). These variations reflect either growth zonation within the grain or postcrystallization mobility of either element. There are a number of crystallographic parameters that may affect trace element distribution in molybdenite. It might be assumed from the molybdenite structure that the fastest growth direction is perpendicular to the c-axis (i.e., outward in the plane of the molybdenite “sheets”). This may cause systematic (or nonsystematic) growth-related concentration variation perpendicular to the c-axis. Such is the case for a young molybdenite crystal from Japan, where significant variations in Re concentration are recorded and contoured for two perpendicular traverses in the plane of the a- and c-axes, with a stated explanation of isomorphic ReS_2 for the high Re values (Terada et al., 1971). Variations parallel to the c-axis may also show considerable scatter produced by concentration jumps related to the formation of new molybdenite layers. Since laser ablation is penetrative, sudden concentration jumps are not entirely surprising. Such sudden changes do occur in some of the scans from the data set (e.g., Fig. 3B). Jumps are significantly more pronounced for ^{185}Re than for ^{184}W . There is no striking difference in the spatial variability of ^{184}W and ^{185}Re signal intensities for scan 11, despite the fact that it is oriented approximately perpendicular to the other scans (Fig. 2).

It is difficult to assess the cause of the signal variation, particularly given the lack of crystallographic control for in situ sample scans. It is possible that Re retains its initial growth pattern marked by sharp concentration variations, while W concentrations are smoothed by postcrystallization diffusion. Another possibility is that Re occurs as small ReS_2 domains in the molybdenite, as was suggested by Terada et al. (1971) for the Japanese molybdenite crystal. Such crystal-chemical control, however, would require gaps in the solid solution series documented by Korzhinsky et al. (1994).

If, on the other hand, we assume the smoothly varying ^{184}W represents the initial growth pattern (no postcrystallization diffusion) and that ^{184}W and ^{185}Re concentrations were initially correlated, as might be expected, then relative ^{185}Re enrichments and depletions must be caused by Re mobility. If Re mobility does occur and radiogenic ^{187}Os remains immobile

(the alternative explanation for variations in apparent ages indicated by LA-ICP-MS scans), the apparent age for a Re-enriched domain will appear younger than its true age due to an increased $^{187}\text{Re}/^{187}\text{Os}$. Conversely, the apparent age for a Re-depleted domain will appear older than the true age due to a decreased $^{187}\text{Re}/^{187}\text{Os}$. Alternatively, if Re and ^{187}Os are both independently mobile, no systematic age variation would be expected. In an effort to test for systematic variations that might reveal patterns of Re mobility, apparent ages were calculated for five scan subsets where the ^{185}Re beam was either higher or lower than the ^{184}W beam (Fig. 3A–E). We see no consistent pattern. Apparent ages are not systematically higher or lower, depending on the relative variations in ^{184}W and ^{185}Re signal intensities. This suggests that either Re and ^{187}Os are both mobile, but do not follow one another in a systematic way, or that Re is relatively immobile. In either case, ^{187}Os mobility is implied.

Rhenium leaching from the 3R-molybdenite polytype was demonstrated by Newberry (1979) and advocated by McCandless et al. (1993) as an explanation for errant Re-Os ages on molybdenite. The more common 2H_1 polytype, however, characterizing the Aittojärvi sample, is less sensitive to leaching. There are other studies in the literature that attribute errant ^{187}Re - ^{187}Os ages (too old) to Re loss (e.g., Luck and Allègre, 1982), but we have revisited many of these localities and have obtained geologically meaningful Re-Os ages that compare favorably with U-Pb ages. As detailed in Stein et al. (2001), many previously published disparate Re-Os ages are most likely the result of inadequately homogenized mineral separates and/or lack of sample-spike equilibration. In summary, while we can find no firm evidence for Re mobility within molybdenite crystals, neither can it be ruled out with certainty.

The last three scans (Fig. 3F–H) are very different from the five scans just discussed. In contrast to the previous five scans, ^{184}W signal intensities are considerably higher and ^{185}Re and ^{184}W show generally systematic and locally antithetic variations along scans. This variation may represent a different growth stage in the molybdenite and may partly capture Re/W variation associated with fractionation of these elements during molybdenite growth. Alternatively, the patterns may record variable concentration (availability) of Re and W during crystal growth. It is not possible to distinguish these two processes.

The weighted mean ages for these last three scans are -135 ± 270 , 165 ± 250 , and 518 ± 345 Ma. Although these scans have higher gas blanks (2.2–12.5%, with an average of ~5%), the 187/185 mass ratio of 1.61–1.62 in the blank is unusually low. The blank correction increases the 187/185 ratio of the sample and thus increases the age. Therefore, the gas blank is not contributing to the low apparent ages. The mass bias correction, applied to all scans, is based on the same solution runs and it also increases the corrected ratio. Furthermore, since the ^{185}Re -signal intensity is within the same range as the first five scans (although at the low end), no systematic difference was expected. The apparent age differences, therefore, must be valid and imply considerable increase of the $^{187}\text{Re}/^{187}\text{Os}$. This increase is due to either Re enrichment or ^{187}Os loss or depletion. Comparing the ^{184}W and ^{185}Re patterns suggests that neither W nor Re was mobile since they are roughly (anti) correlated. Also, the ^{185}Re signal intensity is relatively low in these scans, and could argue against Re enrichment. Accepting

the apparent ages as valid and the relatively uncomplicated scan patterns as a reflection of growth zonation, ^{187}Os is again the most likely candidate for mobility. Therefore, our preferred explanation is that the apparent ages are largely the result of removal or addition of ^{187}Os within analyzed molybdenite subdomains at the micron scale.

This is our preferred explanation because radiogenic ^{187}Os would be expected to accumulate as overcharged $^{187}\text{Os}^{+5}$ ions of inappropriate size relative to the cation space available in molybdenite, as proposed earlier in this paper. We also suggest that older molybdenites, in particular, might accumulate crystal defects in localized areas of high strain, thereby providing space and niches for clustering of radiogenic ^{+5}Os . Among sulfide minerals, this may be a somewhat unique property of molybdenite, given its layered structure. The mechanisms involved are not entirely known, but the outcome is a documented full retention of ^{187}Os , even through deformation and recrystallization. Molybdenite possesses remarkable chemical durability.

Deformation is easily accomplished in soft and delicately bladed molybdenite. In one extreme case, molybdenite can even be deformed by hydrothermal fluids associated with open-space vein formation whereby delicate inward-growing blades, still adhering to their substrate, are swept and bent in the direction of fluid flow within a vein. At the other extreme, molybdenite facilitates deformation by intragranular slip, producing elongate stringers and surface coatings. Whether delicately bent by fluid or intensely smeared by tectonic processes, deformation of molybdenite is characterized by kink bands and the development of delamination cracks that may serve as gathering sites for accumulating radiogenic ^{187}Os . In some crystalline solids, delamination cracks may be bridged by ligament bundles of the material that actually serve to structurally strengthen the solid phase (Barsoum and El-Raghy, 2001). We suggest that molybdenite may have deformation properties that accommodate radiogenic ^{187}Os under extraordinary geologic conditions. The physical accommodation of strain in molybdenite by dislocation glide, kink bands, delamination cracks, and bridging ligament bundles is commonly observed at thin section scale, particularly for molybdenites within shear zones. Just as dislocations related to strain accumulate in localized micron-scale high-strain regions, radiogenic ^{187}Os , which is effectively a crystal defect, may also accumulate in those same regions. Given the structural incompatibility of ^{187}Os in molybdenite, mobility is to be expected. Regardless of how and where accumulating radiogenic ^{187}Os is stored in molybdenite, it is clear from robust NTIMS Re-Os age results for hundreds of samples that ^{187}Os does not leave molybdenite to any significant degree.

We propose three potential physicochemical reasons for the stability of the ^{187}Re - ^{187}Os chronometer in molybdenite. *First*, the low energy beta decay of ^{187}Re with limited recoil effect may keep an oversupply of electrons at hand, thereby providing a “sticky” environment for adherence of the relatively highly charged $^{187}\text{Os}^{+5}$ ion. Radiogenic ^{+5}Os does not fit the cation site based on ionic radii requirements, but the availability of electrons from the weak beta decay of ^{187}Re might reduce $^{187}\text{Os}^{+5}$ to $^{187}\text{Os}^{+4}$, thereby creating ionic-radius compatibility with the molybdenite structure. *Second*, molybdenite’s response to damage during deformation may in fact lead to

increased chemical stability of the mineral. Kink bands and delamination cracks, commonly observed in molybdenite, define clusters of dislocations that may provide sites for the ^{187}Os “impurity” at the micron scale. *Third*, there is no other suitable medium competing for Os, as this element generally has extraordinarily low solubility in hosting silicate phases and aqueous solutions typical for most geologic environments. The possibilities suggested under the first and second explanation need testing in the future. Despite the hard evidence for the remarkable stability of the ^{187}Re - ^{187}Os chronometer in molybdenite (Stein et al., 2001, and references therein), in this paper we have shown that Re-Os isotope systematics, in fact, are disturbed on the micron scale within individual molybdenite crystals. Therefore, spot analyses by LA-ICP-MS will not give reliable age information.

As a final note, we suggest that older molybdenites are more likely to suffer micron to larger scale Re- ^{187}Os decoupling, particularly if they have been subjected to multiple orogenic events. Although Kosler et al. (in press) suggest that LA-ICP-MS dating of molybdenite may be possible for “certain old and Re-rich molybdenites,” our observations and the example provided in this study suggest that this is unlikely. Rather, we suggest that younger molybdenites that have not been subjected to orogenic overprints are more likely to escape decoupling. The proper preparation of mineral separates and Re-Os analyses by ID-NTIMS are necessary to overcome micron- to crystal-scale decoupling, and lead to accurate age results (Stein et al., 2001).

8. Os MOBILITY BEYOND MOLYBDENITE

The stability of the ^{187}Re - ^{187}Os chronometer in molybdenite is due, in part, to the near complete lack of competition for these chalcophile-siderophile elements in the silicate environment. Most molybdenites are in contact with silicate minerals, most commonly quartz and feldspar. This is not exclusively the case, however, and in this section we explore a situation in which Proterozoic molybdenite of moderate to high Re concentration is in contact with cogenetic chalcopyrite in a skarn setting in western Russia. While the Re-Os age for the molybdenite remains intact in this relationship, the Re-Os age for the chalcopyrite is dramatically disturbed.

In Karelia (westernmost Russia), a group of small Sn-Cu-Zn-Pb (Mo-W) ore deposits form the Pitkäranta district (Fig. 4). These deposits are located in exoskarn developed in supracrustal rocks along the west margin of the Salmi batholith, in an area where Salmi biotite granites and rapakivi granites are abundant. The skarn host rocks consist of early Svecofennian (>1900 Ma) supracrustal sequences that rim ~2700 Ma Archean gneiss domes. The Salmi batholith, both rapakivi granite and lesser anorthosite phases, and its associated skarn assemblage, have been dated between 1560–1530 Ma using U-Pb on a variety of mineral phases (Neymark et al., 1994; Amelin et al., 1997). The preferred age for the granitic magmatism, based on U-Pb dating of zircon, is 1545–1530 Ma (Amelin et al., 1997). These ages are confirmed by a single Re-Os molybdenite age, discussed below.

Mineralization at Pitkäranta was long attributed to the Salmi batholith (Törnebohm, 1891; Trüstedt, 1907; Eskola, 1951; Haapala et al., 1991). This assumption was based on its spatial

proximity to the batholith margin, and other geochemical coincidences such as the similarity between trace elements in some ore bodies in the skarn with those from mineralized greisen zones occurring within the granites. One early worker, however, noted that there appeared to be several generations of ore at Pitkäranta, and that potentially they might not share the same origin (Saksela, 1951). A careful look at detailed underground cross sections in Trüstedt (1907) clearly indicates a variety of older intrusions described as pegmatites throughout the workings, but little importance was attached to these in this and subsequent papers. The premise of a link between Pitkäranta mineralization and the Salmi batholith continued into the 1990s, but herein we document that the origin of Pitkäranta mineralization is two-stage and more complicated.

Re-Os dating of molybdenite-bearing ore samples from six different mines in the “Old Mining Field” at Pitkäranta yield a surprising, but unequivocal late Svecofennian age of 1795 ± 8 Ma for the molybdenite (lower two insets, Fig. 4); data in Stein et al., 1996a,b). By association, this late Svecofennian age can be extended to include the W and at least a portion of the Cu mineralization at Pitkäranta. The Re-Os results for molybdenite are similar to a concordant 1797 ± 19 Ma U-Pb age for monazite from the Puruvesi granite ~100 km northwest of Pitkäranta (Huhma, 1986), the closest dated Svecofennian granite, occurring as widespread but sporadic exposures spanning the Russian-Finnish border (Fig. 4). Interestingly, a molybdenite-bearing sample from the Uuksu deposit, hosted ~10 km southeast of Pitkäranta in a greisen vein *within* the batholith yields a Re-Os age equal to that of the Salmi intrusion, as must be the case based on field relationships. While the Re concentrations for ~1800 Ma molybdenites from the “Old Mining Field” range from 130–470 ppm, the Uuksu molybdenite is clearly unique with an extremely low Re concentration of <100 ppb (0.0871 ppm) and its ~1550 Ma age. While we associate high ppm Re concentrations with mantle-involvement often in association with convergent tectonics and oceanic-crustal subduction (Stein et al., 2001), we suggest that extraordinary low Re concentrations reflect melting of posttectonic, over-thickened continental crust, and that elemental associations turn from subduction-associated Cu-Mo-(W)-Au to crustal-associated Sn-W-Mo-(Cu).

In summary, the Re-Os dating of molybdenite provides two geologically fitting ages for Pitkäranta mineralization (~1800 Ma and ~1550 Ma), suggesting that two events (Cu-Mo-W and Sn-Zn-Pb-Cu) have been partly superimposed in space during the complex magmatic history in this region. Furthermore, this study again demonstrates that the Re-Os chronometer is immune to overprinting thermal metamorphism, providing robust age results inside of the high temperature (pyroxene stable) contact metamorphic aureole. A similar case illustrating thermal stability of the Re-Os system in molybdenite has been documented in the contact metamorphic aureole (osumilite stable) adjacent to the Rogaland intrusion in south Norway (Bingen and Stein, 2003).

Curiosity-driven analyses of two chalcopyrite samples from the Klee and Meyer II mines in the Pitkäranta district are pertinent to the mobility issues discussed in this paper. Based on polished thin section examination, this chalcopyrite is a primary sulfide phase intergrown and cogenetic with molybdenite. The chalcopyrite occurs in large homogeneous and

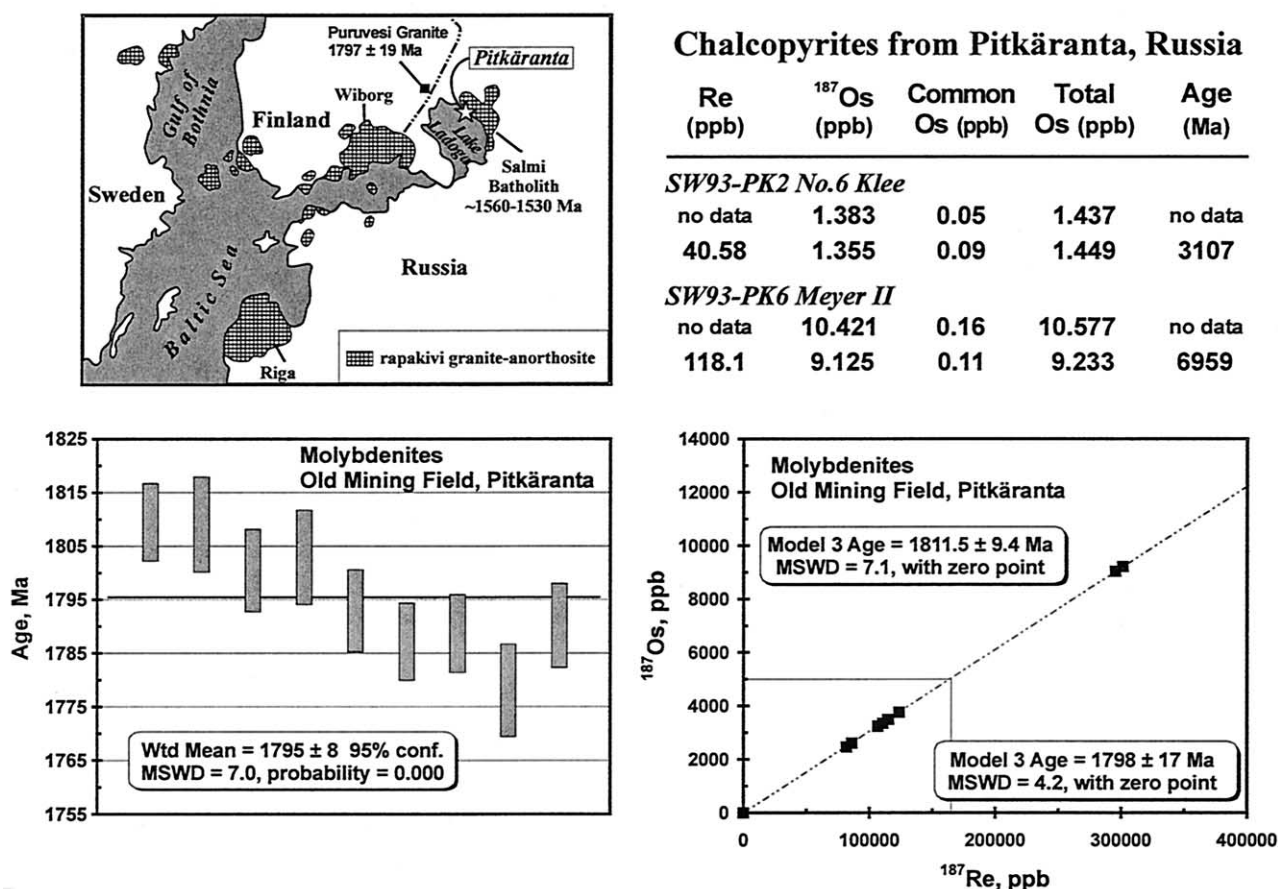


Fig. 4. Re-Os data for two chalcopyrites from the Pitkäranta skarn deposits, western Russia, are shown in the upper right table. Upper left box shows location of the Pitkäranta Sn-Cu-Zn-Pb (Mo-W) district in close proximity to the ~1560–1530 Ma Salmi rapakivi granite-anorthosite. The two lower boxes summarize the Re-Os isotopic data for molybdenites from six different mines (with three replicates) associated with Mo-W (Cu) ore samples hosted in pyroxene-bearing exoskarn adjacent to the Salmi batholith; the analyzed chalcopyrites are contained in two of these samples. Analyzed molybdenite from Mo-W (Cu) samples provide a surprising late Svecofennian age (~1800 Ma), 250 million years older than the fortuitously adjacent Salmi batholith, previously assumed to be the mineralizing intrusion. Re-Os systematics for ~1800 Ma molybdenites, overprinted by high-temperature exoskarn developed in association with the younger Salmi batholith, are fully intact. Re-Os molybdenite data (Stein et al., 1996a,b) summarized in this figure were derived 7 yr ago using the alkaline fusion method (Morgan and Walker, 1989), whereas we now employ the Carius tube method (Shirey and Walker, 1995) for sample dissolution and sample-spike equilibration. Although the alkaline fusion results are technically sound, the reproducibility of samples is less than what we achieve today using the Carius tube approach. Two replicate outliers (not shown) were omitted from the molybdenite data set used for the isochron and weighted average calculations. See text for further discussion of data and geologic interpretation.

uninterrupted patches without inclusions, and locally shares borders with molybdenite. The Re-Os analyses for the two chalcopyrite samples yield low ppb level concentrations for both elements (Fig. 4). Low Re in chalcopyrite coprecipitating with molybdenite is to be expected, and the low Re is proof that the phase analyzed was pure chalcopyrite without molybdenite inclusions. Notably, both chalcopyrites have essentially no common Os suggesting that they are LLHR (low-level, highly radiogenic) samples (Stein et al., 2000). The low Os concentrations for the two chalcopyrites (Fig. 4) are a striking contrast to the ¹⁸⁷Os concentrations in the adjacent molybdenite. Klee and Meyer molybdenite samples yielded a whopping 3764 ± 9 and 2834 ± 7 ppb ¹⁸⁷Os, respectively, more than three orders of magnitude higher than in the corresponding chalcopyrites. The two-sigma uncertainty of 7–9 ppb for the Klee and Meyer

molybdenites is on the order of the entire Os budget in the chalcopyrites. It is obvious that the loss of a few ppb of radiogenic ¹⁸⁷Os from the molybdenite would not affect the age calculation for molybdenite, whereas the gain of even half a ppb of ¹⁸⁷Os by chalcopyrite would drastically increase its age to an impossibly old value. The NTIMS ages for these two chalcopyrites are indeed impossible, in one case exceeding the age of the earth (Fig. 4). Our interpretation is that the chalcopyrite has acquired small amounts of radiogenic ¹⁸⁷Os, facilitated by contact with molybdenite where a suitable cation site for radiogenic ¹⁸⁷Os may be lacking in the crystal structure, as discussed in earlier sections of this paper. Based on similar arguments, it is also possible that some Re originally contained in the chalcopyrite was lost to the adjacent molybdenite, resulting in an impossibly old age for the chalcopyrite, but not

affecting the molybdenite age outside of analytical error. This seems less likely, however, as the distribution of Re between the molybdenite and chalcopyrite was probably fixed by equilibrium processes at the time of crystallization, so that there is little if any driving force for diffusion from one phase to the other. If the excess radiogenic ^{187}Os in the analyzed chalcopyrites were due to molybdenite inclusions or contamination, then there would be a correspondingly high and coupled Re concentration and the chalcopyrite would give an ~ 1800 Ma age, in effect carried by the molybdenite component.

The proposed uptake of ^{187}Os by chalcopyrite also applies to other sulfides that reside in contact with molybdenite. With the lack of available cation sites for radiogenic ^{187}Os in molybdenite, it seems remarkable that the ^{187}Os gain in the chalcopyrite is so slight, given the intimacy of the two minerals, the availability of radiogenic ^{187}Os , and the fact that chalcopyrite is known to accommodate Os during its crystallization (e.g., Morgan et al., 2000). In an experimental study of Os diffusion in pyrrhotite and pyrite, both minerals, but particularly pyrrhotite, readily exchanged Os with an external Os-bearing fluid reservoir at temperatures as low as 300°C (Brenan et al., 2000). Diffusion of Os in chalcopyrite may be slower than in pyrrhotite and pyrite, but this remains to be tested. Also, the grains used in the Brenan et al. (2000) experimental study were in the 10 to $1000\ \mu\text{m}$ range, whereas the Pitkäranta chalcopyrite occurs in >0.5 cm patches and blebs. Uptake of ^{187}Os may be controlled by surface adsorption along grain boundaries in contact with molybdenite, with minor (or slow) diffusion into the chalcopyrite structure.

We suggest that Re-Os analyses of sulfides residing in contact or direct association with molybdenite will most likely lead to geologic ages that are wildly aberrant and too old. In some circumstances, where the isochron approach is employed, excess radiogenic ^{187}Os may provide sulfide isochrons with misleading initial $^{187}\text{Os}/^{188}\text{Os}$ ratios that are too high leading to serious geologic misinterpretation. The chance for problems increases where high levels of radiogenic ^{187}Os are present, such as would be expected in older (Archean-Proterozoic) molybdenites or younger (Phanerozoic) porphyry Cu-Au systems where molybdenites are generally characterized by very high Re concentrations. The safest approach is to avoid Re-Os analytical work on sulfides that are in contact or even general spatial association with molybdenite, as their systematics will most likely be disturbed.

9. SUMMARY AND CONCLUSIONS

In this paper, we summarize the geochemical behavior of Mo, Re, W, and Os in molybdenite, and we explore the ionic species and states of cations to suggest a reason for the absence of common (initial) Os in this mineral. Second, we use LA-ICP-MS to document ^{187}Re - ^{187}Os decoupling, a phenomenon postulated by Stein et al. (1998a, 2001) based on NTIMS dating of molybdenite samples that were obtained from deliberately different mineral separation preparations. Second, we consider the ability of molybdenite to retain radiogenic $^{187}\text{Os}^{+5}$ in its structure, suggesting that the chemical stability in this mineral may actually increase during deformation, and that storage sites for radiogenic ^{187}Os may be created by development of kink bands and delamination cracks. Finally, we provide a geologic

example whereby molybdenite in contact with chalcopyrite retains its age, compared to the chalcopyrite, which acquires an impossibly old age. The loss of an imperceptible amount of radiogenic ^{187}Os from molybdenite swamps the Os budget of adjacent chalcopyrite. From these explorations, we come to the following conclusions:

(1) Molybdenite cannot be dated using the increasingly popular LA-ICP-MS method, as Re and ^{187}Os are decoupled at the micron scale yielding spot ages that are wildly aberrant. Dating whole molybdenite crystals or homogeneous, representative, fine-grained separates by ID-NTIMS, however, provides remarkably robust results, even when the mineral is highly deformed and subjected to granulite facies conditions. The attainment of these ID-NTIMS Re-Os age results is dependent largely on proper preparation of the mineral separate to fully homogenize individual crystals (Stein et al., 1998a, 2001).

(2) Lack of common (initial) Os in molybdenite may result from the reduction of aqueous species with ^{+4}Os to oversized and undercharged ^{+3}Os to ^0Os , which cannot be accommodated by the molybdenite structure.

(3) To retain radiogenic ^{187}Os , we suggest that molybdenite may become physically and chemically strengthened during deformation. The structure of this mineral lends itself to dislocation gliding, leading to kink banding and delamination cracks, where radiogenic ^{187}Os may be stored in crystal defects. In this study, micron scale pockets of radiogenic ^{187}Os enrichment and depletion are detected by LA-ICP-MS.

(4) The low energy beta decay of $^{187}\text{Re}^{+4}$ to $^{187}\text{Os}^{+5}$ may provide an oversupply of electrons that are partly retained in the molybdenite such that radiogenic $^{187}\text{Os}^{+5}$ may have access to “sticky” regions at the atomic scale for adherence. Alternatively, excess electrons may reduce at least some of the $^{187}\text{Os}^{+5}$ to structurally compatible $^{187}\text{Os}^{+4}$.

(5) Molybdenite is unlikely to forfeit Re and/or Os of any size and charge to adjacent silicate phases which provide no sites for siderophile-chalcophile elements. And, aqueous phases mobilize Re and Os only under oxidizing conditions. For situations where molybdenite is in contact with other sulfides, we demonstrate using a geologic example (Pitkäranta, Karelian Russia) that molybdenite ages remain intact relative to cogenetic and adjacent chalcopyrite, whose ages become too old with minor uptake of radiogenic ^{187}Os . Therefore, Re-Os analysis of sulfides in contact or direct association with molybdenite is highly inadvisable, and can lead to ages that are too old, and in the case of Re-Os isochrons, can provide initial $^{187}\text{Os}/^{188}\text{Os}$ ratios that are too high, leading to errant geologic interpretations.

In summary, the Re-Os systematics in molybdenite are an example of the importance of nanogeoscience, whereby “the origins of nearly all things geologic are rooted deeply in nanoscale phenomena” (Lower et al., 2002). While we have learned much about molybdenite in recent years, more work remains to be done, particularly in understanding Re and Os behavior at the atomic level.

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