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Assessment of the ^{187}Re decay constant by cross calibration of Re–Os molybdenite and U–Pb zircon chronometers in magmatic ore systems

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Abstract

The past decade has seen renewed interest in ^{187}Re–^{187}Os geochronology using a variety of matrices including sulfide minerals, shales and meteorites. The most widely used value of the ^{187}Re decay constant (λ ^{187}Re) is $1.666 \pm 0.005 \times 10^{-11}$ a^{-1} ($\pm$0.31%), which is based on cross calibration of Re–Os and Pb–Pb chronometers for certain meteorites [Smoliar M. I., Walker R. J., and Morgan J. W. (1996) Re–Os isotope constraints on the age of Group IIA, IIIA, IVA, and IVB iron meteorites. *Science* **271**, 1099–1102]. However, other recent studies have yielded alternate values of λ ^{187}Re, based upon either direct counting experiments or analysis of meteorites. Here, we provide an independent assessment of λ ^{187}Re, using methodology, sample materials, and preparation of Os standard solutions different from those of Smoliar et al. (1996). Combining Re–Os age data for molybdenite formed in magmatic ore deposits, with the U–Pb zircon age of the magmatic rocks, a refined λ ^{187}Re value is determined by averaging 11 individual cross-calibration experiments spanning ca. 2700 Ma of Earth history. Using the U decay constants of Jaffey [Jaffey A. H., Flynn K. F., Glendenin L. E., Bentley W. C., and Essling A. M. (1971) Precision measurement of half-lives and specific activities of 235U and 238U. *Phys. Rev.* **4,** 1889–1906], a value for λ ^{187}Re of $1.6668 \pm 0.0034 \times 10^{-11}$ a^{-1} is determined. Using the λ ^{238}U value of Jaffey et al. (1971) and λ ^{235}U value of Schoene [Schoene B., Crowley J. L., Condon D. J., Schmitz M. D., and Bowring S. A. (2006) Reassessing the uranium decay constants for geochronology using ID-TIMS U–Pb data. *Geochim. Cosmochim. Acta* **70,** 426–445], a value for λ ^{187}Re of $1.6689 \pm 0.0031 \times 10^{-11}$ a^{-1} is determined. These values are nominally higher (ca. 0.1 and ca. 0.2%) than the value determined by Smoliar et al. [Smoliar M. I., Walker R. J., and Morgan J. W. (1996) Re–Os isotope constraints on the age of Group IIA, IIIA, IVA, and IVB iron meteorites. *Science* **271**, 1099–1102], but within calculated uncertainty. Further refinement of λ ^{187}Re by cross calibrating the molybdenite and U–Pb zircon chronometers should be possible by utilizing high precision, single-grain, chemical abrasion zircon U–Pb analyses.

1. INTRODUCTION

1.1. Background

The past decade has seen rapid expansion in the application of the ^{187}Re–^{187}Os chronometer, and it is now a widely used isotopic system in geosciences. The expansion in Re–Os research results directly from analytical improvements

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in: (1) measurement of Re and Os isotopic compositions precisely and accurately by negative thermal ionization mass spectrometry (NTIMS) (Creaser et al., 1991; Völkening et al., 1991; Walczyk et al., 1991), (2) full chemical equilibration of Os between spike and sample (e.g., Shirey and Walker, 1995), and (3) Re and Os separation techniques (Cohen and Waters, 1996; Birck et al., 1997). The geochemical character of Re and Os (chalcophilic, siderophilic, organometallic) permits chronology and isotopic tracing in geology and cosmochemistry using minerals and matrices that cannot be employed for other isotopic systems (Rb–Sr, Sm–Nd) based on lithophile elements (cf. Ravizza and Turekian, 1989; Stein et al., 1997a,b; Shirey and Walker, 1998; Pearson and Shirey, 1999). Unique to the Re–Os system are accurate and precise age determinations for sulfide minerals in ore systems (e.g., Stein et al., 1997a,b; Selby et al., 2002). A notable example is the successful development of the Re–Os chronometer in molybdenite (Stein et al., 2001), a mineral present in many ore systems and in some metamorphic environments (Stein and Bingen, 2002; Bingen and Stein, 2003; Stein, 2006). For sedimentary rocks, it has been shown that precise and accurate depositional ages can be determined routinely for carbonaceous or pyritiferous shales, which has application in Earth evolution studies, stratigraphic correlation, and timescale research (Cohen et al., 1999; Hannah et al., 2004; Kendall et al., 2004; Selby and Creaser, 2005a). Furthermore, bitumen and oil have been shown to have utility for Re–Os geochronology and tracer studies (Selby and Creaser, 2005a,b). Finally, diamond inclusion Re–Os geochronology has been developed (Pearson et al., 1995).

Given this widespread utility in geochronology, it is fundamental that the value of λ ^{187}Re be known accurately and precisely. The uncertainty in the decay constant is the principal limiting factor for accurate age determination for most radioactive isotopic systems (Begemann et al., 2001). The need to further constrain the absolute value of a decay constant and its uncertainty is particularly important for comparison of isotopic ages derived from different isotopic systems (Min et al., 2000; Villeneuve et al., 2000). The most widely used value for λ^{187}Re in the geosciences (1.666×10^{-11} a^{-1}; Smoliar et al., 1996) has been questioned for its accuracy and precision (Shukolyukov and Lugmair, 1997; Birck and Allègre, 1998). In this study, we derive a value for λ ^{187}Re that is indistinguishable from that of Smoliar et al. (1996), by cross calibrating the U–Pb zircon and Re–Os molybdenite geochronometers from magmatic ore deposits spanning Cretaceous to Archean age.

1.2. The ^{187}Re decay constant (λ ^{187}Re)

The β decay of ^{187}Re to ^{187}Os has been investigated since 1948 (Naldrett and Libby, 1948). Many studies used direct counting experiments and determined λ ^{187}Re values between 2.31×10^{-11} and 1.39×10^{-13} a^{-1} (Sugarman and Richter, 1948; Suttle and Libby, 1954; Watt and Glover, 1962; Wolf and Johnston, 1962; Brodzinski and Conway, 1965; Naldrett, 1984; Ashktorab et al., 1993; Alessandrello et al., 1999; Galeazzi et al., 2001; Arnaboldi et al., 2003) (Table 1). The precision of these studies has been improved by mircocalorimetric determinations (Ashktorab et al., 1993; Alessandrello et al., 1999; Galeazzi et al., 2001; Arnaboldi et al., 2003), but even these modern methods yield results with uncertainties at the several percent level (Galeazzi et al., 2001). In addition, similar protocols (cryogenic bolometry with Re metal and $AgReO_4$) yield precise values that are significantly different, e.g., $1.682 \pm 0.045 \times 10^{-11}$ a^{-1} (Galeazzi et al., 2001) and $1.604 \pm 0.004 \times 10^{-11}$ a^{-1} (Arnaboldi et al., 2003; Audi et al., 2003a,b), making these λ ^{187}Re values unsuitable for high-resolution Re–Os geochronology, particularly when compared with other isotopic systems in use in the Earth Sciences.

Lindner et al. (1986, 1989) determined a λ ^{187}Re value of $1.64 \pm 0.05 \times 10^{-11}$ a^{-1} by measuring in-growth of ^{187}Os in solutions containing precisely known quantities of Re. An

Table 1
^{187}Re decay constant reported in the literature

^{187}Re decay constant	Method	Reference
1.38×10^{-11} to 2.77×10^{-11} a^{-1}	Re–Os molybdenite cross calibration with host rock age	Herr et al., (1954, 1958)
1.61×10^{-11} a^{-1}	Re–Os molybdenite cross calibration with host rock age	Hirt et al. (1963)
2.31×10^{-11} to 1.39×10^{-13} a^{-1}	Direct counting experiments	Sugarman and Richter (1948) Suttle and Libby (1954) Watt and Glover (1962) Wolf and Johnston (1962) Brodzinski and Conway (1965) Naldrett (1984)
$1.53 \pm 0.08 \times 10^{-11}$ a^{-1}	Re–Os meteorite data cross calibration with Pb–Pb meteoric age	Luck and Allègre (1983)
$1.59 \pm 0.05 \times 10^{-11}$ a^{-1}	Direct experimental determination	Lindner et al. (1989)
$1.64 \pm 0.05 \times 10^{-11}$ a^{-1}	Direct experimental determination	Lindner et al. (1989)
$1.65 \pm 0.011 \times 10^{-11}$ a^{-1}	Re–Os meteorite data cross calibration with Pb–Pb meteoric age	Horan et al. (1992)
$1.54 \pm 0.10 \times 10^{-11}$ a^{-1}	Microcalorimetric determinations	Ashktorab et al. (1993)
$1.666 \pm 0.017 \times 10^{-11}$ a^{-1}	Re–Os meteorite data cross calibration with Pb–Pb meteoric age	Smoliar et al. (1996)
$1.66 \pm 0.027 \times 10^{-11}$ a^{-1}	Re–Os meteorite data cross calibration with Pb–Pb meteoric age	Shen et al. (1996b)
$1.658 \pm 0.003 \times 10^{-11}$ a^{-1}	Re–Os meteorite data cross calibration with Pb–Pb meteoric age	Shukolyukov and Lugmair (1997)
$1.61 \pm 0.26 \times 10^{-11}$ a^{-1}	Microcalorimetric determinations	Alessandrello et al. (1999)
$1.682 \pm 0.045 \times 10^{-11}$ a^{-1}	Microcalorimetric determinations	Galeazzi et al. (2001)
$1.604 \pm 0.004 \times 10^{-11}$ a^{-1}	Microcalorimetric determinations	Arnaboldi et al. (2003)

uncertainty of ±3% ($1.64 \pm 0.05 \times 10^{-11}$ a^{-1}) was applied to the Lindner et al. (1989) value of λ ^{187}Re, however, because incomplete equilibration of tracer (^{190}Os) and radiogenic (^{187}Os) Os in batches of the Re-bearing solutions, and systematic uncertainties in the calibration of Os and Re spike and standard solutions.

Geological determinations of λ ^{187}Re have also been made over the past 50 years using terrestrial material and meteorites (Table 1). Geological estimates of λ ^{187}Re were first made from Re–Os molybdenite dating studies. Assuming that the age of the molybdenite was identical to its host rock, Herr et al. (1954) and Herr and Merz, 1958a,b calculated λ ^{187}Re values between 1.38×10^{-11} and 2.77×10^{-11} a^{-1}. Several years later, Hirt et al. (1963) determined a value of 1.61×10^{-11} a^{-1}, in good agreement with determinations that followed more than thirty years later (e.g., 1.666×10^{-11} a^{-1}, Smoliar et al., 1996), a remarkable achievement given the poor age constraints for the studied deposits and the very low precision of analytical techniques available at that time.

The value of λ ^{187}Re has also been evaluated by means of Re–Os isotopic data from iron meteorites (Luck et al., 1980; Luck and Allègre, 1983). Luck and Allègre (1983) presented a value of $1.53 \pm 0.08 \times 10^{-11}$ a^{-1}, based on Re–Os data of Luck et al. (1980) recalculated after recalibration of their Os tracer solution. Using higher-precision NTIMS and Carius tube methodologies, Shen et al. (1996b) determined a λ ^{187}Re value of 1.66×10^{-11} a^{-1} for iron meteorites from various iron meteorite Groups, but an uncertainty of 1.6% (±0.03) exists for this value because of gravimetric issues of Os content of the standard solution made from Os metal used to calibrate the Os spike. Shen et al. (1996b) assumed an age for the meteorites of 4.566 Ga from which to derive this value of λ ^{187}Re.

The most widely used value of λ ^{187}Re in geosciences in the past decade is that determined by Smoliar et al. (1996), who determined a value for λ ^{187}Re of 1.666×10^{-11} a^{1} from the best-fit slope through Re–Os isotopic data for Group IIIA meteorites, by assuming their age to be 4557.8 ± 0.4 Ma, identical to the Pb–Pb age for angrite meteorites (Lugmair and Galer, 1992). The uncertainty in this Pb–Pb age does not include the decay constant uncertainties for ^{235}U and ^{238}U. The assumption that the angrite age is equivalent to the age of IIIA meteorites is supported by ^{53}Mn–^{53}Cr ages for the angrites that are also within ±5 million years of the ^{53}Mn–^{53}Cr age for group IIIAB iron meteorites (Hutcheon and Olsen, 1991; Hutcheon et al., 1992). Smoliar et al. (1996) calculated a ±0.31% uncertainty ($1.666 \pm 0.005 \times 10^{-11}$ a^{1}) for the derived value of λ ^{187}Re from the regression statistics of their Group IIIA Re–Os data, which is an appropriate uncertainty to use for studies of relative Re–Os age difference between samples. However, calibration of the Os spike used by Smoliar et al. (1996) may include a systematic uncertainty of up to ±1.2% (2σ), associated with the non-stoichiometry of the ammonium hexachloro-osmate compound used to prepare the Os standard solution (Morgan et al., 1995). Smoliar et al.'s (1996) assumption that the IIIA meteorites have a Re–Os age identical to the Pb–Pb age for angrites also requires that the Re–Os, Mn–Cr, and U–Pb systems all isotopically closed at the same time, and have not been subsequently disturbed. The Smoliar et al. (1996) λ ^{187}Re value of 1.666×10^{-11} a^{-1} is nominally 1.6% higher than the direct experimental determination (1.64×10^{-11} a^{-1}, Lindner et al., 1989), but the Lindner et al. (1989) value has a ±3% uncertainty which encompasses the Smoliar et al. (1996) determination.

Shen et al. (1996a, 1998) reported that the Re–Os data from pallasites plot along the well-defined IIAB iron meteorite isochron with a slope of 0.07848 ± 0.00018. Shukolyukov and Lugmair (1997) calculated a λ ^{187}Re value of $1.658 \pm 0.003 \times 10^{-11}$ a^{-1} using the Re–Os pallasite data of Shen et al. (1996a), using a Mn–Cr age of 4558.0 ± 1.0 Ma for the Omolon pallasite, along with the assumptions that the Omolon pallasite formed contemporaneously with other pallasites and that the Mn–Cr and Re–Os systems closed the same time. Including the uncertainty in the Os tracer calibration (1.6%; Shen et al., 1996b) for Shukolyukov and Lugmair (1997) λ ^{187}Re determinations, places their estimate of λ ^{187}Re within uncertainty of the Smoliar et al. (1996) determination.

Also, based on Re–Os data from meteorites, Birck and Allègre (1998) proposed that λ ^{187}Re should be adjusted to a value between that determined by Shen et al. (1996b) and Smoliar et al. (1996), but no uncertainty for the Os concentration in the Os standard solution manufactured from $(NH_4)_2Os(Br)_6$ was given.

To further investigate the accuracy and precision of λ ^{187}Re we describe here a cross calibration of the ^{187}Re–^{187}Os molybdenite and U–Pb zircon chronometers from magmatic ore systems. We decided to use this approach because: (1) many recent studies have shown that the Re–Os molybdenite geochronometer is highly robust, (2) molybdenite is a relatively common mineral in magmatic (granitic) ore systems, (3) granitic magmatism can be precisely dated using U–Pb zircon methods, and (4) the U–Pb zircon method is widely regarded as the most accurate and precise method of geochronology, as a result of the highly robust nature of zircon, the dual U–Pb decay scheme utilized, and the most precisely determined decay constants (Jaffey et al., 1971; Heaman and Parrish, 1991; Stein et al., 1997a,b; Cherniak and Watson, 2000; Selby et al., 2002). This independent assessment differs from the methodology of Smoliar et al. (1996) and later studies (e.g., Shukolyukov and Lugmair, 1997).

2. METHODOLOGY

2.1. ^{187}Re–^{187}Os molybdenite chronometer

During the last decade it has been shown that Re–Os dating of molybdenite yields accurate and reproducible ages, and that the ^{187}Re–^{187}Os molybdenite chronometer is remarkably robust, surviving post-mineralization hydrothermal activity, plutonism, metamorphism, and intense deformation (Stein et al., 1998, 2001, 2004; Selby et al., 2002; and others). Further, Bingen and Stein (2003) have shown that the Re–Os molybdenite chronometer was not reset by granulite facies contact metamorphism, implying a "closure temperature" for this mineral close to that of the U–Pb system in zircon (cf. Heaman and Parrish, 1991; Cherniak and Watson, 2000). Recent Re–Os molybdenite studies have proved invaluable for discerning the absolute timing of magmatic-associated mineralization, as age constraints determined from silicate gangue minerals and/or wallrock alteration minerals (e.g., Ar–Ar or Rb–Sr ages) may not record the absolute timing of sulfide deposition because of lower closure temperatures and greater susceptibility to isotopic disturbance (Stein et al., 1997a,b; Watanabe and Stein, 2000; Selby and Creaser, 2001a,b; Selby et al., 2002). However, some workers have proposed that the ^{187}Re–^{187}Os chronometer is unreliable by reporting geologically unreasonable, non-reproducible and/or impossible age results (cf. Luck and Allègre, 1982; McCandless et al., 1993; Suzuki et al., 2000, 2001).

Especially intriguing is the decoupling of Re and ^{187}Os in molybdenite; Os, independently of Re, appears to migrate within, but does not leave the molybdenite grain in significant amounts after molybdenite formation (Stein et al., 2003). Thus, if only a fragment of a crystal is analyzed, the assumption of a closed isotopic system may be violated. Recognition and understanding of this concept has been paramount to obtaining accurate and reproducible Re–Os ages from molybdenite (Stein et al., 2001, 2003; Kosler et al., 2003; Selby and Creaser, 2004). The parent–daughter decoupling can be overcome through appropriate analytical protocols (e.g., sample selection and preparation, and in some cases, sample amount) to assure complete or representative sampling of individual molybdenite crystals (Stein et al., 2001, 2003, 2005; Selby and Creaser, 2004). Problems with geologic understanding and/or sampling protocol may have contributed to the apparent controversy on reliability of Re–Os dating in molybdenite.

Rhenium typically exists at the parts per million level in molybdenite. In contrast, no Os is incorporated into molybdenite during its formation. Thus, measured Os is radiogenic ^{187}Os accumulated *in situ* from ^{187}Re decay. Model molybdenite ages can be calculated from Re–Os isotopic analysis of a single sample using the simplified isotope equation ($t = \ln[^{187}\mathrm{Os}/^{187}\mathrm{Re} + 1]/\lambda$). For molybdenite samples of the same paragenesis, the ^{187}Re–^{187}Os isochron approach can be employed to verify zero initial or common Os (i.e., ^{187}Os) and document isochroneity of related samples (cf. Stein et al., 1997a,b, 1998, 2001; Selby et al., 2002). The ^{187}Re–^{187}Os isochron method is now the mainstream approach for dating molybdenite and establishing genetic relationships in complex terranes (e.g., Selby et al., 2002; Stein et al., 2004).

2.2. Analytical protocol

2.2.1. *Rhenium–osmium molybdenite methodology*

At the University of Alberta Radiogenic Isotope Facility the measurement of the abundance of ^{187}Re and ^{187}Os in molybdenite is by isotope dilution using a mixed tracer solution containing isotopically enriched ^{185}Re and isotopically normal Os, in the form of a gravimetric and isotopic Os standard. By using an isotopically normal Os solution, the abundance of ^{187}Os in molybdenite is calculated by measuring the ^{187}Os abundance after equilibrating ^{187}Os in molybdenite and common Os in the tracer solution (e.g., Suzuki et al., 1992). Using this approach the isotopic analysis of Os can be corrected for instrumental mass fractionation during analysis because the common Os tracer solution offers a pair of Os isotopes whose ratio is known and invariant (c.f. Markey et al., 2003). Ammonium hexachloro-osmate (Johnson and Matthey, 99.999% metal-basis purity) is used for the source of Os in this tracer solution. This compound is known to be non-stoichiometric at levels of ±1% (Papanastassiou et al., 1994; Morgan et al., 1995; Shen et al., 1996b; Yin et al., 2001), but we have found that reduction of this salt to metallic Os in 98% N_2 and 2% H_2 gas at ca. 500 °C for ca. 2 h yields consistent and precise results of the metallic Os weight fraction. For the salt used ("AB2", lot# H25H35) this was determined to be 0.4326% Os $\pm$ 0.0003; $\pm$ 0.07%, 1SD, $n = 5$, slightly less than the stoichiometric value of 0.4333% (Selby and Creaser, 2001a). This gravimetric determination, together with the measured isotopic composition of Os in the compound, are used to determine the ^{187}Os abundance in molybdenite.

The ^{185}Re abundance in the tracer solution is calibrated directly against a gravimetric Re standard solution made from 99.999% Re zone refined metal and shows a reproducibility of ±0.1% 1SD ($n = 6$) (Selby and Creaser, 2001b).

At AIRIE, Colorado State University, measurement of the abundance of ^{187}Re and ^{187}Os in molybdenite samples is obtained by isotope dilution using either individual ^{185}Re and ^{190}Os tracers or a mixed ^{185}Re–^{188}Os–^{190}Os tracer. Spikes were calibrated against gravimetric standard solutions of normal isotopic composition. The source of Os in the standard solutions is ammonium hexachloro-osmate, and the source of Re is potassium perrhenate. Os and Re spike calibrations used the same standard solutions used by Smoliar et al. (1996). Thus, the Os content of the standard solution is known to ca. 1% (Smoliar et al., 1996), and the ^{185}Re content of the spikes is determined to ±0.1% 1SD (Markey et al., 1998).

Rhenium and Os in molybdenite are equilibrated with the mixed tracer isotopes by high-temperature (240 °C) Carius-tube dissolution in inverse *aqua regia*. Rhenium and Os are then chemically separated by solvent extraction or distillation (Os) and anion exchange chromatography (Re), and analysed by NTIMS (Markey et al., 1998, 2003; Selby and Creaser, 2004). Uncertainties for Re–Os isotopic data and abundances are determined by error propagation of uncertainties in Re and Os mass spectrometer measurements, blank abundances and isotopic compositions, spike calibrations, reproducibility of standard Re and Os mass spectrometric values, and weighing uncertainties.

A "control" sample HLP-5, a 2 kg aliquant of a molybdenite powder concentrate (ca. 44 μm) obtained from the mill at the Huanglongpu Mo–Pb–U carbonatite vein-type deposit in the Shaanxi Province, China (Stein et al., 1997a,b; Du et al., 2004; Selby and Creaser, 2004) is routinely analysed to monitor inter-laboratory agreement. This control sample yields a weighted average Re–Os age of 220.52 $\pm$ 0.92 Ma (±0.42% 2σ, MSWD = 1.3, $n = 17$) from the University of Alberta (Selby and Creaser, 2004), which is identical to that reported by Markey et al. (1998) as determined by the AIRIE laboratory (221.0 ± 2.0 Ma, ± 0.90% 2σ, $n = 19$).

2.2.2. *Uranium–lead zircon methodology*

U–Pb zircon dating of the igneous rocks in the magmatic-related mineral deposits discussed here has been determined previously at several worldwide laboratories (see references in footnote of Table 2). In all cases isotope dilution thermal ionisation mass spectrometry (ID-TIMS) was used. For all studies, zircon was isolated from rock samples using standard mineral separation techniques (crushing, Wilfley Table, heavy liquid [methylene iodide], and magnetic [Frantz Isodynamic Separator] methods). In some cases zircons were mechanically abraded to eliminate potentially altered crystal surfaces (Krogh, 1982). Zircon fractions were selected by examination under a high magnification binocular microscope. The U–Pb zircon geochronology used in this study were conducted prior to knowledge of the pre-treatment method of high-temperature annealing forwarded by partial HF digestion at high-temperature and pressure, which has been demonstrated to remove portions of zircons that have lost Pb, without affecting the isotopic systematics of the remaining zircon (Mattinson, 2005). Zircon U–Pb data of the earlier studies used herein followed the protocol of washing the zircon fractions in 4 N HNO_3, H_2O, and acetone, then dissolving the fractions with a mixture of distilled 48% HF and 7 N HNO_3 at ca. 220 °C for ca. 120 h in TFE Teflon vials with Pb and U isotopic (cf. ^{205}Pb–^{235}U; ^{205}Pb, $^{233–235}$U) tracer solutions. Information regarding the calibration uncertainties of U and Pb tracer solutions were not given in any of the studies used here. Standard anion exchange HCl and HBr chromatography was employed for the separation of U and Pb, respectively (cf. Krogh, 1973; Parrish et al., 1987; Mortensen et al., 1995). The purified U and Pb fractions were analyzed by thermal ionization mass spectrometry, and analyses were corrected for mass fractionation, blank contribution, spike, and initial common Pb. The isotopic composition of common Pb in excess of analytical blank was determined using the two-stage model of Stacey and Kramers (1975). The measured isotopic ratios were corrected for mass fractionation based on analysis of NBS 981 and different U isotopic standards. Age determinations quoted by the original studies were completed using the corrected isotopic data, including percent uncertainties at the 1σ level, and error correlation (*rho*; Ludwig, 1980). Various numerical treatments were used, however, (cf. York, 1969; Davis, 1982; Roddick et al., 1987; Ludwig, 1998) to propagate all known sources of uncertainty using the ^{238}U (1.55125×10^{-10} year^{-1}) and ^{235}U (9.8485×10^{-10} year^{-1}) decay constants and the present day ^{238}U/^{235}U value (137.88) (Jaffey et al., 1971).

All U–Pb zircon ages used and quoted in this study are concordia-intercept ages (^{207}Pb/^{206}Pb), using the primary U–Pb isotopic data but with ages recalculated using *Isoplot v 3* (Ludwig, 2003) to include decay constant uncertainties (^{238}U = 0.107% [±0.00166]; ^{235}U = 0.136% [±0.0134], Jaffey et al., 1971). These are presented in Table 2 and EA-1. It has been suggested that λ ^{235}U may be 0.09% higher than the value of Jaffey et al. (1971) (9.8569×10^{-10} year^{-1} ± 0.11% [±0.0108] including λ ^{238}U uncertainty; Mattinson, 2000; Schoene et al., 2006). In addition to using the U decay constants of Jaffey et al. (1971) in this cross-calibration study we also consider U–Pb zircon ages calculated using the suggested λ ^{235}U of Schoene et al. (2006).

3. SAMPLES AND RESULTS

Zircon U–Pb and molybdenite Re–Os age data from 11 magmatic-hydrothermal deposits are presented here (Table 2, Appendix A, Electronic Annex-1). For the deposits studied, there is a close spatial and temporal relationship between magmatism and molybdenite mineralization. In all cases, U–Pb zircon ages record zircon crystallization in the magma of the progenitor pluton, and molybdenite ages record sulfide mineral formation in the related magmatic hydrothermal system, generally as veins within the larger ore system. Though the timing of crystallization of magmatism causing the magmatic-hydrothermal system must be slightly older than sulfide mineralization in the magmatic hydrothermal system itself, only in very young magmatic ore systems can the ages of plutonism and the ages of different vein sets be analytically resolved within the life-span (100–400 thousand years) of typical magmatic-hydrothermal systems (Stein et al., 2002). The data presented here are confined to magmatic-hydrothermal systems older than 90 Ma, with analytical uncertainties of at least 0.2 Ma for both Re–Os molybdenite and U–Pb zircon age determinations.

The agreement between U–Pb zircon and Re–Os molybdenite ages is illustrated in Fig. 1, using the most widely used λ ^{187}Re value of 1.666×10^{-11} a^{-1} (Smoliar et al., 1996). We find an excellent correlation (Slope, 1.0004 ± 0.0023 (2σ); MSWD, 0.17; probability, 0.99) between the Re–Os molybdenite ages determined in our laboratories and U–Pb zircon ages determined using the decay constants of Jaffey et al. (1971) for host plutons from deposits spanning ca. 90 to ca. 2670 Ma (Fig. 1 and Table 2). A statistically indistinguishable correlation (Slope, 0.9984 ± 0.0021 (2σ); MSWD, 0.28; probability, 0.98) is found between the Re–Os molybdenite ages and U–Pb zircon ages calculated using the ^{238}U decay constant of Jaffey et al. (1971) and the ^{235}U decay constant of Schoene et al. (2006).

Using the Re–Os molybdenite data together with the U–Pb zircon ages from each deposit, individual values of λ ^{187}Re can be determined for each magmatic-hydrothermal system. These values of λ ^{187}Re range between $1.664 \pm 0.010 \times 10^{-11}$ and $1.679 \pm 0.035 \times 10^{-11}$ a^{-1}, with a weighted average of $1.6668 \pm 0.0034 \times 10^{-11}$ a^{-1} (MSWD, 0.35; probability, 0.97, 2σ) (Fig. 2). The unweighted mean is $1.6688 \pm 0.0097 \times 10^{-11}$ a^{-1} and the median value is $1.6672 \pm 0.0097 \times 10^{-11}$ a^{-1}. Although the weighted, unweighted, and median values nominally differ, the three calculated λ ^{187}Re values are identical, within uncertainty.

Similar values of λ ^{187}Re are also derived from the Re–Os molybdenite data using U–Pb zircon ages calculated with the λ ^{238}U of Jaffey et al. (1971), but the λ ^{235}U

Table 2
Re–Os molybdenite data and associated U–Pb zircon dates from paired occurrences in the magmatic-hydrothermal environment

Sample	Re (ppm)	^{187}Re (ppm)	^{187}Os (ppb)	Re–Os Age (Ma)[a]	U–Pb Age (Ma)[b]	λ ^{187}Re[n] (e^{-11})	λ ^{187}Re[o] (e^{-11})	% Uncertainty[p] from U–Pb data
Fort Knox, USA[c]	13.58 ± 0.03	8.54 ± 0.02	13.23 ± 0.02	92.9 ± 0.3 [0.4]	92.5 ± 0.2 [0.3] (92.6 ± 0.2[0.3])	1.674 ± 0.011	1.672 ± 0.011	38
Endako, Canada[d]	31.09 ± 0.14	19.54 ± 0.08	47.48 ± 0.19	145.7 ± 0.4 [0.6]	145.1 ± 0.8 [0.9] (145.2 ± 0.8[0.9])	1.673 ± 0.022	1.672 ± 0.022	35
Costelloe Murvey, Ireland[e]	3.163 ± 0.008	1.988 ± 0.005	12.74 ± 0.02	383.3 ± 1.1 [1.6]	380.1 ± 6.7 [7.7] (378.2 ± 6.3[7.1])	1.679 ± 0.035	1.689 ± 0.033	77
Connell Mtn, Canada[f]	643.2 ± 3.4	404.3 ± 2.1	3211 ± 16	474.9 ± 1.2 [1.9]	474.0 ± 5.3 [5.5] (474.8 ± 2.7[2.9])	1.667 ± 0.031	1.666 ± 0.026	45
Aplite, Canada[g]	9.641 ± 0.022	6.059 ± 0.014	269.4 ± 0.4	2611.1 ± 6.9 [10.7]	2611 ± 1.6 [7.4] (2607 ± 1.6[6.3])	1.666 ± 0.010	1.669 ± 0.010	34
Ryan Lake, Canada[g]	11.86 ± 0.05	7.455 ± 0.029	339.7 ± 1.2	2674.8 ± 7.4 [11.3]	2671 ± 5.5 [11] (2665 ± 5.0[9.3])	1.669 ± 0.019	1.671 ± 0.019	28
Tepasto, Finland[h]	4.31 ± 0.01	2.707 ± 0.006	82.46 ± 0.04	1800.9 ± 4.4 [7.1]	1802 ± 13 [15] (1798 ± 13[14])	1.665 ± 0.016	1.669 ± 0.015	64
Øvre Myssa, Norway[i]	29.12 ± 0.02	18.30 ± 0.01	282.0 ± 0.1	917.6 ± 0.7 [2.9]	919 ± 3.8 [5.1] (917 ± 2.6[3.8])	1.664 ± 0.009	1.668 ± 0.007	81
Antoinette, Norway[j]	142.6 ± 0.1	89.63 ± 0.08	2630 ± 4	1735.7 ± 2.2 [5.8]	1739 ± 12 [14] (1735 ± 12[13])	1.670 ± 0.015	1.667 ± 0.014	69
Ragunda, Sweden[k]	0.1921 ± 0.0003	0.1208 ± 0.0002	3.084 ± 0.004	1513.8 ± 3.0 [5.6]	1515 ± 3.7 [7.2] (1512 ± 3.7[6.4])	1.664 ± 0.010	1.667 ± 0.009	59
Salobo, Brazil[l,m]	199.3 ± 0.1	125.24 ± 0.08	5484 ± 2	2572.6 ± 1.8 [8]	2573 ± 4.3 [8.5] (2568 ± 4.0[7.3])	1.666 ± 0.006	1.669 ± 0.005	69

[a] Values in brackets represent full analytical + decay constant uncertainties.

[b] All ages are ^{206}Pb/^{207}Pb ages. Values in square brackets represent full analytical + decay constant uncertainties. Age given in curved bracket are determined using the suggested ^{235}U λ of Schoene et al. (2006). Zircon U and Pb isotopic data used in this study are available from the GCA data repository.

[c] Re–Os data from Alberta (Selby et al., 2002); U–Pb age provided by J. K. Mortensen, University of British Columbia and reported in Murphy (1997) and Bakke (1995).

[d] Re–Os data from Alberta (Selby and Creaser, , 2001b); U–Pb age from Villeneuve et al. (2001).

[e] Re–Os data from Alberta (this study); U–Pb age from Feely et al. (2003).

[f] Re–Os data from Alberta (Lentz et al., 2005); U–Pb age provided by V. McNicoll, Geological Survey of Canada.

[g] Re–Os data from Alberta (Ootes et al., 2002, in press); U–Pb age provided by J. Ketchum, Northwest Territories Geoscience Office.

[h] Re–Os data from AIRIE (CT-564A, this study); U–Pb age from Rastas et al. (2001).

[i] Re–Os data from AIRIE (CT-332A, Bingen et al., 2006); U–Pb age from Shärer et al. (1996).

[j] Re–Os data from AIRIE (CT-210A, this study and Stein et al., 1997a,b); U–Pb age from Mansfeld (1998).

[k] Re–Os data from AIRIE (CT-83A, this study); U–Pb age from Persson (1999).

[l] Re–Os data from AIRIE (CT-415A, Requia et al., 2003); U–Pb age from Machado et al. (1991).

[m] Small analytical correction to Os data compared to Requia et al. (2003).

[n] ^{187}Re decay constant derived using the U–Pb zircon age determined using the U decay constants of Jaffey et al. (1971). Uncertainty in the calculated ^{187}Re λ includes the uncertainties in the ^{187}Os and ^{187}Re abundances and the uncertainty in the U–Pb age.

[o] ^{187}Re decay constant derived using the U–Pb zircon age determined using the ^{238}U decay constant of Jaffey et al. (1971) and the proposed λ value ^{235}U (Schoene et al., 2006). Uncertainty in the calculated ^{187}Re λ includes the uncertainties in the ^{187}Os and ^{187}Re abundances and the uncertainty in the U–Pb age.

[p] Percentage of the uncertainty of the calculated ^{187}Re λ contributed from the uncertainty in the U–Pb zircon ages.

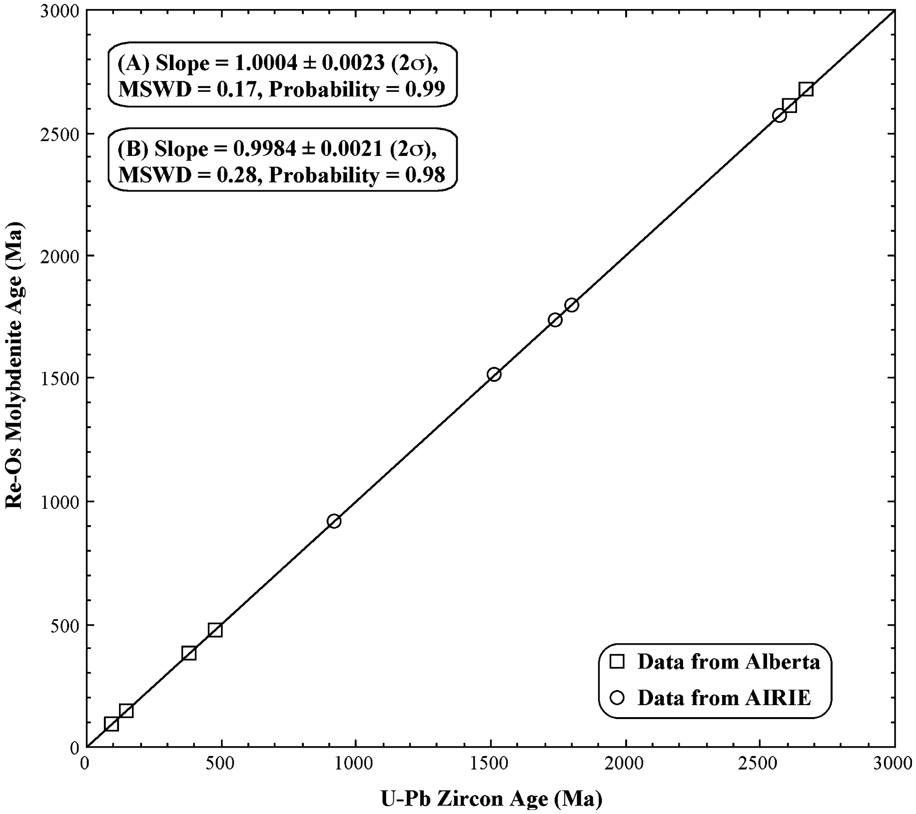

Fig. 1. U–Pb zircon age plotted against Re–Os molybdenite age. (A) Fit of data includes full analytical and decay constant uncertainties. U–Pb zircon ages calculated using the decay constants of Jaffey et al. (1971). (B) Fit of data includes full analytical and decay constant uncertainties, with the U–Pb zircon data calculated using the ^{238}U decay constant of Jaffey et al. (1971) and the ^{235}U decay constant of Schoene et al. (2006). Two sigma uncertainties are smaller than symbol size. Fit calculated using *Isoplot v.3.0* (Ludwig, 2003).

recommended by Schoene et al. (2006). These range from $1.666 \pm 0.026 \times 10^{-11}\ a^{-1}$ to $1.689 \pm 0.033 \times 10^{-11}\ a^{-1}$, with a weighted average of $1.6689 \pm 0.0031 \times 10^{-11}\ a^{-1}$ (MSWD, 0.24; probability, 0.99, 2σ; Fig. 2). The unweighted average is identical to the weighted average ($1.6709 \pm 0.0128 \times 10^{-11}\ a^{-1}$). In this case, the median value ($1.6687 \pm 0.0128 \times 10^{-11}\ a^{-1}$) is nominally lower, but within uncertainty of the means.

4. DISCUSSION

This cross calibration between the U–Pb zircon and Re–Os molybdenite chronometers provides an important independent test of the most widely used value of $\lambda\ ^{187}$Re, as the methodology, sample materials, and (for the University of Alberta laboratory) the preparation of Os standard solutions differ greatly from the study of Smoliar et al. (1996). The weighted average value for $\lambda\ ^{187}$Re determined here using the U decay constants of Jaffey et al. (1971) of $1.6668 \pm 0.0034 \times 10^{-11}\ a^{-1}$ is identical within calculated uncertainty limits to the value derived by Smoliar et al. (1996) of $1.666 \pm 0.005 \times 10^{-11}\ a^{-1}$ (Fig. 3), which is also based on the U decay constants of Jaffey et al. (1971). In addition, the weighted average value for $\lambda\ ^{187}$Re determined here using the $\lambda\ ^{238}$U of Jaffey et al. (1971), but the $\lambda\ ^{235}$U recommended by Schoene et al. (2006) ($1.6689 \pm 0.0031 \times 10^{-11}\ a^{-1}$) is also within calculated uncertainty to the value derived by Smoliar et al. (1996) (Fig. 3).

Calculating the molybdenite Re–Os ages with other values of $\lambda\ ^{187}$Re based on meteoritic studies, such as those proposed by Shukolyukov and Lugmair (1997), results in significant divergence between the U–Pb zircon age of host plutons and the Re–Os age of molybdenite for samples of Archean age. For example, a molybdenite from the Ryan Lake pluton, Yellowknife, Canada yields a Re–Os age of 2674 ± 7.4 Ma [±11.3 including decay constant uncertainty] using the $\lambda\ ^{187}$Re value of Smoliar et al. (1996), indistinguishable from the U–Pb zircon age of 2671 ± 5.5 Ma [±11 including decay constant uncertainty] using the decay constants of Jaffey et al. (1971) (Table 2). Using the $\lambda\ ^{187}$Re value of $1.658 \times 10^{-11}\ a^{-1}$ from Shukolyukov and Lugmair (1997) however, yields Re–Os molybdenite ages 14 and 17 million years older that only agree with the U–Pb zircon age within its uppermost uncertainty limit.

Recent direct counting experiments have resulted in $\lambda\ ^{187}$Re values with much improved precision over previous studies of this type (Galeazzi et al., 2001; Arnaboldi et al., 2003). Nevertheless, they are ca. 1% higher (±0.017) and ca. 3.9% lower (±0.065), respectively, than the $\lambda\ ^{187}$Re value of Smoliar et al. (1996) and the value determined here. For molybdenites of Archean age, this

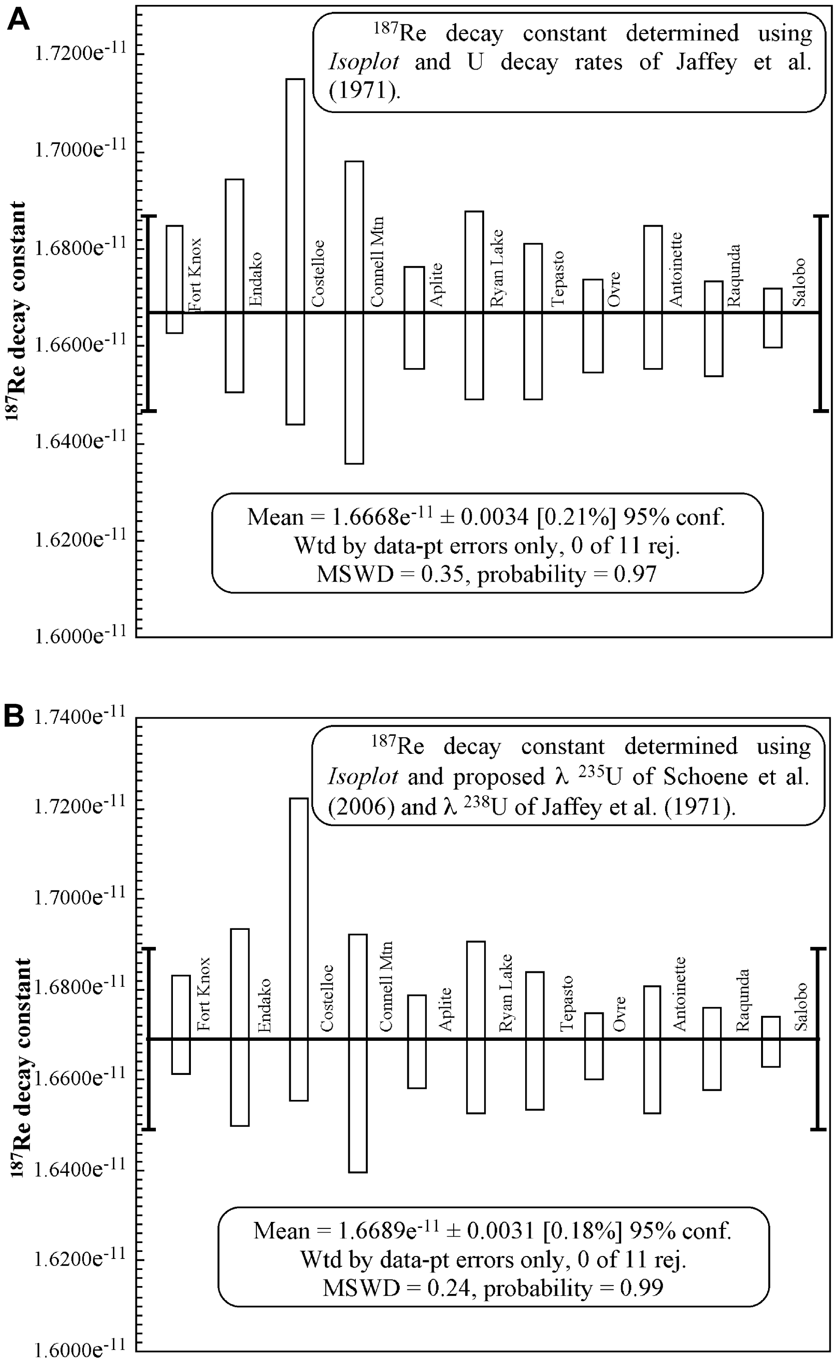

Fig. 2. (A) Weighted average plot of ^{187}Re decay constants derived from the Re–Os data and U–Pb zircon ages, calculated using U decay constants of Jaffey et al. (1971). (B) Weighted average plot of ^{187}Re decay constants derived from the Re–Os data and U–Pb zircon ages calculated using the ^{238}U decay constant of Jaffey et al. (1971) and the ^{235}U decay constant of Schoene et al. (2006). Uncertainties for ^{187}Re λ include all sources of analytical uncertainty and are at the 2σ level. Fit calculated using *Isoplot v.3.0* (Ludwig, 2003).

difference would yield Re–Os ages at least 25 million years younger or 100 million years older than ages calculated with the decay constant of Smoliar et al. (1996), highly disparate to the U–Pb zircon ages for the paragenetically related host plutons. Thus, it appears that despite significantly improved precision for these recent determinations, their accuracy remains problematic.

The weighted average λ ^{187}Re value determined here ($1.6668 \pm 0.0034 \times 10^{-11}$ a^{-1}) is based upon U–Pb zircon ages from host plutons, determined over the past 10 years from a variety of laboratories (Table 2 and Appendix A). For all the deposits studied here the U–Pb age is derived from the regression of U–Pb data obtained from analyses of multi-grain zircons fractions. In many cases, the data

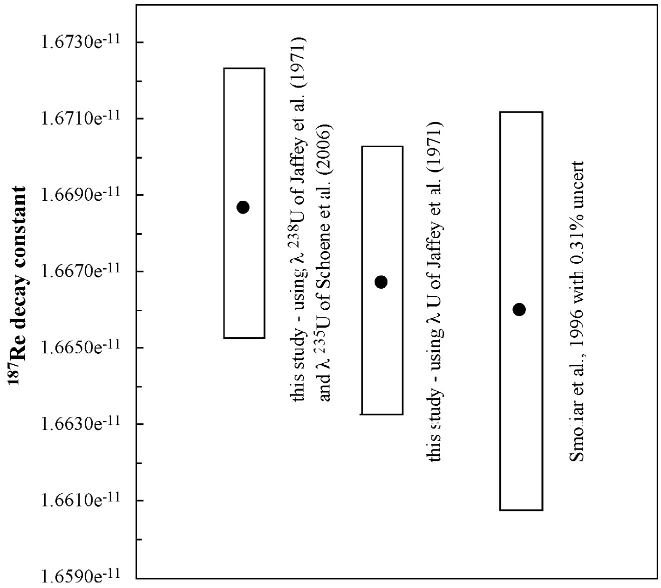

Fig. 3. Plot comparing the ^{187}Re decay constant values derived from this study to the value of Smoliar et al. (1996). Uncertainties are at the 2σ level.

are discordant and show excess scatter, which likely impacts the accuracy and precision of the ^{207}Pb/^{206}Pb age. For some deposits, however, ^{206}Pb/^{238}U ages are almost identical to the ^{207}Pb/^{206}Pb age (e.g., Fort Knox, Salobo), but still result from multi-grain zircon analyses. In some cases, the uncertainty in the derived individual values of λ ^{187}Re is dominated by the partial uncertainty in the U–Pb zircon age determination currently available (Table 2). Recent work shows that Pb loss and/or inheritance effects can be minimized by employing single zircon grain analysis following a pre-dissolution chemical treatment. This procedure improves accuracy and precision of U–Pb zircon ages relative to both multi-grain zircon analyses and single-grain non-treated analyses (Mattinson, 2005; Mundil et al., 2001, 2004). Thus, it is likely that the value of λ ^{187}Re can be further refined through cross calibration of the Re–Os molybdenite and U–Pb zircon chronometers using concordant single-grain ^{206}Pb/^{238}U U–Pb zircon ages that have been chemically treated prior to dissolution (Mundil et al., 2001; Mattinson, 2005). Such data will reduce the added uncertainty from the ^{235}U decay constant (Ludwig, 2000).

Refinement of the precision and accuracy of λ ^{187}Re has important implications for other aspects of Re–Os geochronology. Re–Os geochronology of black shales can provide depositional ages for resolution of problems in stratigraphy, sedimentology and calibration of the earth's time scale (Cohen et al., 1999; Hannah and Stein, 2003; Kendall et al., 2004; Selby and Creaser, 2005a). A study of black shales at Devonian–Mississippian boundary found excellent agreement between the Re–Os depositional age using λ ^{187}Re of $1.666 \pm 0.005 \times 10^{-11}$ a^{-1} (361.3 ± 2.4 Ma, Selby and Creaser, 2005a) and the interpolated U–Pb zircon age (360.7 ± 0.7 Ma, Trapp et al., 2004). Recalculating the Re–Os black shale data using the ^{187}Re λ derived here ($1.6668 \pm 0.0034 \times 10^{-11}$ a^{-1}), yields a revised Re–Os age of 361.2 ± 2.0 Ma, approximately 0.03%, younger than that determined using the λ ^{187}Re of Smoliar et al. (1996).

We have shown here that cross calibration of the Re–Os and U–Pb chronometers by dating molybdenite and zircon from a single magmatic-hydrothermal system is a viable method for determining λ ^{187}Re. This approach offers two key advantages over the most widely employed method, the use of meteoritic material. In many cases, molybdenite and zircon are found together in the same rock specimen, eliminating the need to infer genetic relationships that was necessary in analyses of different meteorite groups. In addition, multiple individual experiments can be performed on deposits spanning a large age range (billions of years) and the combined results used to refine the value of λ ^{187}Re.

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APPENDIX A. SAMPLE DETAILS

For ages reported below, numbers in brackets after the uncertainties reflect the combined analytical plus decay constant uncertainties that contribute to the reported uncertainty in the age. For example, for 2611 ± 6.9[10.7] Ma, ±6.9 represents propagation of all analytical uncertainty alone whereas ±10.7 represents the combined analytical and λ ^{187}Re uncertainties. The same format holds for U–Pb ages discussed in this paper, with U–Pb ages calculated (*Isoplot* V.3; Ludwig, 2003) using the ^{235}U decay constant reported by Schoene et al. (2006) shown in curved brackets, e.g., 2611 ± 1.6[7.4] Ma (2607 ± 1.6[6.3] Ma). The combined error (analytical plus decay constant uncertainty) should be reported for comparing Re–Os ages with ages derived by the U–Pb method.

A.1. ca. 90 Ma, Fort Knox, Alaska

The U–Pb data for the Fort Knox pluton determined by J.K. Mortensen, (University of British Columbia) has not been published, but is discussed in Bakke, 1995; Murphy, 1997. At Fort Knox, Tintina Gold Province, Alaska, gold- and sulphide-bearing quartz veins and associated alteration are restricted to a composite stock, the Fort Knox pluton, dated at 92.5 ± 0.2 [0.3] Ma by U–Pb zircon (Bakke, 1995; Murphy, 1997; J.K. Mortensen, pers. comm., 2006) and 88.1 Ma by ^{40}Ar/^{39}Ar analysis of magmatic biotite (McCoy et al., 1997). Petrography suggests that sulphide minerals, gold and associated wallrock alteration formed simultaneously. Muscovite from sheeted auriferous veins yields argon plateau ages of 88.1–86.8 Ma (McCoy et al., 1997), suggesting a potential age range of ca. 6 million years for gold vein formation. However, molybdenite from early stage veins yields a Re–Os age of 92.9 ± 0.3[0.4] Ma (calculated from the data of Selby et al., 2002). This age is identical, within uncertainty, to the regression of three U–Pb zircon analyses for the host intrusion, 92.5 ± 0.2[0.3] Ma (92.6 ± 0.2[0.3]). The multi-zircon fractions were mainly clear, colourless to pale yellow, euhedral, and ranged from equant, multifaceted grains to stubby prisms. Grains were strongly abraded prior to dissolution to minimize the effects of post-crystallization Pb loss. Measured procedural blanks for U and Pb were 2 and 5 pg. A ^{206}Pb/^{238}U age from Fraction A (92.5 ± 0.2 Ma) is identical to the concordia intercept age and is the most precise estimate for the crystallization age of the Fort Knox pluton (J.K. Mortensen, pers. comm., 2006).

A.2. ca. 145 Ma, Endako, Canada

The Endako porphyry molybdenum deposit, British Columbia, Canada, is hosted by the Endako phase (^{40}Ar/^{39}Ar = 148.4 ± 1.5 Ma, Villeneuve et al., 2001) of the Francois Lake Plutonic Suite. Laminated quartz–molybdenite veins cross cut pre-ore granitic dykes (U–Pb zircon = 147.4 ± 0.6 Ma, Villeneuve et al., 2001) and stockwork quartz veins. Stockwork veins are bordered by K–feldspar alteration assemblages, with the paragenetically later ribbon-textured veins having sericite alteration selvages. Re–Os molybdenite data from ribbon-textured veins yield two distinct ages, ca. 148 and 145 Ma (Selby and Creaser, 2001a). The two Re–Os molybdenite ages are distinguishable within analytical uncertainty, and are in excellent agreement with recent U–Pb and ^{40}Ar/^{39}Ar age determinations for the Endako phase and pre-ore dykes (147–148 Ma), and hydrothermal biotite from the Endako deposit (145 Ma) and the genetically associated Casey phase (145 Ma). These Re–Os data suggest that two episodes of molybdenite mineralization occurred at Endako (ca. 148 and 145 Ma). Evidence for ca. 148 Ma mineralization is not apparent in the ^{40}Ar/^{39}Ar data, perhaps because it has been obscured by the younger thermal event. For example, magmatic biotite in a 147 Ma pre-ore dyke has a ^{40}Ar/^{39}Ar age of 145 Ma, identical to the age of the hydrothermal biotite from the Endako deposit. The similarity between the 148 Ma Re–Os molybdenite age and that of the Endako phase and pre-ore dykes suggests that one stage of mineralization was associated with these bodies. The Re–Os molybdenite age (145.6 ± 0.4 [0.6] Ma, calculated from the data of Selby and Creaser, 2001a) is identical to the U–Pb ^{207}Pb/^{206}Pb zircon age (Geological Survey of Canada, Villeneuve et al., 2001) from the regression of four multi-grain analysis (clear, euhedral, elongate, faceted crystals with small clear inclusions) (145.1 ± 0.8[0.9] Ma (145.2 ± 0.8[0.9]), calculated from the data of Villeneuve et al., 2001) of the genetically related Casey phase. A reliable ^{206}Pb/^{238}U age could not be determined from these analyses due to the use of large multi-zircon fractions, reverse discordance and scatter in the ^{207}Pb/^{235}U ratios, though Villeneuve et al. (2001) report a ^{206}Pb/^{238}U weighted average age of 145.1 ± 0.2 Ma.

A.3. ca. 380 Ma, Costelloe Murvey, Ireland

The Galway Granite is an 80 km long batholith that occupies a key location in the Caledonides of western Ireland. The batholith represents several phases of granite emplacement and is associated with molybdenite mineralization. One phase of the Galway Granite, the Costelloe Murvey granite, is spatially and genetically associated with molybdenite mineralization (Feely et al., 2003). Single- and multi-grain U–Pb zircon analyses yield a crystallisation age for the Costelloe Murvey granite of 380.1 ± 5.5[7.7] Ma, MSWD = 4.3 (378.2 ± 6.3[7.1], MSWD = 4.3) (University of North Carolina, Chapel Hill, Feely et al., 2003). All the U–Pb zircon data are discordant and show excess scatter. Associated molybdenite yields a Re–Os age of 383.3 ± 1.1[1.6] (this study).

A.4. ca. 475 Ma, Connell Mountain, Canada

The Connell Mountain tonalite porphyry is host to Cu–Au–Mo mineralization. The U–Pb age for the tonalite is reported in an abstract by Lentz et al. (2005). The U–Pb data presented in this study were obtained from V. McNicoll of the Geological Survey of Canada. Four multi-grain zircon fractions were analysed, including large elongate crystals and stubby prismatic grains with numerous inclusions. All analyses are discordant. A linear regression of all four analyses has a lower intercept of 474.5 ± 3.5[3.6] Ma, MSWD = 2.7 (474.8 ± 2.7[2.9], MSWD = 2.7), which is interpreted to be the crystallisation age of the pluton. Molybdenite from Connell Mountain yields a Re–Os model age of 474.9 ± 1.2[1.9] Ma (data recalculated from Lentz et al., 2005).

A.5. ca. 920 Ma, Øvre Myssa, Gursli district, Rogaland, Norway

Southern Norway is characterized by widespread vein-style deposits, many of them dominated by molybdenite. These deposits constitute once economic small mines, but most of them have not been worked for nearly a century (Bugge, 1963). The Øvre Myssa mine in the Gursli district is a few hundred meters from the gneissic bedrock contact with the well-known Rogaland anorthosite complex. Mineralization is hosted in gneissic rocks impacted by granulite facies contact metamorphism. Molybdenite from quartz veins hosted in granitic gneiss yields ages of 917 ± 3 and 918 ± 3 Ma (Bingen et al., 2006). The origin of the quartz–molybdenite veins at Øvre Myssa is linked to Rogaland magmatism, most likely originating from contact metamorphism of the gneissic host rocks inducing biotite breakdown and molybdenite deposition (Bingen et al., 2006). Although the intrusion (Garsaknatt) adjacent to the molybdenite locality is not dated, U–Pb zircon ages of ca. 930–920 Ma are reported for the Rogaland anorthosite complex (Laboratoire de Geochronologie, Universite Paris, Schärer et al., 1996). The unit with a U–Pb age that is spatially closest to the dated molybdenite samples. Only two multi-grain zircon fractions from an ilmenite norite from the Tellnes ore body show near concordance, yielding a concordia-intercept age of 919.1 ± 3.8[5.1] Ma (917.2 ± 2.6[3.8] Ma (Schärer et al., 1996)).

A.6. ca. 1500 Ma, Ragunda rapakivi complex, central Sweden

In central Sweden, the Ragunda complex is one of two major rapakivi granite complexes. Together with seven smaller complexes, these rapakivi granites, with ages from 1.53 to 1.47 Ga, postdate the Svecofennian orogeny (Persson, 1999). The last major Ragunda intrusion occurs in the eastern part of the Western Massif outcrops in the vicinity of the village of Ragunda (Persson, 1999). The U–Pb data from multi-grain fractions of euhedral, prismatic, clear to yellow zircons with no inclusions, cores or observable overgrowths are all discordant and yield a concordia-intercept age of 1515. ± 3.7[7.2] Ma, MSWD = 0.82 (1512.1 ± 3.7[6.4] Ma) (Laboratory of Isotope Geology, Swedish Museum of Natural History, Stockholm; Persson, 1999). In the southeast part of Ragunda village, in a quarry where granite was extracted for building stone, molybdenite occurs in 1 cm aplite dikes (Ahl et al., 1997). The hosting granite is a medium- to coarse-grained, red, biotite or biotite-amphibole granite with the biotite varieties locally containing small aplite dikes composed of K–feldspar, quartz, fluorite, and molybdenite (Ahl et al., 1997). Re–Os dating of molybdenite from one of these small aplite dikes yields an age of 1513.8 ± 5.6[7.2] Ma (Table 2).

A.7. ca. 1735 Ma, Antoinette, SE Norway

The mylonite–hosted Antoinette Cu–Mo–(Au) prospect is located in the northernmost part of the Southwest Scandinavian Domain, immediately southwest of the Transcandinavian Igneous Belt (TIB). It is located in the Mjøsa-Vänern mineral belt (Stein et al., 2000). This small prospect is dominated by a highly deformed quartz rock exhibiting intense ductile deformation and containing mm to sub-mm wide stringers of chalcopyrite + bornite + molybdenite transposed during the deformation. The vein is hosted in a shear zone that cuts a tonalitic body, the Mo tonalite, within the Odalen batholith (Stein et al., 1997a,b). The contact between Mo tonalite and the quartz vein varies from moderately sharp to diffuse at the cm scale, and the tonalite is ductily deformed in the immediate vicinity of mineralization. Lesser mineralization is observed at the diffuse contact of the quartz rock with hosting tonalite and within the tonalite. The tonalite body lies within a regional orthogneisses and granitoid, including the surrounding, relatively undeformed Odalen granite. A U–Pb zircon age for the Mo tonalite is reported by Mansfeld (1998); the data, however, have never been published. The U–Pb data from multi-grain zircon fractions are discordant and yield a concordia-intercept age of 1739 ± 12[14] Ma, MSWD = 0.78 (1735 ± 12[13] Ma) (J. Mansfeld, pers. comm., 2006). Stein et al. (1997a,b) published two Re–Os ages for Antoinette molybdenite taken from mylonitized quartz vein (1688 ± 8 Ma) and from the contact between quartz vein and hosting Mo tonalite (1725 ± 8 Ma). These data were acquired by the alkaline fusion method during early development of the molybdenite chronometer, while the AIRIE group was still located at the USGS-Reston. Subsequently, inspired by the lack of age agreement for some samples, additional work was done on Antoinette, including dating of a molybdenite sample distinctly associated with the Mo tonalite intrusion at the contact with the quartz vein. The Re–Os age for this molybdenite sample (NW99-AN1) is 1736 ± 6 Ma (Table 1).

A.8. ca. 1800 Ma, Tepasto, N Finland

In northern Finland, the Tepasto stock is a member of a group of granite complexes named the Nattanen-type (Haapala et al., 1987; Front et al., 1989). Nattanen-type intrusions have alkaline affinities and are slightly peraluminous with bulk geochemistry that crosses I-type, A-type, and S-type granites. The Tepasto granite has been described as a post-orogenic (post-Svecofennian) zoned stock with a microcline-rich aplitic granite phase. Disseminated molybdenite, with minor associated pyrite and chalcopyrite, occurs as coarse-grained rosettes concentrated in the aplitic granite. Quartz-muscovite greisen and quartz-filled fissures with sericitic alteration accompany the mineralisation. Front et al. (1989) associate the volumetrically minor mineralization with a shallow level, largely barren granite stock. Two molybdenite samples were provided by Eero Hanski. The weighted average for three Re–Os ages on two samples is 1796 ± 9 Ma (95% CL, MSWD = 1.4), comparing favourably with two U–Pb zircon ages of 1798 ± 6 (Huhma, 1986) and 1802 ± 10 Ma (Rastas et al., 2001). The more recent U–Pb data from 6 multi-grain zircon fractions are highly discordant and yield an age of 1802 ± 13[15], MSWD = 8.5 (1798 ± 13[14] Ma) (Rastas et al., 2001) in agreement with a single model age for one of the molybdenite samples (1801 ± 4.4[7.1], this study; Table 1).

A.9. ca. 2575 Ma, Salobo, Carajás, Brazil

Re–Os and U–Pb ages are presented in Requia et al. (2003) for mineralization associated with the Old Salobo granite in the Carajás mineral province in northern Brazil. The Salobo deposit is classified as a Fe-oxide Cu–Au (IOCG) type and contains bornite, chalcopyrite, and magnetite as the primary ore assemblage. It is the first recognition of an Archean age IOCG ore deposit. Two molybdenite samples were taken from a vein in a shear zone cutting the Old Salobo granite. As reported in Requia et al. (2003), analyses of two molybdenite separates from one sample yield identical Re–Os ages of 2576 ± 8 Ma, whereas analyses of three molybdenite separates from the second sample yield ages of 2561 ± 8, 2562 ± 8, and 2563 ± 8 Ma. Since publication of Requia et al. (2003) a small analytical correction has been made for Salobo Os data, modifying ages to slightly younger values. The revised Re–Os ages for the Salobo samples are 2573 ± 8 and 2572 ± 8 for the first sample and 2557 ± 8, 2558 ± 8, and 2560 ± 8 for the second sample. The analytically distinct ages for the two samples, were interpreted as (1) intrusion-related mineralization (2572 Ma) linked to the Old Salobo granite, and (2) subsequent renewed molybdenite deposition during deformation (2558 Ma). Two zircon fractions comprising single and parts of zircon crystals yield near concordant data. The near concordant fraction SG-1 yields a ^{206}Pb/^{238}U age of 2572 (Royal Ontario Museum, Toronto; Machado et al., 1991). A concordia-intercept age determined from the two fractions yields an age of 2572.6 ± 4.3[8.5] (2568.3 ± 4.0[7.3]).

A.10. ca. 2700 Ma, Ryan Lake and Aplite, Canada

The Yellowknife Greenstone Belt is host to world-class gold mineralization and until now the absolute age of this mineralization has remained elusive. The quartz diorite to granodiorite Ryan Lake pluton in this belt intrudes >2.72 Ga Kam Group mafic volcanics rocks and lies within the amphibolite grade contact aureole of the Defeat Plutonic suite. Regression of U–Pb data (Royal Ontario Museum, Toronto) from three single zircon fractions defines an age of 2671 ± 5.5[11] Ma, MSWD = 0.1 (2665.4 ± 5[9.3] Ma) for the Ryan Lake quartz diorite, and molybdenite in quartz veining from within the pluton yields a Re–Os model age of 2674 ± 7.4 [11.3] Ma (data recalculated from Ootes et al., 2002, in press). Also within the Yellowknife Greenstone Belt, an aplitic dyke (Duckfish Granite) intrudes the >2.72 Ga volcanic rocks. Regression of the U–Pb data from three single zircon fractions for the aplite dyke yields a crystallisation age of 2611 ± 1.6[7.4] Ma, MSWD = 0.5 (2607 ± 1.6[6.3] Ma), and molybdenite within the same aplite body yields a Re–Os age of 2611 ± 6.9[10.7] Ma (data recalculated from Ootes et al., 2002, in press).

APPENDIX B. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2007.01.008.

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