Rhenium–Osmium Geochronology: Sulfides, Shales, Oils, and Mantle

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Synonyms

Re–Os geochronology; [187]Re–[187]Os geochronology

Definition

Rhenium–osmium geochronology is based on radioactive decay of [187]Re to [187]Os with a half-life of 41.6 b.y. – about 10 times the age of the earth. Both Re and Os are siderophile-chalcophile elements, that is, they are both strongly partitioned into metals or sulfides rather than silicates. This distinguishes them from other widely used geochronometers whose parent-daughter elements reside in silicates. Re–Os geochronology underpins dating of materials from meteorites, the mantle, and metallic ore deposits. Furthermore, both Re and Os are redox-sensitive metals, soluble when oxidized, and fixed by reduction. Thus, both are mobile in Earth's presently oxidized surface environments but are concentrated in sulfides and organic matter in anoxic-euxinic sediments. This is the basis for Re–Os dating of the depositional age of organic-rich sedimentary rocks and provides a temporally constrained record of changing redox conditions through earth history.

Fundamentals of Re–Os Geochemistry

There are two naturally occurring isotopes of Re: stable [185]Re and radioactive [187]Re. Mass fractionation of the two Re isotopes is readily observed during the extreme conditions imposed by mass spectrometry (e.g., Suzuki et al. 2004; Zimmerman et al. 2007). The few reported natural variations, however, are less than 0.3 ‰ (Miller et al. 2009) and thus introduce errors less than other sources of uncertainty for Re–Os geochronology. As with other high-mass elements used in geochronology, we therefore assume uniform present-day abundances of [185]Re (37.398 %) and [187]Re (62.602 %; Gramlich et al. 1973) as an underpinning assumption for radiometric dating.

There are seven naturally occurring isotopes of Os: [184]Os, [186]Os, [187]Os, [188]Os, [189]Os, [190]Os, and [192]Os. Isotope [187]Os is the product of beta decay of [187]Re, with a decay constant of 1.666×10^{-11} year^{-1} (Smoliar et al. 1996). Isotope [186]Os is the product of alpha decay of [190]Pt with a decay constant of 1.542×10^{-12} years^{-1} (Walker et al. 1997). The abundances of the remaining isotopes may be considered constant for present-day Re–Os isotope geochemistry and geochronology. Prior to recognition of small, but measurable contributions of radiogenic [186]Os, Os isotopic compositions were reported as [187]Os/[186]Os. Current convention is to normalize abundances of [187]Os to [188]Os, reporting isotopic variations in terms of the ratio [187]Os/[188]Os.
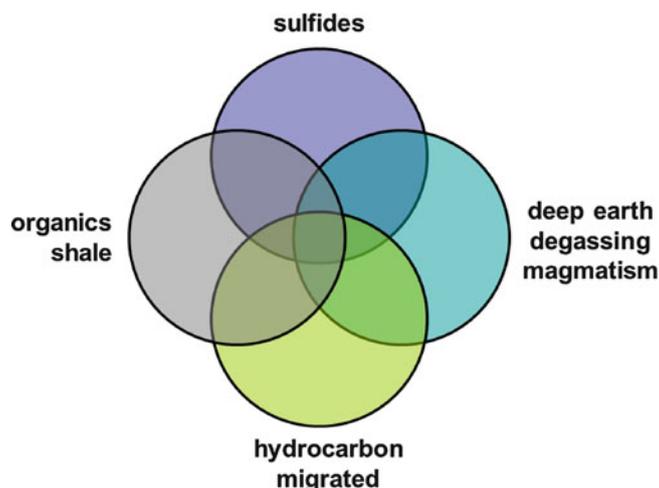
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Fig. 1 Reservoirs important to the terrestrial Re–Os budget

Os is highly compatible in mantle sulfides and metal alloys and is thus strongly sequestered in the earth's mantle relative to the crust. Re, in contrast, is only mildly compatible and is therefore transferred to the crust by partial melts far more efficiently than Os (e.g., Reisberg and Lorand 1995). Thus, $^{187}Re/^{188}Os$ ratios in fertile (undepleted) mantle are low (about 0.4), whereas $^{187}Re/^{188}Os$ ratios in the crust are much higher and extremely variable; crustal $^{187}Re/^{188}Os$ averages about 50 and ranges from one to three orders of magnitude (or more) higher than the mantle (Shirey and Walker 1998). The extreme variability in $^{187}Re/^{188}Os$ ratios offers two key opportunities. First, because $^{187}Re/^{188}Os$ ratios are markedly higher in the crust than in the mantle, decay of ^{187}Re over time produces an enormous range of $^{187}Os/^{188}Os$ ratios in crustal materials. This provides a sensitive tracer of crustal input to mantle or crustal contamination in mantle-derived materials. Second, extremely high $^{187}Re/^{188}Os$ ratios in some materials make them suitable for dating very young samples, despite the long half-life of ^{187}Re.

Figure 1 illustrates earth's Re and Os reservoirs and Fig. 2 details the Re–Os budgets in various reservoirs, along with the potential for cycling among those reservoirs. Whereas subduction cycles crustal Re and Os into the mantle, partial melting and slab dehydration introduce the elements into the crust. The oceans receive Re and Os from seafloor hydrothermal processes, seafloor weathering, riverine inputs from continental weathering, rain of cosmic dust, and the occasional meteorite. Present-day input from continental weathering constitutes about 80 % of the Os budget of seawater (Sharma et al. 1997).

Fundamentals of Re–Os Dating: From Sample to Age

Analyses for high-precision Re–Os ages are acquired using the isotope dilution method, in which a known amount of one isotope of each element is added to the sample prior to analysis. Given the amount and composition of the isotopic "spike" added and the measurement of isotopic ratios in the mixture, it is straightforward to calculate the ratios in the sample. For example, the weight in μg of Re in a sample can be calculated as follows:

$$Re_W = Spk_W \frac{AW_{sam}}{AW_{spk}} \left[\frac{^{185}Re_{spk} - R_M{}^{187}Re_{spk}}{R_M{}^{187}Re_{sam} - {}^{185}Re_{sam}} \right] \tag{1}$$
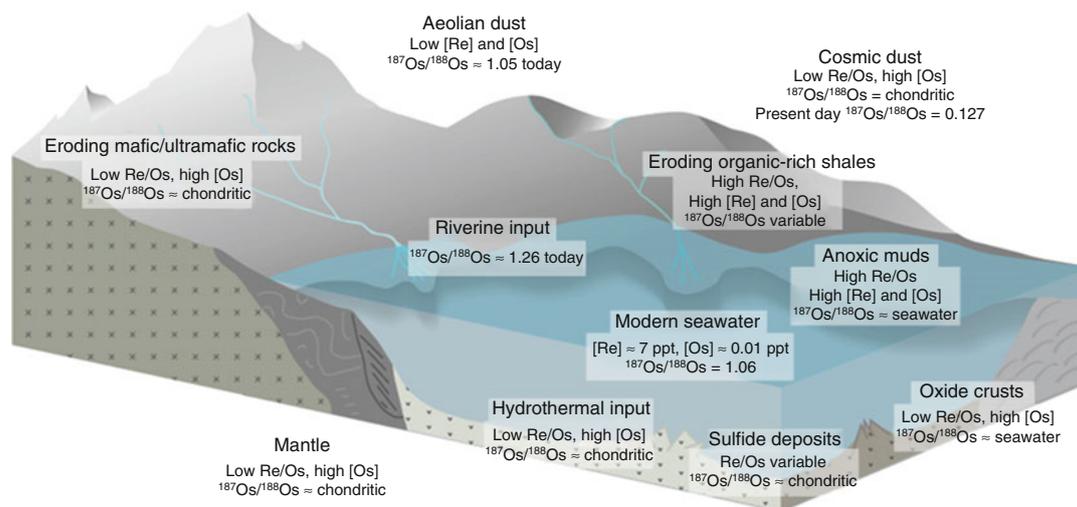
Fig. 2 Re and Os reservoirs with sources and sinks for seawater (From Hannah and Stein 2012). Riverine concentrations of Re and Os depend strongly on the composition of bedrock in the drainage area; flux to the oceans is a mixture of dissolved and suspended load. Therefore, global averages are not available. Data are summarized from a variety of sources, all cited in the main text

where Re_w = weight of Re in the sample, Spk_w = weight of Re in the spike (same units as sample), AW_{sam} = atomic weight of Re in the sample, AW_{spk} = atomic weight of Re in the spike, $^{187}Re_{spk}$ and $^{185}Re_{spk}$ = fraction of each isotope in the spike, $^{187}Re_{sam}$ and $^{185}Re_{sam}$ = fraction of each isotope in the sample, and R_M = measured $^{185}Re/^{187}Re$ ratio. Dividing Re_w by the weight of the sample in grams yields the concentration of Re in μg per gram, or ppm. Derivations, explanations, and examples of applications for this and many other calculations based on isotopic data are given in Faure and Mensing (2005).

Today, isotopic analyses of Re and Os are most commonly acquired in three steps: (1) dissolution of the sample and equilibration with isotopic spikes in a closed vessel; (2) chemical purification of Re and Os, separating each from the matrix and from each other; and (3) isotopic analysis of each element by negative thermal ionization mass spectrometry (NTIMS). For Step 1, the sample and spikes are loaded into thick-walled Pyrex tubes (Carius tube) with inverse aqua regia, sealed, and equilibrated for at least 24 h at 240 °C (Shirey and Walker 1995). To isolate organic matter or sulfides in shale samples without dissolving or significantly leaching detrital minerals, a solution of CrO_3–H_2SO_4 is used in place of inverse aqua regia (Selby and Creaser 2003; Kendall et al. 2004).

For Step 2, Os is separated from the solution in the Carius tube either by distillation (Morgan and Walker 1989) or dissolution in an organic phase (CCl_4 or $CHCl_3$) and back extraction into HBr (Shen et al. 1996; Cohen and Waters 1996; Brauns 2001), followed by microdistillation (Roy-Barman and Allègre 1995; Birck et al. 1997); both utilize the volatility of Os under oxidizing conditions and its quantitative drawdown into HBr. Re is subsequently purified on ion exchange columns (Morgan and Walker 1989).

For Step 3, although NTIMS is almost universally used for high-precision measurement of Os isotopes, some labs use solution multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) to determine the Re isotopic ratio. Spot analyses, such as laser ablation MC-ICP-MS for Re–Os isotopic analyses, are not feasible in most cases for one or both of two reasons. First, most Os concentrations and some Re concentrations are too low, below detection limits for LA-MC-ICP-MS. Second, in some materials – notably in molybdenite – the radiogenic daughter isotope ^{187}Os may diffuse and collect in crystal defects, so that it is spatially decoupled from its parent ^{187}Re (Stein

et al. 2001, 2003; Košler et al. 2003; Selby and Creaser 2004). The resulting ages may be highly erroneous, either too old or too young (see discussion in later section).

Prior to interpretation of the isotopic data, raw measurements of isotopic ratios from mass spectrometry are corrected for instrumental mass fractionation, and all analytical uncertainties must be identified and appropriately calculated. Mass fractionation of Os isotopes is readily corrected for each measurement by using $^{190}Os/^{188}Os = 3.08271$ (Platzner 1999). Because Re has only two isotopes, however, and ^{185}Re is introduced as an isotopic spike, there is no stable, unchanging isotopic ratio in the sample to measure. If MC-ICP-MS is used, however, the sample can be doped with an element of similar atomic weight that has at least two stable isotopes, typically Ir or W, and the mass fractionation of those isotopes used to correct for that of ^{185}Re and ^{187}Re (e.g., Schoenberg et al. 2000; Li et al. 2010). For NTIMS, Re isotope fractionation is determined from repeated measurements of a standard and assumed to be the same for sample analyses. Measured ratios are corrected for mass fractionation and isobaric interferences. Other sources of uncertainty in Re–Os analyses arise from weighing, standard and spike calibrations, and blanks. The 2σ uncertainties for Re and Os abundances and the isotopic ratios are calculated by numerical propagation of all uncertainties.

Given the measured abundances of the parent (^{187}Re) and daughter (^{187}Os) isotopes, each normalized to ^{188}Os, a stable isotope, the age and initial composition of the Os can be calculated from the basic age equation:

$$\left(\frac{^{187}Os}{^{188}Os}\right)_{measured} = \left(\frac{^{187}Os}{^{188}Os}\right)_{initial} + \left(\frac{^{187}Re}{^{188}Os}\right)_{measured} \left(e^{\lambda t} - 1\right) \tag{2}$$

where the measured ratios are determined from mass spectrometry, the initial ratio is the isotopic composition of Os at the time the sample equilibrated with and derived from its source, λ is the ^{187}Re decay constant, and t is the age of the sample in years. In any sample with measureable "common" Os (non-radiogenic Os incorporated into the sample when it formed), the initial Os isotopic composition of the common Os must be known. Thus there are two unknowns: the initial Os isotopic composition and the age. This is overcome by measuring multiple consanguineous samples and fitting a linear regression on an isochron diagram, a plot of the measured $^{187}Re/^{188}Os$ versus $^{187}Os/^{188}Os$ (Fig. 3).

Some samples have very little or effectively no common Os on formation. The mineral molybdenite (MoS_2), for example, takes in large amounts of parent Re, but almost quantitatively excludes Os at the time of crystallization. Other sulfides may also have unusually high $^{187}Re/^{188}Os$ ratios in the thousands or tens of thousands – so-called low-level highly radiogenic (LLHR) samples (Stein et al. 2000). In such cases, for which the Os is nearly 100 % radiogenic, the traditional isochron diagram is meaningless. Any presumed measurement of ^{188}Os clearly carries an extreme uncertainty (since there is too little to measure!). This is described in more detail below in the sections that describe dating molybdenite and LLHR samples.

Historical Background

The promise of highly accurate and precise Re–Os chronology was realized in the mid-1990s after four major, analytical issues were overcome: (1) lack of sensitive mass spectrometry techniques, (2) poor stoichiometry of Os standard materials, (3) difficulty equilibrating spike and sample Re and Os, and (4) uncertainty in the ^{187}Re decay constant. Resolving these issues opened the door to a wide
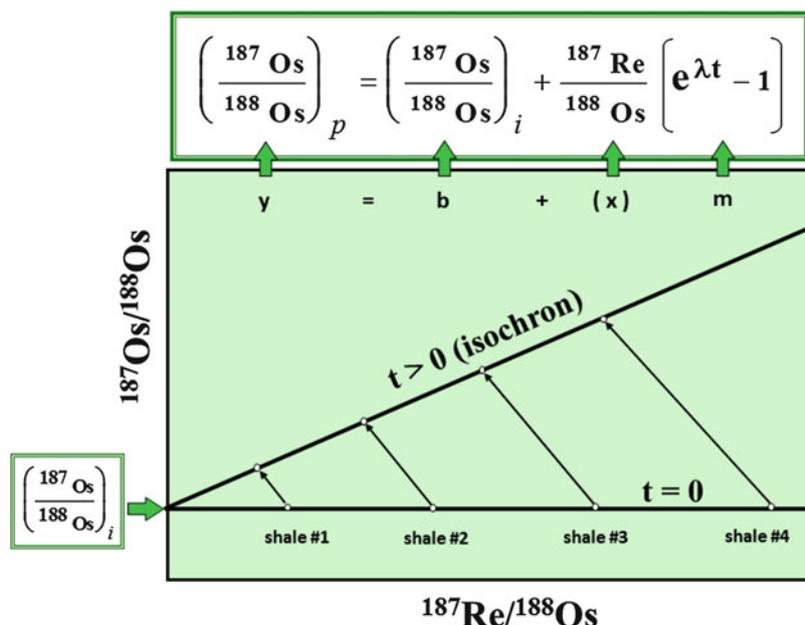
Fig. 3 Example of a Re–Os isochron plot. Four shale samples (or four related sulfide minerals), for example, were deposited at time zero, and all acquired Os from seawater with the same initial ^{187}Os/^{188}Os ratio. Over time, as ^{187}Re decays to ^{187}Os, the position of each point shifts up and to the right. The increase in ^{187}Os/^{188}Os is proportional to the magnitude of ^{187}Re/^{188}Os for each point. Linear regression of the four points at t >0 yields a straight line with the equation shown. The slope ($m = e^{\lambda t}-1$) is a function of the age of the sample and the decay constant. The y-intercept is the initial ^{187}Os/^{188}Os ratio, the ratio that would exist in a sample that had no parent ^{187}Re. The uncertainties on the slope and initial ^{187}Os/^{188}Os ratio depend on the analytical uncertainties for each data point and the goodness of fit (MSWDs, or mean square of weighted deviations) for the regression

range of applications for geologic problems from the mantle to the crust, from magmatic systems to surface processes.

Negative TIMS

Many isotopic methods rely on measurements of positive ions by thermal ionization mass spectrometry (TIMS). Recognition that both Re and Os are much more efficiently ionized as negative ions enabled far more precise measurements of Re and Os isotopic compositions on picogram quantities (Creaser et al. 1991; Völkening et al. 1991). The switch to negative TIMS (NTIMS) was critical to the development of Re–Os isotope geochemistry of crustal materials, as many labs turned to this new and more precise analytical tool. Analysis of Re isotopes by MC-ICP-MS has continued in some labs because it affords the opportunity to correct for instrumental mass fractionation of Re isotopes. In addition, a few labs have developed high-precision methods for analysis of Os isotopes by direct sparging of Os from the reaction vessel into an MC-ICP-MS (e.g., Hassler et al. 2000; Nozaki et al. 2012; Sen and Peucker-Ehrenbrink 2014).

Stoichiometry of Os Standards

Accurate concentration analyses using isotope dilution depend critically on the accuracy of the gravimetric standards used to calibrate spikes. The materials used to make Os standards are notoriously nonstoichiometric, leading to inherent errors in the calculated Os concentrations (Morgan et al. 1995). Alternative materials have been used to overcome this (Shen et al. 1996; Yin et al. 2001), but the inconsistencies remained. Selby and Creaser (2001) adapted an earlier method (Gilchrist 1932) to reduce ammonium hexachloroosmate to a pure osmium metal sponge

and thereby directly measure the Os content of the salt. A further adaptation of this method yields a robust measurement for the Os standard used today at AIRIE (Markey et al. 2007). Nevertheless, the persistent problem with stoichiometry of Os gravimetric standards remains challenging.

Spike Challenges: Equilibration Difficulties and the Mixed Re-double Os Spike

A long-standing challenge was achieving isotopic equilibrium between the sample and Os spike without loss of Os. Loss of Os is especially problematic for open-vessel methods or use of PTFE vessels, through which Os may diffuse. External precision (reproducibility) was greatly improved as laboratory methods moved from less reliable equilibration of spike and sample Re and Os by oxidizing alkaline fusion (Morgan and Walker 1989; Markey et al. 1998) to high-pressure and high-temperature sample dissolution and spike equilibration using inverse aqua regia in a sealed Carius tube (Shirey and Walker 1995).

A particular challenge with spiking is presented by samples with low concentrations of common Os and very high concentrations of radiogenic ^{187}Os. There are no well-measured ratios of Os isotopes that are neither radiogenic nor impacted by the addition of the spike. Thus, there is no mechanism for monitoring mass fractionation or determining the amount of common Os. These problems were resolved simultaneously with development of a mixed Re-double Os spike (^{185}Re–^{188}Os–^{190}Os; Markey et al. 2003). Sufficient ^{188}Os spike is added to match the abundance of ^{187}Os, so that the ^{187}Os/^{188}Os ratio is well measured. In the same spike solution, a small amount of ^{190}Os is used to achieve a well-measured ratio with ^{192}Os, the most abundant isotope in the common Os spectrum. The well-determined ^{188}Os/^{190}Os ratio is used for the fractionation correction, while the balanced ^{190}Os/^{192}Os ratio is used to determine the amount of common Os in the sample. At the same time, use of a mixed Re–Os spike eliminates weighing errors associated with spike addition. This breakthrough has dramatically improved the precision and accuracy of Re–Os ages for young molybdenites and LLHR samples.

Half-Life Hurdles: The ^{187}Re Decay Constant

Establishing the half-life of a parent isotope with certainty is imperative for radiometric dating. Molybdenite, with its extraordinarily high Re concentrations and negligible common Os, contains essentially pure ^{187}Os, thereby providing the first reliable estimates of the half-life of ^{187}Re at about 43.5 b.y. (Herr and Merz 1955; Hirt et al. 1963).

Fifteen years later, the ^{187}Re half-life was determined at 45.6 ± 1.2 b.y. by assuming the slope of a meteorite isochron represented an age of 4.550 Ga (Luck and Allègre 1982). Re–Os ages for 11 molybdenites based on this revised half-life showed that, in a few cases, ages were too old (some older than the age of the earth). These highly inaccurate results were attributed to Re loss due to metamorphic and/or hydrothermal processes (Luck and Allègre 1982) – a major setback for Re–Os dating of molybdenite, as the chronometer was labeled as unreliable.

The half-life of ^{187}Re was again redetermined as 42.3 ± 1.3 Ga by measuring ingrowth of ^{187}Os over several years in a purified kilogram of Re (as perrhenic acid, HReO$_4$; Lindner et al. 1989). Analysis of the same molybdenites that previously gave aberrant ages (Luck and Allègre 1982) now produced ages in good agreement with wall rock ages determined by other isotopic methods, leading to the conclusion that earlier discordant results reflected sample-spike equilibration problems rather than issues with the molybdenite chronometer (Suzuki et al. 1992, 1993).

The 3 % uncertainty on the ^{187}Re half-life determined by Lindner et al. (1989) placed serious limits on Re–Os geochronology. Two labs simultaneously undertook improvements by back-calculating the ^{187}Re decay constant from Re–Os isotope systematics in iron meteorites well dated by other methods. Shen et al. (1996) calculated a ^{187}Re decay constant of 1.66×10^{-11} year^{-1}; while

they do not report an uncertainty for their decay constant, it is tied to the 1.2 % uncertainty on the calibration of their Os tracer. Smoliar et al. (1996) examined Re–Os systematics in group IIIA iron meteorites; by assuming these formed at the same time as angrite meteorites that yield a concordant Pb–Pb model age (Lugmair and Galer 1992), they were able to calculate the ^{187}Re decay constant at $(1.666 \pm 0.017) \times 10^{-11}$ year^{-1}. The assumption that the analyzed group IIIA and angrite meteorites are the same age is supported by agreement within ± 5 m.y. of the ^{53}Mn–^{53}Cr formation intervals. The ± 1.02 % uncertainty calculated for the Smoliar et al. (1996) ^{187}Re decay constant can be reduced to ± 0.31 % if the lab's Os standard can be tied back to the University of Maryland standard used by Smoliar et al. (1996).

Persistent Misperceptions

It is not about closure temperatures! Rather, it is the "container" that assures isotopic closure. The geochemical behavior of Re and Os controls the reliability of the Re–Os chronometers. Neither element is accommodated by silicate minerals, and neither element is soluble in reducing aqueous fluids. Thus, there are only two routes for either Re or Os to escape from its hosting phase: (1) sit adjacent to another phase with a comparable affinity for either Re or Os under conditions that allow diffusion or (2) interact with an oxidizing fluid. An isolated sulfide mineral surrounded by silicates will not lose Re or Os. Surface weathering or attack by any oxidizing fluid, in contrast, promotes disturbance of the Re–Os isotopic system (e.g., Georgiev et al. 2012).

A "Model 1" isochron does not mean "precise and accurate"! Many labs plot isochrons from their data using the freely available software Isoplot (Ludwig 2012). The first model for linear regression used by Isoplot is termed "Model 1" and assumes that scatter of data from the straight line is attributable only to the uncertainties of the individual data points (following York 1969). The program also calculates a "probability of fit" and rejects the Model 1 regression if the probability is <15 %. (The user may change this value to any probability between 5 % and 30 %.) If the Model 1 regression is rejected, Isoplot calculates a "Model 3" age, which assumes an unknown, but normally distributed variation in the initial ^{187}Os/^{188}Os ratio. This change in regression model results in a larger age uncertainty. In fact, the size of the uncertainties for individual data points strongly impacts the choice of model – the larger the uncertainties, the higher the probability of fit, and therefore, the greater likelihood that the Model 1 fit will be accepted. Thus, "better" data – that is, more precise analyses and/or underestimated analytical uncertainties – are less likely to result in a Model 1 regression. Conversely, less precise measurements and/or overestimated analytical uncertainties for each data point readily result in an unwarranted Model 1 regression. Examples of improbably high analytical uncertainties and overly optimistic isochrons are all too common.

A lower MSWD does not always mean a better isochron! Ludwig (2012, footnote on p. 22) eloquently states the meaning of "MSWD":

> MSWD = Mean Square of Weighted Deviates. This does not refer to porcine perverts; it is, roughly, a measure of the ratio of the *observed* scatter of the points (from the best-fit line) to the *expected* scatter (from the assigned errors and error correlations). *The MSWD parameter cannot be compared to the classical R^2 parameter, and is not a measure of how highly correlated the X- and Y-values are.* If the assigned errors are the only cause of scatter, the MSWD will tend to be near unity. MSWD values much greater than unity generally indicate either underestimated analytical errors, or the presence of non-analytical scatter. MSWD values much less than unity generally indicate either overestimated analytical errors or unrecognized error-correlations.

In short, a low MSWD may result from an overestimation of analytical uncertainties. Equally important, an MSWD $\ll 1$ suggests that analytical uncertainties have been underestimated – though it can also indicate an extraordinarily colinear data set. Ideally, for a precise isochron based on good measurements of well-behaved samples, the MSWD will be close to 1.

Applications

The many improvements made during the 1990s for analytical methods and standards opened a world of new applications for Re–Os geochronology. Precision and accuracy of measurements of meteoritic material and mantle xenoliths greatly increased. With the Smoliar et al. (1996) ^{187}Re decay constant, the first NTIMS analyses of molybdenites aligned with U–Pb ages for related zircons (Stein et al. 1997, 2001). High-precision and accurate analyses of low-level basalts, crustal sulfides, and organic matter became a reality. The next sections provide an overview of these applications, each of which is also discussed in separate focused and condensed chapters in this volume. Here we pay particular tribute to the development and application of the Re–Os molybdenite chronometer, as its value is no less than that of zircon dating.

Meteorites and Mantle

Much of the early work on Re–Os systematics in earth materials focused on xenoliths from the earth's mantle and on meteorites (see also entry "▶ Meteorites (Re–Os)"). Prior to the 1990s, analytical limitations required the use of materials with relatively high concentrations of Re and Os. More importantly, the strong fractionation of both Re between earth's mantle and mantle-derived partial melts, and of both Re and Os between silicates and metals, affords ample opportunities to explore the origins of planetary bodies and the evolution of planetary interiors. Re–Os systematics can reveal the age and probable origin of meteorites from the solar nebula, the formation of Fe–Ni cores, and timing of secondary alteration (cf. Walker, this volume). Studies focused on shergottite meteorites, of Martian origin, reveal the evolution of the Martian mantle, early magma ocean, and late accretion (e.g., Brandon et al. 2012).

Re–Os isotopic studies of mantle xenoliths, exposed mantle peridotites, and mantle-derived basalts provide high-quality information on melt-depletion events in the mantle, the evolution of the mantle through time, and the preservation of subcontinental mantle lithosphere. Reisberg et al. (2004) provide an example of multiple processes impacting Os isotope composition of mantle samples preserved as xenoliths, deriving useful model ages for melt extraction, yet questioning the interpretation of these data as mantle stabilization ages. Rudnick and Walker (2009) give an excellent review of the fundamentals, potential pitfalls, and lessons learned in two decades of Re–Os applications in the mantle.

Crustal Sulfides
Molybdenite Geochronology
Molybdenum disulfide (MoS$_2$) or molybdenite is a silver-colored mineral with a distinct bluish tint. The blue tint is particularly notable in samples with high Re. This hexagonal (rarely trigonal) mineral is soft, has a distinct platy cleavage, and can easily be bent with the fingers (Fig. 4). Molybdenite occupies a unique niche – it is the only naturally occurring mineral that takes in significant Re, usually at the level of tens to hundreds of ppm, other than its exceedingly rare Re-rich solid-solution cousin, rheniite (ReS$_2$; Korzhinsky et al. 2004; Tessalina et al. 2008). Molybdenite occurs in a wide range of geologic environments. Almost invariably, it is present in porphyry-style ore deposits worldwide. It may also be found as a minor accessory mineral in silicic-felsic metamorphic rocks and biotite gneisses. Molybdenite is most commonly associated with quartz veins or as disseminated blades or rosettes in felsic magmatic-metamorphic rocks (Fig. 5). The ability to directly date molybdenite gave the economic geology community accurate and precise ages for a wide array of ore deposits and gave the geologic community direct ages for sulfide occurrences in the earth's crust (Stein et al. 2001; cf. review in Stein 2014).
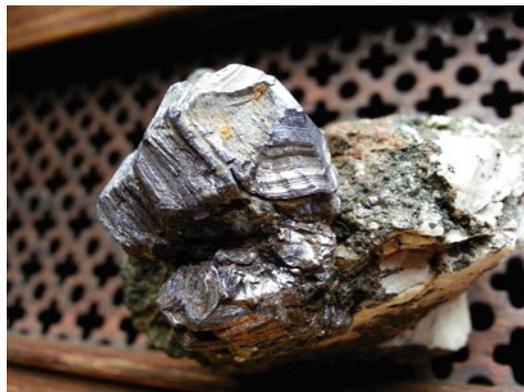
Fig. 4 Molybdenite crystals from Råde, Norway, illustrate hexagonal form and platy texture. This exceptional specimen is about 6 cm across and belongs to the Natural History Museum in Oslo. Crystals as large as 15 cm in diameter have been reported from Råde (Photo by H. Stein)
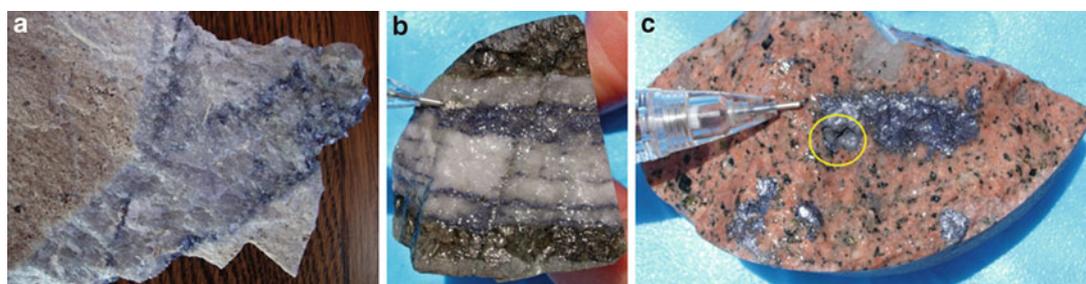

Fig. 5 (**a**) Quartz-molybdenite veins in the Primos rhyolite porphyry, Henderson Mo porphyry deposit, Colorado. Field of view is 10 cm across. (**b**) Banded quartz-molybdenite vein cutting fine-grained biotite hornfels, Myszków Mo deposit, Poland. Thumb and forefinger to right, pencil tip to left for scale. Sample is wet to enhance contrast. (**c**) Porphyritic granite with disseminated molybdenite and minor finely disseminated chalcopyrite (*bottom center*) from the Myszków Mo deposit, Poland. Two drill pits (*inside yellow circle*) show how molybdenite is excavated for Re–Os dating. Pencil tip for scale. Sample is wet to enhance contrast (Photos by H. Stein)

Uniquely, molybdenite has very high Re/Os ratios on crystallization (generally $>10^6$) and takes in essentially no common (i.e., initial) Os. If common Os is present in the sulfide-depositing fluid, it is accommodated by other co-crystallizing sulfides. With vanishingly low common Os (and therefore, no initial ^{187}Os) in molybdenite, the decay equation for calculating a molybdenite age is elegant in its simplicity:

$$^{187}\text{Os}_{\text{measured}} = {}^{187}\text{Os}_{\text{initial}} + {}^{187}\text{Re}_{\text{measured}}\left(e^{\lambda t} - 1\right) \tag{3}$$

reduces to

$$^{187}\text{Os}_{\text{measured}} = {}^{187}\text{Re}_{\text{measured}}\left(e^{\lambda t} - 1\right) \tag{4}$$

Here the model age (t), reflecting the time of crystallization, is the only unknown. The age is therefore readily determined from a single sample of molybdenite. Lambda (λ) is the ^{187}Re decay constant.

The ^{187}Re–^{187}Os radiometric clock held in the mineral molybdenite was explored in earnest in the 1960s (Hirt et al. 1963; Herr et al. 1967). Analytical issues and a poorly determined ^{187}Re decay

constant stalled progress. In the 1990s, early pioneering work in ^{187}Re–^{187}Os dating of molybdenite was carried out by Du Andao, a Chinese chemist, who early on realized the potential of the method for this mineral (Du et al. 1995). Her lab quickly became a venue for many Chinese geologists to simply acquire dates from her for Chinese ore deposits, and a hailstorm of papers reporting molybdenite ages ensued. These geologists depended on her meticulous work and laboratory results. Also in the 1990s, another chemist, Katsuhiko Suzuki, was independently exploring molybdenite as a geochronometer in Japan. His lab became a focal point for mixing geologists and geochemists to jointly tackle geologic problems with Re–Os isotope geochemistry. In the early 1990s, both Drs. Du and Suzuki were limited by the analytical capability offered by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) prior to the advent of multi-collector instruments.

Other groups were also limited by ICP-MS instrumentation and by assessing the accuracy of ^{187}Re–^{187}Os molybdenite ages through their agreement with K–Ar ages (e.g., McCandless and Ruiz 1993). It soon became clear that primary ages in the ore-forming environment were held by molybdenite and not by traditionally dated ore-associated gangue minerals (e.g., alunite and sericite), for which argon-based dating had been employed (Suzuki et al. 1996; Watanabe and Stein 2000; Stein et al. 2001; Selby et al. 2002).

The ages achieved by early workers, nonetheless, were encouraging. But a breakthrough in analytical technology was needed. This was delivered with NTIMS (Negative Thermal Ionization Mass Spectrometry), as two working groups realized that Re and Os could be measured as negative ions (Creaser et al. 1991; Völkening et al. 1991). This analytical breakthrough was immediately utilized to successfully develop the ^{187}Re–^{187}Os chronometer in molybdenite, achieving accurate ages at high precision (Stein et al. 1997; Markey et al. 1998).

In addition to analytical challenges, a limiting factor in putting the molybdenite chronometer to use was the accurate determination of the ^{187}Re decay constant and its uncertainty. Ultimately, the ^{187}Re decay constant of Smoliar et al. (1996) became the established value and is the most widely used today. More recent attempts to further revise the ^{187}Re decay constant by pairing up molybdenite Re–Os and zircon U–Pb ages from the literature (Selby et al. 2007a) rely on two geologic assumptions: (1) molybdenite and zircon formation are contemporaneous, and implicit to the first assumption, (2) there is only one generation of molybdenite and one episode of zircon formation at a locality. In hindsight, geologic reason tells us this assumption is flawed; when multiple dates are available, molybdenite (and zircon) generally shows a range of ages at a single locality. The cleanest data sets are from porphyry-style deposits, but these also may have extended durations (e.g., Los Pelambres, Chile; Stein 2014). Therefore, the ^{187}Re decay constant that ties back to the meteorite community is best used; the complexities of crustal rocks do not lend themselves well to establishing decay constants.

Still other vexing issues lay ahead before ^{187}Re–^{187}Os dating of molybdenite would become mainstream geochronology. Recognition of parent-daughter (^{187}Re–^{187}Os) decoupling within molybdenite crystals presented a new challenge (Stein et al. 2001). Qualitative trial-and-error studies with different grain sizes, different crystals (chopped with a razor, peeled along cleavage planes, or powdered by drilling), different occurrences, and different milligram quantities of molybdenite revealed that geologic sense, not quantity, of molybdenite should drive the sampling. If part of a crystal is sampled, then the whole crystal must be sampled to ensure that all of the parent and daughter are included in the analysis. In fact, acquisition of the molybdenite mineral separate in a geologically meaningful context is the most critical step for molybdenite dating (Stein et al. 2001; Stein 2006, 2014). Unlike the approach for zircon U–Pb dating, whole-rock crushing to acquire a vial of molybdenite grains puts Re–Os dating at risk. If more than one generation of molybdenite is present, even if closely spaced in time, this approach yields variable ages that cannot be well

reproduced. In the same way, if decoupling is present at the scale of the sampling, ages will be variable and cannot be well reproduced. *It is the inability to replicate an age from the same separate that signals decoupling.* The decoupling of ^{187}Re–^{187}Os in molybdenite is generally greater in coarser-grained samples, in older high-Re molybdenites that have accumulated significant radiogenic ^{187}Os, and in deformed molybdenites (Stein et al. 2003). Simply put, the accumulated radiogenic Os is desperate to get comfortable in the molybdenite structure and, at any opportunity, will migrate to crystal defects or dislocations (Stein et al. 2003). The early empirical recognition of parent-daughter decoupling was later verified through LA-ICP-MS of molybdenite (Stein et al. 2003; Selby and Creaser 2004). Thus, laser ablation technology cannot be used for ^{187}Re–^{187}Os molybdenite dating (e.g., Košler et al. 2003). A subsequent atomic level study confirmed the suspected mobility of radiogenic Os within the molybdenite structure (Takahashi et al. 2007).

A unique aspect of ^{187}Re–^{187}Os dating of molybdenite is that this sulfide rarely forms overgrowths (Stein et al. 2004; Aleinikoff et al. 2012). This is not the case for other sulfides; for example, pyrite is notorious for overgrowths. Without the complexity of overgrowths, this makes working with molybdenite far simpler than deciphering some U–Pb histories in zircon and monazite. Another positive feature is that the molybdenite chronometer remains intact, even at granulite facies temperatures (e.g., Bingen and Stein 2003). Compromise of the ^{187}Re–^{187}Os clock in molybdenite should not be associated with temperature, but with chemical stability of sulfide (i.e., oxidation; cf. discussion in Stein 2014).

In nature, however, there are always exceptions when things at first seem simple. Though rare, a small population of molybdenites began to show up with measurable common Os. Not surprisingly, these molybdenites generally occur in the absence of other sulfides that accommodate Os, a platinum group element (PGE), in their structures. Silicate minerals typically do not substitute Os in their structures, so in such circumstances this left molybdenite vulnerable to squeezing Os into its structure. This reality led to the development of a mixed Re-double Os spike, now widely in use, for analyzing molybdenite (Markey et al. 2003). The concept is simple: a single spike solution contains enriched ^{185}Re–^{188}Os–^{190}Os. The ^{185}Re is used to determine the parent ^{187}Re concentration in a molybdenite sample, as there are only two isotopes of Re. The ^{188}Os in the spike solution is used to precisely determine the radiogenic ^{187}Os, just one amu (atomic mass unit) away, and the ^{190}Os is used to determine the ^{192}Os (the most abundant common Os mass). From these measurements, the total Re and Os concentrations in the sample can be reconstructed, and the dating is atomically accurate. Further, the double Os spike eliminates weighing errors for single Re and Os spike solutions and permits a mass fractionation correction for Os (Markey et al. 2003).

A new technology requires a reference material that can be accessed by multiple labs and used for interlaboratory comparison. Early workers used a well-homogenized, milled molybdenite powder from the Huanglongpu Mo deposit in China to assess internal (within lab) and external (between labs) repeatability of age results (Stein et al. 1997; Selby and Creaser 2001; Du et al. 2004). From this, the concept of a molybdenite isochron was derived, with the regression line defined by coupled variation in ^{187}Re and ^{187}Os concentrations and projecting to an intercept of zero initial ^{187}Os (Stein et al. 1997). Subsequently, a milled molybdenite powder from the Henderson mine in Colorado was characterized as a reference material (Markey et al. 2007). Molybdenite from this particular porphyry Mo deposit was specifically chosen for three reasons: (1) undeformed, minimizing decoupling issues, (2) relatively low Re, and (3) young age (27.656 ± 0.022 Ma), limiting the amount of ^{187}Os introduced as a possible lab contaminant. The Henderson molybdenite was endorsed by NIST (RM#8599) and can be purchased through NIST as a reference material for ^{187}Re–^{187}Os age determinations. Importantly, RM#8599 is not a reference material for Re and ^{187}Os

concentrations, only for the accuracy of ^{187}Re–^{187}Os ages. The Re and ^{187}Os concentrations vary, but are perfectly coupled such that the age is highly reproducible (Markey et al. 2007).

While dating ore deposits was the original motivation and a primary application for molybdenite dating, the mineral's widespread occurrence as an accessory phase provides additional opportunities. Molybdenite crystallization can be tied to specific tectonic events, yielding timing, for example, of fluid-flow events during metamorphism (Stein 2006), specific deformation events (Stein and Bingen 2002), and progressive and episodic extensional tectonism (Zimmerman et al. 2008).

In sum, molybdenite presents the geologic community with a simple, yet elegant, radiometric clock through ^{187}Re–^{187}Os. What was novel turned mainstream with NTIMS, the use of a double Os spike, and a certified reference material for the community. Depending on Re concentration in the molybdenite, the chronometer can accommodate samples from Early Archean to well less than 1 Ma. Potential decoupling can be overcome with sensible sampling and thoughtful mineral separation. For a detailed review of molybdenite and sulfide geochronology, rich in examples, consult Stein (2014).

In this brief section, we have focused on the steps leading to breakthroughs and the hurdles in establishing the ^{187}Re–^{187}Os chronometer for this unassuming, soft, pliable, and isotopically strong mineral.

LLHR (Low-Level Highly Radiogenic) Sulfides

The LLHR term was introduced to describe samples with molybdenite-like Os isotopic compositions but with much lower Re concentrations, at the ppb or even ppt level (Stein et al. 2000). That is, the common Os is low enough relative to the radiogenic ^{187}Os that single samples may provide accurate and precise ^{187}Re–^{187}Os ages. The principles are the same as described for molybdenite, with the caveat that the blank correction may be important. The key equation for dating is therefore Eq. 4 (above).

Arsenopyrite (FeAsS) and some pyrites (FeS$_2$) may be LLHR. Because arsenopyrite and pyrite are commonly associated with Au, these two sulfides are sought out for dating gold deposits when molybdenite is absent from the sulfide assemblage. Like molybdenite, arsenopyrite and pyrite may permit ^{187}Re–^{187}Os dating of ore deposits. Further, pyrite is the most common sulfide in the earth's crust, so this mineral has additional value for Re–Os geochronology in general. If sulfides, including arsenopyrite and pyrite, have significant common Os, they can still be dated using the traditional ^{187}Re/^{188}Os versus ^{187}Os/^{188}Os isochron approach, but this requires analyses of multiple contemporaneously formed samples. For further discussion of LLHR samples, refer to Stein (2014). Several key studies brought attention to arsenopyrite as a valuable sulfide for Re–Os dating (Arne et al. 2001; Bierlein et al. 2006; Morelli et al. 2005, 2007, 2010). In addition, Morelli et al. (2010) showed that the Re–Os systematics in arsenopyrite were intact, even at temperature >400 °C. Although unusual, even pyrrhotite can be LLHR, yielding primary ages if the sample does not include other sulfides (Demaiffe et al. 2013).

Dating Shales: Source Rocks for Oil

The Re–Os budget held in crustal rocks is dominated by shales (Fig. 1). Groundbreaking Re–Os work on dating shales relied on whole-rock analyses of organic-rich shales (e.g., Ravizza and Turekian 1989; Creaser et al. 2002). Subsequently, Hannah et al. (2004) made use of syn-sedimentary pyrite with remarkable success on samples of Paleoproterozoic age (2,316 ± 7 Ma). The field of Re–Os geochronology quickly expanded to include dating of the organic (hydrogenous) component of organic-rich shales isolated from the clastic or detrital component of the shale (e.g., Selby and Creaser 2003, 2005a; Kendall et al. 2009; Yang et al. 2009). Re and Os concentrations in the organic

component are easily in the ppb range. The technique soon became well established as a tool to place age pins in the stratigraphic column for geologic time scale calibration. Previously, only U–Pb zircon ages on ash beds had prevailed as absolute time markers in sedimentary sections. Absolute time is also a valuable commodity for correlations where provincial species could not be used to link widely separated paleogeographic terranes (e.g., Xu et al. 2009).

The newfound ability to date shales led quickly to dating key units associated with major earth events; this can help resolve debates over the reach of these events in time and space – whether global or regional, abrupt or protracted. For example, localities with shale records associated with Neoproterozoic glaciation and the theory of a frozen snowball earth could now be time-bracketed with Re–Os dating of shales (e.g., Kendall et al. 2004, 2006, 2013; Rooney et al. 2010, 2011). Other earth events such as biotic crises associated with mass extinctions or major faunal turnovers provide excellent venues for Re–Os dating, as widespread anoxia preserved vast areas of organic material intact with their trace metal record of toxic seawater (e.g., Turgeon and Creaser 2008; Selby et al. 2009; Georgiev et al. 2011; Xu et al. 2014).

Since organic-rich black shales are potential source rocks for hydrocarbons, the petroleum industry became immediately interested in using the method not only as a measure of absolute time but as a correlation tool across basins, continents, and hemispheres. Good isochron regressions define initial $^{187}Os/^{188}Os$ ratios for paleo-seawater, useful measures for what was entering, mixing with, and characterizing the Re–Os budget of oceans on a more global scale (see Fig. 8). Simplistically summarized, the marine geochemical record, including Re–Os chemistry, is transferred to black shales on the seabed. During periods in earth history when the whole of seawater may have been anoxic, including the photic zone (e.g., Grice et al. 2005), the connection between top and bottom is profound. A more stratified ocean with variable oxygenation presents a more complex architecture linking the photic zone and seabed. This scenario holds for anoxic-euxinic waters in lacustrine sediments as well. With adequate ventilation and mixing, the seawater (lake water) Os isotope ratio represents the balance of (1) continental erosion (intimately linked to continental uplift) and (2) hydrothermal input. *Continental erosion* at a particular time in earth history reflects the kinds of rocks that are dominating the erosional cycle, that is, what rivers are delivering to seas. *Hydrothermal input* at a particular time in earth history may be dominated by mafic magmatism penetrating the seabed or terrestrial volcanic systems belching aerosols and particulate matter that ultimately mix at the seawater interface where they may incite algal blooms or otherwise feed microorganisms in the photic zone. While the notion of a global seawater Os isotopic composition is a tidy concept, it soon became apparent that restricted basins and isolated water masses, both horizontally and vertically, both locally and widespread, have the potential to harbor Os isotopic compositions that deviate from an assigned global Os isotopic value. Nevertheless, the concept of a variable Os isotopic composition for seawater through time works well, and the short residency time for Os in seawater gives us an increasingly tuned record of past earth events at high resolution (see Fig. 8).

As discussed throughout this contribution, the Re–Os data are governed by geologically responsible sampling. Drill core samples are highly preferred to outcrop samples to eliminate the possibility of disturbed isotope systematics related to weathering (Georgiev et al. 2012). At a minimum, flawed sampling at the outset compromises results and, more seriously, may disguise potentially meaningful results. Since we do not know the rate of sedimentation, proper sampling of shale means that the smallest possible interval, *but representative*, should be taken. After this interval is powdered, an aliquot of several hundred milligrams is removed for the Re–Os analysis. Sampling too large a stratigraphic interval risks capturing too large an interval of time – this compromises isochroneity and risks reducing the spread of the data points for a statistically well-constrained

isochron regression. Sampling too small a stratigraphic interval risks capture of postdepositional, small-scale isotopic exchange – for example, exchange among organic particles and sulfides after pore waters have been isolated from the overlying water column or redistribution of sediment by burrowing organisms.

What does this mean for Re–Os shale chronology? First, there is no threshold value for the amount of shale to be acquired, pulverized, and homogenized; each interval of core requires its own sampling strategy. Ideally, an isochron is derived from 5 to 8 samples, taken from 20 to 30 cm of core (Fig. 6). Sampling for an isochron should not be carried out over many meters or tens of meters of section. *Generally* speaking, for 20–30 stratigraphic centimeters of section and for ideal, well-laminated black shales without bioturbation, <30 g of pulverized shale sample (i.e., <1 cm stratigraphic span) routinely provides good ages (Fig. 7 and discussion in caption). Again, these are *generalized* parameters, and the sample stratagem depends on depositional rates, stability of the initial Os ratio, and Re/Os ratios in the shale samples. Shales with lower Re require larger aliquots for the analyses, but not necessarily larger bites of the stratigraphic section for homogenization.

Os Isotope Seawater Curve

The Os isotopic composition of the oceans has varied through time because of changes in the balance among the various Os sources, especially inputs from continental weathering (e.g., Peucker-Ehrenbrink and Ravizza 2000) and the several mechanisms for acquiring chondritic Os. Organic-rich sedimentary rocks, especially black shales, hold a record of ancient seawater Os isotopic composition. By far the best evidence that a sedimentary section has remained closed to Os gain, loss, or isotopic exchange is a suite of samples that form a precise isochron. In the last two decades, since high-precision Re–Os geochronology became a reality, a growing archive of initial $^{187}Os/^{188}Os$ ratios and corresponding ages has been acquired from isochrons. Figure 8 shows a plot of seawater $^{187}Os/^{188}Os$ versus age; for comparison, the Sr isotope seawater curve (Howarth and McArthur 1997; McArthur et al. 2001; Shields 2007) is plotted on the same figure. The well-known Sr isotope curve reflects four decades of effort; the Os isotope curve is in its early stages, with much still to be developed. In addition to these data, a number of studies have generated calculated initial $^{187}Os/^{188}Os$ ratios, derived from Re–Os isotopic ratios and a known (or assumed) age (e.g., Peucker-Ehrenbrink et al. 1995). Although a closed isotopic system is not proven, many of these data are likely valid, especially for young samples, and the effect of outliers tends to be swamped by the sheer volume of data. Studies based solely on calculated initial $^{187}Os/^{188}Os$ ratios have effectively illustrated, for example, the effect of a bolide impact at the Cretaceous-Paleogene boundary (Peucker-Ehrenbrink et al. 1995).

Figure 8 reveals a striking difference between the Sr and Os isotope seawater curves: the Os curve is spiky, with sharp highs and lows; the Sr curve is smooth, with more subdued variations. This is a simple result of the relatively long residence time for Sr in the oceans (~2 m.y.; McArthur et al. 2000) and the comparatively short residence time for Os (~28,000 years, Georg et al. 2013; still controversial, Paquay and Ravizza 2012). Short-term effects, such as bolide impacts or inputs from large igneous provinces, readily deflect the Os curve but are washed out by the long residence and mixing of Sr isotopes in seawater. A second critical difference is the continual buildup of Re and thus radiogenic Os in the crust. Neither element was mobilized in surface environments under earth's anoxic Archean atmosphere (Hannah et al. 2004), but both have accumulated since then, sequestered in large amounts in organic-rich sedimentary rocks. While both the Sr and Os seawater curves reflect variable input from continental weathering, Os is strongly controlled by the proportion of organic-rich sedimentary rocks undergoing weathering (Georgiev et al. 2012), whereas the Sr isotope
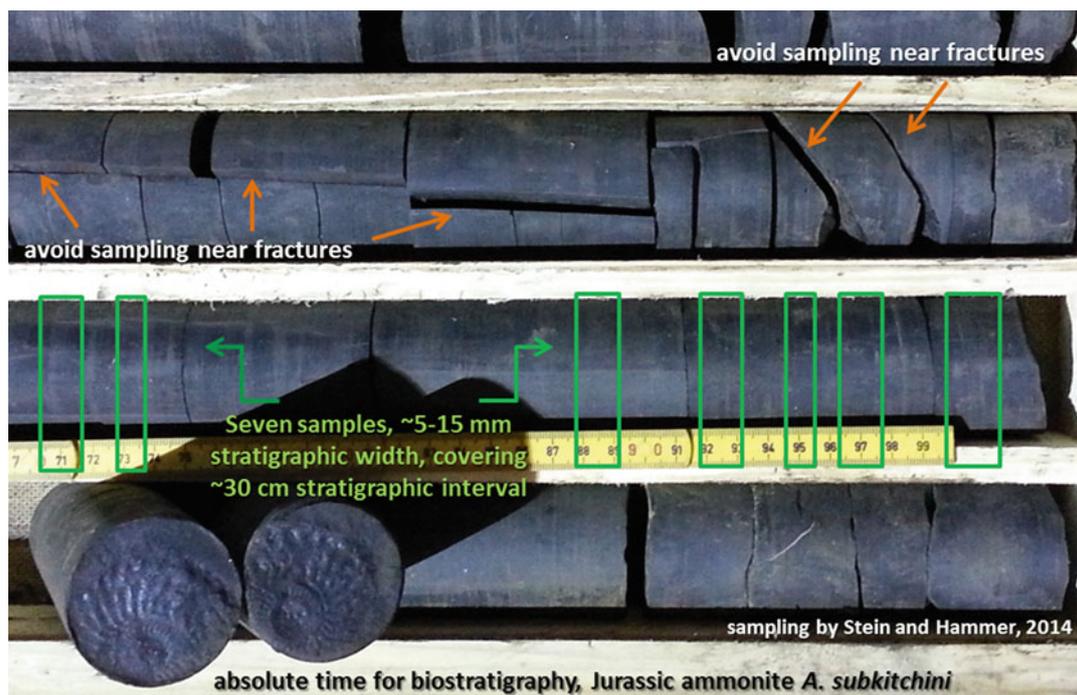
Fig. 6 Sampling shales is the most critical step for Re–Os dating. Drill core showing organic-rich Jurassic *black shale* from Svalbard. The sampling strategy illustrated here is that used by the AIRIE Program. Re–Os analysis of an aliquot from a shale sample acquired from within each *green rectangle* is very likely to yield an accurate and precise isochron age. This particular interval will provide direct age constraints for the Boreal ammonite, *A. subkitchini*

balance is controlled by weathering of carbonates and silicates (Ravizza 2007). The two systems provide complementary data for deducing causes of changes in marine chemistry through time.

Hydrocarbons: What Are We "Dating"?

The proven concentration of Re and Os in organic matter incites immediate interest in the potential for directly "dating" hydrocarbons. Simple thought experiments, however, draw immediate doubts: hydrocarbon systems are by definition open systems. Hydrocarbons are generated by maturation of organic material in a source rock, are expelled, migrate, and may eventually accumulate in a porous reservoir rock with an adequate seal. At what point might Re–Os systematics reveal useful information? How can we know which processes are elucidated by those systematics?

The first attempted Re–Os measurements on organic matter focused on physically separated organic detritus and associated pyrite in the Upper Jurassic Morrison formation (Hannah et al. 2000; Hannah and Stein 2003). All samples yielded high, readily measured concentrations of both Re and Os, with Os and especially Re enriched in organic matter relative to pyrite. Although some useful information could be extracted from closely spaced samples, an approach that subsequently proved useful for dating shales, most of the section was disturbed by open-system behavior. The organic detritus served as a sink for Re and Os dissolved in oxidizing groundwater that flowed through the Morrison sandstones for tens of millions of years.

The first breakthrough was a study by Selby and Creaser (2005b). They analyzed widely spaced samples from the extensive oil sand deposits of Alberta, Canada. A subset of their Re–Os data pointed to an age of 112 ± 5.3 Ma, interpreted as the petroleum emplacement age, and ruling out models suggesting Late Cretaceous hydrocarbon maturation and migration. The conclusions assume that the deposits spanning more than 400 km formed from the same source at the same time, a
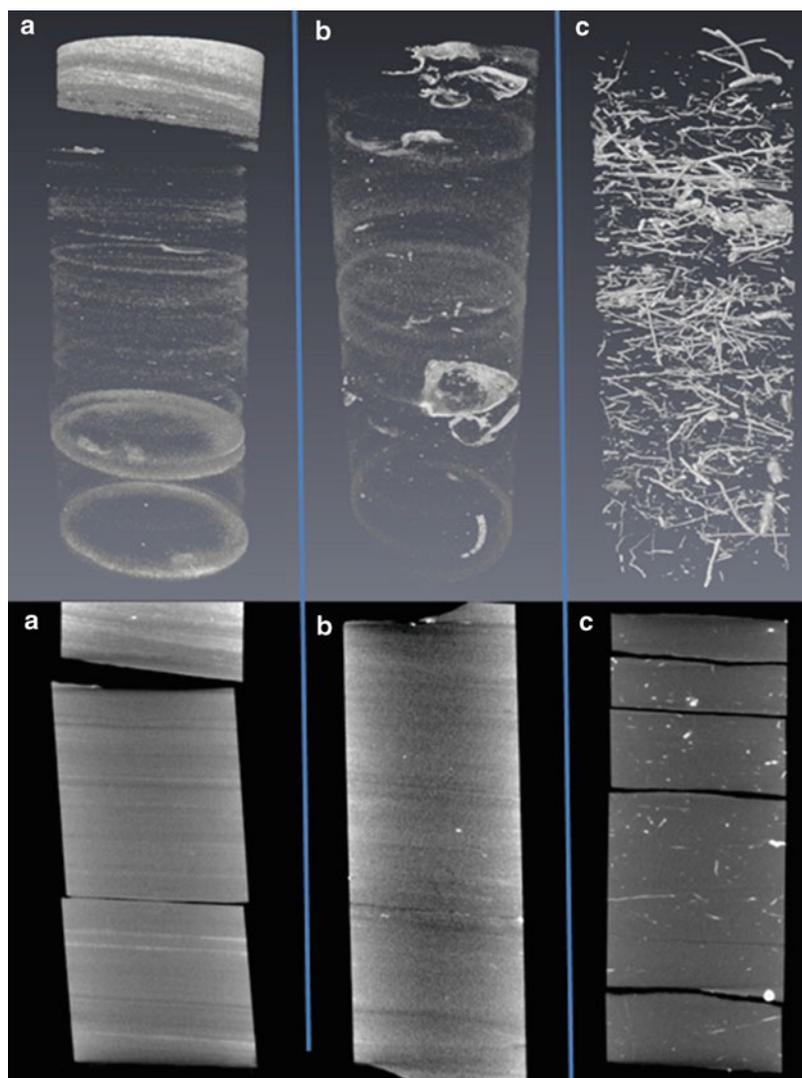
Fig. 7 Sampling shales is the first critical step in Re–Os dating. Three intervals from a drill core, Jurassic black shale, Svalbard. CT images on *top* are paired with corresponding photo of the same drill core piece below. All samples are positioned stratigraphically up toward the top of the page. Cores are 5 cm in diameter. (**a**) IDEAL for Re–Os dating. Beautifully laminated organic-rich black shale with lighter, less organic-rich, siltier intervals visible. (**b**). SUITABLE for Re–Os dating. Laminated black shale with brachiopod shells concave up indicating settling in quiet water; disseminated bright points are pyritized foraminifera indicating anoxic-euxinic conditions in the water column and bottom waters. (**c**) LESS DESIRABLE for Re–Os dating. Organic-rich black shale shows a myriad of fossil burrows, a record of intense bioturbation. As the organisms work their way into and out of the soft sediment bed, any variation in the osmium isotope composition is stirred at the mm to cm scale. With slow sedimentation rates, this has the potential to introduce scatter into an isochron (Samples collected and imaged by H. Stein and Ø. Hammer)

hypothesis supported by distinctive organic geochemistry. A concern is that 9 outliers of the 26 analyses were excluded on the basis of model initial Os ratios – statistically the same as removing any points not lying close to the isochron derived from all data. In addition, the preferred age was partly controlled by a single analysis (out of five) for one unusual deposit. Nevertheless, their landmark effort constituted a significant advance in analytical techniques and demonstrated that useful age information could be extracted from migrated hydrocarbons.
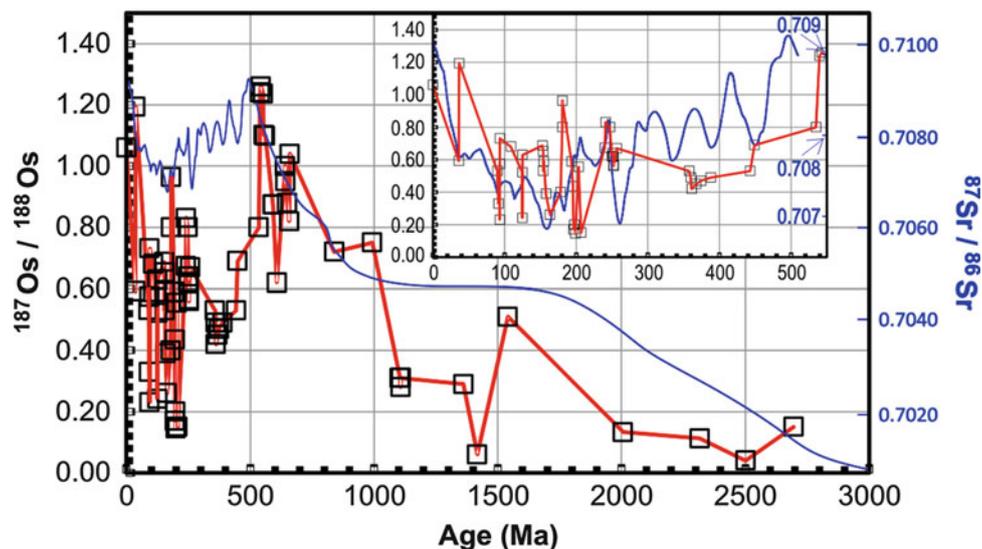
Fig. 8 Variations in the ^{187}Os/^{188}Os and ^{87}Sr/^{86}Sr ratios in seawater through time. Inset shows the Phanerozoic with an expanded scale. The Os isotope *curve* shows only initial ratios from isochrons (see discussion in text). The Phanerozoic Sr seawater curve is from Howarth and McArthur (1997) and McArthur et al. (2001); the Precambrian Sr curve is from Shields (2007). The Os *curve* was compiled by the AIRIE Program from the literature and unpublished data

Subsequent work has documented Re–Os systematics in several hydrocarbon systems, both marine (e.g., Finlay et al. 2011; Lillis and Selby 2013; Hannah et al. 2014) and lacustrine (Cumming et al. 2014). Moreover, geologically reasonable ages for hydrocarbon maturation/expulsion tied to tectonism have been extracted from shales (Stein et al. 2012). Comparison of asphaltene and maltene fractions of individual crude oils (Selby et al. 2007b) and hydrous pyrolysis experiments (artificial hydrocarbon maturation; Rooney et al. 2012) both document minimal differences in both ^{187}Re/^{188}Os and ^{187}Os/^{188}Os between source rock and extracted oil and among hydrocarbon fractions. Unfortunately, the oil generated by hydrous pyrolysis did not contain measurable Re or Os and was not able to fully replicate natural processes (Rooney et al. 2012). Nevertheless, these studies affirm early work that shows little or no disturbance of Re–Os systematics in organic-rich sedimentary rocks upon hydrocarbon maturation (Creaser et al. 2002 and many subsequent papers on shale geochronology).

A major challenge for deriving age information from oils is generating a spread in ^{187}Re/^{188}Os from different components of a single oil. Without this, a statistically significant linear regression cannot be achieved, and thus the age and initial ^{187}Os/^{188}Os cannot be well determined. Selby et al. (2007b) showed that Re and Os are concentrated in the asphaltene fraction, Mahdaoui et al. (2013) further separated asphaltenes by sequential precipitation into strongly and weakly polar fractions. Her results further support observations that separation of lighter oils from asphaltenes does not significantly fractionate Re/Os or ^{187}Os/^{188}Os, but a method is still needed for inducing a spread in Re/Os from a single oil sample. Notably, however, Ni and V concentrations peaked in mid-polarity fractions, while Re and Os dropped continuously from most to least polar. This argues against the commonly held assumption that Re and Os, like Ni and V, are bound in metalloporphyrins.

Re–Os analysis of oils is challenging and very much in its infancy. The potential to place time constraints on maturation, expulsion, and migration of hydrocarbons remains a powerful driver of research.

Summary and Challenges Going Forward

Re–Os geochronology can be used to date earth materials (e.g., sulfides, shales, oils) previously undatable by other isotopic methods. Of pivotal importance, these materials are directly linked to natural resources, both minerals and hydrocarbon, critical to human civilization.

For the immediate future, the challenge is no longer analytical, but geologic. We need to put forward bright and innovative thinking, with the basis for that thinking no longer tied to traditional models, but pointed toward new understanding of how earth's resources are ultimately generated. Re–Os offers more than geochronology. Acquiring an age for an ore deposit, or shale, gives us the last step in a long process. We have the data in hand to start thinking about "how it came about."

Questions for the future must probe deeper than they have in the past. How can Re–Os be used to link the nascent beginnings of resource formation to the end product that is mined or drained from the earth's crust for profit? This is not esoteric information, but needed information for responsible exploration in the next century. What conditions, far and wide, deep and shallow, make it possible to liberate metals and hydrocarbons? This is part of the slippery question of source – where and how does it start? Our thinking should not be limited to the lithosphere and hydrosphere, but must include atmospheric processes. These three spheres collectively govern resources. Not surprisingly, they also govern the timely issue of climate change.

As a first next step and an easy one to take, reconciling seemingly disparate and non-isochronous data is a good place to start new thinking. There is no such thing as bad data; there is only complexity in data sets that should challenge our imaginations, not prompt us to look only toward the easily interpreted data sets. The barrage of analytical data in the last decade should drive new and thoughtful sampling with different questions in hand.

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