

Overview on the Re-Os isotopic method and its application on ore deposits and organic-rich rocks

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Abstract

The Re-Os method has in the last twenty years experienced outstanding improvements and is now widely applied in earth science studies. The unique geochemical characteristics of the isotopic pair allow its application on investigations that vary from cosmochemistry and mantle-crust interactions to weathering and seawater composition. Re-Os has proved to be a valuable geochronometer for mineral deposits owing its chalcophile and siderophile nature that allow direct dating of ore minerals. Moreover, Re-Os isotopic system can provide not only ages for organic-rich sedimentary clastic rocks and oil migration, but also fingerprints the sources of Os inputs to seawater. In this paper, an overview of the method and its main applications is provided with emphasis on geochronology, showing whenever possible Brazilian examples, and providing a wide variety of selected references for those who are interested in greater detail.

Keywords: Re-Os method, geochronology, sulfide, ore deposits, organic-rich rocks, oil.

1. Introduction

The ^{187}Re - ^{187}Os isotopic system, due to rhenium and osmium geochemical characteristics, differ from other commonly used isotopic systems (e.g. Rb-Sr, Sm-Nd, Lu-Hf, U-Th-Pb) in which the elements are lithophile and controlled by silicate minerals. Re and Os are highly chalcophile and siderophile elements, being strongly partitioned into metal or sulfide phases. They are also organometallic with high affinity with organic matter present in sedimentary rocks such as black shales (Ravizza & Turekian 1989, Reisberg & Meisel 2002, Shirey and Walker 1998, Carlson 2005 and Selby et al. 2007b). These characteristics have allowed a diversity of research and application of the Re-Os isotopic system in a broad range of geological problems ranging from cosmochemistry, core-mantle geochemistry and igneous petrogenesis (e.g. Shirey and Walker 1998, Carlson 2005), to continental weathering and seawater Os isotope composition (Pegram et al. 1992, Peucker-Ehrenbrink & Blum 1998, Peucker-Ehrenbrink & Ravizza 2000, Cohen et al. 2004, Oxburgh et al. 2007, Turgeon et al. 2007, Turgeon & Creaser 2008). The Re-Os isotope system has been also widely applied in geochronology to a wide variety of matrices such as mafic rocks (Allègre et al. 1999, Gangopadhyay et al. 2003), oxides (Zhou et al. 2005), sulfide (Stein et al. 1997, Selby & Creaser 2001a,b, Morelli et al. 2004, 2005, Selby et al. 2009a), gold (Kirk et al. 2002), black shale (Ravizza & Turekian 1989, Cohen et al. 1999, Selby & Creaser 2003, 2005a, Kendall et al. 2004, 2006, Azmy et al. 2008, Rooney et al. 2010) and even oil (Selby & Creaser 2005b, Selby et al. 2007b, Finlay et al. 2010a).

2. Basic fundamentals

Rhenium comprises two natural isotopes, ^{185}Re and ^{187}Re , and osmium has seven isotopes, of which two are radiogenic (see Figure 1 for relative abundances of osmium isotopes). ^{187}Os is produced by the β -decay of ^{187}Re and ^{186}Os is produced by the α decay of ^{190}Pt , a minor isotope with a very long half life (between ca. 370 and 490 Ga, still under debate - eg, Tavares et al. 2006). For this review, focus will be on the Re-Os system only.

The ^{187}Re decay constant (λ ^{187}Re) has been assumed to be $1.666 \cdot 10^{-11} \pm 0.0017 \text{ a}^{-1}$ since the study of Smoliar et al. (1996) and was obtained from a cross calibration of Re-Os and Pb-Pb data from meteorites. Recently, the same decay constant was reproduced within calculated uncertainties by Selby et al. (2007a) who conducted an independent study based on cross calibration of Re-Os in molybdenite and U-Pb zircon from magmatic rocks. Uncertainty in the decay constant place limits in the accuracy of age determinations (Begemann et al. 2001) and the recent results of Selby et al. (2007a) help to increase the confidence and reliability of Re-Os calculated ages using the assumed ^{187}Re decay constant, although further refinements continues to be pursued.

3. Analytical Protocols

The Re-Os analytical procedures since early studies encountered difficulties due to: (i) the low amount of rhenium and osmium to be measured, (ii) the OsO_4 volatility at low

temperatures that may cause loss during sample dissolution and equilibration with spike, (ii) the heterogeneous distribution of osmium in some materials leading to low reproducibility, and

After four decades of intense experimentation, analytical improvements during the 1990's led to a rapid expansion in the use of the Re-Os system. As reviewed by Reisberg & Meisel (2002) and recently highlighted by Selby et al. (2007a), the major advances were: (i) the precise and accurate determination of Re and Os compositions by negative thermal ionization mass spectrometry (NTIMS) (Creaser et al. 1991, Völkening et al. 1991, Walczyk et al. 1991), (ii) the effective dissolution of Os carrier phases with complete chemical equilibration with spike (Shirey & Walker 1995) 40 and, (iii) the development of efficient Re and Os separation techniques (Cohen & Waters 1996, Birck et al. 1997).

This overview aims at synthesizing the main aspects of the Re-Os isotopic systematics and at providing a first contact with the method and its applications, particularly in geochronology. Examples from Brazil when available are highlighted to illustrate some applications of the technique. Specific and much more comprehensive reviews on the Re-Os procedures and its applications, particularly on mantle/crust evolution are available, for example, in Shirey & Walker (1998) - for those who are interested in cosmochemistry and mantle evolution; Reisberg & Meisel (2002) - for a full review of analytical procedures; Stein et al. (2001) - for geochronology using molybdenite; Cohen (2004) - for geochronology of organic-rich sediments and Re-Os applied to paleoenvironmental studies; Carlson (2005) - for age and composition of mantle and related magmas and also for an introduction into Pt-Os isotope system, and Rudnick & Walker (2009) - for a deep review on the geochronology of peridotites.

Regarding distribution and geochemical behavior, the highly siderophile characteristic of rhenium and osmium suggests that they are concentrated in the core together with other Highly Siderophile Elements likewise in iron meteorites where both elements are enriched. In natural materials, concentration is variable and ranges from less than ppb to several ppm (Fig. 2).

One of the most relevant characteristic of this system is that osmium is highly compatible and remains in the mantle residue after melting whereas rhenium is moderately incompatible being relatively enriched in the crust. This extreme fractionation between Re and Os, with time, leads to a very large variation in the $^{187}\text{Os}/^{188}\text{Os}$ ratio between crust and mantle. Crust materials have higher $^{187}\text{Os}/^{188}\text{Os}$ than mantle rocks and, consequently, Os isotopes are very sensitive and useful for petrological investigation. For example, small amount of crustal contamination or recycling can be detected in mantle derived magmas. The geochemical behavior including partitioning and sensitivity to oxygen and/or sulfur fugacity during melting and distribution of Re and Os between core, mantle and crust and consequently implications for petrological studies was thoroughly reviewed by Carlson (2005).

Isotopic percentage of Osmium

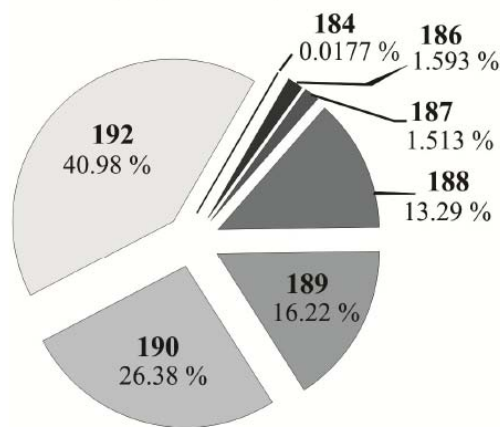


Figure 1

Osmium isotopic abundances in percentage from Shirey & Walker (1998). At the bottom, ¹⁸⁷Re radioactive decay to ¹⁸⁷Os, constant from Smoliar et al. (1996).

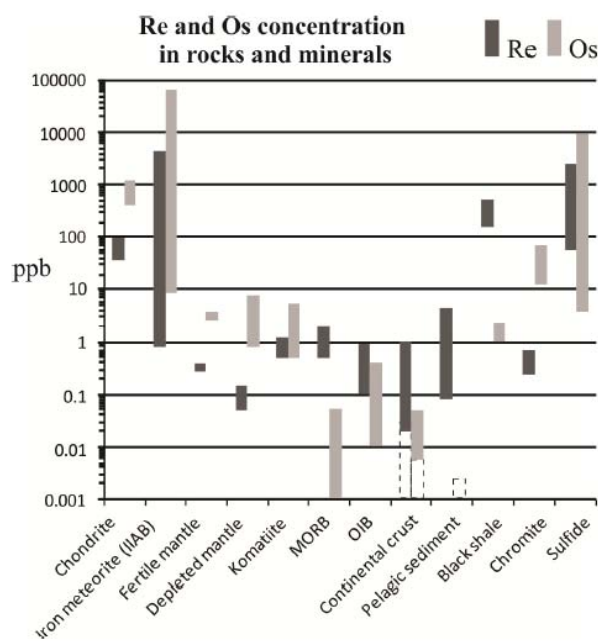
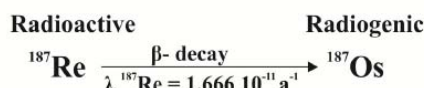


Figure 2

Re and Os typical concentration in rocks and minerals. Concentrations are in ppb. (values from Shirey & Walker (1998) and references therein).

(iv) the highly refractory nature of osmium and its very high ionization potential that make not possible the use of traditional positive thermal ionization procedures.

The analytical techniques were reviewed in detail by Reisberg & Meisel (2002) where readers can find a complete discussion about each different procedure of mass spectrometry, sample dissolution and chemical separation applied to Re-Os measurements and, also, an introduction on spike and standard preparation and calibration, a not simple task due to the non-stoichiometric character of osmium reference materials and difficulties to equilibrate spike and standard (e.g., Markey et al. 2007). Here, only a brief description of the most commonly applied analytical procedures in current use will be presented.

Regarding mass spectrometry, early studies used gas mass spectrometry followed by secondary ion and resonance ionisation mass spectrometry (see Reisberg & Meisel 2002 and references therein). However, since 1991, Re-Os measurements became more accurate and sensitive after the studies by Creaser et al. (1991) and Völkening et al. (1991) that utilized negative thermal ionization mass spectrometry (NTIMS). The NTIMS technique was a turning point for Re-Os method and

opened a large field of work since a wide sort of matrices with low Re-Os could be analyzed. For NTIMS, the osmium and rhenium separates are loaded onto Pt and Pt or Ni filaments, respectively, and measured using peak hopping using the single pulse counting electron multiplier or the Faraday collectors. Nevertheless, more recently, the inductively coupled plasma mass spectrometry (ICP-MS) is being used because new multi-collector equipments with magnetic sector and multiple electron multipliers allow good analytical results (Schoenberg et al. 2000). Although the precision is not as good as in NTIMS, the ICP-MS allow a less complicated chemistry, fast analyses and also lower blanks for rhenium (Reisberg & Meisel 2002). The procedures described below are applied for measurements using NTIMS, but most of them can also be suitable for ICP-MS.

It is important to emphasize that during sample preparation is necessary to avoid possible metal contamination during crushing given the strong siderophile character of rhenium and osmium and their very low abundances in some samples. After crushing, a weighed amount of sample powder is added before digestion together with a weighed quantity of spike. The tracer solution is previously calibrated against standards and

can be used either as a mixed ^{185}Re - ^{190}Os spike (e.g. Carlson et al. 1999, Creaser et al. 2002) or as individual ^{185}Re and ^{190}Os spikes or ^{185}Re spike plus isotopically normal Os (standard) (Selby & Creaser 2001a, Morelli et al. 2004, 2005) or also mixed double-spike (^{185}Re - ^{188}Os - ^{190}Os) (e.g. Markey et al. 2003, Markey et al. 2007) depending on the laboratory and/or composition of the material to be analyzed. The Os content of gravimetric standard solutions used to calibrate any spike is a particular concern, given the non-stoichiometry of most Os compounds used (see Yin 2001 and Markey et al. 2007 for discussion of this problem).

The Carius tube digestion technique (Shirey & Walker 1995) has been the most widely used method and has many advantages such as low blanks and full dissolution. Other techniques like alkaline fusion (Morgan & Walker 1989, Markey et al. 1998) and NiS fire assay (Hoffman et al. 1978, Ravizza & Pyle 1997) have been tried, but high blanks, loss of volatile osmium and problems with equilibration preclude a widespread use of these methods. Dissolution in reducing media using HF-HCl-ethanol and HF-HBr (Walker 1988, Birck et al. 1997) has also been tried with the advantage of very low blanks and no losses of OsO_4 , but is not widely used. Other possible routine is the high pressure asher digestion considered by Reisberg & Meisel (2002) as capable to achieve a more complete dissolution, but needs a more complex and expensive apparatus and for this reason has not been applied frequently. In special circumstances, leaching procedures (sediments, Pegrum et al. 1992, Peucker-Ehrenbrink et al. 1995) may be interesting, but rhenium and osmium fractionation can occur and rigorous control on leaching is necessary. In the Carius tube procedure (Shirey & Walker 1995), sample, spikes and acids are kept at low temperature in a dry-ice-methanol or dry-ice-acetone slurry and sealed in a thick-walled Pyrex tube. The sealed Carius tube is then allowed to warm slowly to room temperature after which it is placed in an oven and heated (average 240°C) for 12 to 48 hours. It allows the dissolution in oxidizing solutions at high temperatures without the loss of volatile OsO_4 and also allows equilibration between sample and spike. However, handling with overpressurized tubes can be dangerous and, for this reason, the tubes are protected by steel explosion shields during heating process. The acids normally used are HNO_3 and HCl in proportions 2:1 or 3:1 (inverse, or Lefort aqua regia), but alternatively CrO_3 and H_2SO_4 can be used (Reisberg & Meisel 2002). The CrO_3 - H_2SO_4 has been widely applied for organic rich samples (Creaser et al. 2002, Kendall et al. 2004, 2006, 2009, Turgeon et al. 2007, Selby et al. 2009b) considering that it minimizes the effect of rhenium and osmium from detrital sources and enables the dating of samples with low total organic matter (< 1%) (Kendall et al. 2004).

After dissolution, the Carius tube cools to room temperature and is again frozen in dry-ice-methanol or liquid nitrogen and the tube tops cracked open and osmium is separated by distillation (not described here, see Reisberg & Meisel 2002 and references therein for further details) or liquid-liquid extraction (Cohen & Waters 1996) or liquid Br_2 with CrO_3 and HNO_3 (cf. Birck et al. 1997). For the liquid-liquid extraction, the cold sample solutions are transferred to 50ml centrifuge tubes to which 3ml of organic solvent (CCl_4 or CHCl_3) is added. The mixture is shaken, centrifuged and the organic solvent removed to a teflon or glass beaker with 4 ml

of concentrated HBr to reduce OsO_4 to a non-volatile form. The procedure is repeated three times to extract all OsO_4 . After a while, the organic solvent is pipetted off and osmium remains dissolved in the HBr, which is dried and the osmium rich fraction is purified by microdistillation (Birck et al. 1997). In this procedure, the dry osmium sample is dissolved in 30 microliters of a mixture of H_2SO_4 and CrO_3 and transferred to the cap of a teflon conical beaker to which 20 microliters of concentrated HBr was placed into the bottom. The beaker is placed on a hot plate upside-down at less than 85°C for 2 or 3 hours, distilling the oxidized osmium into the HBr. The HBr solution is then evaporated to dryness. This method has been widely used and guarantees high purity of osmium analyte which is crucial for NTIMS analysis. The sample is then loaded onto Pt filament, covered by 20 micrograms of BaNO_3 or $\text{Ba}(\text{OH})_2/\text{NaOH}$ activator and then loaded into the mass spectrometer (Carlson et al. 1999, Selby & Creaser 2001a, Creaser et al. 2002).

The rhenium remains on the aqua-regia solution or CrO_3 - H_2SO_4 after osmium extraction. Rhenium extraction is usually made by common anion exchange chromatography (Morgan et al. 1991) but can also be achieved using solvents (not described here, see Reisberg & Meisel 2002 and references therein). For chromatography, the solution is transferred to a beaker and dried. Then, sample is dissolved in 1N HCl, centrifuged and then loaded on a column filled with anion exchange AG1-X8 resin. Rhenium is retained and the column is eluted in HCl followed by HNO_3 . The solution with rhenium can also be purified in a second small column (Carlson et al. 1999) or by a single bead anion extraction using a single large grain of AG1-X8 resin, which will concentrate all rhenium (Selby & Creaser 2003). When CrO_3 - H_2SO_4 residue is used, Cr^{6+} complicates the exchange chromatography and a more detailed procedure needs to be applied in order to reduce Cr^{6+} to Cr^{3+} . One possibility is to bubble SO_2 gas into the solution for one minute (Selby & Creaser 2003, Selby et al. 2005) before normal procedures on the column. Another difficulty is caused by molybdenum (Morgan et al. 1991). The problem can be solved washing the column with HCl and NaCl (Morgan et al. 1991) or using Amyl acetate to retain Molybdenum (Selby & Creaser 2001a). After separation, rhenium is loaded onto Pt or Ni filament and covered with 20 micrograms of BaNO_3 , which is then placed into the mass spectrometer. The use of Ni filament possibly reduces the blanks (Creaser et al. 2002).

Another type of analyses is in situ measurements. The ion probe studies from 1980's were restricted to very rich osmium matrices (Reisberg & Meisel 2002 and references therein), but with the ICP-MS with laser ablation it is now possible to make direct determination of Re-Os isotopes in single sulfide grains from mantle peridotites that are enriched in rhenium and osmium (Pearson et al. 2002, Griffin et al. 2004, Aulbach et al. 2004). However, isobaric interferences, mass bias, lower osmium in some sulfides and "nugget" effect on minerals constitutes additional difficulties for in situ analyses. Nevertheless, recently mass spectrometry improvements, changes in mass bias and isobaric interferences corrections and use of Os solution as reference material has contributing to enhance accuracy and reproducibility (Nowell et al. 2008a,b), although an Os reference material proper for laser ablation is still pursued.

4. γ Os, model ages and its applications

Re-Os method is extremely useful in comparison to other radiogenic isotope systems for tracking sources and dating melt depletion time in peridotites due to geochemical characteristics of both elements that leads to fractionation during mantle melting. Nevertheless, is not easy to obtain isochrons from peridotites or its sulfides because of heterogeneous $^{187}\text{Os}/^{188}\text{Os}$ initial ratio in the mantle and rhenium mobility in some oxidizing circumstances. Application of different types of model ages became relevant and has been applied in many studies (cf. Rudnick & Walker 2009 and references therein).

Considering nomenclature, it is important to be familiar with the most commonly used terms and, also, with

$$\gamma\text{Os}(t) = \left\{ \left[\left(\frac{^{187}\text{Os}/^{188}\text{Os}_{\text{sample}(t)}}{^{187}\text{Os}/^{188}\text{Os}_{\text{chon}(t)}} \right) - 1 \right] \times 100 \right. \quad (1)$$

where $^{187}\text{Os}/^{188}\text{Os}_{\text{chon}(t)}$ is:

$$^{187}\text{Os}/^{188}\text{Os}_{\text{chon}(t)} = ^{187}\text{Os}/^{188}\text{Os}_i + ^{187}\text{Re}/^{188}\text{Os}_{\text{chon}} (e^{\lambda(4.558 \text{ e9})} - e^{\lambda t}) \quad (2)$$

The γ Os is analogous to ϵ_{Nd} in that it is the relative deviation of the sample's Os isotopic composition from that expected for chondritic (or primitive) mantle and they are largely used together in petrological studies. Positive $\gamma_{\text{Os}(t)}$ translates a radiogenic isotopic composition related to an originally high $^{187}\text{Re}/^{188}\text{Os}$ reservoir (e.g. crust) while negative value reflects an unradiogenic composition related to an originally low $^{187}\text{Re}/^{188}\text{Os}$ source (e.g. Re-depleted lithospheric mantle). As Os isotopes are very sensitive to small inputs of crust-derived material, γ_{Os} has been used on petrological studies to evaluate the role of crustal contamination being particularly interesting for investigating the origin of mineral deposits considering the chalcophile and siderophile character of rhenium and osmium (e.g. Ripley et al. 1998, Sproule et al. 1999, Lambert et al. 1998a, 2000, Horan et al. 2001, Lahaye et al. 2001, Marques et al. 2003, Girardi et al. 2006, Day et al. 2008, O'Driscoll et al. 2009, Tao et al. 2010).

One Brazilian example of the use of Os isotopes in petrological problems is the study of chromitites from the Ipeira-Medrado Sill, Jacurici Complex (Marques et al. 2003). The Jacurici parental magma is considered to be very primitive, originated from high degree of mantle melting. The lower and middle part of the sill (LUU-Lower Ultramafic Unit and MCL-Main Chromitite Layer) yield negative ϵ_{Nd} (mean -4.4) for whole peridotite samples and negative γ_{Os} (mean -4.1) for chromite separates. Towards the upper part of the sill (top of MCL and UUU-Upper Ultramafic Unit), the composition modifies and ϵ_{Nd} values become more negative (mean -6.5) for whole-rock peridotite samples and γ_{Os} change from chondritic to positive on chromite separates. The fields of both groups are plotted in figure 3 that exhibits $\epsilon_{\text{Nd}(2038 \text{ Ma})}$ and $\gamma_{\text{Os}(2038 \text{ Ma})}$ variation of magmas evolving from two distinct sources undergoing crustal contamination. The Nd and Os isotope systematics when applied together show compositions which rule out a convective mantle source and argue for an old, enriched, subcontinental lithospheric mantle source for the parental magma which, from the

possible problems when comparing results from different studies. One first issue is the normalization. In earlier studies, ^{187}Os abundances were normalized using ^{186}Os , but as already shown above, ^{186}Os is also radiogenic and has been used in Pt-Os isotopic studies (see Walker et al. 1997, Carlson 2005). In consequence, ^{187}Os has been normalized using ^{188}Os .

One usual notation for tracer studies is the γ Os(t), firstly defined by Walker et al. (1989). It represents the percentage deviation between the sample Os isotopic composition and the average chondritic mantle reservoir (or bulk silicate earth-BSE) composition at a given time t.

middle part of MCL to the top of the sill, experienced up to 30% of crustal contamination. The crustal contamination was interpreted as responsible for triggering chromitite formation (Marques et al. 2003). The use of ϵ_{Nd} and γ_{Os} notations is a practical and convenient way to show petrological variations. The Os isotopic composition of long-established mantle reservoirs and crust has been the subject of several studies and relevant references are Shirey & Walker (1998), Pearson (1999), Carlson (2005) and, more recently, Rudnick & Walker (2009) for mantle and Turgeon & Creaser (2008) and Selby et al. (2009b) for seawater.

Other common parameters used in the osmium isotopic system are the model ages - T_{MA} (Mantle Model Age) and T_{RD} (rhenium-depletion Model Age) - normally used as best estimates for the age of mantle extraction or ages of mantle peridotites and their sulfides. In comparison with Nd, the Os model ages have an advantage in dating melt depletion events. Nd is incompatible and only small amounts remain in residues being easily overprinted by interaction with more evolved magmas. The moderately incompatible behavior of rhenium and strong compatible character of osmium leads to high concentration of osmium in peridotites and virtually no rhenium in highly depleted residues. Thus, osmium is not easily overprinted by metasomatism in the mantle or by later interactions with incompatible rich magmas (Rudnick & Walker 2009).

The T_{MA} (Luck & Allègre 1984) is calculated using equation 3 and is similar to the Nd T_{CHUR} . The T_{MA} represents, therefore, the time of melt extraction from the mantle and is shown by the intersection of the sample $^{187}\text{Os}/^{188}\text{Os}$ isotopic composition and the evolution curve of the mantle Os isotopic composition. It is applied for both mantle (depletion time) and crustal materials (extraction time) (Walker et al. 1989, Shirey & Walker 1998). The T_{MA} represents the true age only if rhenium has not been later modified by any geological process, which is rare in mantle peridotites and their sulfides. The age will be older if rhenium has been added or younger if rhenium has been removed (Rudnick & Walker 2009).

$$T_{\text{MA}} = (1/\lambda) * \ln \left\{ \left[\left(\frac{^{187}\text{Os}/^{188}\text{Os}_{\text{chon}(t=0)}}{^{187}\text{Os}/^{188}\text{Os}_{\text{sample}(t=0)}} \right) / \left(\frac{^{187}\text{Re}/^{188}\text{Os}_{\text{chon}(t=0)}}{^{187}\text{Re}/^{188}\text{Os}_{\text{sample}(t=0)}} \right) + 1 \right] \right\} \quad (3)$$

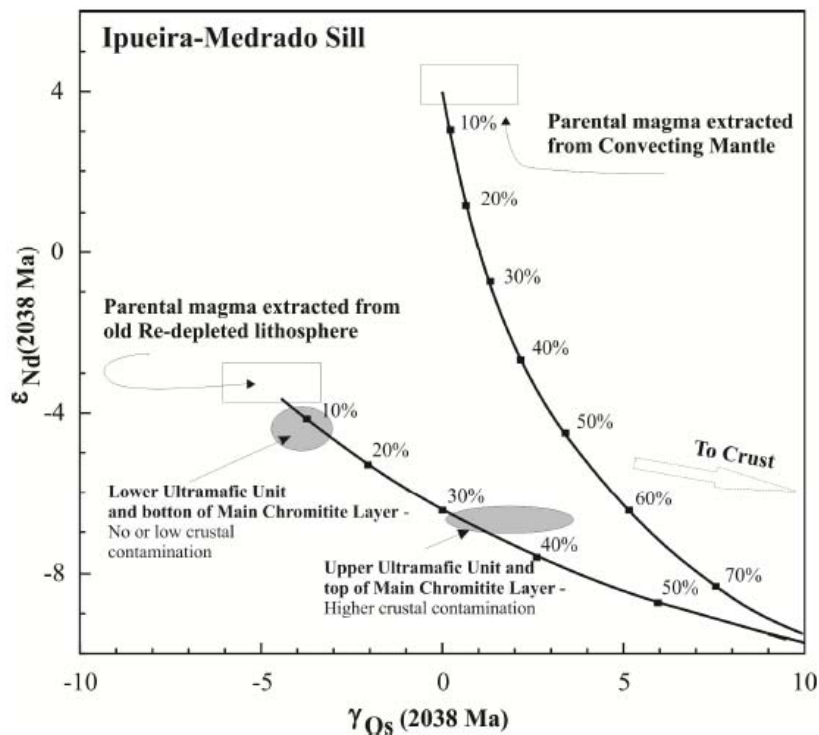


Figure 3

$\epsilon_{\text{Nd}(2038 \text{ Ma})}$ and $\gamma_{\text{Os}(2038 \text{ Ma})}$ variation of magmas evolving from two distinct sources (Re depleted lithosphere and convecting mantle) undergoing crustal contamination (from Marques et al. 2003). Fields of lower and middle part (UUU and base of the MCL) and upper part (UUU and top of MCL) of the Ipueira-Medrado Sill are plotted showing that parental magma possible evolved from an old, enriched, subcontinental lithospheric mantle source and experienced crustal contamination during the Main Chromitite Layer and final crystallization of the sill. Curves were calculated using simple binary mixing. Spots at curves show 10% increments of crustal end-member (see Marques et al. 2003 for further details and end-members compositions).

The T_{RD} (Walker et al. 1989) has been more often used and was conceived to ignore the possible addition of rhenium during emplacement of xenoliths from depleted mantle samples like those from refractory residues. It is very useful for mantle xenoliths that during its final emplacement interacted with basalt or kimberlite magmas, which may cause contamination with rhenium addition (Carlson 2005,

Rudnick & Walker 2009). It is calculated using equation 4, but firstly, the $^{187}\text{Os}/^{188}\text{Os}$ ratio from both sample and chondritic mantle must be recalculated for the time of the possible contamination, i.e time of eruption (Shirey & Walker 1998). Considering $^{187}\text{Re}/^{188}\text{Os}$ of the sample equal to zero, the T_{RD} will represent the minimum age of the true melt depletion time in residue samples.

$$T_{\text{RD}} = (1/\lambda) * \ln \left\{ \left[\left(\frac{^{187}\text{Os}/^{188}\text{Os}_{\text{chon}(t=0)}}{^{187}\text{Os}/^{188}\text{Os}_{\text{sample}(t=0)}} \right) / \left(\frac{^{187}\text{Re}/^{188}\text{Os}_{\text{chon}(t=0)}}{^{187}\text{Re}/^{188}\text{Os}_{\text{sample}(t=0)}} \right) + 1 \right] \right\} \quad (4)$$

The T_{MA} and T_{RD} osmium model ages are exemplified in figure 4a (from Shirey & Walker 1998) considering three different situations. One situation, trajectory A, shows the T_{RD} of a depleted peridotite xenolith contaminated with Re during final emplacement at 0.3 Ga (age of volcanism). First the isotopic composition of sample and chondritic mantle are calculated back to 0.3 Ga (time of the eruption and contamination) and then the Re/Os ratio of the sample is assumed to be zero to obtain the T_{RD} . For this scenario, the T_{MA} is meaningless, shows future age and is not plotted. Thus, in this case, the calculation of T_{RD} enabled to recover, at least, a minimum age of mantle depletion, which were not possible with the traditional model ages calculation. In a second example, trajectory B also illustrates a depleted peridotite but with no or little contamination. In this case, note that recalculation of isotopic composition at time of eruption causes only minimum variation and T_{MA} is older but not much different than T_{RD} . The trajectory C is the simplest and shows the T_{MA} age meaning the extraction time of a crustal rock with high $^{187}\text{Re}/^{188}\text{Os}$ like a basalt.

Peridotite xenoliths from cratonic areas, where high degrees of melting normally took place, probably will have T_{RD} in a very good agreement with the time of mantle extraction and, consequently, with the possible time of lithosphere formation (Carlson 2005, Rudnick & Walker 2009). Nevertheless, if the peridotite xenoliths are not from highly depleted mantle, the T_{RD} will be only a minimum age considering significant amounts of rhenium was left in the residue. Figure

4b, an example used by Walker et al. (1989) and Rudnick & Walker (2009), shows the T_{MA} and T_{RD} model ages considering two different rates of melting at 3.5 Ga. In one situation, a high degree of melting, generating a komatiite magma, causes strong rhenium depletion and the $^{187}\text{Re}/^{188}\text{Os}$ ratio of the residue becomes zero. In this situation, the T_{RD} is equal to T_{MA} and both will be very similar to true age of the melt depletion. However, in other circumstance, when the degree of melting is lower, generating basalts for example, rhenium is left behind and $^{187}\text{Os}/^{188}\text{Os}$ ratio of the residue increases with time leading to only minimum T_{RD} age and not to the real time of depletion. The first situation is expected in peridotite xenoliths from cratonic areas whereas the second is expected in off-craton.

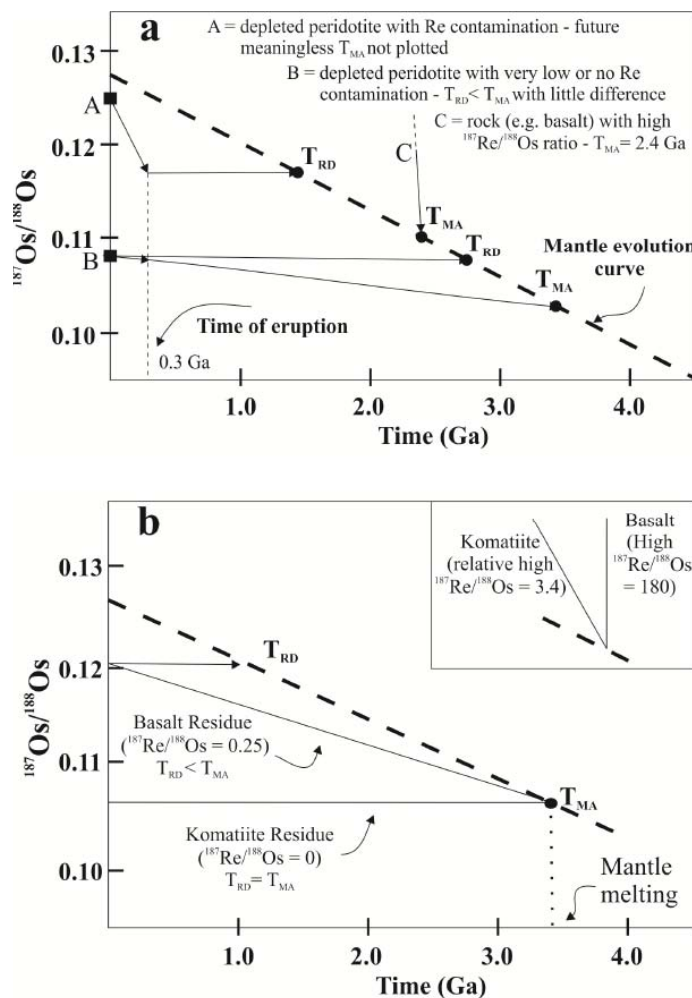
Therefore, in off-craton and where depletion is not homogeneous, the T_{RD} may be less valuable. Geochemical indicators like Mg (Walker et al. 1989, Reisberg & Lorand 1995, Carlson et al. 2007), Al_2O_3 in whole rock or mainly in clinopyroxene (Meisel et al. 1997, Meisel et al. 2001, Gao et al. 2002, Schilling et al. 2008) and other immobile elements like Y and Yb (Reisberg & Lorand 1995, Gao et al. 2002) are normally used against $^{187}\text{Os}/^{188}\text{Os}$ ratio to evaluate the degree of depletion and may constitute an important tool to assess the significance of model ages (cf. Rudnick & Walker 2009). Carlson et al. (2007), for example, applied such method together with other isotopic and geochemical data to better understand the nature of peridotite xenoliths and mafic-ultrapotassic

rocks from southern Brazil. The study indicated that the Alto Paranaíba alkalic province evolved from compositionally and temporally distinct lithospheric mantle when compared to the Goiás alkali province.

Despite the practical use of γ_{Os} and model ages, care must be taken when comparing data from different papers. Differences up to 2.7 units in γ_{Os} and several million years (cf. Carlson 2005) can occur since γ_{Os} and model ages are sensitive to Re-Os parameters assumed as the average of the fertile

mantle reservoir, also known as chondritic mantle or bulk silicate earth. Some works use the Re-Os values from carbonaceous chondrites ($^{187}Os/^{188}Os$ present day=0.1262, Walker et al. 2002) while others use values from primitive upper mantle (or PUM – $^{187}Os/^{188}Os$ present day=0.1296, Meisel et al. 2001) among other possibilities. The reason for this resides in the distinct isotope compositions of chondritic meteorites and no consensus on the best average for the bulk silicate earth (cf. Carlson 2005).

Figure 4
Osmium isotope evolution illustrating:
a) T_{MA} and T_{RD} model ages considering three different circumstances: A. depleted peridotite xenolith contaminated with Re during eruption at 0.3 Ga; B. depleted peridotite xenolith not or poorly contaminated with Re during eruption at 0.3 Ga; and. C. hypothetical basalt with high $^{187}Re/^{188}Os$. See text for further details. Mantle evolution curve plotted considering initial $^{187}Os/^{188}Os$ of 0.09531 from III A iron meteorite at 4.558 Ga an average chondrite $^{187}Os/^{188}Os$ of 0.1270 at present day. Diagram and data after Shirey & Walker (1998). b) T_{MA} and T_{RD} model ages in two different situations after melting. One considering high degree of melting (komatiite extraction) leaving a depleted residue and second after relatively lower degree of melting (basalt extraction) leaving a partly Re-depleted residue. Inset in upper right show trajectory of $^{187}Os/^{188}Os$ from melts with different $^{187}Re/^{188}Os$ initial ratios. Evolution curve from a chondritic mantle. Diagram after Walker et al. (1989) and Rudnick & Walker (2009).



5. Re-Os geochronology applied to ore minerals

Mantle peridotites and its sulfides have not been good matrices to produce true isochrons and model ages have been much more useful instead. Only few good isochron ages have been obtained for Mg rich whole rocks such as komatiites or picrites. On the other hand, other geological materials, especially sulfides (Stein et al. 1997, Selby & Creaser 2001a,b, Mathur et al. 2002, Morelli et al. 2004, 2005, Selby et al. 2009a, Qi et al. 2010) and organic rich rocks (Selby & Creaser 2003,

2005a, Kendall et al. 2004, 2006, Azmy et al. 2008, Rooney et al. 2010) have been able to yield good age determinations.

The age equation for Re-Os isochron (equation 5) is analogous to other isotopic methods like Rb-Sr or Sm-Nd. $^{187}Os/^{188}Os$ is plotted against $^{187}Re/^{188}Os$ and the slope is defined by $(e^{\lambda t} - 1)$. The decay constant normally used, as introduced earlier, is $1.666 \cdot 10^{-11} \pm 0.0017 \text{ a}^{-1}$ from Smoliar et al. (1996).

$$^{187}Os/^{188}Os_{\text{sample}} = ^{187}Os/^{188}Os_{\text{initial}} + ^{187}Re/^{188}Os (e^{\lambda t} - 1) \quad (5)$$

The earlier successful studies (Hirt et al. 1963, Luck & Allègre 1982, Suzuki et al. 1992, 1996, Stein et al. 1997) were dating molybdenite because it is extremely enriched in rhenium and contains almost no initial osmium (Morgan et al. 1968). Rhenium substitutes Molybdenum in the structure and can easily be present in ppb and even in percentage levels (Luck &

Allègre 1982). The high Re/Os ratio, with all osmium being the radiogenic ^{187}Os derived from the decay of ^{187}Re , allows a much more simple dating and molybdenite age can be determined through one single measurement.

After Stein et al. (1998) and later improvements on the method (Selby & Creaser 2001a, Markey et al. 2003), accu-

rate age determinations have been achieved and many studies were then conducted (Markey et al. 1998, Torrealday 2000, Watanabe & Stein 2000, Selby & Creaser 2001a, b, Stein *et al.* 2001, Selby *et al.* 2002, Mathur et al. 2002, Requía et al. 2003, Masterman et al. 2004, Kontak et al. 2005, Marschik et al. 2005, Garrido et al. 2008, Duuring et al. 2009, Porter & Selby 2010, Lawley et al. 2010, Ootes et al. 2010). Good correlation results from areas where ages were obtained by other means like U-Pb in zircons prove the robustness of the Re-Os chronometer. Also, the characterization of reference materials (Stein et al. 1997, Markey et al. 1998, Du et al. 2004) and more recently an inter-laboratory study (Markey et al. 2007) producing a new Henderson molybdenite reference material with age 27.656 ± 0.022 Ma (95% conf.) with excellent reproducibility using different protocols represented a great step to consolidate and normalize the method.

Regarding plotting, molybdenite data on ^{187}Re - ^{187}Os isochron diagram should be displayed anchored in zero considering the absence of common Os in the mineral structure in the time of crystallization and consequently no initial ^{187}Os . Another way is using the weighted average approach for individual model ages, however the uncertainty on individual model ages normally is higher than uncertainty from isochron age. For further details on molybdenite chronometer and plotting considerations, see Stein et al. (2001).

The Re-Os dating of molybdenite represented an enormous advance considering molybdenite is present in many economic deposits, especially porphyry systems. Molybdenite also occurs as accessory mineral in a wide variety of deposits and can remain as a closed system during later hydrothermal alteration and even deformation and metamorphism (Raith and Stein 2000, Stein et al. 2001, Selby et al. 2002, Bigen & Stein 2003) being an important source of information to define the timing of mineralization.

An interesting Brazilian example of application of Re-Os in molybdenite on investigation of ore timing formation was produced by Requía et al (2003) for the Salobo iron oxide copper-gold deposit in the Carajás mineral province where two temporally separated events of molybdenite formation were revealed (Fig. 5). One event yields and age of 2576.1 ± 1.4 Ma ($n=2$) and was coincident with U-Pb ages from Old Salobo Granite (2573 ± 2 Ma, Machado et al. 1991) being interpreted as the main mineralization stage concomitant with granite magmatism. The second fraction yield 2561.7 ± 3.1 Ma ($n=3$) and was considered as formed during late deformational processes.

Although many studies have pointed out the remarkable robustness of the Re-Os system, others suggested that it can be easily disturbed (e.g. Suzuki et al. 2000, 2001). Subsequent studies (Stein et al. 2001, Selby & Creaser 2004), however, show that irreproducibility was probably due to decoupling of rhenium and osmium within single grains of molybdenite. Specific sample preparation protocols can overcome these difficulties and produce accurate and reproducible data (Stein et al. 2001). Coarse grained molybdenite, especially ancient, is more problematic and a large sample must be prepared and properly homogenized to produce reproducible analyses. On the other hand, fine-grained and young grains are less affected by decoupling and good ages can be obtained from lower amounts (milligrams) of samples. Selby & Creaser (2004) and other previous studies (Stein et al. 2003, Kosler et al. 2003) has also shown that due to the heterogeneous distribution of ^{187}Re and ^{187}Os , LA-MC-ICP-MS is not recommended for Re-Os dating of molybdenite as analyses yield erratic ages.

The Re-Os method has also been applied to other sulfides such as pyrite, arsenopyrite and chalcopyrite (Stein et al. 2000, Mathur et al. 1999, Morgan et al. 2000, Arne et al. 2001, Kirk et al. 2002, Morelli et al. 2004, 2005, 2007, Hulbert et al. 2005). Some of these sulfides may have low common Os contents and high Re/Os ratios, with radiogenic ^{187}Os prevailing. Stein et al (2000) named these samples Low Level Highly Radiogenic sulfides (LLHR). The LLHR should be treated as molybdenite, although LLHR sulfides sometimes may contain common Os and some amount of initial ^{187}Os being important (Stein et al. 2001). When common Os concentration is higher than laboratory blanks, data plotted in the $^{187}\text{Os}/^{188}\text{Os}$ versus $^{187}\text{Re}/^{188}\text{Os}$ isochron diagram will yield the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio that may give important source information.

One important issue is the weight of sulfide sample, especially those enriched in iron. The weight must be controlled due to the possible excess of iron (Claus process) that may interfere on osmium oxidation during sample dissolution (Frei et al. 1998). About 200mg of pyrite (Morelli et al. 2004) and up to 500mg of sphalerite (Morelli et al. 2004) or arsenopyrite (Morelli et al. 2005) was tried in those studies and no Claus reaction has been observed.

Arsenopyrite, as molybdenite in earlier studies, produced reliable data (Arne et al. 2001). Morelli et al (2005) reported no internal significant decoupling of rhenium and osmium and showed that some arsenopyrite from Meguma gold district veins (Canada) is free of common osmium. A precise isochron

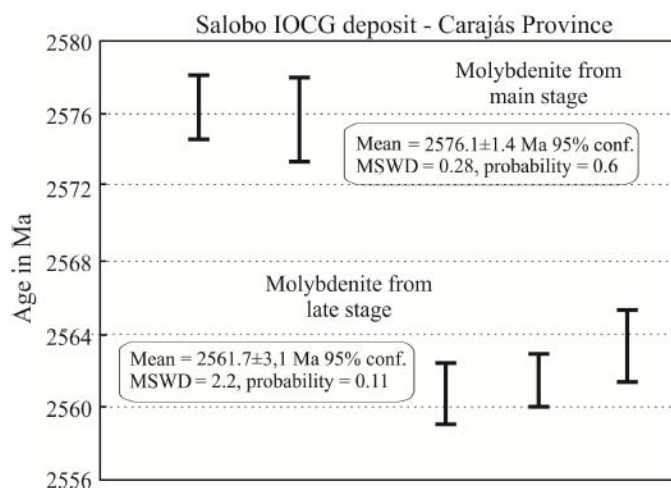
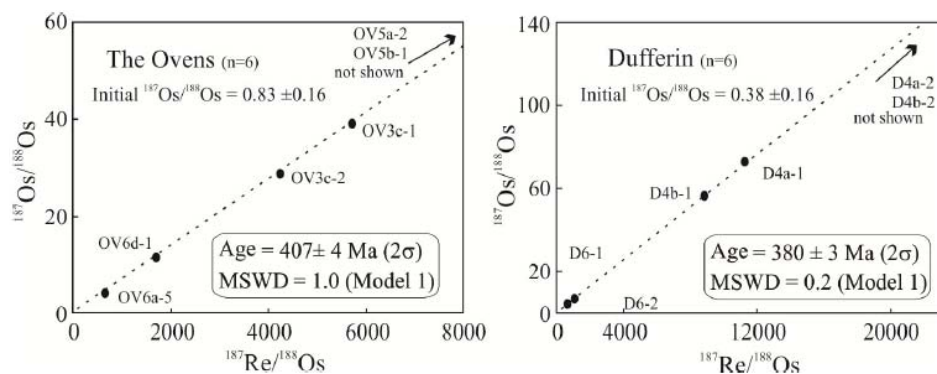


Figure 5
Weighted mean ages for molybdenite samples from the two temporally separated mineralization events, Salobo iron copper-gold deposit, Carajás mineral province. Individual ages plotted as data bars were calculated without uncertainties in the ^{187}Re decay constant (after Requía et al. 2003).

allowed determination of initial Os ratio and arsenopyrite also yield good single mineral model ages. Two distinct ages and initial Os ratios were obtained from southwest (The Ovens area) and northeast (Dufferin area) part of Meguma Terrane showing distinct time and sources for mineralization (see Fig. 6 for details). The study showed that it is possible to date individual veins from lode gold deposits which is interesting for constraining different stages of mineralization in a single deposit. In another study, Morelli et al. (2007) applied coupled Re-Os-He isotope analyses in arsenopyrite from an orogenic gold deposit. The correlation between osmium initial ratios and He isotopes from fluid inclusions in arsenopyrite provide constraints on the source of ore metals and fluids showing further application for Os method in sulfide samples.

Good isochrons were also obtained using other minerals or mixed minerals (e.g. chalcopyrite, bornite, pyrrhotite, magnetite, chromite, Fe-Ti oxides). Some studies have combined more than one type of sulfide (e.g. Lambert et al. 1998b, Frick et al. 2001, Tristá-Aguilera et al. 2006, Schneider et al. 2007, Selby et al. 2009a, Lingang et al. 2011), used a mixture of sulfide and oxide (e.g. Mathur et al. 2002, Marques & Carlson 2008), just oxides (Zhou et al. 2005) or even gold (Kirk et al. 2002). Sulfide from diamonds has also been investigated and can produce good isochron results (e.g. Richardson et al. 2001, Smit et al. 2010) or model ages and initial $^{187}\text{Os}/^{188}\text{Os}$ ratio (e.g. Pearson 1998a, b, Shirey et al. 2002, Aulbach et al. 2009) providing relevant petrological information.

Figure 6
Re-Os data for arsenopyrite from the Meguma Terrane, Nova Scotia, Canada. A. Re-Os isochron diagram showing data from bedding-concordant veins from The Ovens area. The initial $^{187}\text{Os}/^{188}\text{Os}$ ratio suggests predominately crustal source. B. Re-Os isochron diagram showing data from saddle-reef veins from Dufferin area. The lower initial $^{187}\text{Os}/^{188}\text{Os}$ ratio suggests less significant crustal source.



6. Re-Os applied to Organic Rich Rocks

In the last two decades, the technological and methodological advances, discussed earlier, allowed the use of the Re-Os system to a wide variety of different environments. Ravizza & Turekian (1989) and Ravizza et al. (1991), considering the high affinity of both rhenium and osmium with organic matter, defined the principles for the application of Re-Os system to date organic-rich rocks, which was later improved by Cohen et al. (1999) and Creaser et al. (2002).

Both rhenium and osmium, together with some other trace elements (e.g. V, Ni, Mo, U, Au, all PGE), are considered to be concentrated from seawater in anoxic sediments during or just after sedimentation due to reduction reactions at the water-sediment interface or just below, and many of these elements become fixed in the organic matter (Cohen 2004 and Kendall et al. 2004 and references therein). Rhenium concentrations can reach up to 500 ppb and osmium up to 4 ppb (Ravizza & Turekian 1989, Cohen et al. 1999) while detrital contribution is expected to be very low or negligible considering the low amount of both elements in the crust, approximately 400 ppt for rhenium and 50 ppt for osmium (Esser & Turekian, 1993). Also, the Re-Os system remains closed after deposition, even undisturbed during hydrocarbon maturation or chlorite-grade metamorphic conditions (Creaser et al. 2002, Kendall et al. 2004, Selby & Creaser 2003). All these factors constitute the premises for a good chronometer.

Direct determination of absolute ages for clastic sedimentary rocks is an extremely difficult task when the traditional isotopic methods (e.g. U-Pb, Sm-Nd, Rb-Sr) are considered. Isotopic inheritance from the source rocks and post-depositional disturbance are among the most common problems (Creaser et al. 2002). Depositional age sometimes is only possible when

volcanic rocks are interbedded, which not always happen. Therefore, the direct radiometric dating of organic-rich rocks represented an outstanding contribution to stratigraphy and sedimentary studies.

The method is a reliable geochronometer for organic-rich black shales as already shown by several studies (Cohen et al. 1999, Creaser et al. 2002, Selby & Creaser, 2003, 2005a, Kendall et al. 2004, 2006, 2009, Turgeon et al. 2007, Selby et al. 2009b, Rooney et al. 2010, Xu et al. 2009, Georgiev et al. 2011). A contributing factor for the improvement in accuracy was the use of $\text{CrO}_3\text{-H}_2\text{SO}_4$ during dissolution. The use of $\text{CrO}_3\text{-H}_2\text{SO}_4$ minimizes the eventual input of non-hydrogenous Re-Os because it solubilizes mainly the elements from the organic matter, which enhances the results and also provides better estimates of osmium isotopic composition of seawater at the time of deposition (Creaser et al. 2002, Selby & Creaser 2003). The use of $\text{CrO}_3\text{-H}_2\text{SO}_4$ protocol, careful sampling procedures and rigorous blank control yield much more precise ages ($\pm 1\%$ - 2σ) and allow dating shales with low amount of total organic matter (TOC < 1%) (Kendall et al. 2004) and even in rocks with very low amounts of Re and Os (with $\text{Re} < 1$ ppb and $\text{Os} < 50$ ppt, Rooney et al. 2011) expanding the possibilities for Re-Os geochronology.

A Brazilian example of application of Re-Os in organic-rich rocks is the study of the Vazante Group shales that occur associated to a glaciomarine diamictite at the base of the Lapa Formation (Azmy et al. 2008). The glaciomarine diamictite were previously believed to be correlated to the Rasthof cap carbonate from Congo craton and with the "Sturtian" glacial event being younger than 750 Ma (Azmy et al. 2006 and references therein). Although the Re-Os isochron fit displays

some scatter, the age obtained for the black shale modified the previous correlation and constrained the age of the diamictite to Mesoproterozoic (Azmy et al. 2008), an important contribution to Vazante Group stratigraphy. Nevertheless, Marshal et al. (2009) suggest that the glaciogenic rocks contain some detrital organic matter, which could affect the Re-Os isotopic ratio posing problem to the Mesoproterozoic age.

Another important contribution of Re-Os method has been the determination of the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of organic-rich rocks that is considered to be equivalent to the $^{187}\text{Os}/^{188}\text{Os}$ ratio of the seawater at the time of organic matter deposition (Pegram et al. 1992, Peucker-Ehrenbrink & Blum 1998, Peucker-Ehrenbrink & Ravizza 2000, Ravizza & Peucker-Ehrenbrink 2003). The initial ratio is sensitive to variation in the Os inputs to the oceans and can be used as a proxy of the Re-Os paleo sources allowing considerations on the nature of crustal, hydrothermal or even cosmochemical contributions for seawater composition (Fig. 7) (Cohen et al. 1999, Peucker-Ehrenbrink & Ravizza 2000, Ravizza & Peucker-Ehrenbrink 2003, Cohen 2004, Selby et al. 2009b, Georgiev et al. 2011). The fast mixing time in ocean implies in homogeneous isotopic seawater composition at present day (Cohen 2004).

The initial Os isotopic ratio, calculated from Re-Os determinations of organic-rich rocks, can be applied in the same way as the initial Sr ratio has been used for the investigation of continental input on seawater. However, as emphasized by Cohen (2004), osmium is more sensitive and can track extra-terrestrial impacts and also may record short-term changes considering lower time of residence in seawater in comparison to strontium, responding faster to rapid changes in weathering rates and continental input in the ocean. Therefore, Re-Os system has been widely applied to correlate oscillations in

seawater composition with a various kinds of geological events (Turgeon et al. 2007, Oxburgh et al. 2007, Turgeon & Creaser 2008, Xu et al. 2008, Georgiev et al. 2009, Selby et al. 2009b, Rooney et al. 2011) and together with redox sensitive trace elements has been recently used as an important tool for anoxia and mass extinction studies and as a proxy for elevated ocean temperature and acidity (Georgiev et al. 2011).

The Re-Os method has also been applied to dating oil and tracking oil sources (Selby & Creaser 2005b, Selby et al. 2007b, Finlay et al. 2010a,b, 2011). Selby & Creaser (2005b) and Selby et al (2005) published the first results on oils and bitumen, respectively, using the inversed aqua-regia Re-Os protocol from Selby & Creaser (2001) for oils and CrO_3 for bitumen. The Re-Os isotopic determination in oil and similar samples are still under investigation to understand the meaning of ages and initial $^{187}\text{Os}/^{188}\text{Os}$ isotopic ratios (Selby et al. 2007b, Zimmermann et al. 2009, Hannah et al. 2009, Stein et al. 2009, Finlay et al. 2011). Selby et al (2007b) evaluated different types of oils and the distribution of Re-Os and Re-Os isotopic composition in different oil fractions. Light oils with low (<1%) amounts of asphaltene have very low Re-Os contents, precluding analyses. The asphaltene mostly concentrates the rhenium and osmium and its isotopic composition is similar to the expected for whole oil and also for their source rocks (Selby et al. 2007b). Recently, a study of several oils from the United Kingdom Atlantic margin indicated that Re-Os isotopic system actually may track the source of oil and also that obtained ages correspond to ages of generation events (Finlay et al. 2011). Although the Re-Os system applied to oils is still under development, it may, in the near future, become a strategic method for the oil industry.

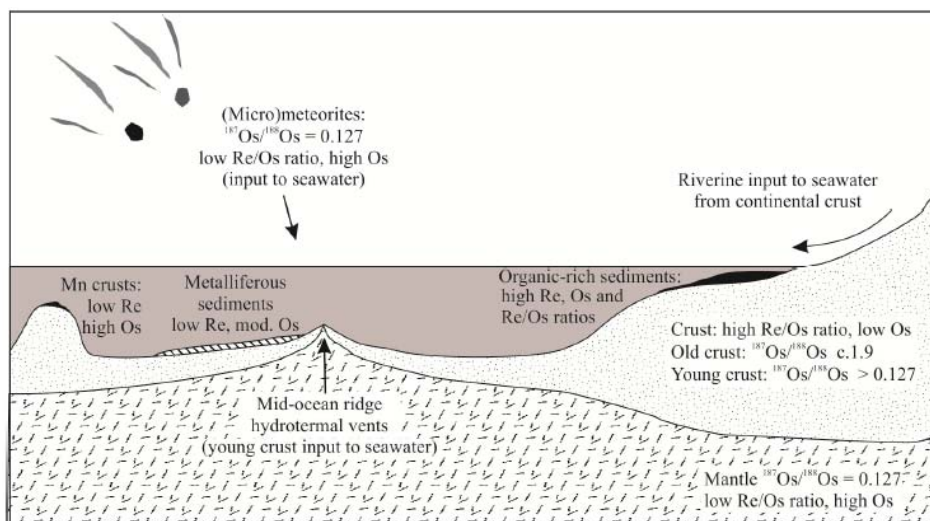


Figure 7
Schematic profile of ocean-continent interface showing the three major osmium sources to seawater (after Cohen 2004).

7. Final Remarks

The Re-Os method has been applied to a large variety of geological environments and shed light on different problems due to its unique geochemical characteristics. In the last twenty years, the technique has been constantly improved and geochronological protocols have reached accuracy and reliability levels allowing direct age determination of ore minerals, organic-rich rocks and oil. In addition to the traditional applications of the method on dating and

petrological studies, further and deeper investigation of isotopic composition of organic rich-rocks, oils and seawater throughout geological time are under fast development opening new knowledge frontiers. For all of these, despite the complicated chemistry that makes the procedure challenging, Re-Os is currently a fascinating technique that has been contributing greatly for better understanding of a wide variety of earth processes.

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