Geol. 655 Isotope Geochemistry

Lecture 11 Spring 2003

GEOCHRONOLOGY VII: OTHER DECAY SYSTEMS

INTRODUCTION

Three other elements have long-lived radioactive isotopes: ^{176}Lu, ^{176}Re, and ^{138}La, which decay to ^{176}Hf, ^{176}Os, and ^{138}Ce and ^{138}Ba respectively. All three of these systems pose significant analytical challenges. The challenges have been largely solved for the Lu-Hf and Re-Os systems and they are increasingly used for geochronology, but little use of the La-Ce-Ba system has been made. In the case of Hf, temperatures required for ionization are quite high; as a result the ionization efficiency by thermal ionization is low, making analysis difficult by this method. This problem has been overcome with the development of multiple-collector magnetic sector inductively coupled plasma mass spectrometers (ICP-MS), in which the analyte is ionized in an Ar plasma rather than thermally. Secondary ion mass spectrometry, in which the Hf is ionized by an ion beam while being heated (hot SIMS) has also been used successfully. Problems with ionizing Os, which as the metal evaporates and ionizes only at extremely high temperatures, limited the use of this system initially, have now overcome through analysis of the negative ion of OsO_3^-, which evaporates at quite low temperature. This technique has proved to be extremely sensitive, making it possible to analyze Os isotope ratios even though Os concentrations are extremely low in most rocks, ranging from a few parts per billion in ultramafic rocks to 0.01 to 0.1 ppb in mafic and acid rocks. The difficulty with the La-Ce system is the ^{138}La/^{138}Ce ratio is is small and furthermore only small natural variations occur in it. Extremely precise measurements of Ce isotopic composition are required to obtain useful information (this can involve 10 or 20 hours of measurement on the mass spectrometer). A few dates have been produced, however. The ^{138}La/^{138}Ba ratio is even lower (the chondritic ratio is on the order of 1×10^{-4}); nevertheless, a relatively precise age on the REE-rich mineral bastnaesite was reported at the International Congress of Geochemistry in Paris in 1988. It seems unlikely that the La-Ce-Ba system will provide useful geochronological information in anything but very special circumstances in the foreseeable future, so the remainder of our discussion will focus on Re-Os and Lu-Hf.

THE LU-HF SYSTEM

Lu is the heaviest rare earth element, with a valence of +3 and an ionic radius of 93 pm. Hf is a member of the group IVB elements, which include Ti and Zr as well. As members of the same periodic group, the three elements show some chemical similarities; this similarity is quite strong in the case of Zr and Hf. Hf has an ionic radius of 0.71Å in six-fold coordination (0.83 in 8-fold coordination) and a valence of +4 (the particularly strong similarity between Hf and Zr results from the similarity of ionic radii: the radius of Zr^{4+} is 0.72Å in six-fold and 0.84 in 8-fold coordination; the radius of Ti^{4+} is much smaller: 0.61Å). Lu can be considered a slightly to moderately incompatible element; Hf is moderately incompatible (its incompatibility is very similar to that of Sm).

The Lu-Hf system shares many of the advantages of the Sm-Nd system: both are relatively insoluble and immobile elements, both are refractory and hence we have reason to believe that the Lu/Hf ratio is the Earth is the same as in chondrites. Indeed, we can define an ε_{Hf} value in a manner exactly analogous to the ε_{Nd}:

$$\varepsilon_{Hf} = \left[\frac{(^{176}Hf/^{177}Hf)_{sample} - (^{176}Hf/^{177}Hf)_{Chon}}{(^{176}Hf/^{177}Hf)_{Chon}} \right] 10000 \qquad 11.1$$

The present-day ^{176}Hf/^{177}Hf chondritic ratio is 0.282772 (Blishert-Toft and Albarede, 1997) when the ^{179}Hf/^{177}Hf ratio is normalized to 0.7325 (fortunately, all laboratories performing Hf isotopic analyses use the same normalization scheme). In a manner exactly analogous to Nd, we can also define ε_{CHUR} and ε_{DM} model ages. One should point out, however, that our confidence about the similarity of the Lu/Hf ratio in the Earth and chondrites is not quite as strong as for Sm/Nd simply because whereas both Sm and Nd are rare earths and behave very similarly, Hf is not a rare earth and differs in its behavior from Lu.

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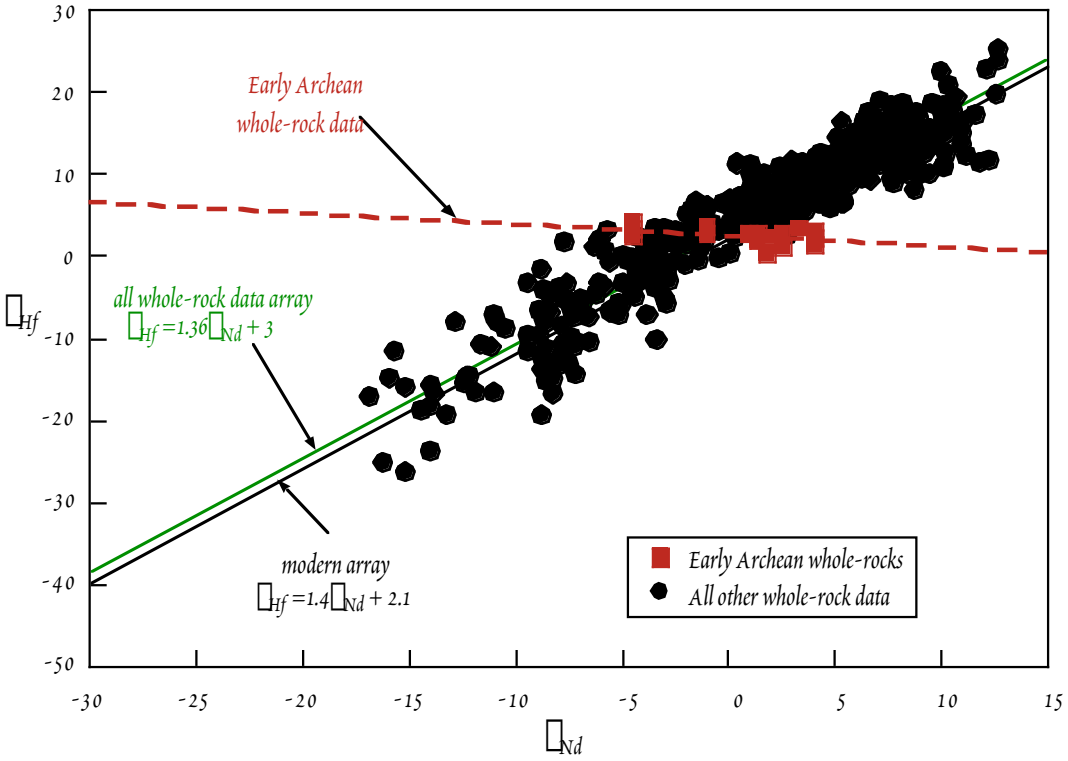


Figure 11.1. ε_{Hf} and ε_{Nd} in crustal rocks of various ages. The two are well correlated, with the variation in ε_{Hf} being about twice that of ε_{Nd}. After Vervoort and Blichert-Toft (1999).

The Lu-Hf system has several advantages over the Sm-Nd system. First, because the half-life of ^{176}Lu is shorter than that of ^{147}Sm (37 Ga vs 106 Ga) and because the range of Lu/Hf ratios in common rocks and minerals is greater than that of Sm/Nd, the variations in ^{176}Hf/^{177}Hf and ε_{Hf} are larger than of ^{143}N/d^{144}Nd and ε_{Nd}. Second, because of the chemical similarity of Hf to Zr, Hf is concentrated in zircon, which as we saw in Lecture 9 is a very robust mineral.

The general similarity between the Lu-Hf system and the Sm-Nd system is demonstrated by Figure 11.1, which shows that ε_{Hf} and ε_{Nd} are well correlated in crustal rocks of all ages, with the exception of early Archean rocks (this is likely due to metamorphic effects on the Sm-Nd system. It also shows that the variations in ε_{Hf} are about twice as large as those of ε_{Nd}.

One important difference between Lu-Hf and Sm-Nd is that whereas Sm/Nd ratios usually do not change much in the weathering of a crystalline rock to form a sediment, Lu/Hf ratios do. In both cases, the elements are reasonably insoluble, and little is carried away by solution. Most of the rare earths end up in clays, but much of the Hf in acid crystalline rocks of the continental crust is in zircon ($ZrSiO_4$), which, as we have already noted, is very resistant to both chemical and mechanical weathering. The clays are, of course, quite fine and can be carried great distances from their source. Zircon remains in the coarse (and hence less mobile) sand fraction. As a result, there are large differences between Lu/Hf ratios in fine and coarse sediments.

As we noted above, two new analytical methods have been developed in the past few years and these allow analysis of much smaller quantities of Hf. The first of these is the "hot SIMS" technique, in which purified Hf is deposited on a filament which is heated, as in normal thermal ionization mass spectrometry (TIMS). In addition, however, the sample is bombarded with ions to assist in ionization (Secondary Ionization Mass Spectrometry or SIMS). The second technique is inductively-coupled plasma mass spectrometry or ICP-MS. ICP-MS instruments utilizing a quadrapole mass analyzer have been in use for nearly 20 years, but are largely restricted to determining trace metal concentrations as the cannot measure isotope ratios precisely enough for most geochronological and geo-

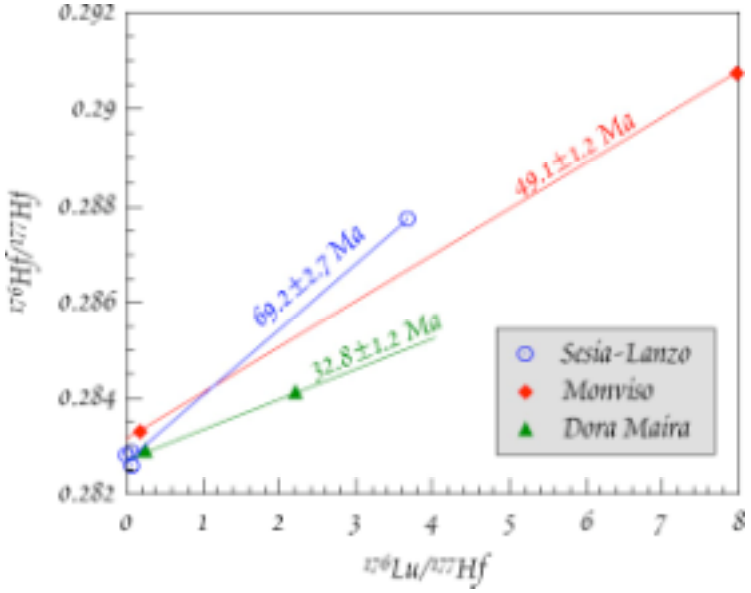


Figure 11.02. Lu-Hf isochrons for eclogites from the Italian Alps. For the Monviso and Dora Maira eclogites, only garnet and whole rocks were measured. For the Sesia-Lanzo eclogite, garnet, clinopyroxene, phengite (a mica) and the whole rock were separately analyzed. In all cases, the garnet has the highest $^{176}Hf/^{177}Hf$. Data were obtained by the ICP-MS technique. After Duchene et al. (1997).

chemical applications. However, ICP-MS instruments employing magnetic sector mass analyzers and having multiple collectors, features shared by almost all modern isotope ratio mass spectrometers, can achieve sufficient precision. As in the hot-SIMS technique, the ionization efficiency is much greater than in thermal ionization. Of these two techniques, ICP-MS has become much more widely used as it is less labor intensive and ICP-MS instruments are cheaper than SIMS instruments. Magnetic sector, multiple collector ICP-MS instruments have only been in use for a half a dozen years or so now and have greatly increased the amount of Hf isotope data available.

An example of the potential uses of Lu-Hf in geochronology using the ICP-MS technique is illustrated by the recent study eclogites in the Italian Alps by Duchene et al. (1997). Three Lu-Hf isochrons obtained for 3 separate eclogites are shown in Figure 11.2. Eclogites consist primarily of clinopyroxene ($(Mg,Fe)CaSi_2O_6$) and garnet ($(Mg,Fe,Ca)_3Al_2Si_3O_{12}$) and form through high pressure metamorphism of basalt. Garnets strongly concentrate Lu, as well as the other heavy rare earths, while rejecting Hf. Thus garnet would appear to be a good target for Lu-Hf geochronology. The high $^{176}Lu/^{177}Hf$ ratios obtained on garnets in this study confirm this. Ages decrease from 69.2 Ma in the structurally highest eclogite to 32.8 Ma in the structurally lowest. This might seem surprising until we think about what is being dated. The ages reflect closure of the Lu-Hf system to diffusion. Closure temperatures are thought to be 600°C or more for this system (Duchene et al., 1977). The age reflects the time temperatures fell below the closure temperature. As the Alps rose, the structurally highest units would naturally cool first and the lowest ones last.

These eclogites must have been deeply buried. The Dora-Maira eclogite may have been buried as deeply as 100 km, judging from the presence of coesite, a high-pressure polymorph of quartz. The Lu-Hf ages, together with zironc and K-Ar ages suggest rates of exhumation as high as 3 cm/yr, rates that are surprisingly high.

THE RE-OS SYSTEM

The Re-Os system is becoming a useful geochronological tool now that the analytical problem has been solved*, although only in special circumstances. Up to now, most of the elements of the decay systems we have discussed have been *lithophile* (derived from Greek words for rock and love) ele-

* Os is very refractory and a very high boiling point. It cannot be thermally ionized as the metal as sufficiently high temperatures cannot be achieved. In the last 15 years, analysis using secondary ionization and laser resonance ionization met with some limited success, but both techniques require instrumentation not found in most isotope geochemistry laboratories. However, work at Cal Tech reported in 1991 showed that ions of OsO_3^- are readily produced by thermal ionization.

ments (the exception is Pb, which is chalcophile). Lithophile means simply that, given the choice, the element prefers a silicate or oxide phase (in fact a better term would be oxyphile) to a sulfide or metal phase. *Chalcophile* elements would choose the sulfide phase and *siderophile* elements would choose a metal phase given the same choices (a final group is the *atmophile* elements: those elements preferring a gas phase). Re and Os are both *siderophile* elements, though both also have some *chalcophile* tendencies. Their siderophile nature accounts for their low concentrations in the crust and mantle: most of the Earth's Re and Os are in the core. Os is one of the platinoid, or platinum-group, elements (the second and third transition series members of Group VIII elements) which include Ru, Rh, Pd, and Ir and well as Os and Pt. Like the rare earths, these elements behave coherently, though their valences and ionic radii differ. The usual valence state of Os is +4 at the Earth's surface; its ionic radius is 0.69. The valence of Re is also +4; its ionic radius is 0.63. However, in the mantle and in magmas, these elements are likely in +1 or 0 valence states. Re is a moderately incompatible element whereas Os is highly compatible one: it partitions into a melt only very sparingly. Hence the crust has a much lower Os concentration than the mantle (the core, of course, should have a higher concentration than both).

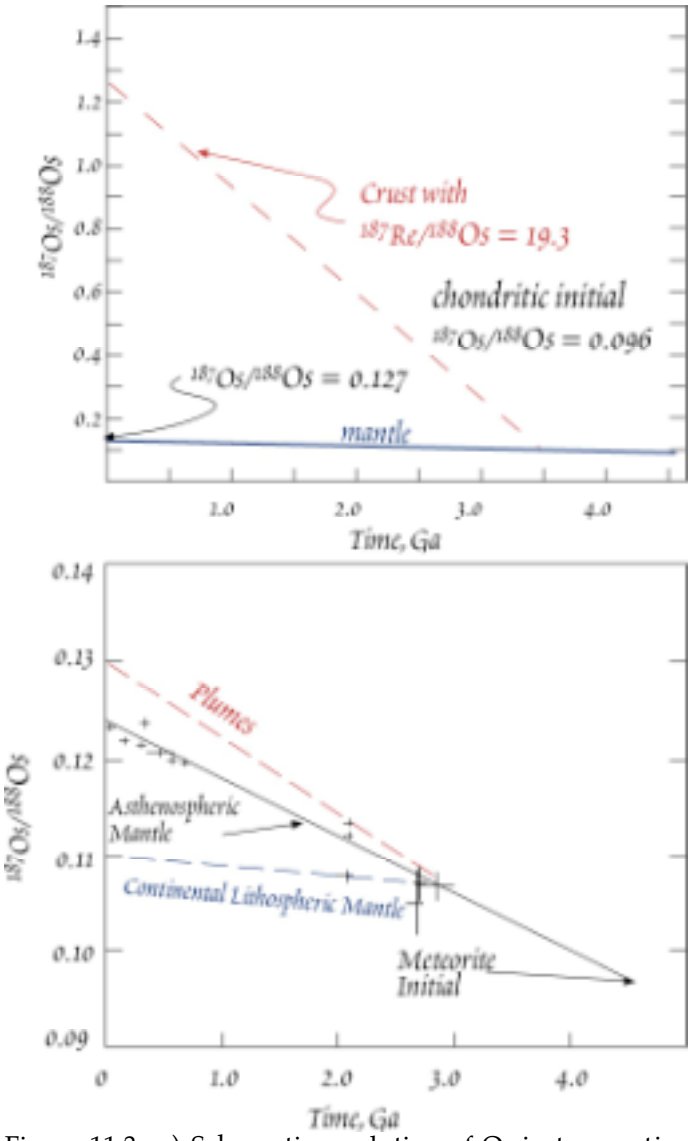


Figure 11.3. a.) Schematic evolution of Os isotope ratios in the mantle and crust. b.) $^{187}Os/^{188}Os$ evolution in the mantle as deduced from analyses of osmiridum and laurite grains in ancient mantle peridotites, initial ratios in peridotites, and modern oceanic peridotites and basalts. The pattern is consistent with other isotopic systems: the asthenospheric mantle is more incompatible element-depleted than mantle plumes, which produce oceanic island basalts. The mantle root of continents (lithospheric mantle), appears to have been depleted in Re by melt extraction.

The older convention for Os isotope ratios, established by Hirt et al. (1963) reports the isotope ratio as $^{187}Os/^{186}Os$ (normalized for fractionation to $^{192}Os/^{188}Os$ of 3.08271). The difficulty is with this normalization is that ^{186}Os is itself radiogenic, being the product of β-decay of ^{190}Pt. ^{109}Pt is sufficiently rare, and its half-life sufficiently long (450 billion years), that in most cases the amount of radiogenic ^{186}Os is insignificant. However, measurable amounts of radiogenic ^{186}Os have been observed, as discussed below. This discovery prompted a shift in the convention and now most laboratories report Os isotope analyses as $^{187}Os/^{188}Os$. Here we will follow the newer convention where possible. $^{187}Os/^{186}Os$ ratios may be converted to $^{187}Os/^{188}Os$ ratios by multiplying by 0.12035.

Figure 11.3 illustrates the evolution of Os isotope ratios in the crust and mantle. As expected from the difference in compatibilities of Re and Os, much higher $^{187}Os/^{186}Os$ ratios are

found in the crust than in the mantle. Interestingly, the Re/Os ratio of the mantle is nearly chondritic (Allègre and Luck, 1980). This is a bit surprising if most of Re and Os have been extracted to the core. If the core and mantle are in equilibrium, then mantle concentrations will be determined by metal-silicate partition coefficients, which are large for both elements. Since the partition coefficients of these two elements are different, the ratio of the two in the mantle should be quite different from chondritic. The approximately chondritic Re/Os ratio of the mantle is, however, consistent with models in which core formation is complete before the Earth entirely accretes. In these models, the highly siderophile elements, such as Re and Os, are quantitatively extracted by core formation. The inventory of highly siderophile elements in the crust and mantle comes from the last 1% of material to accrete to the Earth, which occurs after core formation. An alternative explanation has recently been proposed by Snow and Schmidt (1998). They argue that the nearly chondritic Re-Os ratio of the mantle results from mixing of a small fraction of the outer core back into the mantle.

Since the silicate Earth appears to have a near-chondritic $^{187}Os/^{188}Os$ ratio, it is useful to define a parameter analogous to ε_{Nd} and ε_{Hf} that measures the deviation from chondritic. Walker et al. (1989) defined γ_{Os} as:

$$\gamma_{Os} = \frac{(\frac{^{187}Os}{^{188}Os})_{sample} - (\frac{^{187}Os}{^{188}Os})_{chon}}{(\frac{^{187}Os}{^{188}Os})_{chon}} \times 100 \qquad 11.2$$

Because of the differences in compatibility, Re/Os variations are huge, at least by comparison to the other systems we have considered. The mantle has a Re/Os ratio on the order of 0.1 whereas the crust has a Re/Os ratio on the order of 100. The $^{187}Os/^{188}Os$ ratio of the mantle is about 0.12 whereas the crustal ratio is thought to be between 1.1 and 1.3. Despite these large variations, strictly geochronological applications of Re-Os have been limited because of the very low concentrations of Os in most minerals. Re-Os geochronology has proved used full in dating the formation of iron meteorites, for platinum group metal ores such as the Stillwater Complex in Montana, and for some ultramafic rocks, such as komatiites (komatiites are very MgO-rich lavas that occur almost exclusively in the Archean, i.e., before 2.5 Ga). Figure 11.4 is an example of an isochron obtained on a komatiite from Monro Township in Ontario. In the future, there may be some use for the Re-Os system in dating certain types of sulfide ore deposits. Re is strongly concentrated in molybdenite (MoS_2) and some copper-sulfides. Sulfide deposits have been notoriously difficult to date. The very high Re/Os ratios in molybdenum sulfides should make it possible to exploit this system.

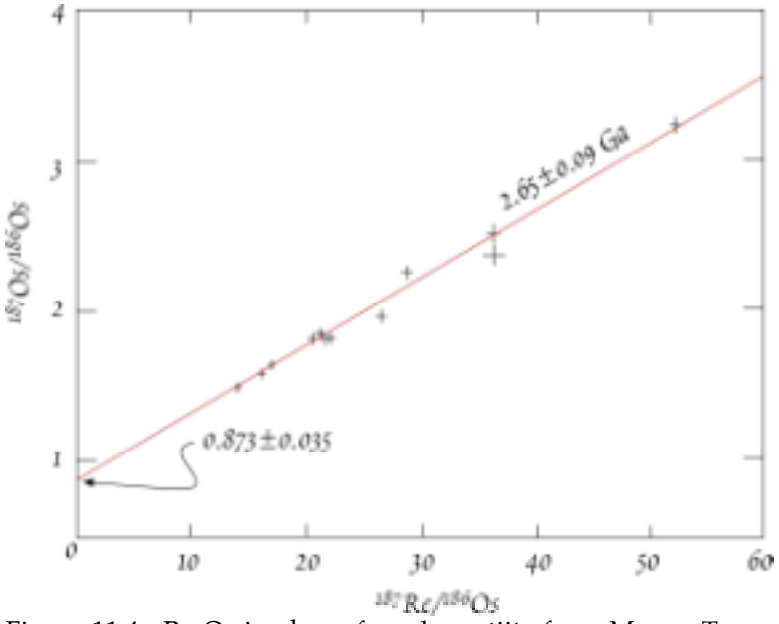


Figure 11.4. Re-Os isochron for a komatiite from Monro Township. After Walker et al. (1988).

Since the mantle $^{187}Os/^{188}Os$ evolution curve is known, at least to a first approximation, an estimate of age, or model age, analogous to Sm-Nd model ages, can be obtained simply by comparing the measured $^{187}Os/^{188}Os$ ratio with the mantle evolution curve. Platinoid metal deposits association with mantle-derived ul-

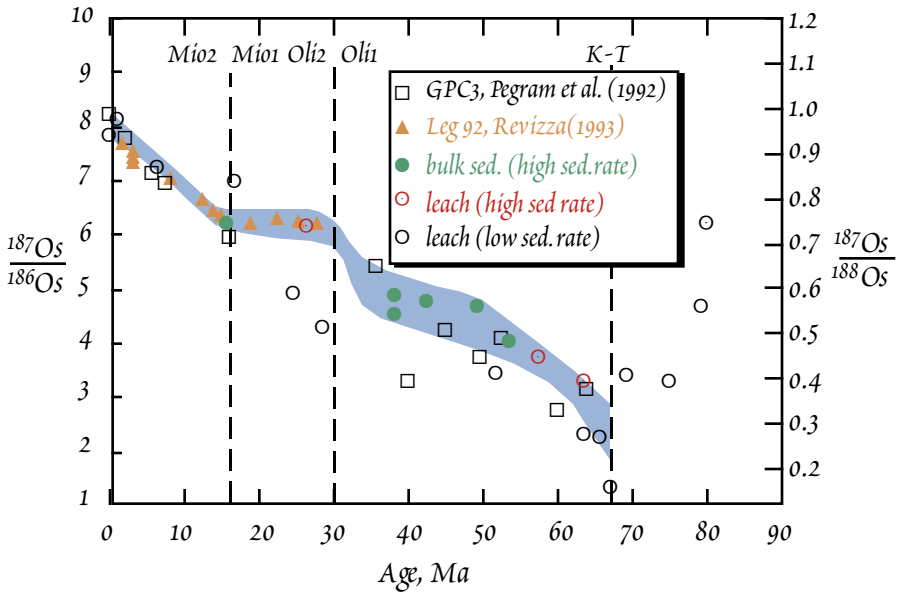


Figure 11.5. Os isotope composition of seawater over the last 80 Ma, from Peuker-Ehrenbrink et al. (1995). Gray field represents the authors best estimates of seawater Os isotopic composition.

tramafic rocks would be one example of where such model ages could be obtained. The PGM's (platinum group metals) occur as very fine (down to a μm or so) metal alloys and sulfides. Os occurs principally as osmiridium (OsIr) and laurite (Ru[Os,Ir]S_2). These minerals have Re/Os close to zero. As a result the $^{187}Os/^{188}Os$ ratio ceases to change once these minerals form (a model age would still be possible even if a small correction for radiogenic growth of ^{187}Os were necessary).

There has also been considerable interest in the Os isotope composition of seawater. The $^{187}Os/^{188}Os$ ratio of modern seawater is about seawater is about 8. Like that of $^{87}Sr/^{86}Sr$, $^{187}Os/^{188}Os$ depends on the balance of continental fluxes (e.g., rivers, with $^{187}Os/^{188}Os$ ~ 1.2) and oceanic crustal fluxes (e.g., hydrothermal activity, with $^{187}Os/^{188}Os$ ~ 0.13). In addition, however, cosmic fluxes ($^{187}Os/^{188}Os$ ~ 0.13), which include both cosmic dust, which continually settles through the atmosphere into the oceans, and large meteorite impacts, may be significant for Os. Because of the low concentrations of Os in seawater, the Os isotopic composition of seawater cannot be measured directly. It can, however, be measured indirectly by analyzing the authigenic component in seawater, such as Mn nodules and the leachable fraction of clays.

Like Sr, the Os isotopic composition of seawater has changed over time (Figure 11.5). There are obvious similarities between the Os isotopic and Sr isotopic evolution of seawater, most notably the increase of both through the Tertiary period (the last 65 million years). This may in part reflect a decreasing hydrothermal flux resulting from decreasing sea floor spreading rates. There are also differences, which reflect the differing geochemical behavior of Sr and Os. The geochemical behavior of both at the surface of the Earth is related to carbon, but while Sr is concentrated in carbonates, Os is concentrated in organic rich sediments. The very low Os isotope ratios at the Cretaceous-Tertiary boundary (65 Ma) may reflect a sudden input of meteoritic Os as a result of the impact of a large meteorite that apparently occurred then.

As noted earlier, ^{186}Os is the decay product of ^{190}Pt. Significant amounts of radiogenic ^{186}Os were first observed by Walker et al. (1991) in copper ores from Sudbury, Ontario. The chondritic $^{186}Os/^{188}Os$ ratio is 0.119828±6; the value in most terrestrial materials is indistinguishable from this value. In Sudbury sulfide copper ore, however, Walker et al. (1991) measured a $^{186}Os/^{188}Os$ ratio of greater than 0.3. This is a result of the strongly chalcophile nature of Pt, and its consequent concentration in sulfides; Os by contrast, is only weakly chalcophile. More recently, Brandon et al. (1998) have reported measurable variations in the $^{186}Os/^{188}Os$ ratio in mantle materials. They found that most mantle ma-

terials have $^{186}Os/^{188}Os$ ratios indistinguishable from the chondritic value, but samples of komatiite (a rare ultramafic lava type) and a xenolith from Kilbourne Hole, Colorado had ratios as high as 0.119842. Excess ^{186}Os has also be found in some Hawaiian basalts, prompting the suggestion that the Hawaiian plume might contain a small core-derived component.

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