OTHER DECAY SYSTEMS

INTRODUCTION

Three other elements have long-lived radioactive isotopes: $^{176}$Lu, $^{176}$Re, and $^{138}$La, which decay to $^{176}$Hf, $^{170}$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, the analytical process is made difficult by its extremely limited aqueous solubility and its nearly identical chemical behavior to Zr (indeed, its chemical similarity to Zr is one reason why Hf was the very last stable element to be discovered and isolated – it was discovered in X-ray spectra in 1923 and the metal first purified in 1925). Although laborious, standard techniques are available for Hf purification. An additional problem is that the 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 (MC-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. Os metal is extremely refractory, evaporating and ionizing only at extremely high temperatures. This limited the use of this system initially, but this has now been overcome through analysis of the negative ion of OsO$_3^-$, which, in contrast to the metal, evaporates and ionizes 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 parts per trillion in crustal rocks (Creaser et al., 1991). The difficulty with the La-Ce system is that the $^{138}$La/$^{138}$Ce ratio 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 $1 \times 10^{-5}$); 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. It has two isotopes, $^{175}$Lu (97.4%) and $^{176}$Lu (2.4%). As an odd-odd nuclei, $^{176}$Lu is unstable relative to both $^{170}$Yb and $^{176}$Hf. However, there is some uncertainty as to whether the decay to $^{170}$Yb occurs at all, and it certainly constitutes less than 3% of the decay. Hf is a member of the group IVB elements, which include Ti and Zr. As members of the same periodic group, the three elements show chemical similarity and this similarity is quite strong in the case of Zr and Hf. Hf has an ionic radius of 71 pm 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 72 pm in six-fold and 84 pm in 8-fold coordination; the radius of Ti$^{4+}$ is much smaller: 61 pm). 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 should be the same as in chondrites. Indeed, we can define an $\varepsilon_{Hf}$ value in a manner exactly analogous to the $\varepsilon_{Nd}$.
As the analytical problems with the Lu-Hf system have been overcome and it has begun to be applied more widely in geochronology and geochemistry, some other problems have emerged. Perhaps most importantly, there is a worrisome amount of uncertainty of the value of the decay constant. Determining the decay rate of a nuclide that decays as slowly as $^{176}$Lu is not easy. There are several possible approaches: measure the build-up of the daughter in a purified sample of the parent, place a sample in a detector and determine the decay rate by counting $\beta$ or $\gamma$ rays, or by “calibration” or “age comparison” – determining Lu-Hf and some other isochron (generally U-Pb) on the same sample suite and use the age obtained by the second method to calculate the Lu decay constant. These approaches have produced results that do not agree as well as one would hope. Counting experiments performed since 1975 have yielded a range of decay constants ranging from $1.70 \times 10^{-11}$ a$^{-1}$ to $1.93 \times 10^{-11}$ a$^{-1}$, a 14% range. The “calibration” approach has also produced a range of values. Tatsumoto et al. (1981) calculated a decay constant of $1.94 \times 10^{-11}$ a$^{-1}$ from a Lu-Hf isochron on eucrite meteorites assuming an age of 4.55 Ga. Scherer et al. (2001) performed a calibration experiment by obtaining U-Pb and Lu-Hf isochrons on 4 rocks suites ranging in age from 0.91 to 2.06 Ga and using the U-Pb ages to determine a decay constant for $^{176}$Lu of $1.865\pm0.015 \times 10^{-11}$ a$^{-1}$. Bizzarro et al. (2003) determined a decay constant of $1.983 \times 10^{-11}$. 

Figure 8.1. Isochron of chondritic and eucritic meteorites. Assuming an age of 4.56 Ga, the isochron corresponds to a decay constant of $1.983\pm0.033$ a$^{-1}$. If the 3 groups of meteorites are considered separately, the calculated slopes are not significantly different from one and other. From Bizzarro et al. (2003).
a $^1$ from an isochron on chondritic and eucritic meteorites and an assumed age of 4.56 Ga (shown in Figure 8.1). Söderlund et al. (2004) calculated a decay constant of $1.867\pm0.008 \times 10^{11}$ yr$^{-1}$ by comparing Lu-Hf and U-Pb isochrons of Proterozoic dolerites from Sweden and Finland. These three careful studies found a range in the decay constant of 4%, not a very satisfactory situation. Furthermore, it seemed that on value of the decay constant applied to meteorites and one value to terrestrial samples, which hardly seemed likely. Part of the problem was resolved by a calibration study using phosphates (such as apatite) in the Acapulco and Richardson meteorites by Amelin (2005). Phosphates have the useful property that the concentrate both U and the rare earths, such as Lu while excluding Pb and Hf. The resulting high U/Pb and Lu/Hf ratios lead to good chronometers (unfortunately, phosphates are also rather soluble, hence isochrons are potentially easily disturbed, although they were not in this study). Comparing Lu-Hf isochrons with previously determined U-Pb ages of 4556.5±1.3 Ma and 4550.7±2.6 Ma, Amelin (2005) found decay constants of $1.864\pm0.016 \times 10^{11}$ yr$^{-1}$ and $1.832\pm0.029 \times 10^{11}$ yr$^{-1}$, in good agreement with the previously determined decay constants from terrestrial samples. That leaves open the question of why previous calibrations based on meteorites gave decay constants that are too high.

On possible answer is that high energy gamma rays, neutrinos, or cosmic rays in the early solar system released $^{176}$Lu nuclei into excited state from which it decays to $^{176}$Hf with a half-life on only 3.7 hours. As yet, however, there is no consensus among scientists on this question.

The problem with the uncertainty in the decay constant obviously directly affects any age calculated from Lu-Hf isochrons. It also affects Lu-Hf in geochemical applications. It leads to uncertainties in calculating $\epsilon_{116}$ values for any time by the present. This matter is made worse by uncertainty over the initial $^{176}$Hf/$^{177}$Hf of the solar system (and the Earth). Bizzarro et al. (2003) obtained an initial ratio from their chondritic isochron of 0.279628±47, whereas Blichert-Toft and Albarede (1997) obtained an chondritic ratio of 0.279742±29. Although the difference might seem small, it amounts to more than 5 epsilon units – enough to be important in interpretation of initial Hf isotope ratios of early Archean rocks, which is in turn important in understanding the early evolution of the crust and mantle.

There is also some uncertainty over the present-day $^{176}$Hf/$^{177}$Hf ‘chondritic ratio’. A good part of the problem is that there is a roughly 20% variation in the Lu/Hf ratio in chondrites (compared to only 3% variation in the Sm/Nd ratio). That in turn reflects the greater difference in chemical behavior between Hf and Lu. Blichert-Toft and Albarede, (1997) and Bizzarro et al. (2003) reported a mean $^{176}$Hf/$^{177}$Hf ratio for chondrites of 0.282772 (when the $^{176}$Hf/$^{177}$Hf ratio is normalized to 0.7325; fortunately, all laboratories use the same normalization scheme for Hf analyses). Bouvier et al. (2008) reported a mean $^{176}$Hf/$^{177}$Hf value of 0.282802 ± 23 for 18 ordinary and carbonaceous chondrites, and a mean $^{176}$Hf/$^{177}$Hf of 0.282828 ± 38 for just the carbonaceous chondrites. While these differences are small, the do represent roughly 2 epsilon units. In addition there is some uncertainty about the Lu/Hf ratio of the Earth. While both Lu and Hf are refractory lithophile elements, our confidence that the Lu/Hf ratio of the Earth is identical to that of chondrites is not quite as strong as for Sm/Nd, and as we have seen, there is reason to doubt the latter. 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. Nevertheless, Hf and Lu are both highly refractory elements (more so that Nd and Sm), and it is difficult to see how they could have been fractionated in the solar nebula.

Despite these problems and uncertainties, the Lu-Hf system has several advantages, in principle at least, 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 $\epsilon_{116}$ are larger than of $^{147}$Nd/$^{144}$Nd and $\epsilon_{Nd}$. Second, because of the chemical similarity of Hf to Zr, Hf is concentrated in zircon, which as we saw in Lecture 6 is a very robust mineral.

The general similarity between the Lu-Hf system and the Sm-Nd system is demonstrated by Figure 8.2, which shows that $\epsilon_{Hf}$ and $\epsilon_{Nd}$ 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 $\varepsilon_{\text{Hf}}$ are about twice as large as those of $\varepsilon_{\text{Nd}}$.

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 felsic crystalline rocks of the continental crust is in zircon ($\text{ZrSiO}_4$), 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 decade 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 quadrupole mass analyzer have been in use for over 20 years, but are largely restricted to determining trace metal concentrations as the cannot measure isotope ratios precisely enough for most geochronological and geochemical 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, MC-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

![Figure 8.2. $\varepsilon_{\text{Hf}}$ and $\varepsilon_{\text{Nd}}$ in crustal rocks of various ages. The two are well correlated, with the variation in $\varepsilon_{\text{Hf}}$ being about twice that of $\varepsilon_{\text{Nd}}$. After Vervoort and Blichert-Toft (1999).](image)
ICP-MS instruments have only been in use for a decade 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 MC-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 8.3. Eclogites consist primarily of clinopyroxene \(((\text{Mg,Fe})\text{CaSi}_2\text{O}_6)\) and garnet \(((\text{Mg,Fe,Ca})_3\text{Al}_2\text{Si}_3\text{O}_{12})\) 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 \(^{176}\text{Lu}/^{177}\text{Hf}\) 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 zircon 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) elements (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 oxophile) 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 va-
ence 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).

The older convention for Os isotope ratios, established by Hirt et al. (1963) reports the isotope ratio as $^{187}\text{Os}/^{186}\text{Os}$ (normalized for fractionation to $^{182}\text{Os}/^{188}\text{Os}$ of 3.08271). The difficulty is with this normalization is that $^{186}\text{Os}$ is itself radiogenic, being the product of $\alpha$-decay of $^{190}\text{Pt}$. $^{189}\text{Pt}$ is sufficiently rare and its half-life sufficiently long (450 billion years) that in most cases the amount of radiogenic $^{186}\text{Os}$ is insignificant. However, measurable amounts of radiogenic $^{186}\text{Os}$ have been observed, as discussed below. This discovery prompted a shift in the convention and now all laboratories report Os isotope analyses as $^{187}\text{Os}/^{188}\text{Os}$. $^{187}\text{Os}/^{186}\text{Os}$ ratios may be converted to $^{187}\text{Os}/^{188}\text{Os}$ ratios by multiplying by 0.12035.

Figure 8.4 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 $^{187}\text{Os}/^{188}\text{Os}$ 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 $\varepsilon_{Nd}$ and $\varepsilon_{Hf}$ that measures the deviation from chondritic. Walker et al. (1989) defined $\gamma_{Os}$ as:

$$\gamma_{Os} = \frac{(^{187}Os / ^{188}Os)_{sample} - (^{187}Os / ^{188}Os)_{Chond}}{(^{187}Os / ^{188}Os)_{Chond}} \times 100$$

Thus the gamma parameter is exactly analogous to the epsilon one, but where the latter is deviations in parts per ten thousand, the former is percent deviations.

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 crustal materials can have Re/Os ratios of 100 or even more. 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 useful 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 8.5 is an example of an isochron obtained on a komatiite from Monro Township in Ontario. Re is strongly concentrated in some sulfides and arsenides, making the system ideal for dating a variety of ore deposits, including sulfides and gold deposits (e.g., Arne et al., 2001).

Re-Os Dating of Diamonds

Another novel application of the Re-Os system is dating diamonds by dating sulfide inclusions within them. Since Re and Os are somewhat chalcophile, they can be concentrated in mantle sulfide minerals such as pyrrhotite, chalcopyrite, and pentlandite. These minerals are sometimes found as small inclusions in diamond (Figure 8.6). Encapsulated in diamond, individual inclusions become closed systems and accumulate $^{187}$Os is proportion to the amount of $^{185}$Re they contain. Figure 8.7 shows a 2.9 Ga Re-Os isochron derived from inclusions in diamonds from the Kimberley mine in South Africa. Studies such as these have shown that diamond formation in the mantle occurs in discrete events, most likely related to subduction (Shirey et al., 2004).

Figure 8.5. Re-Os isochron for a komatiite from Monro Township. After Walker et al. (1988).
Since the mantle $^{187}\text{Os}/^{188}\text{Os}$ 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 $^{187}\text{Os}/^{188}\text{Os}$ ratio with the mantle evolution curve. Platinoid metal deposits association with mantle-derived ultramafic 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 $\mu$m 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 $^{187}\text{Os}/^{188}\text{Os}$ ratio ceases to change once these minerals form (a model age would still be possible even if a small correction for radiogenic growth of $^{187}\text{Os}$ were necessary).

There has also been considerable interest in the Os isotope composition of seawater. The $^{187}\text{Os}/^{188}\text{Os}$ ratio of modern seawater is about 8. Like that of $^{87}\text{Sr}/^{86}\text{Sr}$, $^{187}\text{Os}/^{188}\text{Os}$ depends on the balance of continental fluxes (e.g., rivers, with $^{187}\text{Os}/^{188}\text{Os}$ ~ 1.2) and oceanic crustal fluxes (e.g., hydrothermal activity, with $^{187}\text{Os}/^{188}\text{Os}$ ~ 0.13). In addition, however, cosmic fluxes ($^{187}\text{Os}/^{188}\text{Os}$ ~ 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 8.8). 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.

Re-Os Dating of Hydrocarbons

There is undoubtedly no geologic material that is as essential to modern society as petroleum. Petroleum, however, consists almost exclusively of hydrocarbons, i.e., compounds of C and H, making its formation a challenge to date. Economic petroleum deposits can form if a series of conditions are met: an environment in which relatively high concentrations of organic matter are preserved in sediment as kerogen during deposition of the source rock; subsequent burial and conversion of the kerogen to hydrocarbons through gentle heating, and migration and concentration of the petroleum thus produced in a sufficiently porous reservoir rock. Through a variety of methods (some of which involve isotopic analysis), it is often possible to identify the source rock, and standard correlation techniques can determine the age of source rock deposition. The age of other steps in the process, particularly the timing of generation and migration, have been much harder to determine. Researchers have recently had some success in dating hydrocarbon migration using Re-Os.

Perhaps surprisingly, noble metals, and Re and Os in particular, can be present in relatively high concentrations in petroleum. Work by Selby et al. (2007) found that Re and Os are primarily present in asphaltene fraction of petroleum. Asphaltenes are heavy (molecular masses around 750u) polycyclic aromatic hydrocarbons. Although detailed studies have not been done, it seems likely that Re and Os are bound in porphyrins in the asphaltene fraction. Porphyrins are rings of pyrroline and pyrole groups (5-sided hydrocarbon rings containing N or NH) that can complex a metal ion in the center of the ring. Such organometallic complexes play vital biological roles. In the chlorophyll porphyrin, essential for harvesting photic energy in plants, Mg occupies this site; in the porphyrin structure that is part of the hemoglobin protein, essential for oxygen transport in blood, Fe occupies this site. Porphyrins in hydrocarbons can have high concentrations (up to a ppm or so) of transition metals such as Ni, V, and Mo.
Re concentrations in petroleum can be as high as 50 ppb, and it is more strongly concentrated than Os, whose concentration reaches only 300 ppt. Consequently, $^{187}\text{Rb} / ^{188}\text{Os}$ ratios can exceed 1000, and that in turn results in high $^{187}\text{Os} / ^{188}\text{Os}$ ratios.

Selby and Creaser (2005) used Re-Os to ‘date’ petroleum of the Western Canada Sedimentary Basin (WCSB). As may be seen in Figure 8.9, apparent isochrons yield ages of 111 to 121 Ma, depending on which samples are included. We say “apparent” isochrons because the mean square weighted deviations (MSWD) is greater than 1, indicating that not all deviations from regression can be accounted for by analytical error. In other words, there is real geologic variation from the isochron model. Selby and Creaser (2005) argue that, given the regional scale involved, this is more likely due to incomplete homogenization of the initial isotope ratio than to subsequent disturbances of Re/Os ratios. Precisely what event is being dated here is, however, somewhat unclear. Hydrocarbons in the WCSB are thought to have been derived from source rocks on the western side of the basin and then migrated east. It seems reasonable that hydrocarbon generation and migration could homogenize $^{187}\text{Os} / ^{188}\text{Os}$ ratios, although perhaps imperfectly, but it is unclear what mechanism produced the high $^{187}\text{Re} / ^{188}\text{Os}$ ra-

Figure 8.9. A. Re-Os isochron diagram for 24 samples of oil from the WCSB. The slope when all data are included corresponds to an age of 116±27 Ma. A slightly older but more precise age is obtained when the Prevost data is excluded. B. Including just those samples whose calculated $^{187}\text{Os} / ^{188}\text{Os}$ at 110 Ma is 1.4 to 1.5 yields a yet more precise age of 111.6±5 Ma. C. Location map for samples. From Selby and Creaser (2005).
The \(^{188}\text{Os}/^{186}\text{Os}\) ratio in mantle materials is 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 \(^{188}\text{Os}\) has also be found in some Hawaiian basalts, prompting the suggestion that the Hawaiian plume might contain a small core-derived component.

REFERENCES AND SUGGESTIONS FOR FURTHER READING


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