Geol. 655 Isotope Geochemistry

lecture 7 Spring 2003

GEOCHRONOLOGY III

THE SM-ND SYSTEM

^{147}Sm decays to ^{143}Nd by alpha decay with a half-life of 106 Ga (λ = 6.54 x $10^{-12}y^{-1}$). Because the half-life is so long, the resulting variations in Nd isotopic composition are small and require precise measurement. Sm and Nd are both intermediate rare earth elements (Figure 1). The distinctive feature of the rare earth elements is that inner electron shells (specifically the 4f and 5d shells) are being filled as atomic number increases. Normally an electron is added to the outermost shell when atomic number increases. It is the outer electron shells that dictate the chemical behavior of elements. Since the outer electron shells of the rare earths have identical configurations, we would expect them to behave quite similarly. This is indeed the case. The rare earths generally have a +3 valence; the most important exceptions being Eu, which is +2 under some conditions, and Ce, which is +4 under some conditions. The primary chemical difference between the rare earth elements is the ionic radius, which shrinks systematically from 1.15 Å for La (A=57) to 0.93Å for Lu (A=71). Since the rare earths form predominately covalent bonds with oxygen in the solid earth, their ionic radius is a key factor in their geochemical behavior. Thus there is a systematic variation in their abundances in rocks, minerals, and solutions (see box on rare earth plots). The ionic radii of Sm and Nd, which are separated by Pm (an element that has no stable or long-lived isotope), differ by only 0.04Å (Nd=1.08, Sm=1.04). The ionic radii and relatively high charge of the rare earths make them fairly unwelcome in many mineral lattices: they can be considered moderately incompatible, with Nd being slightly more incompatible than Sm. Ce is generally the most abundant rare earth and forms its own phase in rare instances. Some rare earths, particularly the heavier ones, are accommodated in lattice structures of common minerals; for example the partition coefficient of Lu in garnet is in the range of 4-10 (depending on the composition of the magma and the garnet). In mafic minerals, the lighter rare earths, which have the largest ionic radii, tend to be excluded more than the heavies, but in plagioclase, the heavies are the most excluded (though partition coefficients generally do not exceed 0.1). The high valence state of the rare earths results in relatively strong bonds. This, together with their tendency to hydrolyze (that is, surround themselves with OH^- radicals), results in relatively low solubilities and low mobilities.

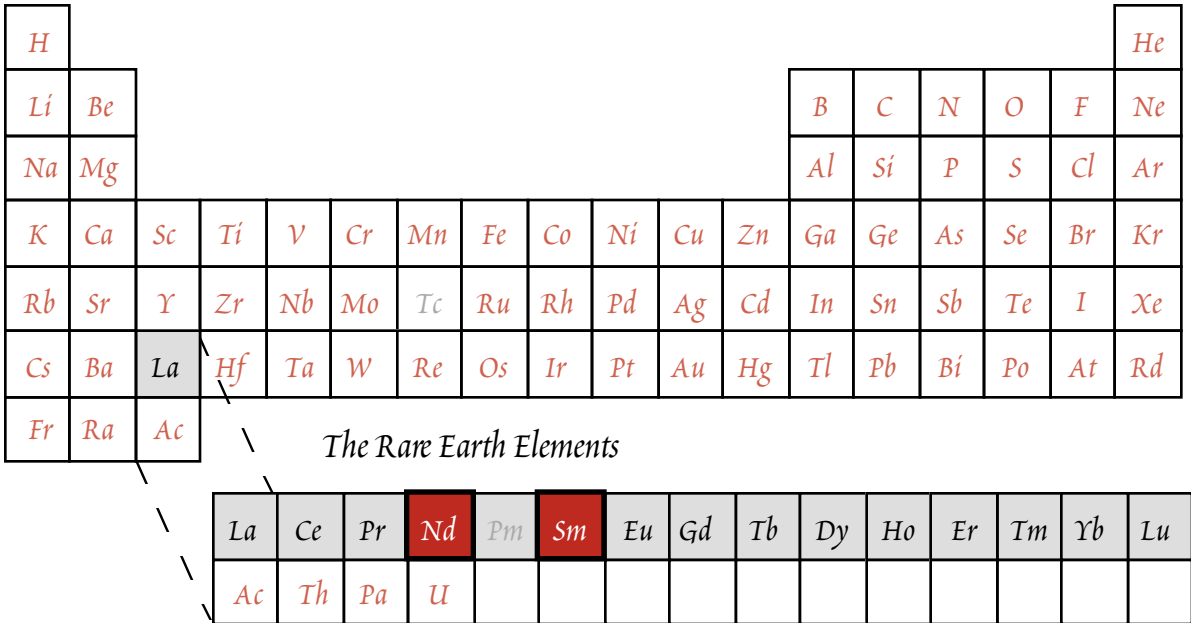


Figure 7.1. Periodic table highlighting the rare earths (gray background) and Nd and Sm.

RARE EARTH PLOTS

The systematic contraction in the ionic radii of the rare earth elements leads to systematic variation in their behavior. This is best illustrated by viewing their abundances on rare earth, or Masuda-Coryell, plots. The plots are constructed by first "normalizing" the concentrations of the rare earth, i.e., dividing but the concentration of the element in a standard. Generally, this standard is the abundance in chondritic meteorites, but other values are also used (for example, rare earths in sediments and seawater are often normalized to average shale). This normalizing process removes the sawtooth pattern that results from odd-even nuclear effects, and also the effect of decreasing concentration with atomic number. Those concentration variations, illustrated in Figure 7.2, reflect differences in nuclear stability and the nucleosynthetic process, and therefore affect the abundances of rare earths in all matter. Removing these effects by normalization highlights differences in concentration due to geochemical processes. After normalizing, the log of the abundance of each element is plotted against atomic number, as is illustrated in Figure 7.3.

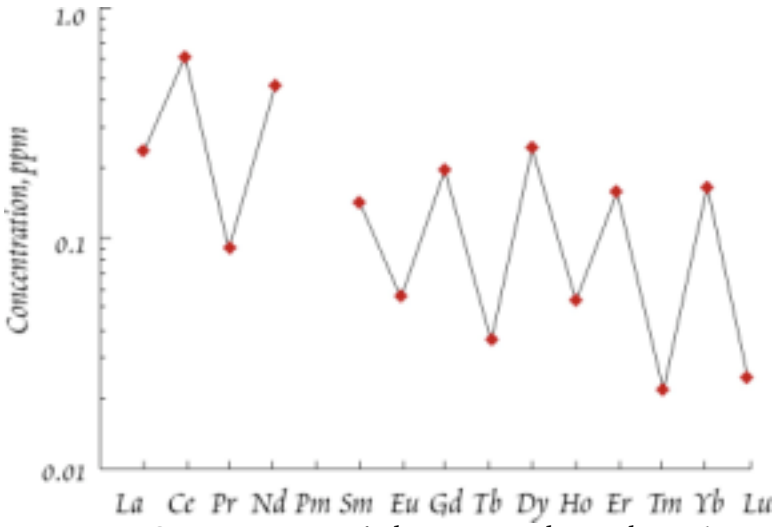


Figure7.2. Concentrations of the rare earths in the carbonaceous chondritic meteorite Orgueil.

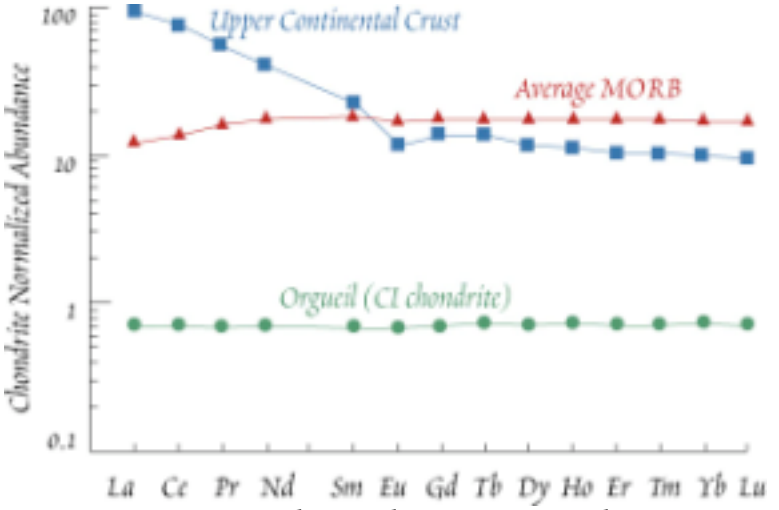


Figure 7.3. A rare earth plot showing rare earth patterns for orgueil, average upper continental crust, and average mid-ocean ridge basalt (MORB).

The rare earths are refractory elements (which is to say they have low vapor pressures or low boiling points); what is more relevant is that they form refractory compounds. As is the case with other refractory elements, it can be assumed that their relative abundances in the Earth are the same as in chondritic meteorites. This assumption is strengthened in the case of the rare earths because of the general similarity of their chemical behavior: i.e., we do not believe that processes in the early solar system fractionated the rare earths. The important point is we have good reason to believe the $^{147}Sm/^{144}Nd$ ratio of the Earth is the same as the chondritic value, 0.1967, which corresponds to a Sm/Nd of about 0.32. A general assumption is that the solar system was isotopically homogeneous when the Earth formed. This is to say that the initial $^{143}Nd/^{144}Nd$ ratio of the Earth should be identical to the initial $^{143}Nd/^{144}Nd$ ratio of other bodies formed 4.55 Ga ago, including meteorite parent bodies. Since the initial ratio and the Sm/Nd ratio of all bodies in the solar system are identical,

the present-day ratios of $^{143}Nd/^{144}Nd$ should also be identical, and they should have been identical at every point in their histories, provided they are closed systems.

Thus we believe we know the Earth's Sm/Nd ratio, present-day $^{143}Nd/^{144}Nd$ ratio, and the evolution of $^{143}Nd/^{144}Nd$ through time. It turns out that this is a very useful thing from both a geochemical and geochronological standpoint. It also leads to a useful notation for Nd isotope ratios. Because we know the bulk-earth $^{143}Nd/^{144}Nd$ at any instant in time, it is useful to consider relative deviations of $^{143}Nd/^{144}Nd$ from the bulk-earth value. These deviations are small, so we write them in deviations in parts in 10,000. This is the ε (epsilon) notation. The ε_{Nd} value is defined as follows:

$$\varepsilon_{Nd} = \left[\frac{\left(^{143}Nd/^{144}Nd\right)_{sample} - \left(^{143}Nd/^{144}Nd\right)_{CHUR}}{\left(^{143}Nd/^{144}Nd\right)_{CHUR}} \right] \times 10000 \qquad 7.1$$

where CHUR stands for 'chondritic uniform reservoir'; i.e., $(^{143}Nd/^{144}Nd)_{CHUR}$ is the value of the ratio in chondrites. We can calculate an ε_{Nd} for any point in time. For the present, the value of $(^{143}Nd/^{144}Nd)_{CHUR}$ is 0.512638 when $^{146}Nd/^{144}Nd = 0.7219$[1]. The range in ε_{Nd} values in virtually all whole rocks is +14 to -20. The gross features of the evolution of Nd isotope ratios are illustrated in Figure 7.4.

The similarity of the chemical behavior in Sm and Nd means that the range in Sm/Nd and $^{143}Nd/^{144}Nd$ ratios is generally quite limited. For this reason, and because of the difficulty in separating these elements, this system has been used for only 20 years. (We should note at this point that Mother Nature was kind to isotope geochemists and did not make any Pm, the element that occurs between Nd and Sm. Purification of Nd and Sm would have otherwise been more difficult).

The limited variation in Sm/Nd is certainly the major drawback of this system for geochronology. As things turn out, however, Sm-Nd compliments Rb-Sr nicely. Sm/Nd variations tend to be largest in mafic and ultramafic rocks and smallest in acid rocks, exactly the opposite of Rb/Sr. A relatively wide spread in Sm/Nd may be achieved if garnet, or a garnet-rock is included in the samples analyzed. Garnets tend to have rela-

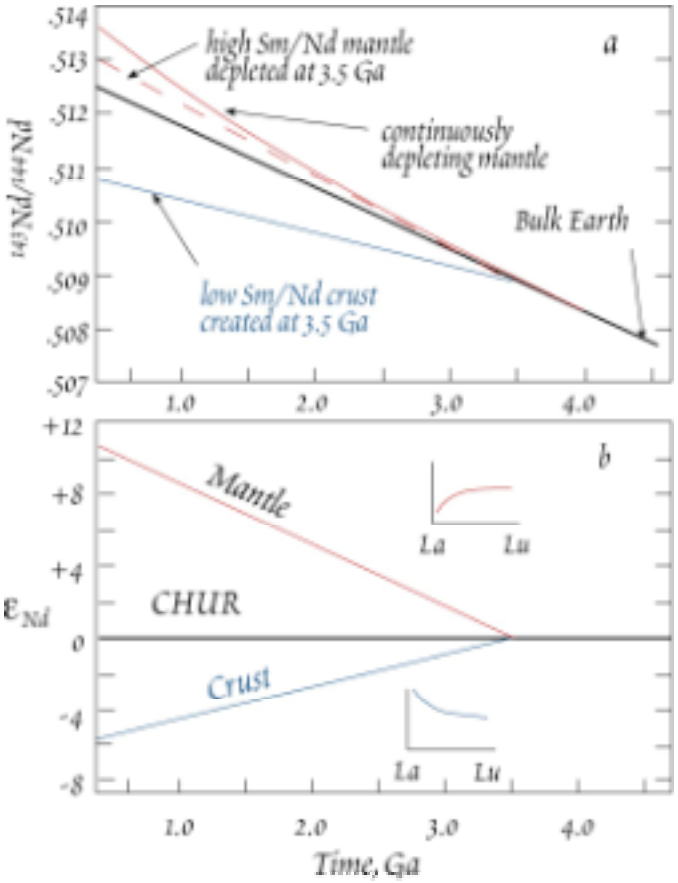


Figure 7.4. (a) Nd isotope evolution in mantle and crust. Bold line shows the evolution of the bulk earth or CHUR (chondritic uniform reservoir); also shown is the evolution of crust created at 3.5 Ga, the corresponding residual mantle, and the evolution of a continuously depleted mantle. (b) Evolution of bulk earth, crust, and mantle when $^{143}Nd/^{144}Nd$ is transformed to ε_{Nd}.

[1]There are essentially two normalization schemes (i.e., mass fractionation corrections) for Nd. Cal Tech, and some former Cal Tech students, normalize to $^{146}Nd/^{142}Nd = 0.636151$. Using this scheme, the present-day $^{143}Nd/^{144}Nd$ chondritic value is 0.511847. All other laboratories, including Cornell, use $^{146}Nd/^{144}Nd = 0.7219$. The value of ε_{Nd} for a given rock should be the same, however, regardless of normalization.

tively high Sm/Nd ratios. Failing this, inclusion of both plagioclase and pyroxene can result in a satisfactory spread in Sm/Nd ratios. Because the range in Sm/Nd ratios tends to be small, even small variations in initial $^{143}Nd/^{144}Nd$ can result in erroneous ages. There are several such cases in the literature.

Perhaps the greatest advantage of Sm/Nd is the lack of mobility of these elements. *The Sm-Nd chronometer is therefore relatively robust with respect to alteration and low-grade metamorphism*. Thus the Sm-Nd system is often the system of choice for mafic rocks and for rocks that have experienced low-grade metamorphism or alteration.

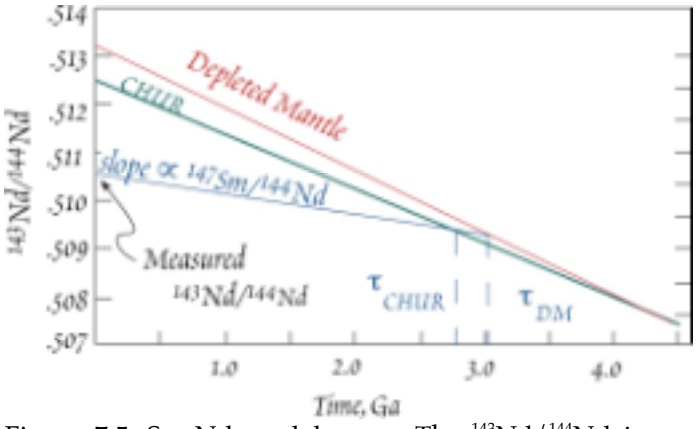


Figure 7.5. Sm-Nd model ages. The $^{143}Nd/^{144}Nd$ is extrapolated backward (slope depending on Sm/Nd) until it intersects a mantle or chondritic growth curve.

SM-ND MODEL AGES AND CRUSTAL RESIDENCE TIMES

A general assumption about the Earth is that the crust has been created from the mantle by magmatism. When a piece of crust is first created, it will have the $^{143}Nd/^{144}Nd$ ratio of the mantle, though it's Sm/Nd ratio will be lower than that of the mantle (a consequence of Nd being more incompatible and partitioning more into the melt than Sm). Let's make the simplistic assumption that the mantle has the same Nd isotopic history as CHUR. This means a piece of crust will have the same $^{143}Nd/^{144}Nd$ as the mantle and as CHUR when it is created, i.e., $\varepsilon_{Nd} = 0$. If we know the present-day Sm/Nd and $^{143}Nd/^{144}Nd$ ratio of this piece of crust, we can estimate its age. Figure 7.5 illustrates how this is done graphically, let's see how this is done mathematically. What we want to find is the intersection of line describing the evolution of the sample and that describing the evolution of the mantle. To do so, we simply need to subtract one equation from the other.

The closed system isotopic evolution of any sample can be expressed as:

$$^{143}Nd/^{144}Nd_{sam} = {}^{143}Nd/^{144}Nd_0 + {}^{147}Sm/^{144}Nd_{sam}(e^{\lambda t} - 1) \qquad 7.02$$

The chondritic evolution line is:

$$^{143}Nd/^{144}Nd_{CHUR} = {}^{143}Nd/^{144}Nd_0 + {}^{147}Sm/^{144}Nd_{CHUR}(e^{\lambda t} - 1) \qquad 7.03$$

The CHUR model age of a system is the time elapsed, $t = \tau$, since it had a chondritic $^{143}Nd/^{144}Nd$ ratio, assuming the system has remained closed. We can find τ by subtracting equation 7.03 from 7.02, which yields:

$$^{143}Nd/^{144}Nd_{sam} - {}^{143}Nd/^{144}Nd_{CHUR} = \left\{{}^{147}Sm/^{144}Nd_{sam} - {}^{147}Sm/^{144}Nd_{CHUR}\right\}(e^{\lambda\tau} - 1) \qquad 7.04$$

Another way of thinking about this problem is to imagine a $^{143}Nd/^{144}Nd$ vs. time plot: on that plot, we extrapolate the sample's evolution curve back to the chondritic one. In terms of the above equations, this intersection occurs at $(^{143}Nd/^{144}Nd)_0$.

Solving equ. 7.04 for τ:

$$\tau_{CHUR} = \frac{1}{\lambda}\ln\left[\frac{{}^{143}Nd/^{144}Nd_{sam} - {}^{143}Nd/^{144}Nd_{CHUR}}{{}^{147}Sm/^{144}Nd_{sam} - {}^{147}Sm/^{144}Nd_{CHUR}} + 1\right] \qquad 7.05$$

An age obtained in this way is called an *Nd model age* (the model is that of chondritic evolution of the mantle), or a *crustal residence age*, because it provides an estimate of how long this sample of Nd has been in the crust. Note that we explicitly assume the sample has remained a closed system, in the sense of no migration in or out of Sm or Nd. Because of the immobility of these elements, the assumption generally holds, at least approximately.

We can obtain somewhat better model ages by making more a sophisticated assumption about the Nd evolution of the mantle. Since the crust is enriched in Nd relative to Sm, the mantle must be depleted in Nd relative to Sm (analyses of mantle-derived rocks confirm this). So the chondritic assumption must be wrong. We can assume instead a model of $^{143}Nd/^{144}Nd$ growth in the mantle that is more rapid than chondritic, i.e., a higher Sm/Nd ratio. Once we decide on Sm/Nd and present-day $^{143}Nd/^{143}Nd$ ratios for this 'depleted-mantle' (the latter can be estimated from the $^{143}Nd/^{143}Nd$ of MORB, mid-ocean ridge basalts), we can calculate a model age relative to the depleted mantle by substituting the depleted-mantle terms for the CHUR terms in 7.2 and 7.3.

To calculate the depleted mantle model age, τ_{DM}, we use the same approach, but this time we want the intersection of the sample evolution line and the depleted mantle evolution line. So equation 7.05 becomes:

$$\tau_{DM} = \frac{1}{\lambda}\ln\left[\frac{^{143}Nd/^{144}Nd_{sam} - {}^{143}Nd/^{144}Nd_{DM}}{^{147}Sm/^{144}Nd_{sam} - {}^{147}Sm/^{144}Nd_{DM}} + 1\right] \qquad 7.06$$

The depleted mantle (as sampled by mid-ocean ridge basalts) has an average ε_{Nd} of about 10, or $^{143}Nd/^{144}Nd = 0.51315$. The simplest possible evolution path, and the one we shall use, would be a closed system evolution since the formation of the Earth, 4.55 Ga ago (i.e., a straight line on a $^{143}Nd/^{144}Nd$ vs. time plot). This evolution implies a $^{147}Sm/^{144}Nd$ of 0.2137.

Because the Sm/Nd ratio is so little affected by weathering, and because these elements are so insoluble, Sm/Nd ratios in fine-grained sediments do not generally differ much from the ratio in the precursor crystalline rock. Thus, the system has some power to 'see through' even the process of making a sediment from a crystalline rock. The result is we can even compute crustal residence times from Nd isotope ratio and Sm/Nd measurements of fine-grained sediments. This generally does not work for coarse-grained sediments though because they contain accessory minerals whose Sm/Nd ratios can be quite different from that of the whole rock.

REFERENCES AND SUGGESTIONS FOR FURTHER READING

Dickin, A. 1995. *Radiogenic Isotope Geochemistry*. Cambridge: Cambridge University Press.

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