

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/234148718>

# Geochemical and Cosmochemical Applications of Nd Isotope Analysis

Article in *Annual Review of Earth and Planetary Sciences* · November 2003

DOI: 10.1146/annurev.earth.07.050179.000303

---

CITATIONS

58

---

READS

60

4 authors, including:



Joseph Hamilton

ana-min

99 PUBLICATIONS 9,161 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:



FTIR mineral analysis of drill cuttings [View project](#)

# GEOCHEMICAL AND COSMOCHEMICAL APPLICATIONS OF Nd ISOTOPE ANALYSIS<sup>1</sup>

\*10105

*R. K. O'Nions, S. R. Carter, N. M. Evensen, and P. J. Hamilton*

Lamont-Doherty Geological Observatory, Columbia University,  
Palisades, New York 10964

## INTRODUCTION

The realm of the isotope geochemist consists of the 288 naturally occurring isotopes. The portions of interest to the geochemist are those isotopes that show measurable variations relatable to natural processes, and this domain has expanded as analytical refinements have permitted the measurement of progressively smaller variations in isotopic abundance. The most recent isotopic system to come within the expanding frontiers of geochemistry is that of the rare earth element neodymium (Nd). Although the analysis of Nd isotope variations is only a few years old, it has proven its worth in a variety of terrestrial and extraterrestrial studies, and is rapidly becoming a standard geochemical technique, capable of providing information not accessible by other means.

The primary cause of natural variations in the isotopic composition of Nd is the  $\alpha$ -decay of the long-lived isotope  $^{147}\text{Sm}$  to  $^{143}\text{Nd}$ . The variations thus produced have been employed as a geochronologic tool as well as a tracer of geochemical provenance. In addition, variations in other isotopes of Nd have apparently resulted from incomplete mixing of the products of various nucleosynthetic regimes during formation of the solar nebula, from the  $\alpha$ -decay of the short-lived extinct radioactivity  $^{146}\text{Sm}$ , and from the spontaneous fission of U. The ability to discern the often minor effects resulting from these causes depends heavily upon the advances in mass spectrometry made during the last decade.

This paper discusses the natural processes capable of inducing varia-

<sup>1</sup> L.-D.G.O. Contribution No. 2729. This work has been supported by NSF Grant EAR-75-20891.

tions in the isotopic composition of Nd, the techniques used for precise measurement of the variations, and a variety of applications of Nd isotope analysis in geochemistry and cosmochemistry.

## PROCESSES GOVERNING THE ISOTOPIC COMPOSITION OF Nd

### *Nucleosynthesis*

Neodymium is one of the 14 naturally occurring rare earth elements (REE). Its even atomic number ( $Z = 60$ ) favors nuclear stability, and it possesses seven stable isotopes, at mass numbers 142, 143, 144, 145, 146, 148, and 150. The general features of the nucleosynthesis of Nd are readily inferred from Figure 1. In the classic scheme of Burbidge et al (1957), the s-process nuclides are formed by the successive addition of neutrons until terminated by an unstable  $\beta$ -emitter, which carries the process to a new element having the next higher value of  $Z$ .  $^{142}\text{Nd}$  through  $^{146}\text{Nd}$  are s-process nuclides, while  $^{147}\text{Nd}$  is a short-lived (11 day half-life) nuclide decaying to  $^{147}\text{Pm}$  and thence to  $^{147}\text{Sm}$  (Pm has no stable isotopes). The r-process consists of the much more rapid addition of neutrons, with neutron capture occurring on a time scale shorter than the  $\beta$ -decay half-lives of the resulting nuclides, so that very neutron-rich nuclides are formed, which subsequently  $\beta$ -decay to the valley of nuclear stability.  $^{148}\text{Nd}$  and  $^{150}\text{Nd}$  are isolated from the s-process by  $^{147}\text{Nd}$ , and so can only be formed by the r-process. However,  $^{143}\text{Nd}$  through  $^{146}\text{Nd}$  can also be formed by the r-process. Neutron-rich nuclides of mass 142 will  $\beta$ -decay to stable  $^{142}\text{Ce}$  before reaching  $^{142}\text{Nd}$ , which is therefore shielded from r-process contributions. None of the isotopes of Nd are sufficiently proton-rich to require the somewhat mysterious p-process of proton addition for their formation, but there is some evidence (Lugmair et al 1978) for a p-process contribution to the lighter isotopes of Nd, either directly or through the  $\alpha$ -decay of the short-lived p-process nuclides  $^{146}\text{Sm}$  and  $^{150}\text{Gd}$  to  $^{142}\text{Nd}$ .

Each process described above is believed to occur in a different cosmic environment. Variations in the proportions of material derived from different nucleosynthetic regimes, therefore, will result in variations in the isotopic abundances of the corresponding nuclides (e.g. in the ratio of s-only  $^{142}\text{Nd}$  to r-only  $^{148}\text{Nd}$ ). The relative abundances of nuclides derived from a *single* process (e.g. the ratio of the r-process  $^{148}\text{Nd}$  to r-process  $^{150}\text{Nd}$ ) will not change, however. This latter property is useful in searching for Nd isotopic variations resulting from nucleosynthetic causes, since instrumental fractionation can be corrected by normalizing to the  $^{148}\text{Nd}/^{150}\text{Nd}$  ratio, which is unaffected by variable s-process con-

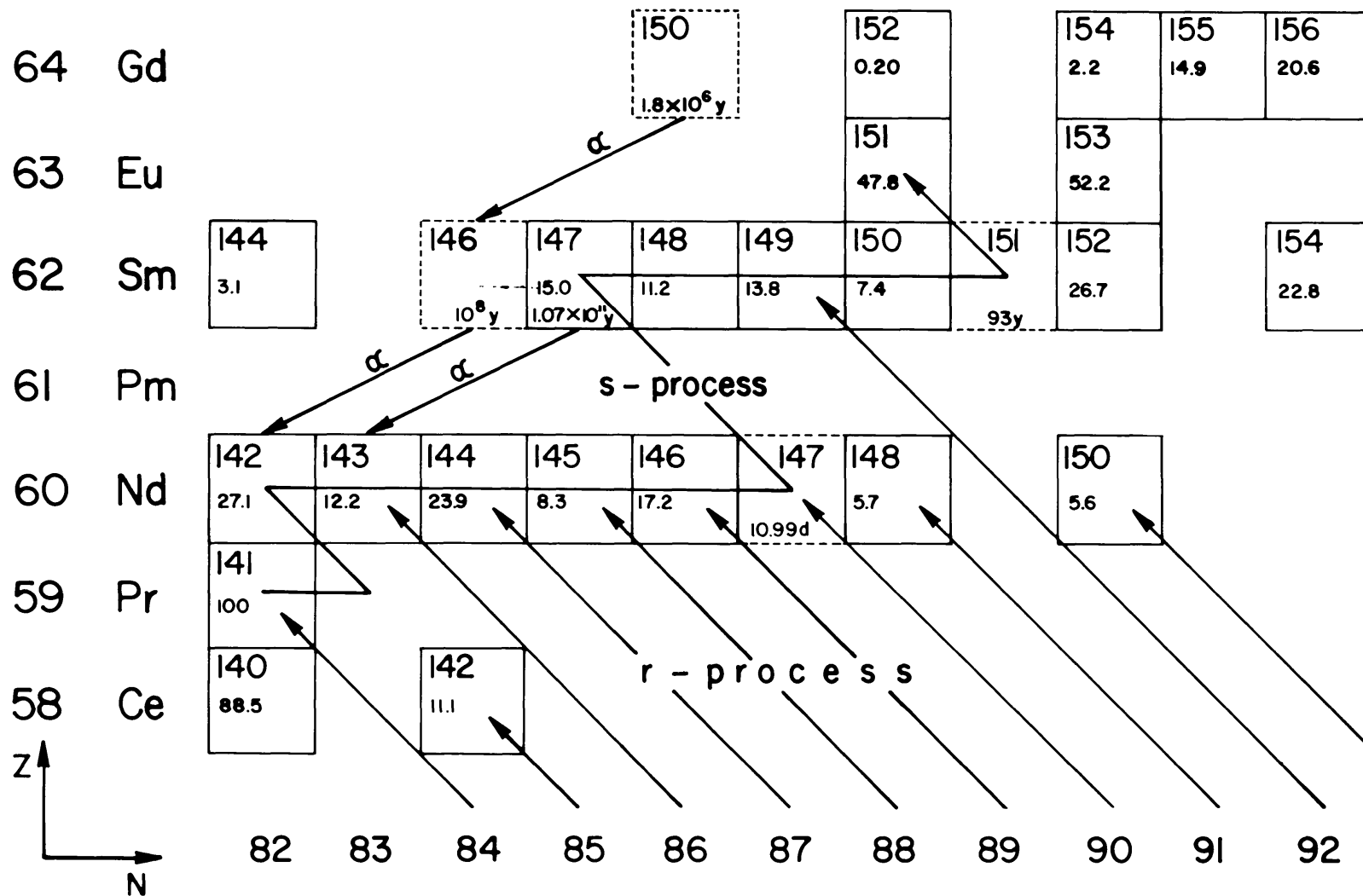


Figure 1 A portion of the nuclide chart showing nuclear processes of relevance to the abundances of Nd isotopes. Atomic number  $Z$  is plotted against neutron number  $N$ . Naturally occurring isotopes with their percent abundances are enclosed by heavy lines, unstable isotopes by dashed lines. Only those unstable isotopes involved in nuclear processes of interest are shown. A portion of the s-process path of nucleosynthesis appears as a zig-zag line from lower left to upper right; r-process paths are parallel lines from lower right, terminating at the first stable nuclide. Several  $\alpha$ -decay paths are shown; the half-lives of the parents are given at the bottom of the corresponding square.

tributions. McCulloch & Wasserburg (1978b,c) and Lugmair et al (1978) independently observed variations in the isotopic composition of Sm and Nd in an inclusion from Allende. This inclusion has an excess of r-process nuclides, the excesses forming smooth functions of atomic mass (Figure 2). The effect of odd and even mass numbers on nuclear stability is clearly seen, and results in lower abundances of odd-mass nuclides. A small p-process contribution may also be present, but the inference of its presence is somewhat model-dependent.

The existence of the pure r-process as originally visualized by Burbidge et al has recently been questioned by Blake & Schramm (1976), who suggest that neutron fluxes lower than those required for the idealized

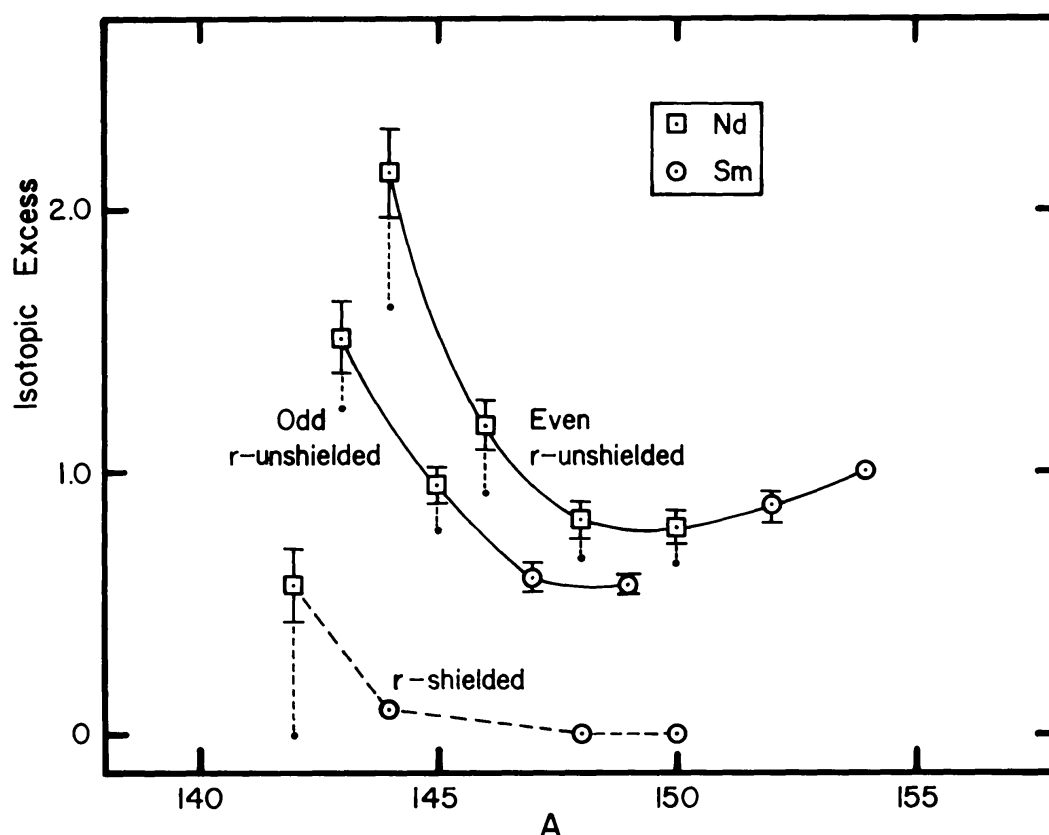


Figure 2 Excess abundances of Sm and Nd isotopes in Allende inclusion EK 1-04-1, plotted against mass number  $A$  (after Lugmair et al 1978). Sm points (circles) are obtained by normalizing the measured Sm isotopic composition of EK 1-04-1 to match the ratio of s-only isotopes  $^{148}\text{Sm}/^{150}\text{Sm}$  determined for a terrestrial standard. Excesses of other Sm isotopes over the values in the standard are then plotted relative to  $^{154}\text{Sm}$  excess  $\equiv 1$ . Nd data were normalized to the terrestrial standard ratio of the r-only isotopes  $^{148}\text{Nd}/^{150}\text{Nd}$ . Assuming excess of r-shielded  $^{142}\text{Nd}$  to be zero, excesses of other Nd isotopes are shown as small dots below the squares. The squares indicate excesses obtained by fitting r-unshielded Nd isotopes to the Sm excesses; the  $^{142}\text{Nd}$  excess obtained in this case may represent a differential p-process contribution.

r-process can reproduce the observed distribution of nuclides equally well or better. Their n- (or neutron-) process is essentially a mixture of the classical s- and r-processes, and requires less extreme and more astrophysically reasonable sites than the pure r-process.

### *Radioactive Decay*

The abundance of a given nuclide at any point in time reflects the relative rates of synthesis and decay, integrated over all past time. Once significant nucleosynthesis has ceased, many of the resultant nuclides begin to decay at rates which vary over many orders of magnitude. For radioactive decay to produce observable variations in isotopic abundances of the daughter nuclide

1. variable parent-daughter ratios must exist over some interval while the parent nuclide is decaying,
2. the variations thus produced must be preserved, i.e. any subsequent mixing must be incomplete,
3. the analytical techniques employed must be capable of resolving these variations.

The first condition requires that some fractionation process be operative while significant amounts of the parent nuclide are still present—hence the half-life must be sufficiently long to allow this. Since any decay involving charged particles (e.g.  $\alpha$ - and  $\beta$ -decay) results in a daughter of differing atomic number, parent-daughter fractionation can be induced by a variety of cosmochemical and geochemical processes. The second requirement implies that at least some of the fractionated phases be persistent to the present day. If the half-life of the nuclide involved is short, this means that the fractionations must have persisted since a similarly brief interval following nucleosynthesis. The third condition merely relates quantitatively the analytical resolution available to the size of the induced variations. The magnitude of effects produced is dependent upon the range of parent-daughter ratios, the half-life of the parent, and the interval over which the variations in parent-daughter ratio were present.

In the case of Nd, the only naturally occurring nuclides decaying to isotopes of Nd are  $^{147}\text{Sm}$ ,  $^{148}\text{Sm}$ , and  $^{149}\text{Sm}$ , which undergo  $\alpha$ -decay to  $^{143}\text{Nd}$ ,  $^{144}\text{Nd}$ , and  $^{145}\text{Nd}$  respectively. Sm and Nd are rare earths and hence similar chemically, so that variations in the Sm/Nd ratio by more than a factor of two are not common in nature. The long-lived ( $T_{1/2} \sim 10^{16}\text{y}$ )  $^{148}\text{Sm}$  and  $^{149}\text{Sm}$  are not capable of producing measurable variations in  $^{144}\text{Nd}$  or  $^{145}\text{Nd}$  even over cosmological intervals ( $\sim 10^{10}\text{y}$ ). However, the half-life of  $^{147}\text{Sm}$ , about  $10^{11}\text{y}$ , is sufficiently short to produce small but readily measurable differences in  $^{143}\text{Nd}$  abundance

over time spans of  $10^8$  y or more. This provides the basis for the Sm-Nd technique of age determination, to be discussed in detail shortly.

The other decay scheme of possible cosmochemical interest involving Nd is the  $\alpha$ -decay of  $^{146}\text{Sm}$  to  $^{142}\text{Nd}$ .  $^{146}\text{Sm}$  is unstable, but its half-life of  $\sim 10^8$  y is relatively long. If fractionation of Sm/Nd took place within a few  $10^8$  y after nucleosynthesis of the REE, any fractionated phases still extant should show measurable anomalies of  $^{142}\text{Nd}$ , in addition to any variations caused by differential p-process contributions (see Figure 1).

If at time = 0, a number  $^x\text{Nd}_0$  of  $^{142}\text{Nd}$  or  $^{143}\text{Nd}$  atoms are present, together with  $^y\text{Sm}_0$  atoms of  $^{146}\text{Sm}$  or  $^{147}\text{Sm}$  respectively, then after a time  $t$  has elapsed a proportion  $(1 - e^{-\lambda_y t})$  of the parent isotope will have decayed, where  $\lambda_{146} = 6.93 \times 10^{-9} \text{y}^{-1}$  and  $\lambda_{147} = 6.54 \times 10^{-12} \text{y}^{-1}$ . Then the total number of  $^x\text{Nd}$  atoms at time  $t$  is

$$^x\text{Nd}_t = ^x\text{Nd}_0 + ^y\text{Sm}_0(1 - e^{-\lambda_y t}).$$

The equation may be divided through by any nonradiogenic isotope of Nd, say  $^z\text{Nd}$ , and since  $^z\text{Nd}_0 = ^z\text{Nd}_t$ , we have:

$$\left(\frac{^x\text{Nd}}{^z\text{Nd}}\right)_t = \left(\frac{^x\text{Nd}}{^z\text{Nd}}\right)_0 + \left(\frac{^y\text{Sm}}{^z\text{Nd}}\right)_0 (1 - e^{-\lambda_y t}). \quad (1)$$

In subsequent discussion,  $z = 144$  will be assumed, with the understanding that any non-radiogenic Nd isotope could be substituted.

For the case of  $^{147}\text{Sm}$ - $^{143}\text{Nd}$ , one generally makes the substitution

$$^{147}\text{Sm}_0 = ^{147}\text{Sm}_t e^{\lambda t},$$

so that

$$\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)_t = \left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)_0 + \left(\frac{^{147}\text{Sm}}{^{144}\text{Nd}}\right)_t (e^{\lambda t} - 1). \quad (2)$$

This equation is linear in the parameters  $(^{143}\text{Nd}/^{144}\text{Nd})_t$  and  $(^{147}\text{Sm}/^{144}\text{Nd})_t$ , so that for a given  $(^{143}\text{Nd}/^{144}\text{Nd})_0$  and  $t$ , a plot of  $^{143}\text{Nd}/^{144}\text{Nd}$  vs  $^{147}\text{Sm}/^{144}\text{Nd}$  as measured at present (the "Nd evolution diagram") is a straight line, with intercept  $(^{143}\text{Nd}/^{144}\text{Nd})_0$  and slope  $e^{\lambda t} - 1$ . This is the basis of the isochron plot familiar from the Rb-Sr system and equally applicable to the Sm-Nd system. Note however that the range of Sm/Nd in natural systems is normally less than that of Rb/Sr; in particular, very low Sm/Nd ratios are seldom found, so that the initial  $^{143}\text{Nd}/^{144}\text{Nd}$  must be obtained from a considerable extrapolation to the ordinate, whereas it is often possible to obtain phases of very low Rb/Sr in which the measured  $^{87}\text{Sr}/^{86}\text{Sr}$  is very close to the initial value.

In the case of the  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  system, the time from nucleosynthesis

( $t = 0$ ) to the present ( $t \geq 4.5$  G.y.) is many half-lives of  $^{146}\text{Sm}$ , so the term  $\exp(-\lambda t) \approx 0$  in Equation (1), and we have,

$$\left(\frac{^{142}\text{Nd}}{^{144}\text{Nd}}\right)_t = \left(\frac{^{142}\text{Nd}}{^{144}\text{Nd}}\right)_0 + \left(\frac{^{146}\text{Sm}}{^{144}\text{Nd}}\right)_0.$$

If we assume the ratio of  $^{146}\text{Sm}$  to some stable, nonradiogenic isotope of Sm, say  $^{144}\text{Sm}$ , to have been constant at  $t = 0$ , we may write

$$\left(\frac{^{142}\text{Nd}}{^{144}\text{Nd}}\right)_t = \left(\frac{^{142}\text{Nd}}{^{144}\text{Nd}}\right)_0 + \left(\frac{^{144}\text{Sm}}{^{144}\text{Nd}}\right)_t \left(\frac{^{146}\text{Sm}}{^{144}\text{Sm}}\right)_0. \quad (3)$$

Again we have an equation linear in the quantities  $(^{142}\text{Nd}/^{144}\text{Nd})_t$  and  $(^{144}\text{Sm}/^{144}\text{Nd})_t$ , assuming constant  $(^{142}\text{Nd}/^{144}\text{Nd})_0$ , in which case samples of varying Sm/Nd will define a straight line with intercept  $(^{142}\text{Nd}/^{144}\text{Nd})_0$ . However, the slope no longer has time significance, but rather defines the  $^{146}\text{Sm}/^{144}\text{Sm}$  ratio at time zero, the time at which the  $^{142}\text{Nd}/^{144}\text{Nd}$  was last homogeneous.

### *Nuclear Fission*

Fission of the actinide elements results in two major fragments of unequal and somewhat variable mass. The heavier fragments of each pair generally have masses in the range of the lighter REE, so that fission products contain a significant proportion of various Nd isotopes. Spontaneous fission occurs only for certain isotopes of transuranic elements, notably the extinct radioactivity  $^{244}\text{Pu}$ . Evidence of  $^{244}\text{Pu}$  fission has been found in some meteorites, in the form of anomalous isotopic compositions of Xe. Because of the volatility of Xe, phases with high Pu/Xe were formed while  $^{244}\text{Pu}$  was still extant, and thus a fairly high proportion of their Xe is fission-produced. However no such extreme Pu/Nd enrichment is likely, so that the small amount of  $^{244}\text{Pu}$  present at solar system formation could not produce significant change in Nd isotope abundances.

Slow neutron-induced fission of natural U is a rare but not unknown process in nature. The Oklo natural reactor represents a rare combination of circumstances in which a sufficient natural concentration of U has been moderated at some past times by sufficient water to allow a chain reaction to be sustained. The resulting high concentrations of fission products have led to marked changes in the isotopic composition of the REE (Loubet & Allègre 1977).

### *Measurement of Nd-Isotope Compositions*

Although neutron activation analysis is capable of detecting large ( $\sim 1\%$ ) differences in the isotopic composition of an element, mass spectrometry



remains the technique of choice for the precise determination of small isotopic variations. The geochemical applications of Nd isotopes have in fact been entirely dependent upon the advances in high-precision isotope ratio mass spectrometry first applied to Sr (Wasserburg et al 1969, Papanastassiou & Wasserburg 1969).

Because of the many isobars of the REE (Figure 1), good chemical separation of Nd from the adjacent REE, Ce and Sm, is required for successful mass spectrometry.  $^{142}\text{Ce}$ ,  $^{144}\text{Sm}$ ,  $^{148}\text{Sm}$ , and  $^{150}\text{Sm}$  are capable of causing interferences on the corresponding Nd isotopes. The REE are readily separated from other elements by standard ion-exchange techniques (e.g. Schnetzler et al 1967, Hooker et al 1975), but the separation of Nd from the other REE is more difficult. A variety of cation- and anion-exchange techniques have been developed, but in general require careful control of some parameters such as temperature or pH (e.g. Lugmair et al 1975a, Richard et al 1976, O'Nions et al 1977).

Mass spectrometry is performed on either metal or oxide species; each technique has its potential isobaric interferences, and use of the oxide species requires corrections to the data for the mutual interferences produced by the three isotopes of O. In either case correction must be made for instrumental mass fractionation during mass spectrometry. As with Sr, the usual procedure is to choose an isotope pair (not including the daughter isotope) that can be assumed constant in nature, compare its value during the analysis with a standard value, and extrapolate the observed fractionation to the ratio of interest (usually assuming a linearly mass-dependent fractionation). Unlike the case of Sr, however, there is no general agreement on a normalizing ratio or its standard value for Nd. This is a potential cause of confusion in comparing Nd measurements from various laboratories, and conversion must often be made. If two laboratories use the same normalizing ratio but assume different values for it, the conversion is straightforward, but if different normalizing ratios are used, the conversion requires knowledge of the isotopic composition of normal Nd (Table 1). In our laboratory and throughout this paper

**Table 1** Nonradiogenic isotope ratios in natural neodymium<sup>a</sup>

142/144	$1.1382602 \pm 58$
145/144	$0.3489695 \pm 50$
146/144	$0.7241103 \pm 53$
148/144	$0.2430801 \pm 36$

<sup>a</sup> Weighted means and errors from DePaolo & Wasserburg (1976a). Ratios normalized to  $^{150}\text{Nd}/^{142}\text{Nd} = 0.2096$ .

results are quoted relative to  $^{144}\text{Nd}$  (e.g.  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios) and corrected to a  $^{146}\text{Nd}/^{144}\text{Nd}$  ratio of 0.7219, the mean of a large number of Nd analyses made in our laboratory. Use is also commonly made of derived parameters that relate observed ratios to various simple models; these are defined when introduced. At present, Nd ratios are generally measured with 95% confidence limits of 0.005% or less. Lugmair & Marti (1978) reviewed measurements of the  $^{147}\text{Sm}$  half-life and obtain a weighted mean value of  $1.06 \times 10^{11}\text{y}$ , corresponding to a decay constant of  $6.54 \times 10^{-12}\text{y}^{-1}$ . This is the value that has been used for all published  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  chronometry, and appears consistent with the recently revised U decay constants (Lugmair & Marti, 1978).

## COSMOCHEMICAL APPLICATIONS

### *Information from $^{146}\text{Sm}$ - $^{142}\text{Nd}$*

The practical utility of Nd isotope studies was first demonstrated in cosmochemical applications. Following the suggestion by Kohman (1954) that  $^{146}\text{Sm}$  might have existed as an extinct radioactivity, searches for  $^{142}\text{Nd}$  anomalies were carried out by Murthy (1964) with negative results and by Notsu et al (1973), who claimed to have found effects in the achondrite Juvinas attributable to  $^{146}\text{Sm}$  decay. More precise work by Lugmair et al (1975a) failed to confirm these results, and placed an upper limit of 0.013 on the  $^{146}\text{Sm}/^{144}\text{Sm}$  ratio at the time of solidification. The actual  $^{146}\text{Sm}/^{144}\text{Sm}$  determined by a best fit line to their data, using Equation (3), was  $0.0054 \pm 0.0072$ , indistinguishable from zero. Subsequently, Lugmair & Marti (1977) measured  $^{142}\text{Nd}/^{144}\text{Nd}$  in mineral separates from the unusual achondrite Angra dos Reis, and found a barely resolvable effect from  $^{146}\text{Sm}$  decay. Their results are plotted on a  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  evolution diagram in Figure 3; the slope of the best fit line (Equation 3) corresponds to an initial  $^{146}\text{Sm}/^{144}\text{Sm}$  of  $0.0047 \pm 0.0023$ , in agreement with their Juvinas data. Thus  $^{146}\text{Sm}$  may be tentatively added to the small list of extinct radioactivities for which actual evidence has been obtained.

### *$^{147}\text{Sm}$ - $^{143}\text{Nd}$ Dating of the Moon and Meteorites*

The Nd measurements of Notsu et al (1973) on Juvinas allowed them to calculate an isochron age of  $4.3 \pm 2.5$  ( $2\sigma$ ) G.y. for this meteorite. Because of the long  $^{147}\text{Sm}$  half-life and the limited spread in Sm/Nd obtainable from mineral separates, very precise measurements of  $^{143}\text{Nd}/^{144}\text{Nd}$  are required to closely define an age. The more precise Juvinas data obtained by Lugmair et al (1975a) enabled them to define an age of  $4.56 \pm 0.08$  G.y., with a corresponding initial  $^{143}\text{Nd}/^{144}\text{Nd}$  of  $0.50677 \pm 0.00010$ . This work

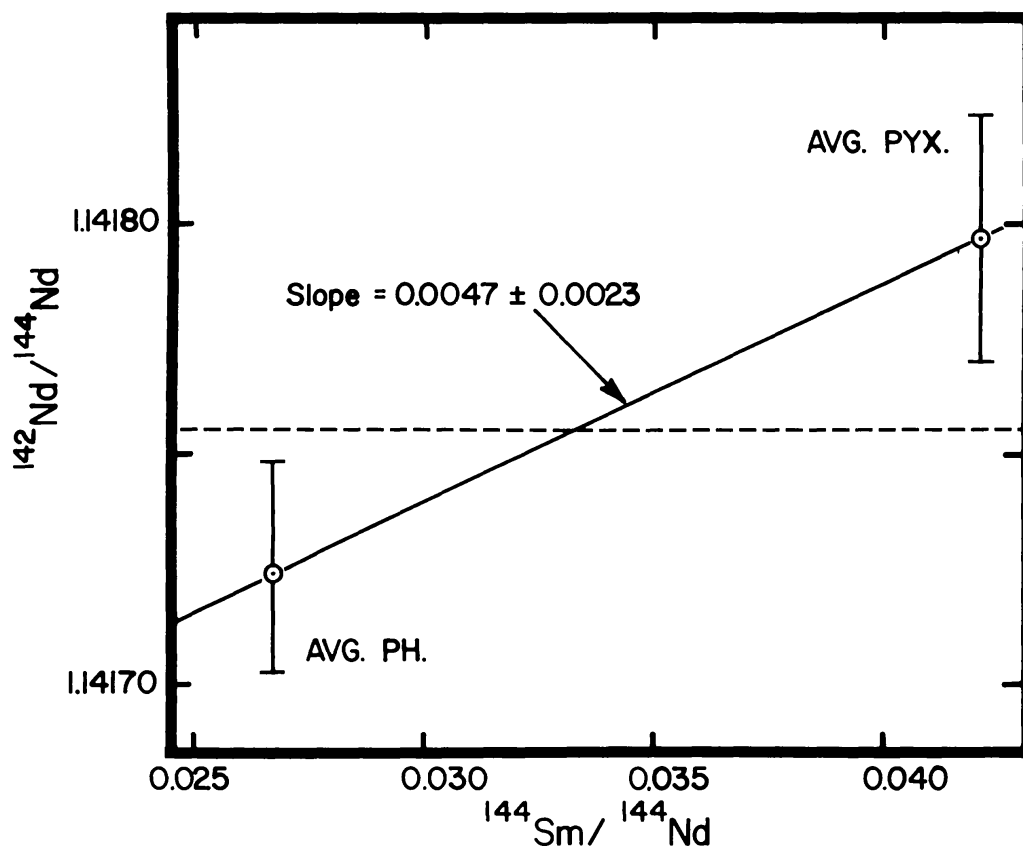


Figure 3 Plot of  $^{142}\text{Nd}/^{144}\text{Nd}$  versus  $^{144}\text{Sm}/^{144}\text{Nd}$  for phosphate and pyroxene components from the Angra dos Reis achondrite (after Lugmair & Marti 1977). The slope of the line corresponds to the  $^{146}\text{Sm}/^{144}\text{Nd}$  ratio in Angra dos Reis at the time of its formation and is significantly greater than zero attesting to the former existence of  $^{146}\text{Sm}$  in the solar system.

demonstrated conclusively that Sm-Nd dating was capable of precision comparable to that obtainable from Rb-Sr.

The Sm-Nd and Rb-Sr systems have proven complementary in many areas of application. In the case of the meteorites, achondrites are very difficult to date by Rb-Sr because of their low Rb-Sr ratios, but lend themselves readily to Sm-Nd dating. (Chondrites, on the other hand, have been dated by Rb-Sr, but their low REE contents make Sm-Nd dating more difficult.) So a new class of meteorites was opened to chronologic studies, and subsequent to Juvinas several other achondrites (e.g. Figure 4) have been dated by Sm-Nd internal isochrons (Lugmair & Scheinin 1975, Lugmair & Marti 1977, Unruh et al 1977, Nakamura et al 1977).

The ages obtained range from 4.55–4.60 G.y. except that of Stannern, which may be slightly disturbed and yields an age of  $4.48 \pm 0.07$  G.y. (Lugmair & Scheinin 1975). These ages are in excellent agreement with U-Pb dates on achondrites (e.g. Unruh et al 1977, Wasserburg et al 1977)

and delimit the time of achondrite formation much more narrowly than Rb-Sr studies (Papanastassiou & Wasserburg 1969, Birck & Allègre 1978). The broader significance of the Sm-Nd studies of meteorites, however, has been in establishing the initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of solar system material, a parameter of central importance in the application of the analysis of Nd isotopes to problems of planetary evolution. The most precisely determined initial Nd for an achondrite is that for Angra dos Reis (Lugmair & Marti 1977; Figure 4), with a value of  $0.50682 \pm 5$ , but there is agreement among all initial values within their respective errors. This initial value assumes the importance for Nd isotope systematics that the achondritic initial  $^{87}\text{Sr}/^{86}\text{Sr}$  (BABI; Papanastassiou & Wasserburg 1969) has for Sr. From it, a model age can be derived for any sample of known  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$ , or the time-integrated Sm/Nd ratio required to produce the present  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio can be calculated. Extensive use of these concepts will be made in the discussion of terrestrial Sm-Nd work.

The dating of lunar samples was another early application of Nd isotope systematics (Lugmair et al 1975b). Lunar samples have been intensively

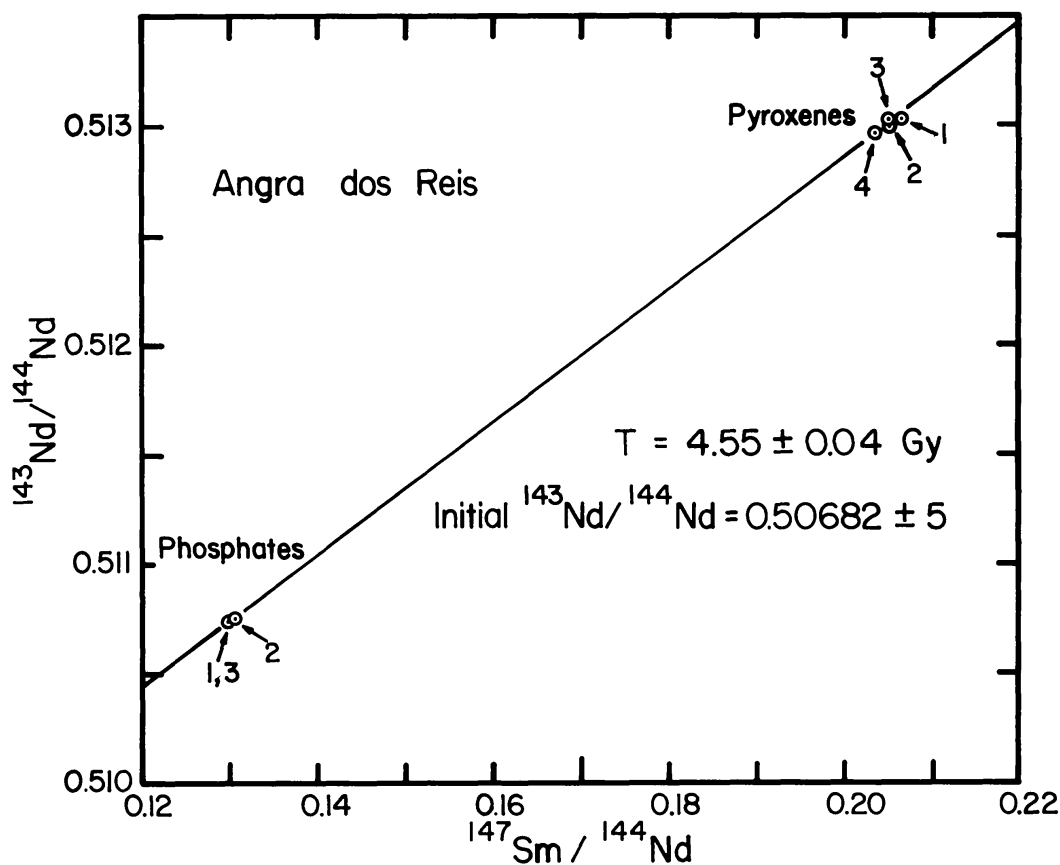


Figure 4 Sm-Nd evolution diagram for separated components of the achondrite Angra dos Reis (after Lugmair & Marti 1977).

studied, and are amenable to dating by Sm-Nd, Rb-Sr, K-Ar, and U-Th-Pb, and so offer a potential testing ground for comparison of ages and isotopic systematics in general. Only limited comparisons are available to date, however, and while Rb-Sr and Sm-Nd ages have been found to agree well in most cases (Nakamura et al 1976, Nakamura et al 1977, Papanastassiou et al 1977), a considerable discrepancy has appeared with sample 76535. This is a troctolite from the Apollo 17 site that has been dated by Rb-Sr (Papanastassiou & Wasserburg 1976) and Sm-Nd (Lugmair et al 1976). The puzzling feature is that the Rb-Sr age ( $4.61 \pm 0.07$ ) is older than the Sm-Nd age ( $4.26 \pm 0.06$ ; Figure 5), despite the fact that experience with terrestrial rocks has shown the Sm-Nd system to be much less readily disturbed by metamorphism than the Rb-Sr system (see discussion below).

Initial  $^{143}\text{Nd}/^{144}\text{Nd}$  values for lunar samples have been used to understand the Sm/Nd fractionations undergone by lunar source areas prior to formation of the rocks. The difficulties of this approach are greater than in the case of Rb-Sr because of the much smaller fractionations of Sm/Nd that are encountered and because of the greater extrapolation normally required to obtain initial Nd values. Nevertheless it appears clear that the initial  $^{143}\text{Nd}/^{144}\text{Nd}$  for the moon is similar to that for the

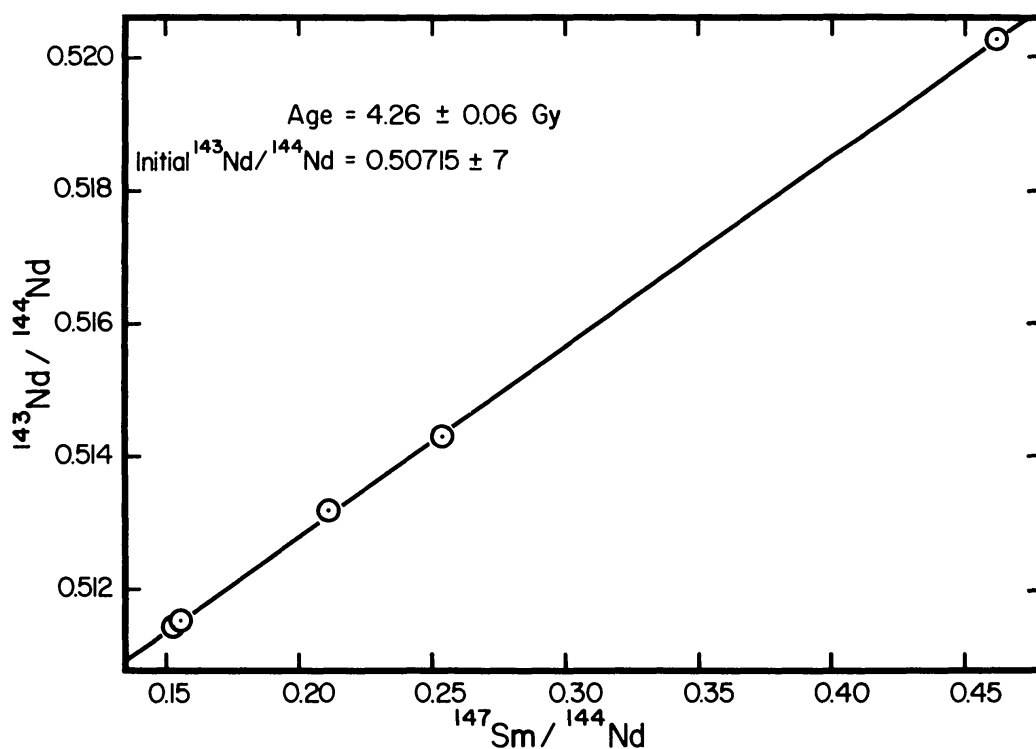


Figure 5 Sm-Nd evolution diagram for separated components of a lunar troctolite returned by the Apollo 17 mission (after Lugmair et al 1976).

achondrites, and that the bulk moon may have a Nd evolution comparable to the achondrites (i.e. a similar initial Nd and Sm/Nd ratio, the latter in turn equivalent to the chondritic ratio). There is some evidence for differential evolution of crust and mantle, with Sm/Nd ratios lower and higher respectively than chondritic since some time early in lunar history (Lugmair & Marti 1978).

Cosmochemistry has not only provided the first application of the analysis of Nd isotopes but also has provided the framework within which the extensive Nd studies that have been made on terrestrial samples can be interpreted in terms of the broader processes of planetary formation and evolution.

## GEOCHRONOLOGICAL APPLICATIONS

Subsequent to the application of the  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  decay scheme to extra-terrestrial materials by Lugmair and co-workers, others have successfully applied the scheme to the dating of Archaean (> 2.5 G.y.) terrestrial rocks. Dating of such materials using alternative parent-daughter systems such as Rb-Sr has frequently been hampered by post-crystallization alteration and metamorphism leading to the differential movement of parent and daughter isotopes. Thus temporal relationships between the various components of Archaean terrains such as the granitic-gneisses and greenstone belts, which are usually equivocal on structural grounds, have not always been readily resolved using Rb-Sr and U-Pb methods.

In marked contrast to the modification of alkali and alkaline earth element abundances during post-crystallization alteration, the rare earths seem to be comparatively unaffected by such processes (Herrman et al 1974, Kay et al 1970, Smewing & Potts 1976, O'Nions & Pankhurst 1976, Frey et al 1968, O'Nions et al 1977). This point is well illustrated by Sm-Nd ages obtained thus far on Archaean rocks. At the time of writing, four Sm-Nd whole-rock isochrons have been determined on Archaean rocks at the Lamont-Doherty Geological Observatory (Hamilton et al 1977, 1978a,b,c). These studies were intended both to assess the value of the Sm-Nd method for dating Archaean basic and acid rocks and to resolve some important geochronological problems.

Specifically the following have been dated:

(a) Rhodesian greenstone belts

Age =  $2.64 \pm 0.14$  G.y.,  $I = 0.50919 \pm 18$  (Hamilton et al 1977);

(b) Isua supracrustals, West Greenland

Age =  $3.770 \pm 0.042$  G.y.,  $I = 0.507831 \pm 46$  (Hamilton et al 1978a);

(c) Onverwacht Volcanics, Southern Africa

Age =  $3.54 \pm 0.03$  G.y.,  $I = 0.50809 \pm 4$  (Hamilton et al 1978c);

(d) Lewisian gneisses, Scotland

Age =  $2.92 \pm 0.05$  G.y.,  $I = 0.508959 \pm 49$  (Hamilton et al 1978b).

A detailed discussion of these results is not entered into at this juncture; however, the considerable advantages of Sm-Nd whole-rock dating compared with other whole-rock methods such as Rb-Sr, U-Pb, and Pb-Pb

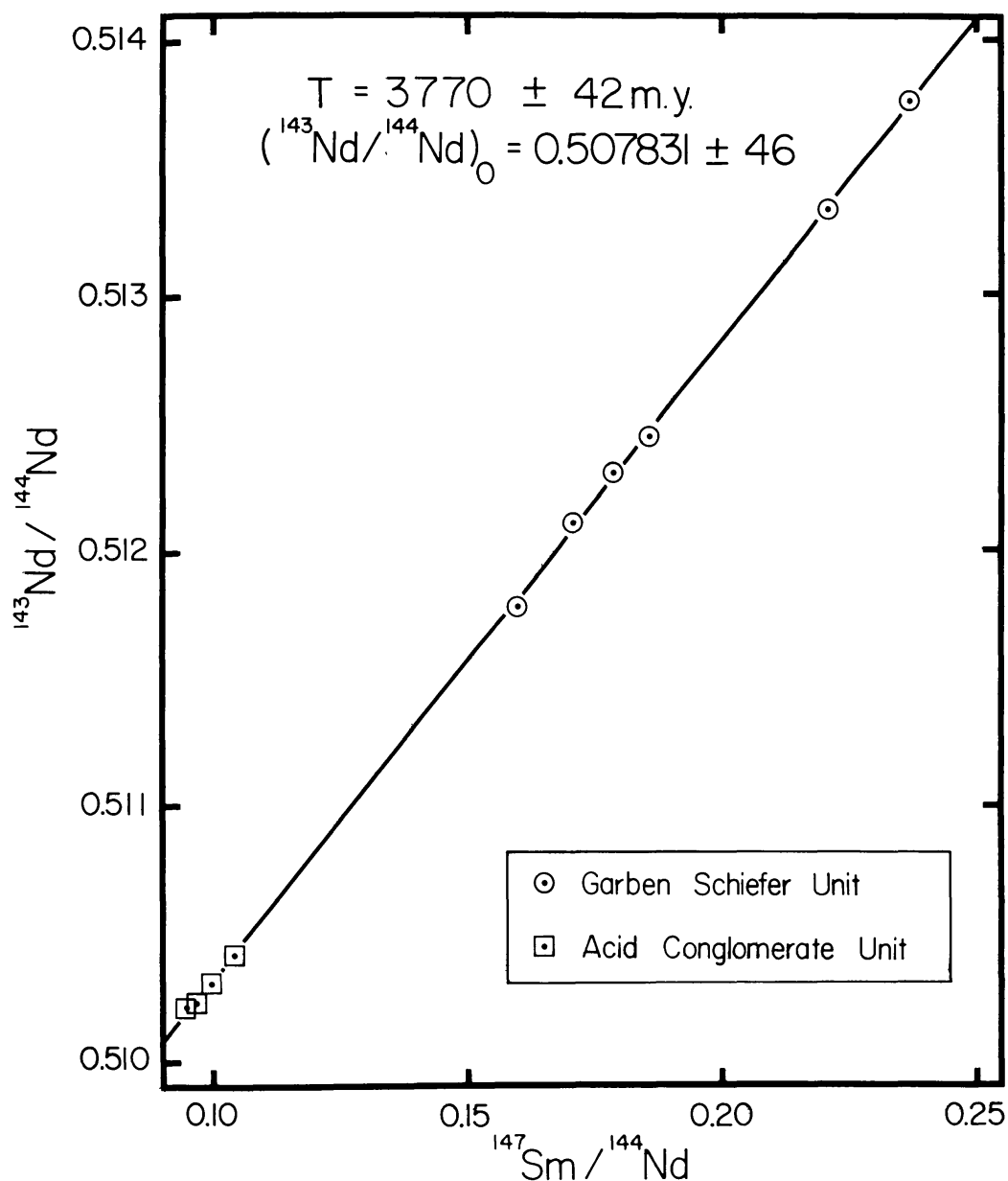


Figure 6 Sm-Nd evolution diagram for acid (conglomerate unit) and basic (garben schiefer) metavolcanics from the Isua supracrustals, West Greenland (after Hamilton et al 1978a).

is illustrated with respect to the results obtained on the Isua supracrustals and the Onverwacht Volcanics.

The Isua area of West Greenland contains the oldest known terrestrial rocks. Sm-Nd data for samples from the Isua supracrustal succession (the acid conglomerate and basic garben schiefer units) are plotted on a Sm-Nd evolution diagram in Figure 6. The age obtained ( $3.77 \pm 0.04$  G.y.) is in agreement with the results obtained from zircons (Baadsgaard 1973, Baadsgaard, Lambert & Krupicka 1976, Michard-Vitrac et al 1977) that Amitsoq tonalitic gneisses were formed about 150 m.y. after the deposition and metamorphism of the supracrustal succession at Isua. In this respect the Sm-Nd result is less equivocal than the available Rb-Sr and Pb-Pb whole-rock ages (Moorbath et al 1973, 1975, 1977), which are less precise.

Attempts to date the Onverwacht Volcanic series of Southern Africa provide a further comparison of the application of the Rb-Sr and Sm-Nd systems. A comparatively well-preserved komatiite yielded an internal Rb-Sr isochron age of  $3.5 \pm 0.2$  G.y. (Jahn & Shih 1974). Highly scattered data obtained on ultrabasic and basic whole-rock samples and acidic

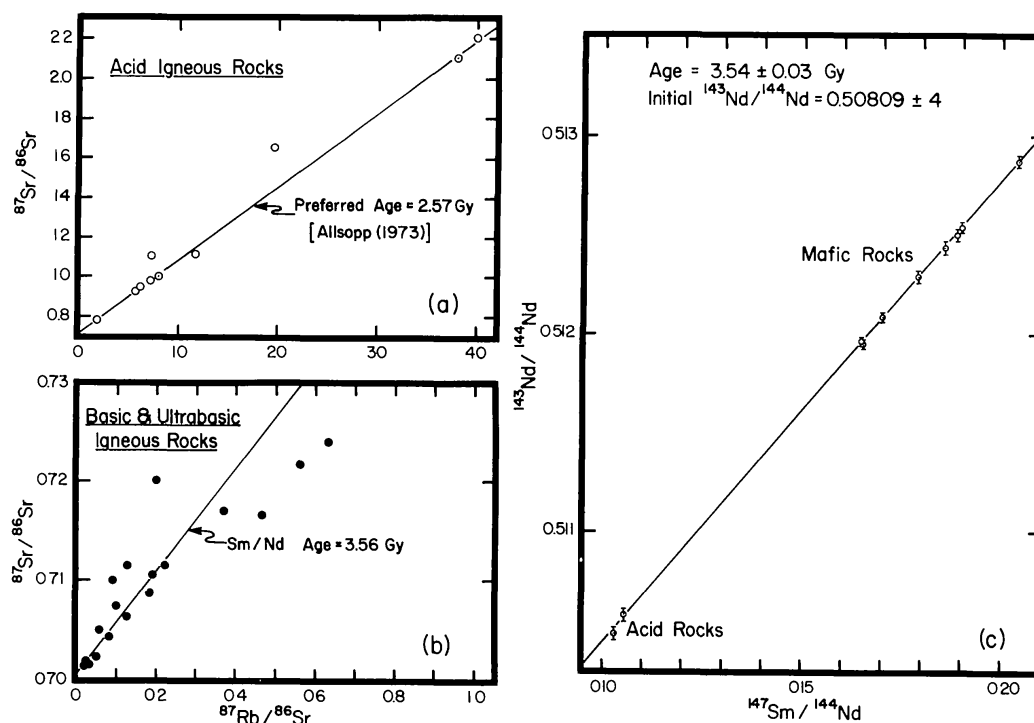


Figure 7 Comparison of Rb-Sr and Sm-Nd evolution diagrams for the Onverwacht Volcanics. (a) Rb-Sr evolution diagram for basic and ultrabasic samples of the Onverwacht Volcanics. Data from Allsopp et al (1973) and Jahn & Shih (1974). (b) Rb-Sr evolution diagram for acid samples of the Onverwacht Volcanics. Data sources as in (a). (c) Sm-Nd evolution diagram for ultrabasic, basic, and acid samples of the Onverwacht Volcanics (Hamilton 1978c).



volcanics suggest that Rb-Sr redistribution occurred about 2.6 G.y. ago (Figure 7a and b). In marked contrast Sm-Nd data for ultrabasic, basic, and acid volcanics yield a whole-rock isochron age of  $3.54 \pm 0.03$  G.y. and an initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  $0.50908 \pm 4$ , with no indication of younger events (Figure 7c).

It can be seen, therefore, that although limited Sm/Nd fractionation and the long half-life of  $^{147}\text{Sm}$  presently limit the use of the Sm-Nd system for dating more recent samples, it does provide a useful tool for the dating of ancient rocks, which almost inevitably have suffered alteration since their formation.

## EVOLUTION OF THE EARTH'S CRUST AND MANTLE

The Earth has evolved into two distinct reservoirs of rare earth elements: the mantle (upper and lower) and the continental crust. The continental crust is enriched in light REE relative to the cosmic abundances (Table 2) whereas the suboceanic mantle has much lower overall REE abundances and is commonly depleted in light REE.

From Rb-Sr and U-Pb isotope investigations it has been demonstrated that the continental crust is a secondary geological feature that has developed in a quasi-continuous manner from about 3.8 G.y. ago (see reviews by Moorbath 1975, O'Nions & Pankhurst 1978, and McCulloch & Wasserburg 1978, for example). A fuller understanding of the complementary nature of these two reservoirs and their time-dependent changes has become possible as a result of Nd isotope studies of terrestrial rocks (see O'Nions et al 1979a,b for additional review of this subject).

DePaolo & Wasserburg (1976a) showed that the initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios computed for a number of well-dated single whole-rock samples

**Table 2** Sm and Nd abundance data

	Sm (ppm)	Nd (ppm)	Sm/Nd (atomic)
CI chondrite average <sup>a</sup>	0.154	0.4738	0.31
Bulk Earth (Model 1) <sup>b</sup>	0.32	0.97	0.31
Bulk Earth (Model 2) <sup>c</sup>	0.74	2.2	0.31
Continental crust <sup>d</sup>	3.7	16	0.22

<sup>a</sup> Evensen et al 1978.

<sup>b</sup> Assumes Earth has solar REE/U ratios and Earth's heat loss equals heat production (after O'Nions et al 1978a).

<sup>c</sup> Assumes solar Ca/U and REE/U ratios for Earth (O'Nions et al 1979a).

<sup>d</sup> Assumes crust has average composition of island arcs (after Taylor 1977).

ranging in age from 3.6 G.y. to approximately 1 G.y. were derived from a reservoir having  $\text{Sm}/\text{Nd} \approx 0.308$  (the chondrite average value of Nakamura et al 1976). Whole-rock Sm-Nd isochrons obtained on the Isua meta-volcanics, West Greenland (Figure 6), the Onverwacht lavas, Southern Africa (Figure 7), and Bulawayan volcanics, Rhodesia (Hamilton et al 1977), have initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios that are consistent with DePaolo & Wasserburg's (1976a) claim (Figure 8). If it is assumed that the Earth developed from material that had a  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio identical to Angra dos Reis at the time of its formation 4.55 G.y. ago (Figure 4), then the initial ratios of the Isua and Onverwacht volcanics provide independent estimates of the bulk Earth Sm/Nd ratio equal to  $0.306 \pm 6$  and  $0.298 \pm 4$  respectively for the period between 4.55 and their formation. Because only small amounts of the Earth's total inventory of REE had been partitioned into stable continental crust by about 3.5 G.y., these Archaean meta-volcanics should provide a reliable estimate of Sm/Nd in the bulk Earth.

Development of continental crust has increased the Sm/Nd ratio of the residual mantle and *in toto* it should have a  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio greater

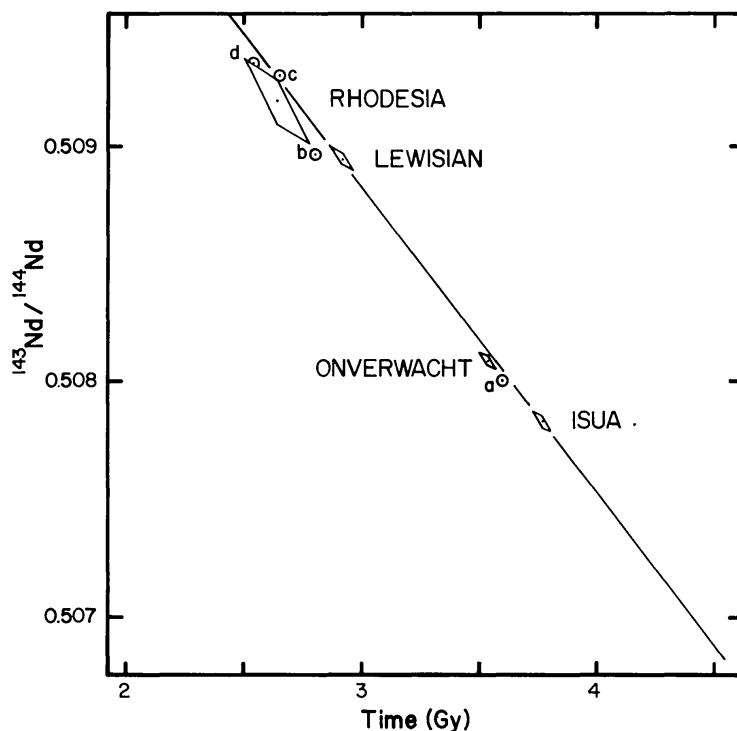


Figure 8 Initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of Archaean rocks. The ages and initial ratios of the Isua, Onverwacht, Lewisian, and Rhodesia samples were determined from Sm-Nd whole-rock isochrons (Hamilton et al 1977, 1978a,b,c). The initial ratios of the Amitsoq gneiss, Great Dyke, and Fiskenaesset anorthosite were computed from single whole-rock analyses using ages derived by other parent-daughter systems (DePaolo & Wasserburg 1976a). Collectively these data are consistent with a chondritic Sm/Nd ratio for the Earth: the line plotted is for  $\text{Sm}/\text{Nd} = 0.308$ .

than the bulk Earth value (estimated at 0.51262). The range of  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios in oceanic basalts (Figure 9) indicates that the partition of REE into the crust has not had a uniform effect on the mantle; various segments have made contributions of differing magnitudes and at different times.

The Nd-isotopic evolution of the continental crust contrasts markedly with that of the suboceanic mantle, as illustrated by the 3.6 G.y. Amitsoq gneisses from West Greenland (Figure 10). The Amitsoq gneisses, like acid gneisses in general, are light REE enriched, and have average Sm/Nd and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios considerably lower than the bulk Earth, at the present day (Figure 9). McCulloch & Wasserburg (1978) computed the times of separation of crustal material from a chondritic reservoir using measurements of Sm/Nd ratios and Nd-isotope compositions obtained on composite gneiss samples from Precambrian shields. The ages obtained from these model calculations are in good agreement with other geochronological estimates of the age of the shield segments. The corollary of this observation is that the large areas of shield represented by these composite samples were generated from reservoirs that evolved with chondritic Sm/Nd ratios. This point is further illustrated by the age and initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio obtained for the Lewisian gneisses of northwestern Scotland (Figure 8).

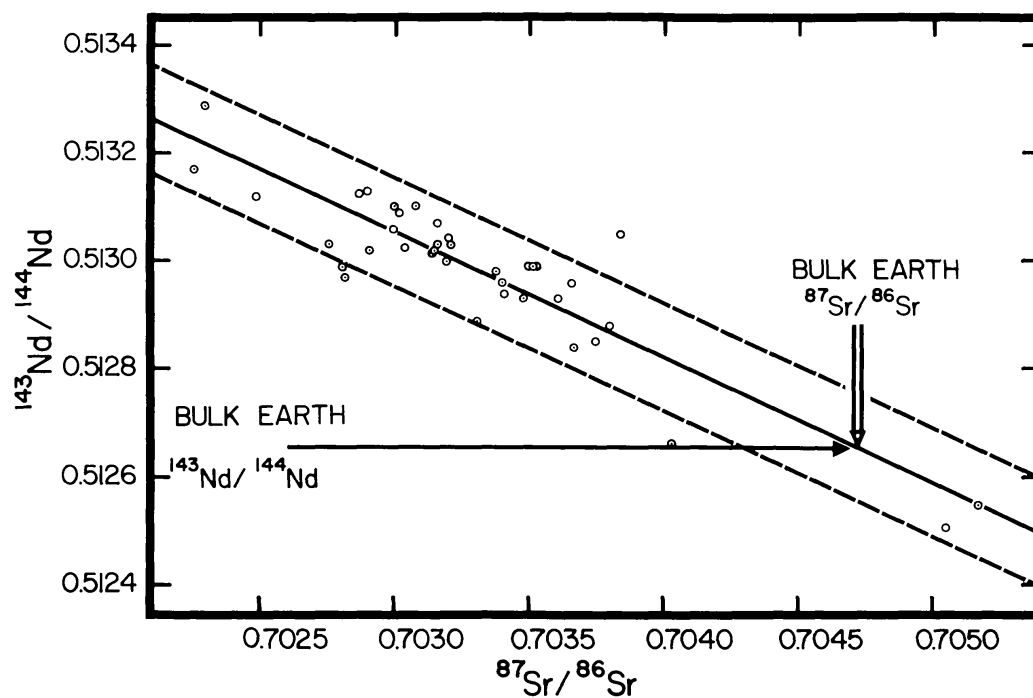


Figure 9  $^{143}\text{Nd}/^{144}\text{Nd}$  versus  $^{87}\text{Sr}/^{86}\text{Sr}$  for unaltered oceanic ridge and oceanic island basalts. The dashed lines encompass 90% of the data. The present-day bulk Earth  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of about 0.7047 can be deduced from the intersection of the present-day bulk Earth  $^{143}\text{Nd}/^{144}\text{Nd}$  (0.51265) with the best-fit line (solid line) of the oceanic data. Data from DePaolo & Wasserburg (1976a) and O'Nions et al (1977).

The apparent uniformity of Sm/Nd in the mantle reservoir from which continental crust was extracted during the Archaean is perhaps surprising in view of the fact that the reservoir must change in response to continental

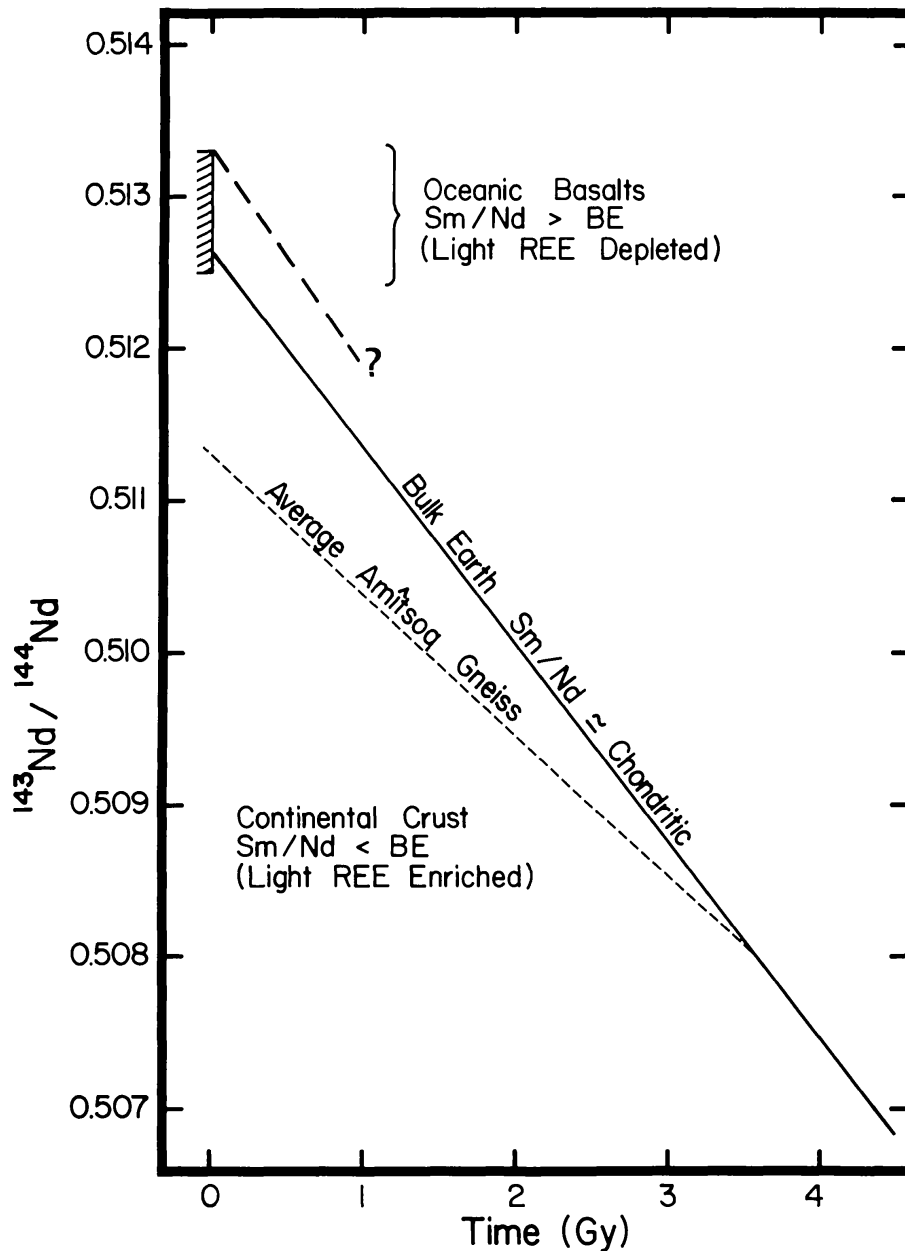


Figure 10 Evolution of  $^{143}\text{Nd}/^{144}\text{Nd}$  in the Earth's crust and mantle. The bulk Earth is assumed to have a Sm/Nd ratio of 0.308 (see Figure 8) and to have developed from material with an initial  $^{143}\text{Nd}/^{144}\text{Nd} = 0.50682$  identical to that of Angra dos Reis 4.55 G.y. ago (Lugmair & Marti 1977), such that its present-day  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio is predicted to be 0.51262. The range of Recent oceanic basalts is indicated and they are seen to be largely derived from source regions having higher Sm/Nd than the bulk Earth ( $\equiv$  light REE depleted). The continental crust has evolved with a Sm/Nd ratio less than the bulk Earth ( $\equiv$  light REE enriched) as illustrated for 3.7 G.y. Amitsoq gneiss from West Greenland (average Sm/Nd ratio computed from O'Nions & Pankhurst 1974).

growth. This apparent uniformity may reflect the combined effects of large reservoir size (e.g. whole mantle) and uniform extraction of REE in the Archaean such that the change in Sm/Nd in the whole mantle was insignificant. Alternatively the uniformity may reflect isolation of mantle source regions such that they escaped earlier fractionation events. Differentiating between these two possibilities presents an intriguing problem for the future.

## Nd ISOTOPES AS TRACERS IN PETROGENESIS

Because the continental crust has grown by nonuniform extraction of REE from the mantle and has evolved with a markedly lower Sm/Nd ratio, there is a diversity of  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios in the Earth which serve as powerful tracers of provenance in various petrogenetic problems. Some instances in which the determination of Nd-isotope compositions has helped elucidate the petrogenesis of terrestrial rocks are reviewed here.

### *Petrogenesis of Oceanic Basalts*

Nd-isotope compositions of oceanic basalts exhibit a significant range and have now been investigated quite extensively. Although Nd-isotope compositions alone can place important constraints on the petrogenetic relationships of oceanic basalts, they have been particularly useful where considered in conjunction with  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. Thus in the ensuing discussion the constraints imposed by both  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are reviewed. Sr- and Nd-isotope data published by DePaolo & Wasserburg (1976a,b), Richard et al (1976), O'Nions et al (1977), and Hawkesworth et al (1977) are summarized in Figure 9. The most striking and noteworthy features of these data are the strong anticorrelation of  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, the generally higher  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of submarine ocean ridge basalts and the paucity of oceanic basalts with  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios less than the predicted bulk Earth value of 0.5126. These features suggest that *virtually all* oceanic basalts have been generated from mantle source regions with time-integrated Sm/Nd ratios greater than the bulk Earth value (corresponding to light REE depletion). Because submarine ocean ridge basalts are more voluminous than ocean island basalts and also have higher  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios, only trivial amounts of the suboceanic upper mantle can be in an undifferentiated or pristine condition. The anticorrelation of  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios requires that Rb/Sr and Sm/Nd have fractionated coherently during the differentiation and evolution of the mantle, and leads to an estimate of the Rb/Sr ratio in the bulk Earth as indicated in Figure 9. DePaolo & Wasserburg (1976b) and O'Nions et al (1977) independently estimated this ratio to be approximately 0.03.

The genetic relationships of oceanic island and ridge basalts can be conveniently made in reference to the Rb/Sr and Sm/Nd ratios of the bulk Earth utilizing the values  $\Delta\text{ND}$  and  $\Delta\text{SR}$ . These were defined by O'Nions et al (1978a) and Carter et al (1978a) as follows:

$$\Delta\text{ND} = \frac{(^{147}\text{Sm}/^{144}\text{Nd})_{\text{SS}} - (^{147}\text{Sm}/^{144}\text{Nd})_{\text{BE}}}{(^{147}\text{Sm}/^{144}\text{Nd})_{\text{BE}}} \cdot 10^2$$

where the subscripts BE and SS refer to the bulk Earth and single stage values respectively,

$$(^{147}\text{Sm}/^{144}\text{Nd})_{\text{SS}} = \frac{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{M}} - I}{(e^{\lambda t} - 1)}$$

where  $I$  is the assumed initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of terrestrial material 4.55 G.y. ago (Lugmair & Marti 1977), and for a Recent basalt  $t = 4.55$  G.y.

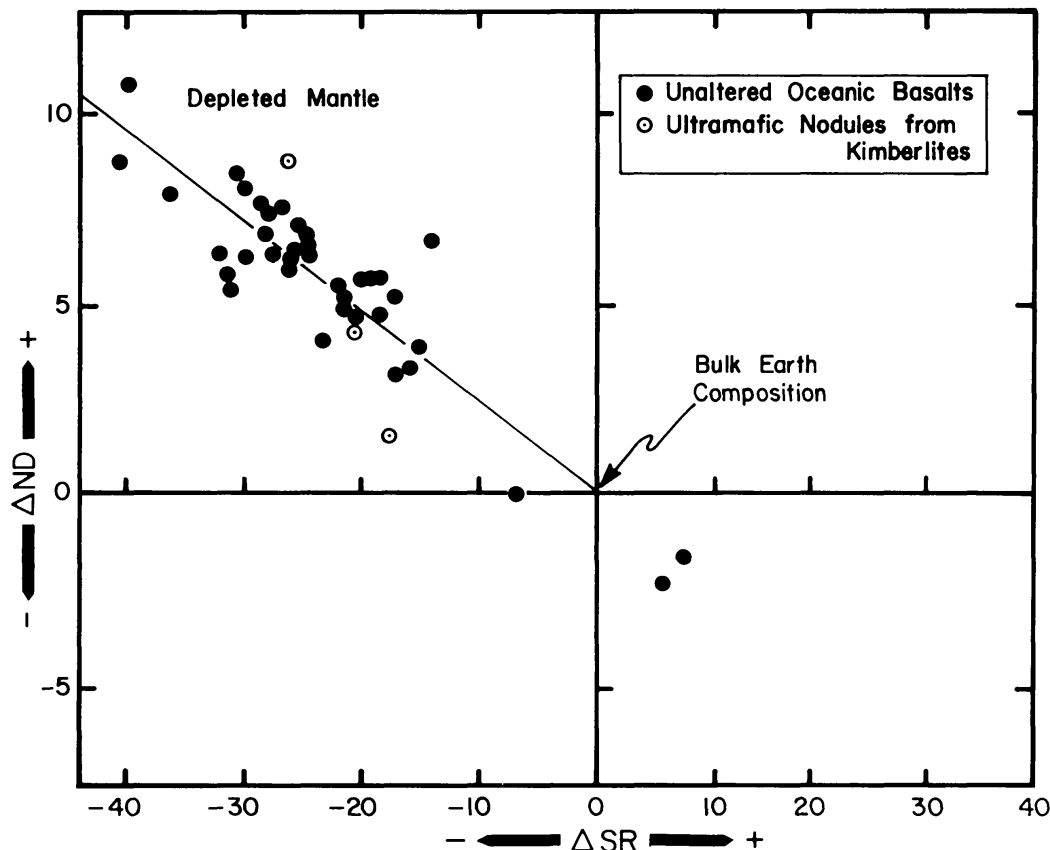


Figure 11 Plot of  $\Delta\text{ND}$  and  $\Delta\text{SR}$  for Recent uncontaminated oceanic basalts and garnet lherzolite xenoliths from South African kimberlites. See text for definitions of  $\Delta\text{ND}$  and  $\Delta\text{SR}$ . The  $\Delta\text{ND}$  and  $\Delta\text{SR}$  parameters of the garnet lherzolites (Thaba Putsoa and Premier) are calculated for their initial  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. All samples plotted fall close to the bulk Earth point or within the  $-\Delta\text{SR}$ ,  $+\Delta\text{ND}$  quadrant, which indicates that they were derived from depleted source regions. Data from O'Nions et al (1977, and Lamont-Doherty Geological Observatory, unpublished).

$\Delta\text{ND}$  and  $\Delta\text{SR}$  values for Recent oceanic basalts are shown in Figure 11. A basalt generated from undifferentiated mantle will have  $\Delta\text{ND} = \Delta\text{SR} = 0$  and plot at the origin of Figure 11. The majority of the basalts have negative  $\Delta\text{SR}$  and positive  $\Delta\text{ND}$  values consistent with their time-integrated or single stage Rb/Sr and Sm/Nd ratios, which are lower and higher respectively than the bulk Earth values. It is immediately clear from this diagram that very few basalts have been generated from undifferentiated mantle.

### *Continental Basalts and Subcontinental Mantle*

Interpretations of the isotope geochemistry of continental basalts are frequently hampered by uncertainties concerning the extent of contamination by continental crust. Some recent interpretations of their Rb-Sr isotope geochemistry for example imply that contamination effects are negligible (Brooks et al 1976, Brooks & Hart 1978), whereas Carter et al (1978b) have claimed on the basis of  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios that some Tertiary basalts from northwestern Scotland have been severely contaminated. In favorable circumstances crustal contamination can be elegantly demonstrated in continental basalts as indicated in Figure 12. In this diagram the  $\Delta\text{ND}$  and  $\Delta\text{SR}$  values for 2.9 G.y. Lewisian granulite and amphibolite facies basement in northwestern Scotland are illustrated. It is noteworthy that the range of  $\Delta\text{SR}$  values is much larger than the range of  $\Delta\text{ND}$  values in the Lewisian, reflecting the wide variation of Rb/Sr ratios between granulites and amphibolites and the more similar Sm/Nd ratios. Also illustrated in Figure 12 is the area occupied by oceanic basalts, and thus by inference suboceanic upper mantle. The contrasting isotopic evolution of continental crust and mantle alluded to previously in this article is well illustrated in this diagram. Some Tertiary basalts from northwestern Scotland (e.g. Mull) have  $\Delta\text{ND}$  and  $\Delta\text{SR}$  values similar to Recent oceanic basalts, while others such as Skye, Eigg, and Muck basalts are markedly displaced from the oceanic basalt region towards the areas occupied by the Lewisian basement. Carter et al (1978b) have claimed on the basis of this evidence that these northwestern Scotland basalts have been contaminated by Lewisian basement. Volcanics from Roccamonfina, Italy (Carter et al 1978a), are shown for comparative purposes in Figure 12, and at this stage the possibility that the  $\Delta\text{ND}$  and  $\Delta\text{SR}$  values of these volcanics reflect some form of enriched mantle and/or have been contaminated by continental crust cannot be resolved. Granitic and gabbroic intrusives from northwestern Scotland have  $\Delta\text{ND}$  and  $\Delta\text{SR}$  values suggesting that Lewisian amphibolite facies gneisses are a significant component, which is consistent with previous petrogenetic models (Carter et al 1978b).

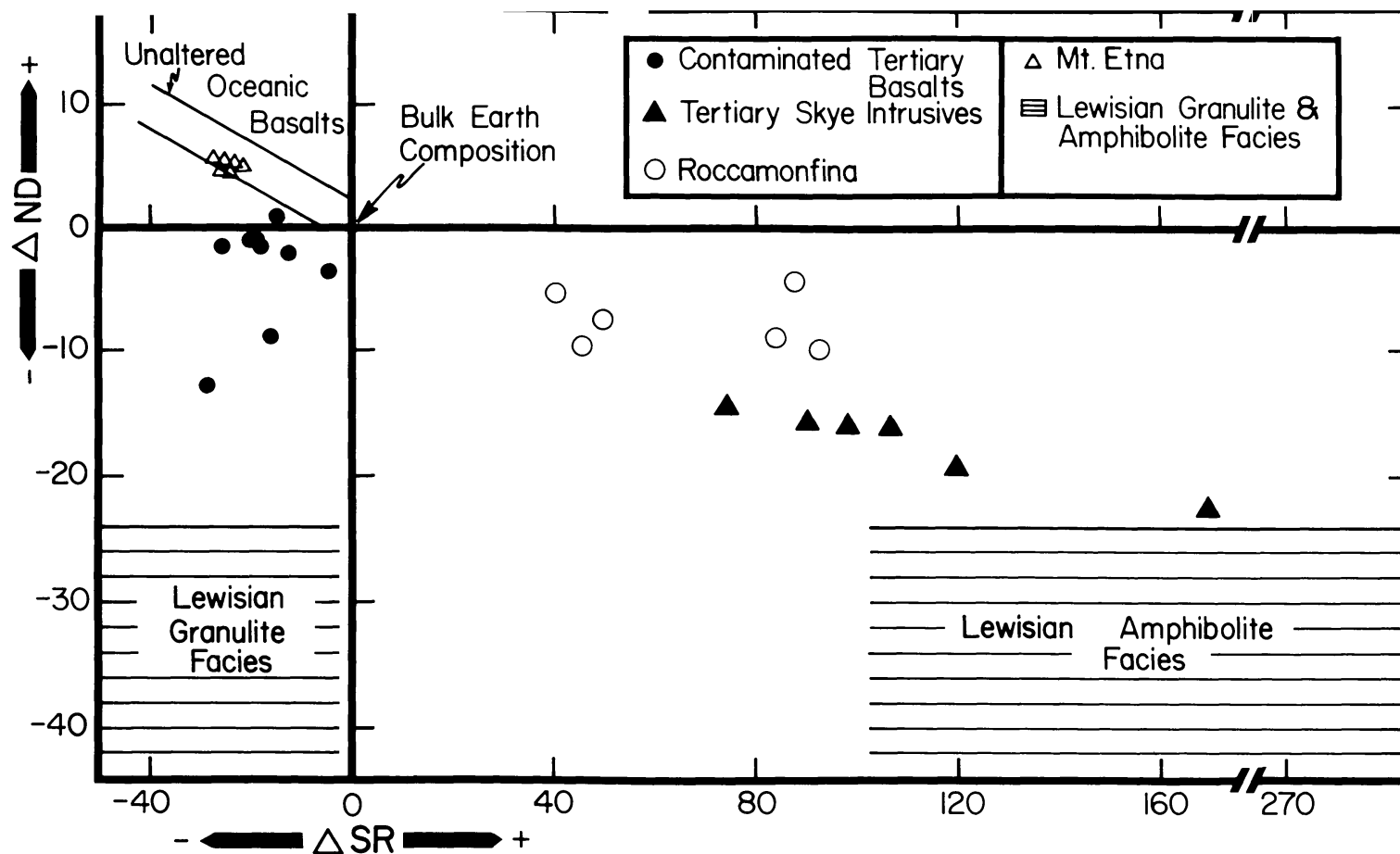


Figure 12  $\Delta$ ND versus  $\Delta$ SR parameters of various continental volcanics and continental basement rocks, illustrating the effects of crustal contamination of mantle-derived magmas. For the definition of the  $\Delta$  parameters, see text. The Lewisian basement of northwestern Scotland has low  $-\Delta$ ND values and a wide range of  $\Delta$ SR values. The granulite facies have  $-\Delta$ SR values and the amphibolite facies have  $+\Delta$ SR values. The unique character of the granulite facies ( $-\Delta$ ND/ $-\Delta$ SR) identifies it as the crustal component that contaminated the Scottish Tertiary basalts, which also fall in the  $-\Delta$ ND/ $-\Delta$ SR quadrant. The Skye intrusives, which fall in the  $-\Delta$ ND/ $+\Delta$ SR quadrant, contain a high proportion of Lewisian amphibolite facies and a small component of mantle-derived magma.

The Etna (Sicily) basalts fall on the unaltered oceanic basalt trend in the  $+\Delta$ ND/ $-\Delta$ SR quadrant and are therefore considered to be uncontaminated products of depleted mantle. The Roccamonfina (Italy) volcanics fall in the  $-\Delta$ ND/ $+\Delta$ SR (enriched in Rb and light REE), but it is not possible to ascertain whether they have been contaminated by continental crust or are the products of enriched mantle. Data from Carter et al (1978a,b) and Hamilton et al (1978b).



The possible contamination of continental basalts, so clearly evident in the case of the northwestern Scotland basalts, confuses attempts to compare the evolutionary histories of suboceanic and subcontinental mantle. An alternative approach to the investigation of subcontinental mantle is via the study of mantle-derived lherzolites transported to the surface as xenoliths in kimberlites and other volcanics. There are comparatively few relevant Nd-isotope data, but those that are available are plotted in Figure 11. The particular samples are garnet lherzolites from Southern African kimberlites that range in age from 1.1 G.y. to 60 M.y. These all have  $\Delta ND$  and  $\Delta SR$  values coincident with those for oceanic basalts, which indicates a similar evolutionary history.

### *Oceanic Ferromanganese Deposits*

There are two broad classes of oceanic ferromanganese deposits, namely the Fe-rich sediments occurring at mid-ocean ridge crests and the manganese nodules more characteristic of the abyssal depths of the oceans.

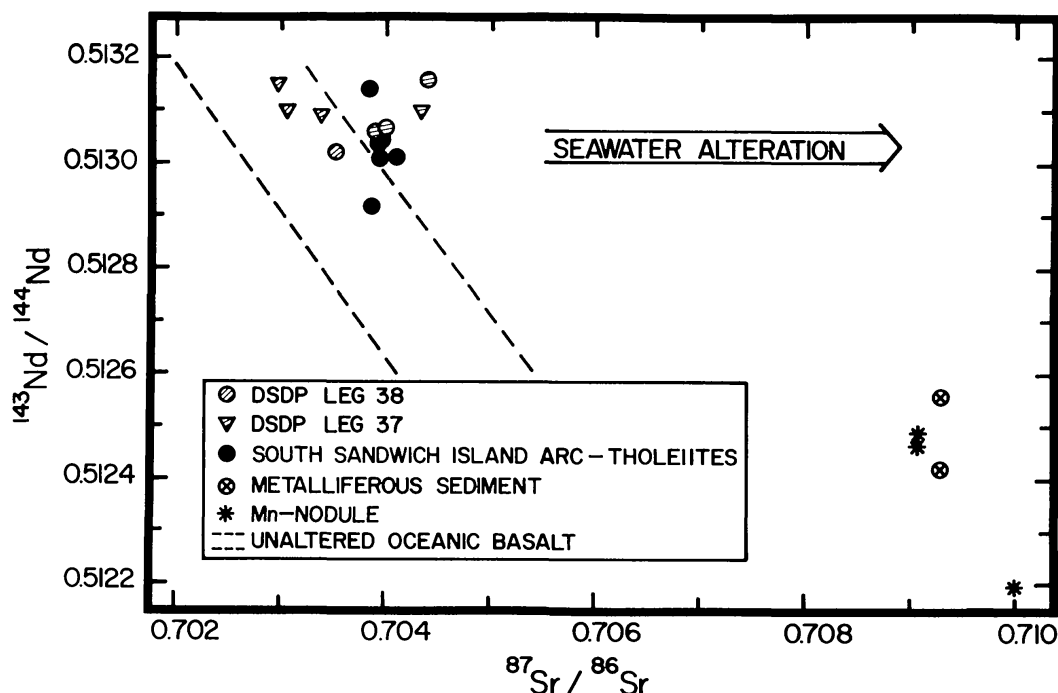


Figure 13 Comparison of  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in unaltered oceanic basalts (dashed lines; see Figure 10), altered ocean floor basalts, and island-arc volcanics with Mn nodules and Fe-rich metalliferous sediments. Alteration of ocean floor basalts increases the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios but has little effect on  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios.  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in Mn nodules and Fe-rich sediments are similar, and require a substantial proportion of both Nd and Sr from a continental source. The isotope composition of island-arc tholeiites suggests that they contain a component of altered ocean floor basalt. Data from DePaolo & Wasserburg (1977), Hawkesworth et al (1977), and O'Nions et al (1978b).

The source of metals in these ferromanganese deposits is a subject of considerable debate; both continental weathering and the basaltic ocean crust feature as possible sources of metals in various hypotheses. Elucidation of the provenance of metals in ferromanganese deposits will require knowledge of the flux for each metal concerned from the continents (via rivers and aerosols) and from the oceanic crust, together with their residence times in the oceans. Clearly this is a long-term goal, however some progress has been made in elucidating the provenance of Nd in ferromanganese deposits from measurements of  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios (O'Nions et al 1978b), which adds to earlier studies of Sr and Pb isotopes. The  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios obtained by O'Nions et al (1978b) are presented in Figure 13 and compared with the range for unaltered oceanic basalts and ocean floor basalts altered by seawater. The  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of both the manganese nodules and Fe-rich sediments are similar (indicating an apparently homogeneous provenance for Nd), and have lower  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios than ocean floor basalt.

The effect of seawater alteration on the Nd- and Sr-isotope compositions of ocean floor basalts is also indicated in Figure 13. Whereas the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are readily modified by seawater contamination (seawater contains approximately  $8 \times 10^{-6} \text{g.g}^{-1} \text{Sr}$ ), the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios do not appear to be affected, presumably in part because of the substantially lower concentration of Nd in seawater (approximately  $3 \times 10^{-12} \text{g.g}^{-1}$ ). Thus whereas the basaltic ocean crust behaves as a sink for marine Sr (derived largely from the continents) and ultimately cycles it into the mantle, it does not appear to be a substantial sink for Nd. The  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of the manganese nodules suggests that seawater Nd is comparatively well mixed isotopically and has a large component derived from the continents, since the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of the basaltic oceanic crust is about 0.5130.

### *Island-Arc Tholeiites*

Only a few island-arc tholeiite samples have been analyzed for  $^{143}\text{Nd}/^{144}\text{Nd}$  to date (Hawkesworth et al 1977, DePaolo & Wasserburg 1977), and these are shown in Figure 13. The particular samples studied are from the South Sandwich Islands and New Britain, and both areas have samples that plot to the right of the trend defined by unaltered ocean basalts, which suggests that altered ocean floor is a component of their source region.

## CONCLUSIONS

Variations in the isotopic composition of natural Nd have been identified with high-precision solid-source mass spectrometry. These variations

have resulted from the  $\alpha$ -decay of  $^{147}\text{Sm}$  ( $\lambda = 6.54 \times 10^{-12}\text{y}^{-1}$ ),  $^{146}\text{Sm}$  ( $\lambda = 6.93 \times 10^{-9}\text{y}^{-1}$ ), incomplete mixing of r- and s-process Nd isotopes, and fission of natural U. Evidence for incomplete mixing of different Nd isotopes has been obtained from the Allende meteorite, and for the former existence of  $^{146}\text{Sm}$  in the solar system from  $^{142}\text{Nd}$  excesses in the achondrite Angra dos Reis. The Nd isotope fission products of uranium are only known from the highly unusual Oklo natural reactor.

The  $\alpha$ -decay of  $^{147}\text{Sm}$  to  $^{143}\text{Nd}$  has been rapidly exploited as a cosmochronological and geochronological dating tool. It has some advantages over other systems such as Rb-Sr and U-Pb in both the coherence of Sm and Nd in natural fractionation processes, and the favorable abundances of Sm and Nd in some situations where those of Rb and Sr are unfavorable for dating.

In the Earth the isotopic composition of Nd varies both within the mantle and between the continental crust and mantle, and is a valuable indicator of provenance of rare earths in a variety of materials and thus an aid to the elucidating of their petrogenesis. The potential applications of Nd isotopes have still not been fully exploited and to date only a small number of laboratories have participated in their exploitation. Nd-isotope studies will now undoubtedly become a routine technique alongside the more established Rb-Sr and U-Pb investigations as more laboratories join the chase.

#### Literature Cited

- Allsopp, H. L., Viljoen, M. J., Viljoen, R. P. 1973. Strontium isotopic studies of the mafic and felsic rocks of the Onverwacht Group of the Swaziland Sequence. *Geol. Rundsch.* 62: 902
- Baadsgaard, H. 1973. U-Th-Pb dates on zircons from the early Precambrian Amitsoq gneisses, Godthaab District, West Greenland. *Earth Planet. Sci. Lett.* 19: 22-28
- Baadsgaard, H., Lambert, R. St. J., Krupicka, J. 1976. Mineral isotopic age relationships in the polymetamorphic Amitsoq gneisses, Godthaab District, West Greenland. *Geochim. Cosmochim. Acta* 40: 513-27
- Birck, J. L., Allègre, C. J. 1978. Chronology and chemical history of the parent body of basaltic achondrites studied by the  $^{87}\text{Rb}$ - $^{87}\text{Sr}$  method. *Earth Planet. Sci. Lett.* 39: 37-51
- Blake, J. B., Schramm, D. M. 1976. A possible alternative to the r-process. *Astrophys. J.* 209: 846-49
- Brooks, C., Hart, S. R. 1978. Rb-Sr mantle isochrons and variations in the chemistry of Gondwanaland's lithosphere. *Nature* 271: 220-23
- Brooks, C., James, D. E., Hart, S. R. 1976. Ancient lithosphere: Its role in young continental volcanism. *Science* 193: 1086-94
- Burbidge, E. M., Burbidge, G. R., Fowler, W. A., Hoyle, F. 1957. Synthesis of the elements in stars. *Rev. Mod. Phys.* 29: 547-650
- Carter, S. R., Evensen, N. M., Hamilton, P. J., O'Nions, R. K. 1978a. Continental volcanics derived from enriched and depleted source regions: Nd- and Sr-isotope evidence. *Earth Planet. Sci. Lett.* 37: 401-8
- Carter, S. R., Evensen, N. M., Hamilton, P. J., O'Nions, R. L. 1978b. Neodymium and strontium isotope evidence for crustal contamination of continental volcanics. *Science* 202: 743-47
- DePaolo, D. J., Wasserburg, G. J. 1976a. Nd-isotope variations and petrogenetic models. *Geophys. Res. Lett.* 3: 249-52
- DePaolo, D. J., Wasserburg, G. J. 1976b. Inferences about magma sources and mantle structure from variations of  $^{143}\text{Nd}/^{144}\text{Nd}$ . *Geophys. Res. Lett.* 3: 743-46
- DePaolo, D. J., Wasserburg, G. J. 1977. The

- sources of island arcs as indicated by Nd and Sr isotopic studies. *Geophys. Res. Lett.* 41: 465–68
- Evensen, N. M., Hamilton, P. J., O’Nions, R. K. 1978. Rare-earth abundances in chondritic meteorites. *Geochim. Cosmochim. Acta* 42: 1199–1212
- Frey, F. A., Haskin, M. A., Poetz, J. A., Haskin, L. A. 1968. Rare-earth abundances in some basic rocks. *J. Geophys. Res.* 73: 6085–98
- Hamilton, P. J., O’Nions, R. K., Evensen, N. M. 1977. Sm-Nd dating of Archaean basic and ultrabasic volcanics. *Earth Planet. Sci. Lett.* 36: 263–68
- Hamilton, P. J., O’Nions, R. K., Evensen, N. M., Bridgwater, D., Allaart, J. H. 1978a. Sm-Nd isotopic investigations of the Isua supracrustals, West Greenland: implications for mantle evolution. *Nature* 272: 41–43
- Hamilton, P. J., O’Nions, R. K., Evensen, N. M., Turney, J. 1978b. Sm-Nd systematics of Lewisian gneisses: Implications for the origin of granulites. *Nature*. In press
- Hamilton, P. J., Evensen, N. M., O’Nions, R. K., Erlank, A. J., Smith, H. S. 1978c. Sm-Nd dating of Onverwacht Group volcanics, South Africa. *Nature*. In press
- Hawkesworth, C. J., O’Nions, R. K., Pankhurst, R. J., Hamilton, P. J., Evensen, N. M. 1977. A geochemical study of island-arc and back-arc tholeiites from the Scotia Sea. *Earth Planet. Sci. Lett.* 36: 253–63
- Herrmann, A. G., Potts, M. J., Knake, D. 1974. Geochemistry of the rare earth elements in spilites from the oceanic and continental crust. *Contrib. Mineral. Petrol.* 44: 1–16
- Hooker, P., O’Nions, R. K., Pankhurst, R. J. 1975. Determination of rare-earth elements in U.S.G.S. standard rocks by mixed-solvent ion exchange and mass spectrometric isotope dilution. *Chem. Geol.* 16: 189–96
- Jahn, B. J., Shih, C. Y. 1974. On the age of the Onverwacht Group, Swaziland Sequence, South Africa. *Geochim. Cosmochim. Acta* 38: 873–85
- Kay, R., Hubbard, N. J., Gast, P. W. 1970. Chemical characteristics and origins of oceanic ridge volcanics. *J. Geophys. Res.* 75: 1585–1613
- Kohman, T. P. 1954. Geochronological significance of extinct natural radioactivity. *Science* 119: 851–52
- Loubet, M., Allègre, C. J. 1977. Behavior of the rare earth elements in the Oklo natural reactor. *Geochim. Cosmochim. Acta* 41: 1539–48
- Lugmair, G. W., Marti, K. 1977. Sm-Nd-Pu timepieces in the Angra dos Reis meteorite. *Earth Planet. Sci. Lett.* 35: 273–84
- Lugmair, G. W., Marti, K. 1978. Lunar initial  $^{143}\text{Nd}/^{144}\text{Nd}$ : differential evolution of the lunar crust and mantle. *Earth Planet. Sci. Lett.* 39: 349–57
- Lugmair, G. W., Scheinin, N. B. 1975. Sm-Nd systematics of the Stannern meteorite. *Meteoritics* 10: 447–48 (Abstr.)
- Lugmair, G. W., Scheinin, N. B., Marti, K. 1975a. Search for extinct  $^{146}\text{Sm}$ , I. The isotopic abundance of  $^{142}\text{Nd}$  in the Juvinas meteorite. *Earth Planet. Sci. Lett.* 27: 79–84
- Lugmair, G. W., Scheinin, N. B., Marti, K. 1975b. Sm-Nd age and history of Apollo 17 basalt 75075: evidence for early differentiation of the lunar exterior. *Proc. Lunar Sci. Conf. 6th* 6: 1419–29
- Lugmair, G. W., Marti, K., Kurtz, J. P., Scheinin, N. B. 1976. History and genesis of lunar troctolite 76535 or: how old is old? *Proc. Lunar Sci. Conf. 7th* 7: 2009–33
- Lugmair, G. W., Marti, K., Scheinin, N. B. 1978. Incomplete mixing of products from r-, p-, and s-process nucleosynthesis: Sm-Nd systematics in Allende inclusion Ek 1-04-1. *Lunar and Planetary Science IX*, pp. 672–74. Lunar Science Institute, Houston, Texas
- McCulloch, M. T., Wasserburg, G. J. 1978a. Sm-Nd and Rb-Sr chronology of continental crust formation. *Science* 200: 1003–11
- McCulloch, M. T., Wasserburg, G. J. 1978b. Barium and neodymium isotopic anomalies in the Allende meteorite. *Astrophys. J.* 220: 15–19
- McCulloch, M. T., Wasserburg, G. J. 1978c. More anomalies from the Allende meteorite: samarium. Preprint
- Michard-Vitrac, A., Lancelot, J., Allègre, C. J., Moorbath, S. 1977. U-Pb ages on single zircons from the early Precambrian rocks of West Greenland and the Minnesota River Valley. *Earth Planet. Sci. Lett.* 35: 449–53
- Moorbath, S. 1975. Evolution of Precambrian crust from strontium isotopic evidence. *Nature* 254: 395–98
- Moorbath, S., O’Nions, R. K., Pankhurst, R. J. 1973. Early Archaean age for the Isua iron formation, West Greenland. *Nature* 245: 138–39
- Moorbath, S., O’Nions, R. K., Pankhurst, R. J. 1975. The evolution of early Precambrian crustal rocks at Isua, West Greenland—geochemical and isotopic evidence. *Earth Planet. Sci. Lett.* 27: 229–39
- Moorbath, S., Allaart, J. H., Bridgwater, D., McGregor, V. R. 1977. Rb-Sr ages of early

- Archaean supercrustal rocks and Amitsoq gneisses at Isua. *Nature* 270:43
- Murthy, V. R. 1964. Stable isotope studies of some heavy elements in meteorites. In *Isotopic and Cosmic Chemistry*, ed. H. Craig, S. L. Miller, G. J. Wasserburg, pp. 488–515. Amsterdam: North-Holland.
- Nakamura, N., Tatsumoto, M., Nunes, P. D., Unruh, D. M., Schwab, A. P., Wildeman, R. R. 1976. 4.4-b.y.-old clast in Boulder 7, Apollo 17: a comprehensive chronological study by U-Pb, Rb-Sr and Sm-Nd methods. *Proc. Lunar Sci. Conf. 7th.* 7: 2107–29
- Nakamura, N., Unruh, D. M., Gensho, R., Tatsumoto, M. 1977. Evolution history of lunar mare basalts: Apollo 15 samples revisited. *Lunar Science VIII*, pp. 712–13. Lunar Science Institute, Houston, Texas
- Notsu, K., Mabuchi, H., Yoshioka, O., Matsuda, J., Ozima, M. 1973. Evidence of the extinct nuclide  $^{146}\text{Sm}$  in “Juvinas” achondrite. *Earth Planet. Sci. Lett.* 19: 29–36
- O'Nions, R. K., Pankhurst, R. J. 1974. Rare-earth element distribution in Archaean gneisses and anorthosites, Godthåb area, West Greenland. *Earth Planet. Sci. Lett.* 22: 328–38
- O'Nions, R. K., Pankhurst, R. J. 1976. Sr isotope and rare-earth element geochemistry of DSDP Leg 37 basalts. *Earth Planet. Sci. Lett.* 31: 255–61
- O'Nions, R. K., Pankhurst, R. J. 1978. Early Archaean rocks and geochemical evolution of the Earth's crust. *Earth Planet. Sci. Lett.* 38: 211–36
- O'Nions, R. K., Hamilton, P. J., Evensen, N. M. 1977. Variations in  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in oceanic basalts. *Earth Planet. Sci. Lett.* 34: 13–22
- O'Nions, R. K., Evensen, N. M., Hamilton, P. J., Carter, S. R. 1978a. Melting of the mantle past and present: isotope and trace element evidence. *Philos. Trans. R. Soc. Lond.* 258: 547–59
- O'Nions, R. K., Carter, S. R., Cohen, R. S., Evensen, N. M., Hamilton, P. J. 1978b. Pb, Nd and Sr isotopes in oceanic ferromanganese deposits and ocean floor basalts. *Nature* 273: 435–38
- O'Nions, R. K., Carter, S. R., Evensen, N. M., Hamilton, P. J. 1979a. Upper mantle geochemistry. In *The Sea*, ed. E. Emiliani, Vol. VII. In press
- O'Nions, R. K., Carter, S. R., Evensen, N. M., Hamilton, P. J. 1979b. Isotope geochemical studies of North Atlantic Ocean basalts and their implications for mantle evolution. In *Second Maurice Ewing Volume*. Am. Geophys. Union. In press
- Papanastassiou, D. A., Wasserburg, G. J. 1969. Initial strontium isotopic abundances and the resolution of small time differences in the formation of planetary objects. *Earth Planet. Sci. Lett.* 5: 361–76
- Papanastassiou, D. A., Wasserburg, G. J. 1976. Rb-Sr age of troctolite 76535. *Proc. Lunar Sci. Conf. 7th.* 7: 2035–54
- Papanastassiou, D. A., DePaolo, D. J., Tera, F., Wasserburg, G. J. 1977. An isotopic triptych on mare basalts: Rb-Sr, Sm-Nd, U-Pb. *Lunar Science VIII*, pp. 750–52. Lunar Science Institute
- Richard, P., Shimizu, N., Allègre, C. J. 1976.  $^{143}\text{Nd}/^{146}\text{Nd}$  a natural tracer, an application to oceanic basalts. *Earth Planet. Sci. Lett.* 31: 269
- Schnetzler, C. C., Thomas, H. H., Philpotts, J. A. 1967. Determination of rare-earth elements in rocks and minerals by mass spectrometric, stable isotope dilution technique. *Anal. Chem.* 39: 1888–90
- Smewing, J. D., Potts, P. J. 1976. Rare-earth abundances in basalts and metabasalts from the Troodos Massif, Cyprus. *Contrib. Mineral. Petrol.* 57: 245–58
- Taylor, S. R. 1977. Island-arc models and the composition of the continental crust. In *Island Arcs, Deep Sea Trenches and Back Arc Basins*, ed. M. Talwani, W. Pitman. Ewing Series, Am. Geophys. Union
- Unruh, D. M., Nakamura, N., Tatsumoto, M. 1977. History of the Pasamonte achondrite: relative susceptibility of the Sm-Nd, Rb-Sr and U-Pb systems to metamorphic events. *Earth Planet. Sci. Lett.* 37: 1–12
- Wasserburg, G. J., Papanastassiou, D. A., Nenow, E. V., Bauman, C. A. 1969. A programmable magnetic field mass spectrometer with on-line data processing. *Rev. Sci. Instrum.* 40: 288–95
- Wasserburg, G. J., Tera, F., Papanastassiou, D. A., Huneke, J. C. 1977. Isotopic and chemical investigation on Angra dos Reis. *Earth Planet. Sci. Lett.* 35: 294–316