Sources of Phosphorous in Rivers of the Namoi Basin, New South Wales: Nd-Sr Isotopic and Rare-Earth Element Constraints

CANDACE E. MARTIN and MALCOLM T. MCCULLOCH (both at: Research School of Earth Sciences, The Australian National University, Canberra ACT 0200 Australia)

Abstract The supply of excess nutrients, in particular phosphorous, is cause of major concern in the Darling River and its tributaries. In an attempt to distinguish between natural versus anthropogenic sources of phosphorus in rivers, we report here the first application of neodymium (Nd) and strontium (Sr) isotopic variations in the Namoi River catchment, a major tributary of the Darling River. The lowest Sr and highest Nd isotopic compositions are found in Tertiary basalts and older Paleozoic sediments from the Peel River catchment upstream of Chaffey Dam with ε_{Nd} values of +4.1 to +6.1 and $^{87}Sr/^{86}Sr$ ratios of 0.70345 to 0.70537. Basaltic and sedimentary soil composites have a larger range of generally intermediate compositions (ε_{Nd} = +2.3 to -2.7 and $^{87}Sr/^{86}Sr$ = 0.70560 to 0.70965), whereas phosphate rich fertilizers have distinctive, strongly negative ε_{Nd} (-5.7 to -7.0) and high $^{87}Sr/^{86}Sr$ (0.70807 to 0.70902). The intermediate compositions of the soil composites may reflect the addition of phosphate fertilizer or geologic processes associated with rock weathering. Filtered waters from the Peel and MacDonald Rivers have a range of low to intermediate Sr isotopic ratios of 0.70488 and 0.70543, respectively. These results are consistent with basaltic sources being the dominant source of Nd and Sr, particularly in the Peel River above the Chaffey Reservoir. Mixing calculations for the sediment in Chaffey Reservoir are consistent with 10-15% addition of fertilizer-derived Nd and Sr to a predominantly basaltic sediment source. Because P is a major constituent of fertilizers whereas it is present in relatively low concentrations in rocks and sediments, the proportion of P derived from fertilizer is greater than the mass fraction of fertilizer. In contrast to the Chaffey Reservoir case, the higher Sr isotopic composition of the Namoi River (0.70671 to 0.70700) requires an additional component, which may be either phosphate fertilizer, sedimentary derived soils, or a combination of these. Combined Nd-Sr isotope systematics can be used to distinguish between natural and anthropogenic sources of P in the Namoi catchment.

1. INTRODUCTION

The composition of naturally occurring radiogenic isotopic tracers such as neodymium (Nd) and strontium (Sr) can vary within different rock, sediment and soil types. Part of the ^{87}Sr in materials is produced by radioactive decay of its parent nuclide ^{87}Rb (half-life 4.89 x 10^{10} years) and similarly some ^{143}Nd is produced by decay of ^{147}Sm (half-life 1.06 x 10^{11} years). Because of differences in age and Rb/Sr or Sm/Nd ratio, materials develop measurable differences in Sr and Nd isotopic composition. Elemental and isotopic abundances of radiogenic tracers have been used to constrain processes deep within Earth as well as at and near the surface.

Manufactured products are derived from naturally occurring mineral resources. These products can retain elemental and isotopic abundances which are characteristic of the place from which they were derived. If such distinctive products are introduced into a catchment area which is naturally different, we can extend geochemical tracing to investigating the extent of anthropogenic effects in a catchment.

In this work, we use Nd and Sr isotopic tracers to investigate the sources of phosphorous (P) in the Namoi River catchment. In igneous rocks, much of the Nd and Sr are located in the same phases which contain P, particularly in the mineral apatite or in glass. During chemical weathering, these elements will both be liberated by decomposition of igneous minerals and will either be released to solution or taken up in new minerals or trapped by adsorption onto the surface of particles. Unlike light elements such as oxygen, no mass-dependent separation of Sr or Nd isotopes takes place;

therefore weathering processes do not affect Sr and Nd isotopic compositions of the starting materials. An additional source of P, Nd and Sr in the drainage basin is from the use of phosphate fertilizers for agricultural purposes. Phosphate fertilizers are produced from naturally occurring marine derived phosphorite or guano deposits from locations such as Nauru Island in the Pacific Ocean as well as from Jordan and Florida. These materials are known to have high Nd and Sr concentrations [e.g., Goldberg et al., 1963; Grandjean et al., 1987] which would therefore be expected in the fertilizers produced from them. Furthermore, Nd and P are expected to behave similarly in geochemical processes on Earth's surface, as both elements are readily partitioned from surface waters onto the surfaces of particles.

The fundamental question we address in this study is: what are the relative contributions of P from rock weathering, the natural source, and from the application of fertilizers in the area, the anthropogenic source, in this drainage basin? These sorts of data are fundamental inputs to hydrologic models.

2. SAMPLES AND PROCEDURES

The Namoi River has been chosen for this study as its catchment is made up of a number of diverse bedrock types and sediments. Along the Peel River in the vicinity of Chaffey Dam, the dominant bedrock types are Tertiary (less than 65 million years old) basaltic igneous rocks and Devonian-Carboniferous (approximately 300 to 400 million years old) metamorphosed sedimentary rocks. Soils have developed on both rock types.

A map of the Peel River catchment above Chaffey Dam, showing the sample locations, is illustrated in Figure 1. Rocks are hand samples which were crushed and homogenized. Two of the three soil samples are composites of samples taken from four to six different locations. The composite sedimentary soil is the 2-10 μm fraction; the basaltic soil sample is the less than 2 μm size fraction. Note that the terms basalt soil and sedimentary soil refer to the rock types located at or near the site of soil collection: it does not refer to any mineralogical or chemical evidence of the source of the soil particles. The sample size of rock, sediment and soil analyzed was about 50-100 mg.
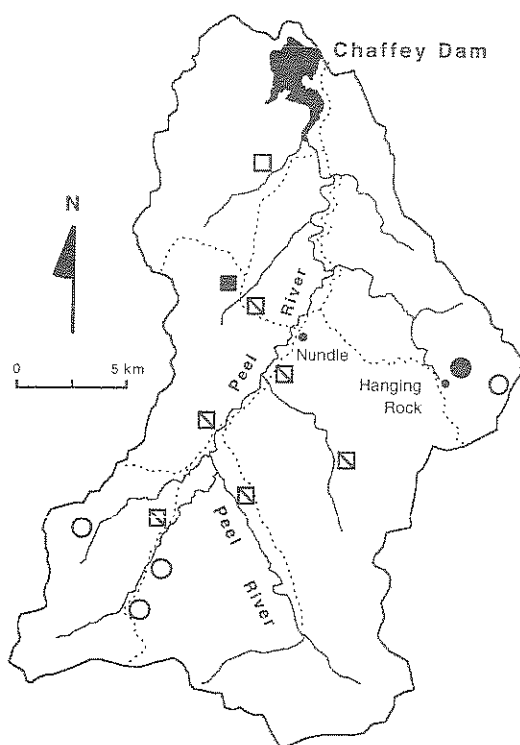

Figure 1. Location map of the field area, showing sampling locations for basaltic rock (closed circle), metasedimentary rock (closed square), composite basaltic soil (open circles), composite sedimentary soils (box with slash) and unsized sedimentary soil (open square). In addition, a sediment sample was obtained from Chaffey Reservoir and water was sampled at the Peel River where it enters the reservoir.

For at least the past 11 years, fertilizer has been applied to approximately half of the Peel River catchment, particularly in the western half, in amounts of up to 60 kg/ha/y [data compiled by the Landholders of the Chaffey Catchment]. Except for the easternmost sedimentary soil composite location, all areas from which soil samples were collected have been treated with fertilizer. A variety of phosphate fertilizers which are used in the area were also analyzed for Nd and Sr isotopic compositions and trace element concentrations. Samples of 100-200 mg were dissolved, and from the solution separate splits (equivalent to about 25 to 50

mg of sample) were taken for isotopic analysis and for concentration determination.

Water samples were taken in April 1995, one from the Peel River just south of the Chaffey Reservoir, one from the MacDonald River near Aberbaldie, two from the Namoi, one at approximately 10 km east of Gunnedah (labeled Namoi-G) and the other at about 10 km south of Boggabri (labeled Namoi-B). An algal bloom was in progress at Chaffey Reservoir when the water sample was collected, and along the Namoi a massive fish death had been reported earlier in the same week. 2 L samples were collected for Sr isotopic analysis of the "dissolved" load. The water samples were filtered within a week of collection to less than 0.45 μm using cellulose nitrate filter paper, and acidified to 2% HNO_3. Although colloidal material would have passed through this size of filter, it is assumed here that the colloids have been through a dissolution stage and therefore are still representative of the dissolved stream load. Approximately 4 to 5 g splits of the solution were taken for the isotopic and concentration analysis.

Chemical procedures used for analysis were those in standard practice at RSES. Nd and Sr isotopic compositions and concentrations were obtained using a Finnigan MAT 261 thermal ionization mass spectrometer. Concentrations of all the REE and Sr as well as other trace elements in the fertilizer samples were determined using a Plasmaquad ICP-MS instrument using internal standards.

3. RESULTS

Isotopic and concentration results are listed in Table 1. The isotopic results for the different rock and soil types and fertilizers are plotted in Figure 2. There is a large variation in Nd and Sr isotopic ratios, which are inversely correlated. An inverse relationship between Sr and Nd isotopes is commonly observed, and in the case of rivers has been interpreted to be the result of weathering of terranes of different ages [Goldstein and Jacobsen, 1987]. The data presented for this catchment plot at the high ε_{Nd} end of the worldwide Nd-Sr isotopic data set for rivers by Goldstein and Jacobsen [1987]. The Tertiary basalt has $\varepsilon_{Nd} = +6.2$ and $^{87}Sr/^{86}Sr = 0.70345$, which are expected values for mantle-derived rocks of this type and age. The sedimentary rock has $\varepsilon_{Nd} = +4.1$ and $^{87}Sr/^{86}Sr = 0.70537$. These results are comparable to results on crustal rocks such as granite and metasediments in the Tamworth area analyzed by Hensel et al. [1985]. Soils developed on both sedimentary and basaltic rocks have ε_{Nd} which are lower and $^{87}Sr/^{86}Sr$ which are higher than the corresponding rocks, with ε_{Nd} of about -2 to +2.

In contrast to the basalt and sedimentary rocks in this area, phosphate fertilizers have rather uniform ε_{Nd} (-5.7 to -6.5) and $^{87}Sr/^{86}Sr$ (0.7080 to 0.7090). In comparison to the natural materials in the drainage basin, the fertilizers have a very wide range in concentration of both Nd and Sr, from 0.93-75 ppm and 18-1028 ppm, respectively. This range in concentration may be due to differences in elemental behavior during chemical processing of phosphorite or guano, or it may be due to differences in the original materials. The REE concentrations are highest in triple superphosphate (TSP), which has the highest P concentration, and in general

decreases with decreasing P concentration of the fertilizer. This suggests that the rare earth elements are associated with the phosphate in the fertilizer and that the non-phosphate component of the fertilizer acts as a simple dilutent of the REE concentrations. The REE abundances of the fertilizers are plotted relative to the average composition of post-Archean Australian shales (PAAS) [McLennan, 1989] in Figure 3. Also shown for comparison in Figure 3 is the abundance pattern of representative phosphorites [Goldberg et al., 1963; Grandjean et al., 1987]. The general similarity between the abundance levels in the phosphate fertilizers and phosphorite suggests that little fractionation between REE and P takes place during the manufacture of fertilizer. Grandjean et al. [1987] found Sr concentrations of 425-4752 ppm in fish remains that comprise phosphorites. These Sr concentrations are somewhat high relative to the range of 18.1 to 1028 ppm Sr in the fertilizers, suggesting that some Sr is removed from phosphorite (by dissolution) during fertilizer production. The fertilizer on average has 300 ppm Sr with $^{87}Sr/^{86}Sr$ of 0.70865 (±0.00036, 1σ) and 18 ppm Nd with ε_{Nd} of -6.47 (±0.47, 1σ).

Sediment sampled at Chaffey Dam has ε_{Nd} = +4.1 and $^{87}Sr/^{86}Sr$ = 0.70704, similar to but not exactly the same as the results obtained for the rock types in the area. Concentrations of Nd and Sr are similar to the rocks and soils. The sediment from the Namoi is quite different from the Chaffey sediment, having ε_{Nd} = -2.49 and $^{87}Sr/^{86}Sr$ = 0.70879. Isotopically the Namoi sediment is most similar to the sedimentary soils from the Chaffey catchment.

All water samples have Sr concentrations which are low compared to the rocks and soils, but equal to or higher than the worldwide river average of 60 ppb (parts per billion) determined by Goldstein and Jacobsen [1987]. Qualitative ICP-MS scans also taken of the waters indicate they have less than 50 ppt (parts per trillion) of Nd, which is low relative to the worldwide river average of 41 ppt. The lowest dissolved $^{87}Sr/^{86}Sr$ (0.70488) is in the water from the Peel River; this value is slightly higher than the sediment in the reservoir. On the other hand, Namoi R. waters from near Gunnedah and Boggabri have $^{87}Sr/^{86}Sr$ ratios of about 0.707, which are lower than the Namoi sediment value. The upper MacDonald River has a dissolved $^{87}Sr/^{86}Sr$ of 0.70543, similar to the Peel River.

4. DISCUSSION AND ISOTOPIC MODELLING

Due to the large difference between the Nd and Sr isotopic compositions of the rocks in the Chaffey catchment compared to fertilizers, these results can be used to constrain the amount of fertilizer-derived components which could be contributing to the sediments and waters. These calculations depend only on knowing the concentrations and isotopic compositions of trace elements in the different materials. The simplifying assumption of bulk mixing of two components will first be considered.

An isotopic mixing curve between basalt and the average fertilizer (curve 1) is shown in Figure 2. Because the Nd/Sr ratio is higher in the fertilizer (0.06) than in the basalt (0.03), the mixing line is slightly concave upwards. The mixing curve passes through the results for Chaffey Reservoir sediment. This model is therefore consistent with the sediment in Chaffey Reservoir being comprised of 10 to 15 %

Table 1. Results

Sample	$^{87}Sr / ^{86}Sr$	ε_{Nd}	Sr (ppm)	Nd (ppm)
ROCKS				
basalt	0.70345	+6.15	336	11.7
sedimentary	0.70537	+4.11	453	16.8
SOILS				
basaltic composite	0.70560	+2.31	256	23.0
sedimentary	0.70845	-2.49	222	23.3
sedimentary composite	0.70965	-2.67	154	19.6
SEDIMENTS				
Chaffey Dam	0.70404	+4.11	404	27.4
Namoi R.	0.70879	-2.49	143	31.7
RIVER WATERS				
Peel	0.70488	-	0.256	-
Namoi (G)	0.70700	-	0.632	-
Namoi (B)	0.70671	-	0.603	-
MacDonald	0.70543	-	0.062	-
FERTILIZERS				
DAP	0.70880	-6.51	46.7	7.36
SSP	0.70807	-5.70	244	0.932
TSP	0.70878	-7.00	1028	75.3
Big Crop 32	0.70857	-6.50	18.1	2.09
Big Crop S 32	0.70902	-6.57	145	3.94

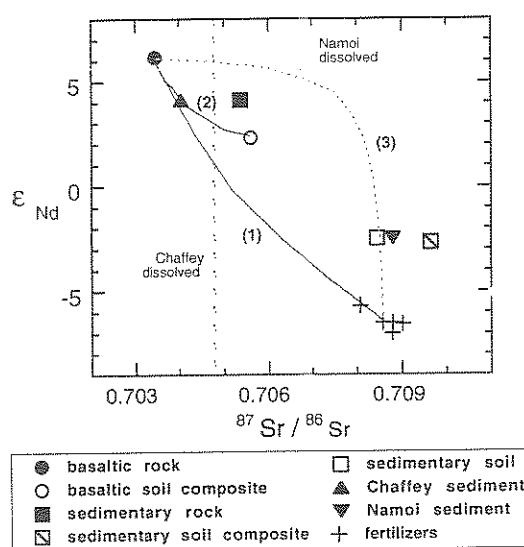|		
● basaltic rock	□	sedimentary soil
○ basaltic soil composite	▲	Chaffey sediment
▨ sedimentary rock	▽	Namoi sediment
◨ sedimentary soil composite	+	fertilizers

Figure 2. Plot of Nd vs. Sr isotopic variations in rocks, soils sediments, and waters from the Namoi River basin and in fertilizers used in the area. Also indicated as shaded regions are the Sr isotopic composition of Peel River and Namoi River waters. The mixing curves (1 and 2) are calculations based on "bulk" mixing of solid components. The dashed curve (3) shows the relations for mixing between a basaltic and a dissolved component enriched in more soluble Sr from fertilizers.
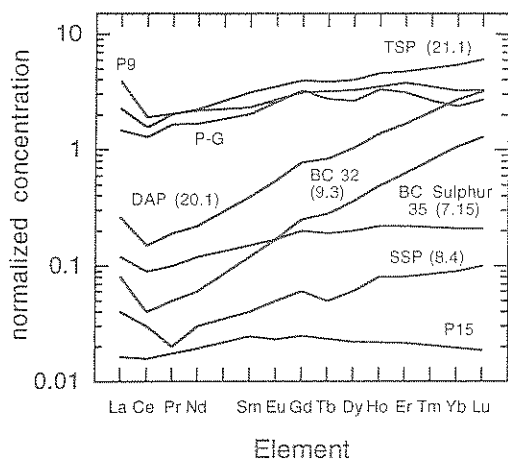
Figure 3. Rare earth element diagram for fertilizer samples, normalized to the concentration in PAAS, an average for post-Archean shales as discussed by McLennan [1989], with the wt. % P in each fertilizer indicated in parentheses. Also shown are phosphorites labeled P-G [Goldberg et al.,1963], and the limits of rare earth concentrations in group 1 phosphorites defined by P9 and P15 [Grandjean et al., 1987].

basin, the mixing relations would be very different. The Nd/Sr ratio of most stream waters is less than 0.001, and therefore mixing of, for example, basalt with the waters would produce a strongly concave downward mixing curve, such as curve 3 shown in Figure 2. Note that the Namoi River sediment falls directly on such a mixing line, but cannot be distinguished on the basis of these data alone from being purely derived from sedimentary soils similar to those analyzed in the Chaffey catchment area.
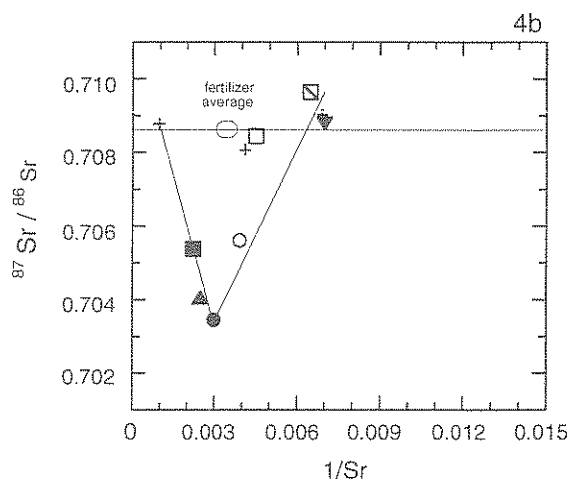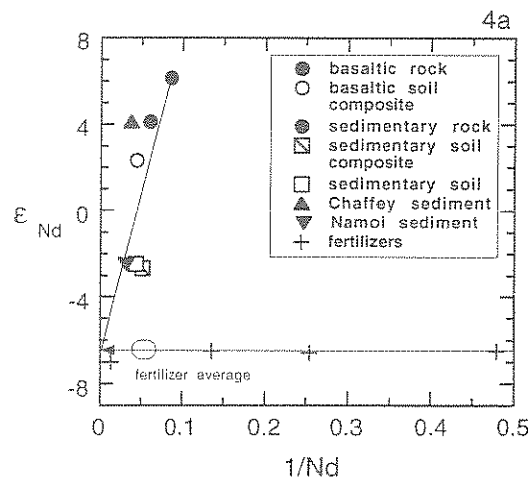

Figure 4. Mixing diagrams for Nd (4a) and Sr (4b). Symbols are the same as in Figure 2. (Not all fertilizers are shown on the Sr diagram.) The average isotopic composition of fertilizer is shown as a horizontal line on each diagram, and the average reciprocal concentrations are shown as ovals.

fertilizer derived material and the remaining 90 to 85 % of basalt. In mass balance terms, over the past ten years at least, enough fertilizer has been supplied to the catchment to make this a reasonable possibility. It is important to note that the effect this amount of fertilizer would have on the phosphorus budget of the sediment is very significant, because the fertilizers analyzed contain at least 7 wt. % P, whereas most rocks, soils and sediments contain less than 0.5 wt. % P.

Another possibility is apparent from Figure 2, where a mixing curve between basaltic rock and basaltic soil (curve 2) is also shown. The Chaffey Reservoir sediment also plots on this mixing curve, and would require that the sediment is a mixture of 35% basaltic soil with 65% basaltic rock. The sedimentary soils in the area could also be a significant contributor to the isotopic systematics of the Chaffey sediment. This begs the question of the cause of the measured isotopic differences between bedrock and soil. It cannot be simply due to preferential weathering of minerals with different isotopic compositions, because the basalts are too young to have developed such a large isotopic contrast. Rather, the soils are interpreted to contain, in addition to material from the rock type on which they developed, at least one isotopically distinct component which was derived from elsewhere. This component may be windblown dust. Further examination of the soils may determine if such a component is present. However, it is more likely that the soils themselves contain a significant fertilizer component in an analogous manner to the Chaffey sediment.

It is possible that fertilizer-related components will be released into solution more easily than the minerals present in rocks and soils. If Sr and Nd were released to waters from fertilizer and then mixed with the solid constituents of the drainage

The mixing process does not necessarily occur as a bulk process, because of possible dissolution and precipitation of Sr and Nd. One way of assessing the extent to which concentrations as well as isotopic compositions of samples

can be satisfied by a particular mixing scenario is to plot isotopic composition versus the inverse of concentration. Such plots for both Nd and Sr are shown in Figure 4. Bulk two component mixing on such a diagram is constrained to fall along a straight line. The lines drawn illustrate reasonable mixing curves for these materials. In Figure 4a, the Nd results are fairly well correlated and are consistent with mixing, provided that Nd is scavenged onto the particles. Because Nd, like P, is highly particle reactive, such a process is reasonable. In Figure 4a, the mixing line for such a process plots at a reciprocal Nd concentration of 0. This corresponds to an "infinite" concentration in the fertilizer-derived material due to particle scavenging, as indicated by the horizontal arrow passing through the fertilizer data toward the y-axis.

Figure 4b shows the situation for Sr, which unlike Nd is not strongly particle reactive. Sr has finite concentrations in the fertilizer mixing endmember, consistent with its higher concentration in the dissolved load. Mixing between basalt and fertilizers of variable concentration, within the range of those analyzed, would satisfy the mass balance for Chaffey Reservoir sediment and considered in conjunction with the isotopic modeling shown in Figure 2, indicates this is a very likely scenario.

Consideration of the dissolved load Sr isotopic results are supportive of the interpretations made on the basis of the solid phase analysis. In world rivers analyzed by Goldstein and Jacobsen [1987], either the suspended sediment and its corresponding dissolved load are identical in $^{87}Sr/^{86}Sr$, or the suspended load has a higher $^{87}Sr/^{86}Sr$ than the water. In the Namoi, the sediment has a higher $^{87}Sr/^{86}Sr$ than the dissolved load, similar to the Goldstein and Jacobsen findings. We note that in the Peel River at the Chaffey Reservoir, in contrast, the water has a higher $^{87}Sr/^{86}Sr$ than the sediment. Addition of soluble Sr from fertilizer with high $^{87}Sr/^{86}Sr$ is consistent with this finding.

5. CONCLUSIONS AND RECOMMENDATIONS

The Namoi basin has proven to be a good site for investigating the utility of combined Nd and Sr isotope systematics to looking for fertilizer inputs to rivers. The rocks and soils show significant ranges in ε_{Nd} and $^{87}Sr/^{86}Sr$ which do not overlap with phosphate fertilizers, making the isotopic compositions of stream sediments a sensitive tracer of anthropogenic P contamination of rivers. In this study, isotopic and elemental modeling based on the solid phase analysis suggests that the Chaffey Reservoir sediment may be comprised of 10-15% fertilizer derived material. The higher $^{87}Sr/^{86}Sr$ found in the dissolved load of the Peel River at Chaffey Reservoir is also consistent with soluble fertilizer addition. Because the P content of fertilizers is generally higher than that of rocks and sediments, the effects on P are expected to be larger than the proportion of fertilizer added. Ongoing measurements of both solid materials and the dissolved load in rivers will further constrain the sources of the sediments and ultimately phosphorous in the Namoi basin.

6. ACKNOWLEDGMENTS

7. REFERENCES

Goldstein, S.J., and S.B. Jacobsen, The Nd and Sr isotopic systematics of river-water dissolved material: Implications for the sources of Nd and Sr in seawater. *Chem. Geology (Isotope Geoscience Section)*, 66, 245-272, 1987.

Goldberg, E.D., M. Koide, R.A. Schmitt, and R.H. Smith, Rare-earth distributions in the marine environment. *J. Geophys. Res.*, 68(14), 4209-4217, 1963.

Grandjean, P., H. Cappetta, A. Michard, and F. Albarède, The assessment of REE patterns and $^{143}Nd/^{144}Nd$ ratios in fish remains. *Earth Planet. Sci. Lett.*, 84, 181-196, 1987.

Hensel, H.-D., M.T. McCulloch, and B.W. Chappell, The New England Batholith: constraints on its derivation from Nd and Sr isotopic studies of granitoids and country rocks. *Geochim. Cosmochim. Acta*, 49, 369-384, 1985.

McLennan, S.M., Rare Earth Elements in Sedimentary Rocks: Influence of Provenance and Sedimentary Processes, in *Geochemistry and Mineralogy of Rare Earth Elements*, (Reviews in Mineralogy, v. 21) edited by B.R. Lipin and G.A. McKay, pp.169-200, Mineralogical Society of America, Washington, D.C., 1989.

8. NOTATIONS AND UNITS

Nd isotopic ratios are usually reported as deviations (in parts per 10,000) in the measured $^{143}Nd/^{144}Nd$ of a sample relative to a standard; these values are referred to as ε_{Nd}. Our data are normalized to an average chondritic meteorite (CHUR) value of $^{143}Nd/^{144}Nd = 0.512680$ derived from the measured $^{143}Nd/^{144}Nd$ of the BCR-1 basaltic rock standard. Sr isotopic compositions are reported as $^{87}Sr/^{86}Sr$ ratios. Analytical uncertainties are better than ±0.2 in ε_{Nd} and ±0.00001 in $^{87}Sr/^{86}Sr$. Concentrations reported are in micrograms per gram or ppm (parts per million).