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The "North American shale composite": Its compilation, major and trace element characteristics

L. PETER GROMET
Department of Geological Sciences, Brown University, Providence, RI 02912

ROBERT F. DYMEK*
Department of Geological Sciences, Harvard University, Cambridge, MA 02138

and

LARRY A. HASKIN, RANDY L. KOROTEV
Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences,
Washington University, St. Louis, MO 63130

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Abstract—The compilation and major element composition of the "North American shale composite" (NASC) are reported for the first time, along with redeterminations for the REE and selected other elements by modern, high precision analytical methods. The NASC is not strictly of North American origin; 5 of the constituent samples are from Africa and Antarctica, and 15 are from unspecified locations. The major element composition of the NASC compares quite closely with other average shale compositions. New analyses of the NASC document that significant portions of the REE and some other trace elements are contained in minor phases (zircon and possibly other minerals) and that their uneven distribution in the NASC powder appears to have resulted in heterogeneity among analyzed aliquants. The results of this study show that the REE distributions of detrital sediments can be dependent to some extent on their minor mineral assemblages and the sedimentological factors that control these assemblages. Consequently, caution should be exercised in the interpretation of the REE distributions of sediment samples as they may be variable and biased relative to average REE distribution of the crustal rocks supplying detritus. These effects appear to be largely averaged out in sediment composites, with the result that their REE distributions are more likely to be representative of their provenances.

INTRODUCTION

A COMPOSITE of 40 shales was prepared at the request of the late Paul Gast in the 1950's. Although its compilation has never been described and documented in print, selected geochemical properties of this composite have been reported, particularly for the rare earth elements (REE) (HASKIN and FREY, 1966; HASKIN and HASKIN, 1966; HASKIN *et al.*, 1968). Since that time, the REE abundances of the so-called "North American shale composite" (NASC) have been used, in effect, as a standard of comparison in a number of geochemical studies.

The original interest in the REE distributions of fine-grained detrital sediments stemmed from the expectation that they represented average crustal relative REE abundances (GOLDSCHMIDT, 1938). It was possible therefore to evaluate the REE distribution in the upper crust (that part exposed to erosion) by determining the REE contents of sediment composites. The work of MINAMI (1935), HASKIN and GEHL (1962), BALASHOV *et al.* (1964), HASKIN and FREY (1966), and HASKIN *et al.* (1968) established that the relative REE abundances of several sediment composites (including the NASC) were very similar to one another, but as a group were distinctly enriched in the lighter REE compared to the REE distribution in chondritic meteorites and presumably that for the bulk Earth. The relative enrichment of upper crustal rocks in the light REE was attributed to the differentiation process that formed and modified the Earth's crust (*e.g.*, HASKIN and GEHL, 1962; TAYLOR, 1962; HASKIN and FREY, 1966), although the details of these processes and how they led specifically to the relative REE abundances observed in the NASC and other sediments are not really understood.

More recently, studies of REE distributions in shales and other detrital sedimentary and metasedimentary rocks have been extended to include samples from most of the continents, from a variety of geological environments, and materials as old as the earliest Archaean (*e.g.*, WILDEMAN and HASKIN, 1973; RONOV *et al.*, 1974; CULLERS *et al.*, 1975; NANCE and TAYLOR, 1976, 1977; BAVINTON and TAYLOR, 1980; TAYLOR and MCLENNAN, 1981a; BOAK, 1983; BOAK *et al.*, 1982, 1983; DYMEK *et al.*, 1983; MCLENNAN *et al.*, 1984). These studies have confirmed that post-Archaean sediment composites as a group have rather uniform REE characteristics, although sediments with sources restricted to certain limited environments can deviate considerably from these values (*e.g.*, RONOV *et al.*, 1974; NANCE and TAYLOR, 1976). By virtue of their broad similarity over several continents, the relative REE patterns of

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* Present Address: Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130

the NASC and other post-Archaean sediment composites have been considered to be representative of the post-Archaean upper crust. As such, these patterns have constituted an important benchmark for models of crustal evolution based on sedimentary REE patterns (*e.g.*, TAYLOR, 1977; TAYLOR and MCLENNAN, 1981b).

In light of the extensive and continuing use of NASC REE abundances in the literature, a more comprehensive characterization of that composite and its geochemical characteristics using current methods appears warranted. One of us (LAH) had received some unpublished information from Gast on the constituent rocks of the composite and this information is now presented. The major element chemistry of the NASC (RFD) is reported for the first time, and a comparison of its chemistry to that of other sediment composites is discussed. New REE analyses of the NASC using isotope dilution mass spectrometry (LPG) and improved neutron activation analysis techniques (LAH and RLK) are reported. These analyses have significantly higher precision than previously reported determinations, reflecting improvements in the methods of REE analysis that have been made over the last two decades. The new analyses document significant heterogeneity among analyzed aliquants of the composite for the REE and some other elements. A series of analytical experiments is described whereby the origin of this heterogeneity is found to lie in the small and variable amounts of REE-concentrating minerals in the NASC, a finding of considerable significance to the interpretation of sediment REE distributions in general. Despite this heterogeneity, the new REE analyses reveal some fine structure in the NASC REE distribution that is important to the interpretation of its provenances.

COMPILATION OF THE NASC

The composite of sediments that has come to be known as the "North American shale composite" was prepared at the request of Paul W. Gast during his tenure at the University of Minnesota. At that time he had access to numerous rock samples that had been analyzed for major elements in the rock analysis laboratory there. He caused aliquants of analyzed samples to be compounded into various composites, including the NASC, to enable measurement of average properties of different rock types. Several grams each of these composites were given to one of us (LAH) in the middle 1960's; sometime later, major element compositions and information on where the constituent samples had been collected were also provided. Gast referred to the composite merely as "sediments", but noted that it consisted mainly of North American Paleozoic shales. In addition, a composite referred to as "metamorphics", also discussed in the present paper, was described by GAST (pers. commun.) as somewhat metamorphosed North American shales.

In fact, the NASC samples did not all originate in North America: five were from Antarctica and Africa, and no place of origin was given for more than a third. The geographical distribution of the 40 sediments of the NASC was given as follows: Minnesota (6); Montana (1); New Hampshire (1); New Mexico (1); New York (4); Ohio (1); Oklahoma (2); South Dakota (1); West Virginia (3); Antarctica (2); North Rhodesia (3); no location (15). More specific locations were not provided.

Limitations on the significance of this composite are evident. It was never intended as a representative sampling of North America or any place else. It was intended merely to provide a first-cut indication of some more or less averaged properties of shales. Only the agreement of its REE distribution with those of composites from other regions gives the REE distribution of the NASC credibility as representative of the Earth's post-Precambrian upper continental crust.

The geographical distribution of the composite of 55 metamorphosed shales was given as follows: Arizona (3); Colorado (1); Labrador (2); Maine (2); Minnesota (7); New Brunswick (6); Newfoundland (1); New Hampshire (5); New York (7); Texas (1); Virginia (2); Washington (1); Antarctica (2); Venezuela (1); no location (14).

The major element compositions of the material provided by Gast are included in Table 1.

ANALYTICAL PROCEDURES AND RESULTS

Major element analyses

The major element composition of the NASC was determined by microprobe analysis of glass prepared by fusion of 100 mg each of sample powder and $Li_2B_4O_7$ flux, using procedures described in DYMEK and GROMET (1984). Results of analyses on two separate aliquants of NASC are listed in Table 1 (columns 1 & 2), where they are reported on a 100% volatile-free, reduced iron basis. Entries for each oxide represent the mean (and standard deviation) for 12 analyses on each glass; the two average compositions agree within experimental error.

Also listed in Table 1 (column 5) are the results of multiple analyses by the same methods on USGS standard rock AGV-1 conducted over a 2½ year period. The closeness of agreement between our results and the recommended values (column 6) establishes the general reliability of the analytical procedures; similar results have been obtained on W-1 and G-2.

Column 3 lists a wet-chemical analysis for the NASC provided by GAST (pers. commun. to LAH), also reported on a volatile-free, reduced iron basis. Except for MnO, the agreement with the microprobe analysis is excellent; the cause of this single discrepancy is unclear. Column 4 lists the analysis for the metamorphosed shale composite as provided by Gast (reported again on the volatile-free, reduced iron basis). The difference between the bulk composition of this composite and the NASC is noteworthy; in terms of major elements at least, they represent somewhat different materials.

Neutron activation analyses for REE

The initial analysis for REE in the NASC was done by FREY (1966) (see HASKIN and FREY, 1966) using radiochemical separation of the individual REE. Such early results do not carry the level of precision now obtainable,

Table 1. Major element composition of the "North American shale composite" (NASC), "metamorphosed shale composite", and AGV-1*.

	1	2	3	4	5	6
SiO_2	64.80 (.18)	64.82 (.30)	64.82	60.48	60.52 (.34)	60.41
TiO_2	0.78 (.03)	0.79 (.04)	0.80	0.91	1.09 (.04)	1.06
Al_2O_3	16.90 (.07)	16.88 (.13)	17.05	16.58	17.46 (.18)	17.66
FeO	5.70 (.14)	5.59 (.18)	5.70	8.10	6.20 (.24)	6.26
MnO	0.06 (.02)	0.07 (.03)	0.25	0.13	0.10 (.03)	0.10
MgO	2.85 (.08)	2.86 (.06)	2.83	6.35	1.54 (.04)	1.57
CaO	3.56 (.12)	3.68 (.11)	3.51	2.31	5.04 (.09)	5.02
Na_2O	1.15 (.03)	1.12 (.06)	1.13	1.80	4.37 (.07)	4.36
K_2O	3.99 (.09)	3.87 (.19)	3.97	3.17	2.98 (.08)	2.93
P_2O_5	0.11 (.03)	0.17 (.03)	0.15	0.17	0.53 (.04)	0.50

*Weight percent oxides, recalculated to 100% on a volatile-free and reduced iron basis.

1,2. "NASC," electron microprobe analysis of 100 mg aliquants fused with lithium tetraborate, this work (average and standard deviation for 12 analyses on each aliquant).
3. "NASC", wet chemical analysis, Minnesota rock analysis lab (P.W. Gast, pers. comm.).
4. Composite of metamorphosed, mostly North American "shales"; wet chemical analysis, Minnesota rock analysis lab (P.W. Gast, pers. comm.).
5. AGV-1, electron microprobe analysis of 1 g aliquant fused with lithium tetraborate, this work (average and standard deviation for 15 groups of analyses totaling 85 individual analyses; wt% BaO = 0.17±.04).
6. AGV-1, recommended values (Flanagan, 1973; wt% BaO = 0.13).

although some of the differences between this and later analyses are probably related to sample heterogeneity as discussed later in this report. Over a period of 10 years, additional aliquants were analyzed by an improved version of the radiochemical separation procedure (HASKIN *et al.*, 1968), by separation and radioassay of the REE as a group (KOSIEWICZ, 1973, pers. commun.; procedures of DENECHAUD *et al.*, 1970), and by instrumental neutron activation (JACOBS, 1976, pers. commun.; procedures of JACOBS *et al.*, 1977). The results of these analyses are listed in Table 2 along with a new analysis determined by a recently refined instrumental neutron activation technique that is more precise than the former methods (LINDSTROM and KOROTEV, 1982).

Note that the REE concentrations given in columns 1–5, Table 2 do not converge to a single set of values. However, with the exception of individual elements in some of the older analyses (*e.g.*, Pr, Eu and Tb in column 1; Pr and Ho in column 2; Ce and Ho and/or Er in column 3), the results define generally smooth chondrite-normalized distribution patterns characterized by strong relative fractionation in the light REE, a negative Eu anomaly, and slight or no relative fractionation among the heavy REE (see Fig. 1). The spread of values among the different analyses is well outside the known precision for several of the better determined elements, suggesting the possibility of sample heterogeneity.

Isotope dilution mass spectrometric analyses

The isotope dilution analyses reported here follow the procedures of GROMET (1979) with the exception that sample dissolution was carried out either by reaction with

Table 2. REE concentrations in aliquants of the "North American shale composite" (NASC).

	NEUTRON ACTIVATION ANALYSES					MASS SPECTROMETRY ISOTOPE DILUTION ANALYSES						
	1	2	3	4	5	6	7	8	9	10	11	12
La	39	32	39	32.3	31.1	---	---	---	---	---	---	---
Ce	76	73	72	72	66.7	67.8	66.6	2.86	63.7	69.2	70.0	8.31
Pr	10.3	7.9	---	---	---	---	---	---	---	---	---	---
Nd	37	33	36	---	27.4	34.4	29.4	1.00	28.4	31.0	30.7	4.75
Sm	7.0	5.7	6.9	6.4	5.59	6.69	5.66	0.324	5.34	5.88	5.75	1.22
Eu	2.0	1.24	1.28	1.15	1.18	1.39	1.19	0.109	1.08	1.17	1.15	0.264
Gd	6.1	5.2	6.4	---	---	5.60	5.40	1.08	4.32	4.55	4.51	1.24
Tb	1.3	0.85	1.08	0.78	0.85	---	---	---	---	---	---	---
Dy	---	---	6.0	---	---	5.75	5.33	2.04	3.27	3.51	3.34	0.907
Ho	1.40	1.04	1.36	---	---	---	---	---	---	---	---	---
Er	4.0	3.4	3.2	---	---	3.34	3.21	1.36	1.85	1.93	1.86	0.388
Tm	0.58	0.50	---	---	---	---	---	---	---	---	---	---
Yb	3.4	3.1	3.5	3.3	3.06	3.21	3.07	1.17	1.90	2.00	1.96	0.293
Lu	0.6	0.48	0.53	0.55	0.456	---	---	---	---	---	---	---
sample wt.(mg)	1000	1070	1000	20	107.41	229.88	50.20	50.20	50.20	81.53	49.40	218.92

* Weight basis is for shales including H_2O and CO_2; values in μg/g.

1. RNAA, individual element separation (Haskin and Frey, 1966).
2. Improved RNAA, individual element separation (Haskin et al., 1968).
3. RNAA, REE group separation (Kosiewicz, 1973, pers. comm.).
4. INAA (Jacobs, 1976, pers. comm.).
5. Improved INAA, this work.
6. MSID, HF bomb dissolution, this work.
7. MSID, sum of 8 and 9, this work.
8. MSID, HF insoluble (open beaker), this work.
9. MSID, HF soluble (open beaker), this work.
10. MSID, HF soluble (open beaker), this work.
11. MSID, HF soluble (open beaker), this work.
12. MSID, dil. HNO_3 soluble (open beaker), this work.

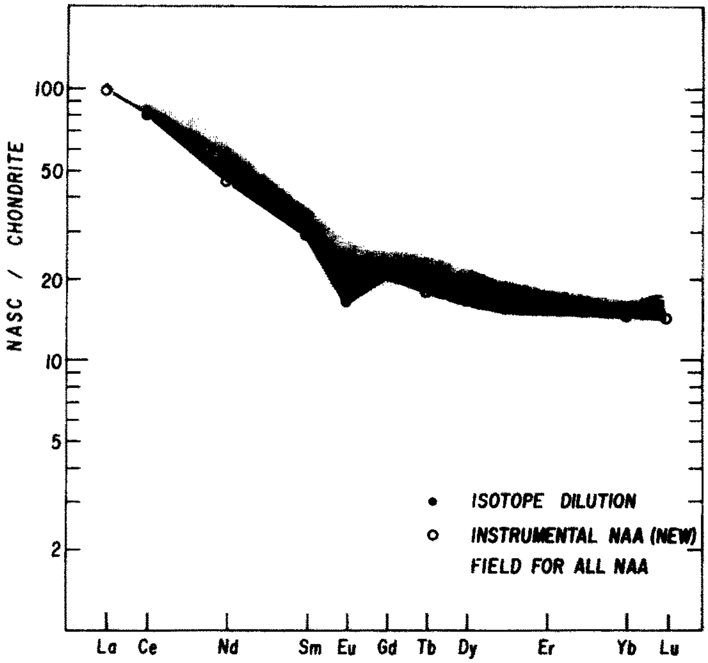

FIG. 1. REE distributions for the NASC. The results of the most recent instrumental neutron activation analysis (column 5, Table 2) and two isotope dilution analyses (columns 6 and 7, Table 2) are plotted. The field shown represents the range of all neutron activation analyses of the NASC (columns 1-5, Table 2), with some smoothing of a few apparently anomalous values. In this and subsequent figures, the samples are normalized to the chondrite values of HASKIN *et al.* (1968) for monoisotopic elements and Leedy (MASUDA *et al.*, 1973) divided by 1.20 for multi-isotopic elements.

HF in open Teflon beakers, or by reaction with HF in enclosed Teflon bombs of the type used for zircon dissolution (*e.g.*, KROGH, 1973). The initial analysis was carried out on an aliquant dissolved in an open beaker. A very small quantity of fine black residue (estimated visually at no more than a few volume percent) was left after evaporation with $HClO_4$ and redissolution in dilute HNO_3. This residue was assumed to consist entirely of unreacted graphite, and the resulting analysis (column 10, Table 2) was reported incorrectly as that of NASC (GROMET and DYMEK, 1982). A second aliquant was dissolved in an enclosed Teflon bomb without leaving any residue; this analysis yielded REE concentrations that are similar to the first analysis for the lighter REE, but are significantly higher for the heavier REE (column 6, Table 2).

In order to determine if a resistant phase (or phases) harboring some of the heavier REE was surviving HF attack in an open beaker, two additional isotope dilution analyses were performed. The first was designed to determine the REE content of the residue. An aliquant of powder was attacked twice with HF in an open beaker before the addition of isotopically altered spike (in the preceding analyses, spiking was done before attack to ensure as complete an equilibration of spike and dissolved sample as possible). A fine black residue remained, as before. This residue was separated from the dissolved fraction of the sample by repeated cycles of washing the residue with 2N HNO_3, centrifuging, and pipeting off the supernate. The supernate washings were combined, spiked and processed for analysis. The residue was spiked separately and dissolved with HF in a Teflon bomb, leaving no residue. The REE contents of the dissolved fraction and residue (columns 9 and 8, Table 2) are reported as concentrations relative to the total sample weight (the residue itself could not be weighed). REE concentrations of the dissolved fraction are slightly lower but in general agreement with the REE contents determined in the first open beaker dissolution. Lesser amounts of the REE are found in the residue, but it is comparatively enriched in the heavier REE (Fig. 2). This small quantity of residue holds approximately *one third* of the heavier REE in the NASC. The summation of the REE contained in the dissolved fraction and residue (column 7, Table 2) agrees fairly closely with the analysis carried out in a bomb and with the most recent INAA results (column 5, Table 2) (see Figs. 1 and 2).

Another split of powder was dissolved in an open beaker, principally so that the residue could be examined with a petrographic microscope. This provided an opportunity to obtain an additional REE analysis of the fraction of powder soluble in HF in an open beaker (column 11, Table 2). The residue from this dissolution was mounted in an oil of 1.80 index of refraction. The presence of dispersed graphite hampered observations, but several small grains of zircon were identified on the basis of an index greater than that of the oil, stubby prismatic form, high birefringence, parallel extinction and length-slow orientation. Several larger, colorless, prismatic grains with an index less than that of the oil, parallel extinction and length-slow orientation were observed. These characteristics and an insolubility in HF suggest this phase is an aluminosilicate, probably sillimanite. Two isotropic grains with an index less than that of the oil were present. These isotropic grains are not likely to be garnet (this mineral dissolves in concentrated HF under prolonged attack), but are perhaps a spinel.

A final split of NASC was leached gently in warm 2N nitric acid for 20 minutes to determine the easily soluble or desorbable fraction of REE. The REE contents of the leachate, reported as concentrations relative to the total powder weight, are given in column 12, Table 2. The leachate contains from 10% to 20% of each REE in the NASC. The remaining residue was washed of fines and processed through a heavy liquid separation (methylene iodide) so that grains with densities greater than 3.3 g/cm^3 could be observed. Most of the grains present were silicates

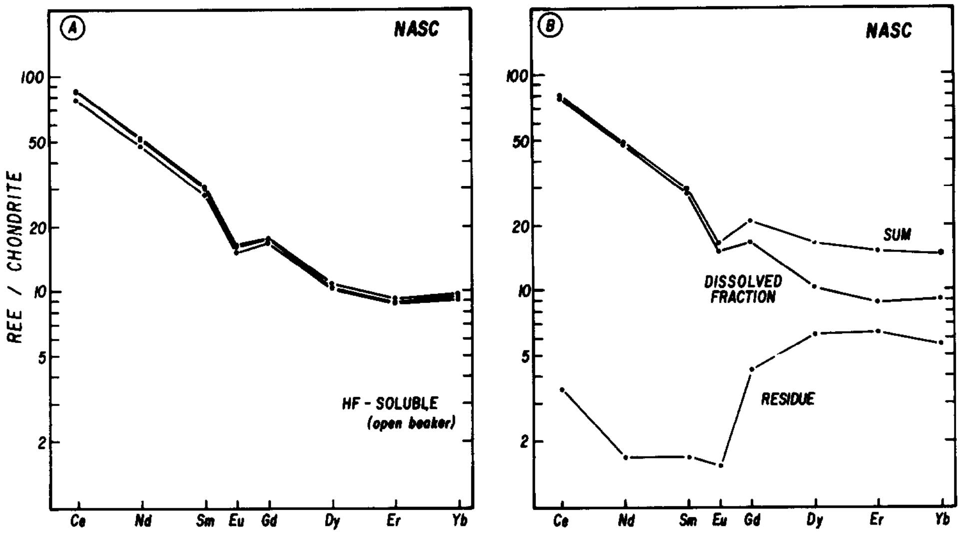

FIG. 2. A) REE distributions for three separate open beaker HF-dissolutions of the NASC (columns 9–11, Table 2). B) REE distributions for the dissolved and residue fractions (columns 9 and 8, Table 2) resulting from an open beaker dissolution experiment and their sum (column 7, Table 2). Details of the experiment are described in the text.

that are soluble in HF. In a population of approximately 200 grains, 9 grains of zircon were identified. Grains with the properties corresponding to an aluminosilicate were not observed, undoubtedly because their expected density is less than that of methylene iodide. Two isotropic grains and a few opaque grains were observed.

Neutron activation analyses of the metamorphosed shale composite

On learning of the importance of REE-concentrating minerals in the NASC and recognizing the disparities among several REE analyses, it was appropriate to consider performing analyses on multiple aliquants of the NASC for a large number of elements in order to identify further the effects of heterogeneity. Recent improvements in the precision of INAA procedures (LINDSTROM and KOROTEV, 1982) and extensive studies of multiple aliquants of standardized samples together with multiple radioassay of single aliquants (KOROTEV, unpub.) have enabled us to determine accurately the extent of our ability to detect heterogeneity among aliquants of single powdered samples. The precision for multiple analyses of most of the 29 elements determined by the current technique is one percent or less (as sample standard deviation given as percent of observed value).

Unfortunately, the quantity of NASC remaining in the vial was too small for such an experiment, so the apparently similar composite of metamorphosed shales was used; one aliquant of the NASC was also analyzed. Table 3 lists data for 29 elements for four aliquants of the metamorphosed shale composite (columns 1–4), its average (column 5), its sample standard deviation in percent (column 6), and results of a previous analysis for REE (column 8). Column 9 gives the concentrations for USGS standard rock BCR-1 analyzed concurrently with the shale samples, and column 10 gives recent "consensus" values (GLADNEY *et al.*, 1983) for comparison. Column 11 gives data obtained on an aliquant of the NASC by JACOBS (pers. commun.), using an earlier version of the INAA procedure, and column 12 gives values determined by the current procedure.

Column 7 of Table 3 contains estimates of analytical precision for those elements whose concentrations were calculated from multiple radioassays of either the four metamorphosed shale aliquants (longer-lived radioisotopes) or of the NASC aliquant. Values given are relative sample standard deviations in percent. These were calculated for Sc, Cr, FeO, Co, Rb, Sb, Cs, Ba, Ce, Nd, Eu, Tb, Yb, Lu, Hf, Ta, and Th as follows: each aliquant of powder and a standard were assayed on two different Ge(Li) detectors during the first period of radioassay (7–12 days after irradiation) and again during the second period of radioassay (28–33 days after irradiation), providing four independent concentration values (relative to the standard) for each of the above elements. From these four values, a mean concentration and standard deviation were calculated for each element in each aliquant. The mean concentrations for each of the four aliquants of the metamorphosed shale composite are listed in columns 1–4; the standard deviations for the four individual aliquants were averaged and are listed in column 7. These mean standard deviations, based on the repeatability of radioassay, approximate the precision expected for replicate determinations of separate aliquants of a perfectly homogeneous material against a perfectly homogeneous standard. Similar estimates of standard deviation expected for perfectly homogeneous samples and standards could not be made for the remaining elements as they were measured only during the first or second radioassay. (Their activities had either died out prior to the second period of radioassay or were not intense enough during the first.) However, the single aliquant of the NASC and the standard were assayed three times using three separate detectors during the first and second period of radioassay. This provided similar information for all 29 elements. The resulting estimates for those elements discussed earlier are not listed as they are quite similar to those obtained from multiple assay of the four aliquants of the metamorphosed shale composite. The estimates for the remaining elements (Na_2O, K_2O, CaO, Ni, As, Br, Sr, Zr, La, Sm, W and U), based on the short-lived isotopes and weak long-lived isotopes, are listed in column 7. The validity of these estimates is supported further by results of extensive other recent analytical work (KOROTEV, unpub.)

For the elements Na_2O, K_2O, Sc, FeO, Co, Ni, Rb, Cs, Ta, and U, the values in column 7 are not significantly different from the actual sample standard deviations for four aliquants given in column 6. Thus, within our ability to measure, the composite is homogeneous at an aliquant size of 75 mg for those elements. For the elements Cr, Sr, Sb, Ba, most REE, Hf, and Th, the values in column 6 are some 3 times larger than those in column 7, good evidence

Table 3. Neutron activation analysis results for the "metamorphosed shale composite", the "North American shale composite" (NASC), and BCR-1*.

	METAMORPHOSED SHALE COMPOSITE								BCR-1		NASC	
	1	2	3	4	5	6	7	8	9	10	11	12
Na_2O	1.680	1.674	1.676	1.665	1.674	0.4	1.3	---	3.29	3.27±.11	1.05	1.008
K_2O	3.0	2.8	3.0	3.1	3.0	4	4	---	N.D.	1.69±.08	4.0	3.8
CaO	2.2	1.9	2.0	1.8	2.0	10.9	0.7**	---	6.0±.6	6.95±.15	---	3.3
Sc	17.87	17.96	18.16	18.09	18.0	0.7	0.4	---	32.7	32.8±1.7	14.6	14.9
Cr	412	419	414	421	417	1.0	0.3	---	11.3	16 ±4	130	124.5
FeO	7.81	7.87	7.84	7.90	7.86	0.5	0.7	---	12.6	12.1±.3	5.1	5.09
Co	28.6	28.0	28.2	28.1	28.2	0.9	0.6	---	38.2	36.3±1.6	27	25.7
Ni	217	235	229	226	227	3.3	9.6	---	<50	13 ±4	---	58
As	11.5	11.2	11.9	11.1	11.4	3.1	1.2	---	<4	0.64±.14	---	28.4
Br	0.75	0.70	0.74	0.97	0.79	15	8.8	---	N.D.	0.07±.03	---	0.69
Rb	129	130	128	130	129	0.7	0.4	---	54 ± 4	47.1±.6	---	125
Sr	176	198	204	190	192	6.3	0.7	---	347±20	330 ±5	---	142
Zr	173	180	158	148	165	8.7	3.7	---	185±25	191 ±5	---	200
Sb	0.74	0.80	0.83	0.79	0.79	4.6	1.4	---	0.70	0.62±.10	---	2.09
Cs	6.15	6.00	6.08	6.17	6.10	1.3	0.8	---	1.01	0.97±.13	---	5.16
Ba	523	514	521	550	527	3.0	0.9	---	698	678 ±16	---	636
La	30.7	33.5	33.8	32.6	32.6	4.3	0.2	34.0	24.9	25.0±.8	32	31.1
Ce	67.8	73.7	75.9	73.3	72.7	4.7	1.1	73.8	54.3	53.7±.8	72	66.7
Nd	29.7	31.8	32.9	30.8	31.3	4.4	1.8	35.1	28.0	28.7±.6	---	27.4
Sm	5.75	6.26	6.38	6.25	6.16	4.5	0.4	6.05	6.63	6.58±.17	6.4	5.59
Eu	1.25	1.27	1.30	1.28	1.27	1.6	0.9	1.51	1.96	1.96±.05	1.15	1.18
Tb	0.87	0.89	0.90	0.89	0.89	1.3	2.3	0.88	1.07	1.05±.09	0.78	0.85
Yb	2.97	2.86	2.68	2.71	2.80	4.9	1.6	2.71	3.37	3.39±.08	3.3	3.06
Lu	0.437	0.423	0.405	0.401	0.417	4.0	1.0	0.41	0.509	0.512±.02	0.55	0.456
Hf	4.57	5.35	4.63	4.61	4.79	7.8	1.0	---	5.08	4.9 ±.3	6.3	6.30
Ta	0.853	0.849	0.828	0.860	0.848	1.6	3.6	---	0.77	0.79±.09	1.2	1.12
W	1.4	N.D.	1.5	N.D.	1.5	---	---	---	N.D.	0.40±.09	---	2.1
Th	9.33	10.72	10.86	10.38	10.3	6.7	0.6	---	6.01	6.0 ±.6	12.2	12.3
U	2.60	2.44	2.49	2.38	2.48	3.8	3.1	---	1.78	1.71±.16	---	2.66
Sample Wt.(mg)	77.48	75.40	78.57	75.05	306.5	---	---	1,070	44.15	---	20	107.41

*Concentration values are for undried samples (i.e., including CO_2 and H_2O) in weight percent for oxides (total element as oxide) and μg/g for other elements. Values in columns 1-5, 9, and 12 were determined against multielement reference standards 1633a (NBS coal flyash), DTS-1 (USGS dunite), and AN-G (GIT-IWG anorthosite). Concentration values used for each element are listed in Table 1 of Korotev et al. (1984) with the following additions: K_2O(2.27%), As(145), Sb(6.15), Br(2.31), Rb(134), Cs(10.42) in 1633a and W(110) in AN-G, and the following changes: La(77.9), Ce(169), Nd(76.8), Sm(16.1), Eu(3.57), Tb(2.57), Yb(7.73), and Lu(1.115) in 1633a.

1-4. Separate aliquants of the metamorphosed shale composite, this work.
5,6. Mean and sample standard deviation (in %) of 1-4.
7. Expected sample standard deviation (in %) for 75 mg aliquants based on multiple counts of sample-standard pairs on different detectors. **The value for CaO is based on 3 determinations of NASC (column 12) which were fortuitously much more precise than would be expected on the basis of counting statistics. The latter predict about 11% uncertainty for the values in columns 1-4.
8. Improved RNAA analysis (Haskin et al., 1968).
9. BCR-1, this work, with one standard deviation estimate of analytical precision for those elements for which this value exceeds 5%. N.D.=low concentration could not be determined in presence of Na^{24}.
10. "Consensus" values and stated uncertainty from Gladney et al. (1983) for BCR-1.
11. "NASC," (Jacobs, 1976, pers. comm.).
12. "NASC," this work.

for heterogeneity. For the remaining elements, ambiguity prevails, the differences being too large to ignore but not large enough to establish with confidence that heterogeneity has been observed.

DISCUSSION

Comparison of the bulk compositions of the NASC and other average shales

The major element composition of the NASC determined in this study is compared to the compositions of selected other average shales and shale composites in Table 4 and Fig. 3. In general, the bulk composition of the NASC compares quite closely with these previously published estimates of average shale compositions, particularly that of CLARKE (1924) (Col. 2). The relatively high SiO_2, Al_2O_3 and K_2O contents that characterize most of these sediment composites are features expected of a typical chemically mature argillaceous sediment (*c.f.* GARRELS and MACKENZIE, 1971). The large range in CaO abundances in these composites is probably caused by variable carbonate contents and/or calcite/dolomite ratios.

A plot of SiO_2/Al_2O_3 *versus* K_2O/Na_2O (Fig. 3) reveals some important characteristics of the NASC. Its SiO_2/Al_2O_3 ratio is centered within the range established for shales. The K_2O/Na_2O ratio for the NASC is within range of average Proterzoic and Phanerozoic shales, which as a group appear distinctly higher in K_2O/Na_2O ratio than reported averages of Archaean shales (compare columns 9 & 10 with 1–8). These chemical ratios suggest that the NASC bulk composition has the qualities of an average of averages. In terms of SiO_2/Al_2O_3 and K_2O/Na_2O ratios, the NASC most clearly resembles the Canadian Proterozoic (Aphebian) average (Col. 7). Perhaps the sediments comprising the NASC and the Canadian Proterozoic (Aphebian) average share many aspects of their provenance.

Table 4. Major element compositions of selected average shales and shale composites*

	1	2	3	4	5	6	7	8	9	10
SiO_2	64.80	64.21	59.75	56.78	67.78	64.09	66.90	63.04	62.13	65.47
TiO_2	0.70	0.72	0.98	0.92	0.70	0.82	0.78	0.94	0.78	0.49
Al_2O_3	16.90	17.02	17.79	16.89	16.59	16.65	16.67	18.63	18.11	16.11
FeO	5.66	6.71	5.59	6.56	4.11	6.03	5.87	7.66	7.33	5.85
MnO	0.06	0.5	-----	0.08	-----	0.07	0.06	0.12	0.10	0.07
MgO	2.86	2.70	4.02	4.56	3.38	2.54	2.59	2.60	3.57	2.50
CaO	3.63	3.44	6.10	8.91	3.91	5.65	0.53	1.31	2.22	4.10
Na_2O	1.14	1.44	0.72	0.77	0.98	1.27	1.50	1.02	2.68	2.80
K_2O	3.97	3.58	4.82	4.38	2.44	2.73	4.97	4.57	2.92	2.37
P_2O_5	0.13	0.19	0.12	0.13	0.10	0.12	0.14	0.10	0.17	0.14

*All compositions recalculated to 100% volatile-free basis.

1. NASC, weighted average of microprobe analyses (this study).
2. Average shale (Clark, 1924).
3. Average North American Paleozoic shale (Ronov and Migdisov, 1971).
4. Average Russian Paleozoic shale (Ronov and Migdisov, 1971).
5. Average North American Mesozoic/Cenozoic shale (Ronov and Migdisov, 1971).
6. Average Russian Mesozoic/Cenozoic shale (Ronov and Migdisov, 1971).
7. Average Canadian Proterozoic (Aphebian) shale (Cameron and Garrels, 1980).
8. Average Russian Proterozoic shale (Ronov and Migdisov, 1971).
9. Average Canadian Archean Shale (Cameron and Garrels, 1980).
10. Average Archean shale (Ronov and Migdisov, 1971).

The final important features shown on Fig. 3 are the six shale composites utilized by CAMERON and GARRELS (1980) to construct their average Canadian Proterozoic (Aphebian) shale, and the eight shale composites utilized for their average Canadian Archaean shale. The dispersion evident in these data illustrates the degree to which significant chemical variations can be masked in compiling comprehensive composites or averages. A similar amount of diversity in compositional characteristics may well exist in the individual shales used in the compilation of the NASC. Because the compositional characteristics of such composites need not correspond to any individual sample in the compilation, some caution in the interpretation of these composites is warranted.

REE heterogeneity in the NASC and the role of minor minerals

The analyses for the NASC now available, whether grouped by method of analysis or taken collectively, clearly indicate that this material is heterogeneous for the REE. The two complete analyses by isotope

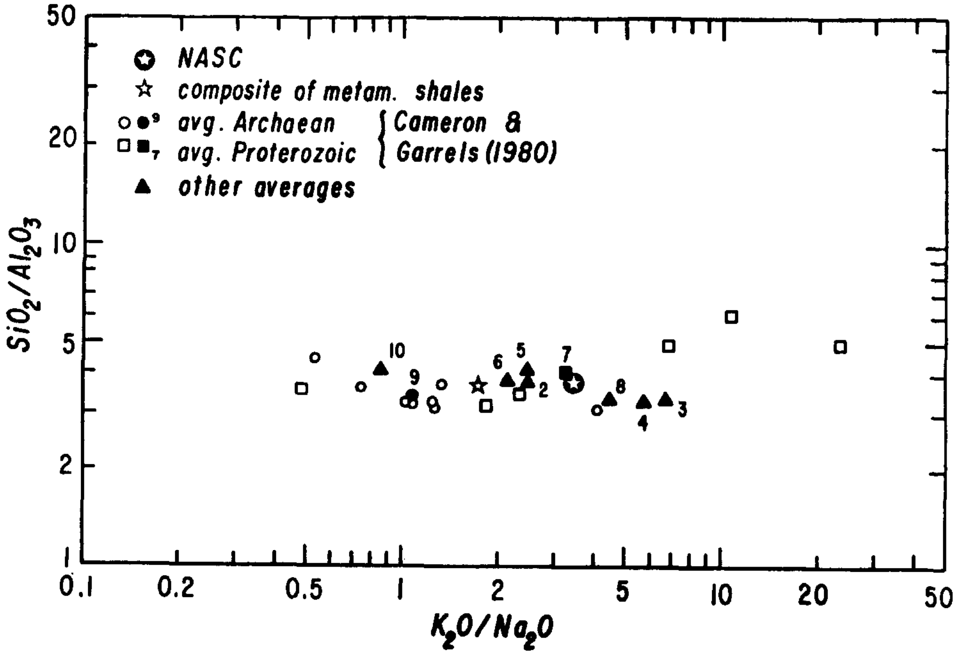

FIG. 3. SiO_2/Al_2O_3 vs. K_2O/Na_2O (weight ratios) for the NASC, the composite of metamorphosed shales, and selected other shale averages. The numbers adjacent to filled symbols correspond to the entries listed in Table 4. Open symbols represent individual local average shale compositions used by CAMERON and GARRELS (1980) to compile the grand average of Canadian Archaean and Proterozoic (Aphebian) shales.

dilution have systematic differences for several elements that are larger than the analytical errors that can be attributed to them (≤2%; GROMET, 1979). The remarkably smooth REE pattern shape for each determination confirms that random analytical errors for individual elements are small and do not contribute significantly to the observed differences. The differences among the neutron activation analyses are also systematic and outside their analytical errors both for the NASC and the metamorphosed shales. The deviations from smoothness of patterns from the earlier neutron activation work are mostly within the somewhat larger errors associated with those analyses. Thus analytical capabilities have for some time exceeded the quality of the composite for REE, although the composite appears to be significantly homogeneous for major elements.

The results of the trace element analyses provide strong evidence that minor phases in the NASC contain significant portions of the REE. The dissolution experiments document that an HF-resistant minor phase (or phases) holds approximately one third of the heavier REE. The microscopic observations suggest that zircon is a likely site for the REE in the undissolved residue. The other HF-resistant phases (aluminosilicate, graphite, opaques and possibly spinel) are expected to contain insignificant proportions of the REE on the basis of crystal chemical characteristics. Garnet, if it is indeed present in the residue, is a possible exception. However, the overall agreement among three separate REE analyses of the HF-soluble fraction (Fig. 2a)—despite varying lengths and intensities of attack—indicates that the HF-resistant and HF-soluble fractions each holds generally consistent and reproducible portions of the REE in the composite, and that the heavy REE-bearing, HF-resistant phase or phases are not being partially attacked. This is consistent with the insolubility of zircon in HF in an open beaker and inconsistent with the at least reluctantly reactive nature of garnet under such conditions.

The extent to which the REE in the HF-resistant fraction are contained in zircon can be evaluated further. An INAA analysis of the NASC gives a Zr concentration of 200 ppm (Table 3), indicating that the maximum amount of zircon in the NASC is approximately 0.041 weight %. If this quantity of zircon contained all the REE in the residue, the average zircon grain would have 6940 ppm Ce and 2840 ppm Yb. To determine if these implied REE concentrations are reasonable for crustal zircons, a comparison to values observed in zircon from a variety of crustal rock types is presented. A summary of available analyses is given in Table 5. The brevity of the table reflects the few studies reporting REE concentrations in zircon. The very large range in zircon Ce and Yb abundances, despite the few examples that have been studied, is notable. It must be emphasized that this limited compilation cannot be considered representative of the range or the mean of REE concentrations in crustal zircons, although it does establish a minimum range. With this limitation in mind, the Yb content inferred for the average NASC zircon is observed to be within the range of reported values (30–4100 ppm Yb) whereas the Ce content inferred for the average NASC zircon exceeds the highest reported value (2270 ppm Ce) by a factor of three.

This comparison suggests that zircon could account for much but probably not all of the heavier REE in the residue, and a lesser proportion of the lighter REE. It seems likely that other HF-resistant, strongly REE-enriched trace phases, as yet unidentified, also are present in the residue and contribute to the REE found there.

An alternative or additional source for the *lighter* REE in the residue could come from the associated soluble fraction if it was incompletely removed during the repeated washings in dilute acid. For example, if 5% of the REE in the soluble fraction were retained in the residue by adsorption or occlusion, all of the Ce (but less than 10% of the heavier REE) in the residue would be accounted for. Perhaps the somewhat lower REE contents found in the soluble fraction associated with the analyzed residue (Table 2, col. 9) compared to the other soluble fractions (Table 2, cols. 10 and 11) reflect this. (The latter two analyses were spiked before dissolution, effectively eliminating REE adsorption on or occlusion in the residue as a problem.)

Table 5. Zircon REE Contents (in μg/g)

Ce	Yb	Rock Type/Locality	Reference
104-127	529-598	Dacites/Japan	Nagasawa (1970)
16-24	392-720	Granites/Japan	
450	950	Bishop (felsic) tuff (early)/USA	Hildreth (1979)
2270	608	Bishop (felsic) tuff (late)/USA	
300-400	1400-3000	Skye Epigranites and Granophyre/U.K.	Exley (1980)
300-2000	2300-4100	Arkose/U.K.	
42	253	Granodiorite/USA	Gromet & Silver (1983)
19-47	119-144	Beach sands/India	Murali et al. (1983)
11-50	30-250	Plutonic igneous rocks/India	

Given that our observations require a significant fraction of the heavier REE in the NASC to be contained in one or more accessory phases, their uneven distribution in the NASC powder is a potential source of the observed heterogeneity in REE concentrations. In order to evaluate this, the physical state of the NASC powder was examined with the aid of a microscope. This revealed that the powder is characterized by a considerable range in grain size, and that among the coarser fractions there is an abundance of 0.1 mm to 0.3 mm-sized grains. This is cause for some concern as the disparity in the size of these grains and the very fine fractions of the powder can lead to partial segregation of the different size fractions during grinding and general handling. This problem is recognized in the preparation of most materials used for rock standards in that they are very finely and thoroughly ground. Unfortunately, such was not the case for the NASC or its constituent samples.

As a result, the non-uniform distribution of grains of different minerals in NASC powder must be considered as the probable cause of some chemical heterogeneity in the powder and aliquants taken from it. The magnitude of the heterogeneity is expected to be small for elements dispersed among the major minerals in the powder, but substantial for those elements contained in minor and trace phases. The problem is expected to be most severe for elements concentrated in phases that are particularly hard, have poor cleavage and a density very different from that of the majority of grains. In light of this and previous observations, it appears that the uneven distribution of zircon could well be the principal cause of the observed variations in heavy REE contents of the NASC. Presumably at least one other minor phase, one that concentrates light REE, is also involved as those elements are heterogeneously distributed. The REE analysis of the dilute acid leachate (column 12, Table 2) indicates that as much as 20% of some of the lighter REE and 10% of some of the heavier REE are contained in an easily soluble phase (*e.g.*, authigenic apatite?) or are adsorbed on mineral surfaces.

Further evidence that minor phases are the source of the heterogeneity, and that analytical error is not, is obtained indirectly from the analytical experiments on the four aliquants of the metamorphosed shale composite. The large number of elements analyzed in that experiment permits correlations in the concentrations of heterogeneously distributed elements to be identified. Despite relatively narrow concentration ranges observed among the four aliquants, strong coherence is seen between those element pairs that on crystal chemical grounds are expected to have correlated behavior. Values for correlation coefficients are shown in Table 6 for all element pairs yielding correlation coefficients $>|0.8|$ as well as for a few that are not. Light REE are well correlated with each other and with Sc, Th and Sb; Yb and Lu are correlated with each other and with Zr; Cr is well correlated with FeO. With only four samples and a very narrow range of variation in concentration, some correlations may not be meaningful, whether plausible or not, and some correlations will be poorer than expected (*e.g.*, Zr-Hf). For a coherent group such as the REE, for which chemical properties change gradually as a function of atomic number, the consistent pattern of correlations (light REE with each other and with Th, heavy REE with each other and Zr) and anticorrelations (light REE *versus* heavy REE and Zr) are statistically meaningful, plausible, and supportive of the idea that uneven distribution of zircon and other minor minerals is responsible for most of the observed sample heterogeneity among analyzed aliquants of the shale composites (note that the four determinations of Zr in the metamorphosed shale composite vary by 20%). Analytical errors are present in the older neutron activation data, and in some cases are greater than initially realized, but most of the differences among sets of results (Table 2) are a result of sample heterogeneity.

Table 6. Correlation coefficients (r) for pairs of elements in 4 aliquants of the metamorphosed shale composite.

La-Ce	.97	Ce-Sc	.87	Sm-Yb	-.86
La-Nd	.94	Yb-Lu	.98	Sm-Lu	-.83
La-Sm	.97	Yb-Zr	.80	Ce-Zr	-.40
La-Eu	.89	Cr-Fe	.98	Sc-Yb	-.99
La-Tb	.90	Zr-Hf	.64	Fe-Co	-.83
La-Th	.996	Ce-Yb	-.87	Fe-Na	-.96
La-Sb	.95	Ce-Lu	-.81	Ba-Na	-.81
				Cs-Hf	-.88

Recommended values for the NASC?

The presentation of a set of recommended values for the REE contents of the NASC with the precision and accuracy available with modern analytical techniques is precluded by the heterogeneity of the NASC powder. The three high precision analyses available are an insufficient sampling to insure that the heterogeneity has been averaged out. Additional analyses are not possible as the supply of NASC powder is nearly exhausted.

If a lesser degree of precision and accuracy is acceptable, as would be the case for general comparison to other REE patterns, the values for the three new analyses (columns 5, 6 and 7, Table 2) could be averaged, or if just those elements determined by isotope dilution are desired, the two complete isotope dilution analyses (columns 6 and 7) could be averaged. These averages provide a more precise relative REE pattern than the earlier analyses, particularly for several of the heavier REE as their precision was much poorer in the earlier work. Either of these averages falls within the range of the earlier analyses except in the case of Ce, which is lower in each of the three new analyses than in earlier analyses as well as in two of the HF-soluble (open beaker) fractions (columns 10 and 11, Table 2).

Concentrations of numerous other elements in the NASC are given in column 12, Table 3. These concentrations constitute a single analysis of a material known to be heterogeneous for certain trace elements and should be viewed with a corresponding degree of caution.

Implications for shale REE geochemistry

The results described above have some important implications for the interpretation of the REE pattern of the NASC, and of the REE patterns of other shales and sediments in general. The first concerns the presence of a significant portion of the REE, especially the heavier REE, in minor minerals. To the extent that this minor mineral fraction is detrital in origin, the heavy REE contents of sediments containing them are dependent on the factors that control the abundance and composition of the detrital resistate mineral assemblage. Such factors include sorting and winnowing by wave and current action during and after transportation and deposition. These processes are known to operate in the fluvial cycle, in the shallow marine environment of continental basins, platforms and shelves, and also to some extent on continental slopes, rises and the ocean floor (*e.g.*, KENNET, 1982). As a result, sediments produced in a wide variety of environments can be susceptible to these effects.

It should be noted here that the localization of a significant portion of the REE in minor minerals is not an observation limited to the NASC. For example, a detailed study by CULLERS *et al.* (1979) on REE in size fractions of sediments from the mid-continent of North America has shown that heavy minerals in these sediments can be a variable but appreciable reservoir of the REE, particularly the heavy REE. This effect was most pronounced in the silt-sized fractions, and as the examination of the NASC powder revealed, silt and sand-sized grains are common in the shales constituting the NASC.

An additional factor relevant to this problem is the growing appreciation of the importance of minor mineral assemblages as major sites for REE and other trace elements in plutonic igneous rocks (*e.g.*, BUMA *et al.*, 1971; SIMMONS and HEDGE, 1978; EXLEY, 1980; MITTLEFEHLDT and MILLER, 1983; GROMET and SILVER, 1983; NOYES *et al.*, 1983). Plutonic igneous rocks are a major component of the Earth's crust and as such must contribute significantly to sediment composites thought to be representative of that crust. The weathering of plutonic rocks whose REE are contained to varying degrees in resistate minor minerals will produce a sediment whose REE budget is controlled to some degree by that minor mineral assemblage. Unless the processes operating during weathering, transport and deposition have resulted in a sediment with the same proportional representation of these minor phases as was present in the source, the REE patterns of such sediments will be biased relative to the average REE pattern of the crustal rocks supplying detritus. In light of this, it is possible that variations in REE abundances and pattern shapes in some sediments may reflect localized changes in the abundance of minor phases rather than yielding information about variable proportions of rock types in sediment source areas. A similar caution may also apply to the REE patterns of those sediments in which a portion of the REE is contained in authigenic and/or diagenetic minerals, or where the detrital minerals have been affected by authigenic or diagenetic processes (*e.g.*, PIPER, 1974; CULLERS *et al.*, 1975, 1979). Other factors recognized as having an effect on the REE patterns of sediments include climate, intensity of weathering, acid-base character of weathering profiles and stream waters and depositional environment (*e.g.*, BALASHOV *et al.*, 1964; RONOV *et al.*, 1974; NESBITT, 1979; CULLERS *et al.*, 1979).

All of the above factors complicate the inference of sediment provenance from REE characteristics. While some or all of these factors may be averaged out in broadly sampled sediment composites (see following section), they are much less likely to be so masked in individual sediment samples. In fact, a considerable variability has been observed in the REE patterns of individual sediment samples in many studies (*e.g.*, HASKIN *et al.*, 1966a,b, 1968; CULLERS *et al.*, 1974, 1975, 1979; NANCE and TAYLOR, 1976), even if just shales or specific size fractions from shales of the same formation are considered. We concur with CULLERS *et al.* (1979) that our understanding of the interplay of factors affecting the REE contents of sediments is incomplete and that the interpretation of sedimentary REE patterns must be approached with caution.

A contribution to the interpretation of the NASC REE pattern

The rather limited variation in the relative REE patterns of post-Archaean sediment composites from many continental platforms and basins (*e.g.*, BALASHOV *et al.*, 1964; HASKIN *et al.*, 1966; NANCE and TAYLOR, 1976) (see Fig. 4) is a remarkable and significant observation. It is difficult to explain this observation without appealing to the fact that the crustal rocks exposed to erosion on each continent must have had on average very similar REE patterns, and that, as inferred by many workers, the REE patterns of the composites closely approximate the average REE pattern of these crustal rocks. This implies that for these composites, the largely local factors discussed in preceding sections are averaged out.

If composites such as the NASC are considered representative of the upper crust, the three new REE determinations of the NASC provide some improved constraints on the average REE pattern of the upper crust of "North America". Despite the heterogeneity discussed above, the improved accuracy of these data documents the smoothly fractionated nature of the

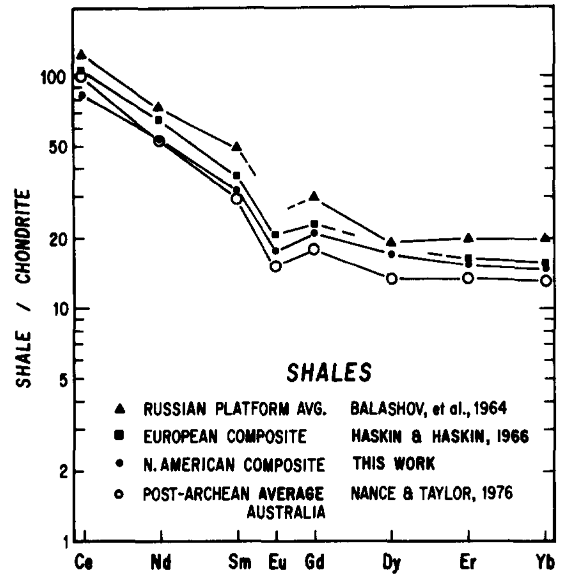

FIG. 4. REE distributions for shale averages or composites from four continents. The NASC REE distribution is derived from an average of columns 6 and 7, Table 2.

NASC REE pattern (Fig. 1). The persistence of a modest fractionation relative to chondrites across the heavier REE (Gd-Yb), a feature masked within the analytical uncertainties of prior measurements, is clearly shown. A significant aspect of this finding is that it permits rocks with moderately to steeply fractionated heavy REE patterns to constitute an important part of the upper crust. In fact, extensive North American granitic terrains are known to have an abundance of rocks with these characteristics (*e.g.*, ARTH and HANSON, 1975; BARKER *et al.*, 1976; FREY *et al.*, 1978; GROMET, 1979; GROMET and SILVER, 1983 and in prep.) and they should be represented in the crustal average. Inasmuch as no abundant, complementary material with a positive slope in the heavy REE is known and available to cancel the negative slope in the granitic rocks, the unfractionated heavy REE pattern originally inferred for the NASC from the early analyses was an unresolved problem.

We note that the modestly fractionated heavy REE pattern of the NASC does not limit the abundance of rocks with strongly fractionated REE patterns to small percentages of the crust; such rocks typically have very low heavy REE contents, allowing the rocks with less steeply fractionated patterns and higher heavy REE abundances largely to control the heavy REE fractionation of the average. This feature is schematically illustrated in Fig. 5 by showing REE patterns calculated for simple mixtures of two granodiorites from the Peninsular Ranges batholith. The granodiorites are representative of two major end-member REE types in the batholith (GROMET, 1979): patterns with moderate light REE enrichment and

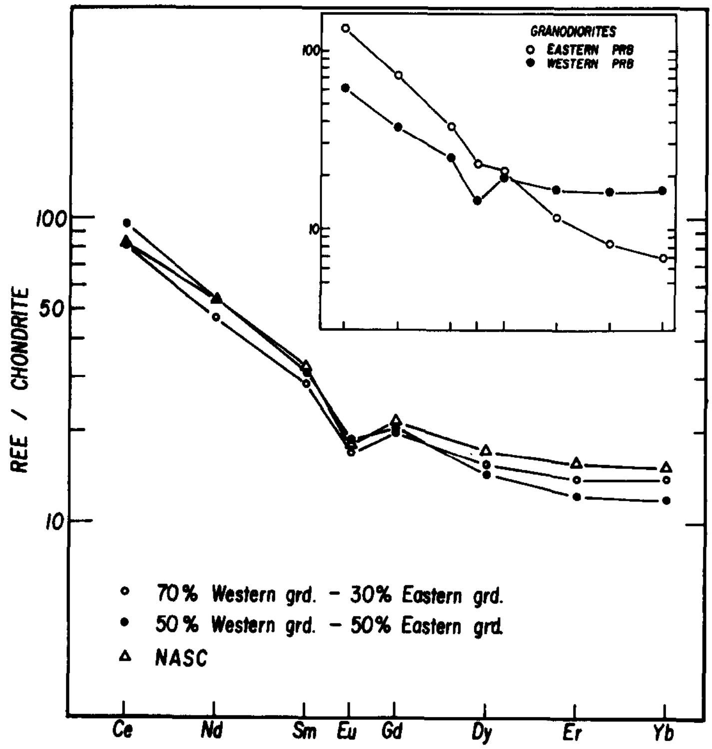

FIG. 5. Calculated REE patterns of mixtures of two granodiorites from the Peninsular Ranges batholith (GROMET, 1979). REE patterns of the two granodiorites, which are representative of the western and eastern regions of the batholith, are shown in the inset. Note that the REE pattern shape of the 70-30 mixture compares quite closely to that of the NASC, especially in the heavy REE.

nearly unfractionated heavy REE are characteristic of rocks from the western part of the batholith, and patterns with strong light REE enrichment and strongly fractionated, lower concentrations of the heavy REE are characteristic of rocks from the eastern part of the batholith. A 70-30 mixture of these two granodiorites yields a REE pattern quite close to the relative distribution found in the NASC especially in the heavy REE. The purpose of this calculation is not to argue that NASC-like REE patterns could arise by crudely mixing detritus derived from the Peninsular Ranges, but simply to point out that rocks with very strongly fractionated, heavy REE-poor REE patterns like the eastern granodiorite ($Ce_N/Yb_N = 18.6$) can be a major contributor to post-Archaean sediments along with other rocks possessing less fractionated, higher heavy REE abundances.

A caution

Although the REE patterns of the NASC and other similar sediment composites share features suggesting they are representative of the continental crust exposed to erosion, extension of this inference to sediment composites in general should be avoided unless reasonable justification can be provided. The reason for this is that the inference of representativeness of the continental crust is based on and appears only to apply to composites with broad geographic coverage and a predominance of continental platform and basin sediments in their compilation. The same argument cannot be made for sediment composites whose provenance is limited, such as where tectonic setting has imposed a pronounced bias on sediment provenance. For example, sediments in active "geosynclinal" areas typically sample a high proportion of local lithologies, many of which are volcanogenic. The REE patterns of these sediments commonly differ from those of continental platform and basin sediments regardless of age (*e.g.*, RONOV *et al.*, 1974; NANCE and TAYLOR, 1977). Isotopic studies also have indicated a dominance of local sources for such sediments (MCCULLOCH and WASSERBURG, 1978). Because of this bias, sediment composites from geosynclinal regions are unlikely to provide an average of the entire exposed continental crust at the time of their formation, although such composites may well be representative of their geographically and geologically more limited provenances.

The above considerations and caution are probably relevant to the interpretation of REE patterns of Archaean sediments, which as a group may have lower light REE contents than post-Archaean composites (TAYLOR and MCLENNAN, 1981a,b) and lack pronounced negative Eu anomalies (*e.g.*, WILDEMAN and HASKIN, 1973). The degree to which these REE characteristics are representative of Archaean crust may be limited by the observations that many Archaean detrital sediments, including "shaley" types, have features characteristic of locally derived sediments (*e.g.*, PETTIJOHN, 1943, 1972; HENDERSON, 1972; LOWE, 1980; BOAK *et al.*, 1982, 1983; BOAK, 1983), and that, as pointed out by DYMEK *et al.* (1983), there is an apparent underrepresentation of sediments from Archaean high-grade terrains in published REE studies of Archaean sediments. TAYLOR and MCLENNAN (1981a) have suggested, however, that Archaean sediments provide a fairly broad sampling of Archaean crust on the basis of an indicated uniformity in Archaean sediment REE patterns in several studies and evidence or indications of non-local components in some Archaean sediments. Additional studies of the REE characteristics of Archaean sediments will be useful in further evaluation of these concepts.

SUMMARY AND CONCLUSIONS

New analyses of the *mostly* North American shale composite document that minor phases contain significant portions of the REE in this material, and suggest that the observed heterogeneity in REE abundances for different aliquants is the result of uneven distribution of such phases in the NASC powder. Dissolution experiments show that approximately one third of the heavier REE are held in an HF-resistant minor phase or phases, probably to a large extent in zircon, and that as much as 20% of some of the lighter REE and 10% of the heavier REE are contained in an easily soluble phase (apatite?) or are adsorbed on mineral surfaces. The NASC is considerably more homogeneous in major element composition, which compares quite closely with other average shale compositions.

The new high-precision isotope dilution and INAA analyses of the NASC indicate its REE pattern is smoothly fractionated and that some relative fractionation persists through the heavier REE. If the NASC relative REE abundances are representative of the upper crust of North America (despite pitfalls in the compilation and homogeneity of the composite), the fractionation in the heavier REE allows granitic rocks with steeply fractionated REE distributions (which are known to constitute an important fraction of the upper crust of North America) to have a reasonable representation in the NASC provenances.

The results of this study raise a caution that the REE distributions of detrital sediments can be dependent to some extent on the sedimentological and other factors that influence the abundance and composition of the minor mineral assemblages. These effects appear to be most pronounced for individual sediment samples, but are muted or eliminated for well-constructed sediment composites. REE characteristics of sediment composites therefore are more likely to be representative of their provenances, but only those sediment composites whose provenances sample the exposed continental crust in an unbiased manner will be representative of that crust. Samples of individual sediments do have value in that they reflect the many processes contributing to their origin, albeit our ability to decipher them fully is limited at present. With comparatively rapid, easy and accurate analytical methods now available, the richness of information ultimately available from individual sediments should provide a better understanding of the many factors that influence their geochemical characteristics.

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REFERENCES

ARTH J. G. and HANSON G. N. (1975) Geochemistry and origin of the Early Precambrian crust of northern Minnesota. *Geochim. Cosmochim. Acta* **39**, 325–362.

BALASHOV YU. A., RONOV A. B., MIGDISOV A. A. and TURANSKAYA N. V. (1964) The effect of climate and facies environment on the fractionation of the rare earths during sedimentation. *Geochem. Int.* **5**, 951–969.

BARKER F., ARTH J. G., PETERMAN Z. E. and FRIEDMAN I. (1976) The 1.7 to 1.8 b.y. old trondhjemites of southwestern Colorado and northern New Mexico: geochemistry and depths of genesis. *Geol. Soc. Amer. Bull.* **87**, 189–198.

BAVINTON O. A. and TAYLOR S. R. (1980) Rare earth geochemistry of Archean metasedimentary rocks from Kambalda, Western Australia. *Geochim. Cosmochim. Acta* **44**, 639–648.

BOAK J. L. (1983) Petrology and geochemistry of clastic metasedimentary rocks of the Isua Supracrustal Belt, West Greenland. Ph.D. Dissertation, Harvard University.

BOAK J. L., DYMEK R. F. and GROMET L. P. (1982) Early crustal evolution: constraints from variable REE patterns in metasedimentary rocks from the 3800 Ma Isua Supracrustal Belt, West Greenland. *Lunar and Planetary Science XIII*, 51–52.

BOAK J. L., DYMEK R. F. and GROMET L. P. (1983) Petrology and rare earth element geochemistry of clastic metasedimentary rocks from the Isua Supracrustal Belt, West Greenland. *Geol. Surv. Greenland Bull.* **112**, 23–33.

BUMA G., FREY F. A. and WONES D. R. (1971) New England Granites: trace element evidence regarding their origin and differentiation. *Contrib. Mineral. Petrol.* **31**, 300–320.

CAMERON E. M. and GARRELS R. M. (1980) Geochemical compositions of some Precambrian shales from the Canadian Shield. *Chem. Geol.* **28**, 181–197.

CLARKE F. W. (1924) The data of geochemistry. *U.S. Geol. Surv. Bull. 770.*

CULLERS R. L., YEH L.-T., CHAUDHURI S. and GUIDOTTI C. V. (1974) Rare earth elements in Silurian pelitic schists from northwest Maine. *Geochim. Cosmochim. Acta* **38**, 389–400.

CULLERS R. L., CHAUDHURI S., ARNOLD B., LEE M. and WOLF C. W. (1975) Rare earth distributions in clay minerals and in the clay-sized fraction of the Lower Permian Havensville and Eskridge shales of Kansas and Oklahoma. *Geochim. Cosmochim. Acta* **39**, 1691–1703.

CULLERS R. L., CHAUDHURI S., KILBANE N. and KOCH R. (1979) Rare earths in size fractions and sedimentary rocks of Pennsylvanian-Permian age from the mid-continent of the U.S.A. *Geochim. Cosmochim. Acta* **43**, 1285–1301.

DENECHAUD E. B., HELMKE P. A. and HASKIN L. A. (1970) Analysis for the rare earth elements by neutron activation and Ge(Li) spectrometry. *J. Radioanal. Chem.* **6**, 97–113.

DYMEK R. F. and GROMET L. P. (1984) Nature and origin of orthopyroxene megacrysts from the St. Urbain anorthosite massif, Quebec. *Can. Mineral.* **22**, 297–326.

DYMEK R. F., BOAK J. L. and GROMET L. P. (1983) Average sedimentary rock rare earth element patterns and crustal evolution: some observations and implications from the 3800 Ma Isua Supracrustal rocks, West Greenland. In *Workshop on Early Crustal Genesis*, pp. 23–26. The Lunar and Planetary Institute, Houston.

EXLEY R. A. (1980) Microprobe studies of REE-rich accessory minerals: implications for Skye granite petrogenesis and REE mobility in hydrothermal systems. *Earth Planet. Sci. Lett.* **48**, 97–110.

FLANAGAN F. J. (1973) 1972 values for international geochemical samples. *Geochim. Cosmochim. Acta* **37**, 1189–1200.

FREY F. A. (1966) Rare-earth elements in basic and ultrabasic rocks. Ph.D. Thesis, University of Wisconsin-Madison.

FREY F. A., CHAPPELL B. W. and ROY S. D. (1978) Fractionation of rare-earth elements in the Tuolumne Intrusive Series, Sierra Nevada batholith, California. *Geology* **6**, 239–242.

GARRELS R. M. and MACKENZIE F. T. (1971) *Evolution of Sedimentary Rocks.* Norton, New York.

GLADNEY E. S., BURNS C. E. and ROELANDTS I. (1983) 1982 compilation of elemental concentrations in eleven United States Geological Survey rock standards. *Geostandards Newsl.* **7**, 3–226.

GOLDSCHMIDT V. M. (1938) Skrifter norske videnskaps-akad. Oslo I. *Mat.-Naturv. Kl.* **1938**, 4, 1.

GROMET L. P. (1979) Rare earth abundances and fractionations and their implications for batholithic petrogenesis in the Peninsular Ranges Batholith, California, USA, and Baja California, Mexico. Ph.D. Dissertation, California Institute of Technology.

GROMET L. P. and DYMEK R. F. (1982) A redetermination of REE in the North American Shale Composite and implications for crustal models. *EOS* **63**, 467.

GROMET L. P. and SILVER L. T. (1983) Rare earth element distributions among minerals in a granodiorite and their petrogenetic implications. *Geochim. Cosmochim. Acta* **47**, 925–939.

HASKIN L. A. and GEHL M. A. (1962) The rare-earth distribution in sediments. *J. Geophys. Res.* **67**, 2537–2541.

HASKIN L. A. and FREY F. A. (1966) Dispersed and not-so-rare earths. *Science* **152**, 299–314.

HASKIN M. A. and HASKIN L. A. (1966) Rare earths in European shales: A redetermination. *Science* **154**, 507–509.

HASKIN L. A., FREY F. A., SCHMITT R. A. and SMITH R. H. (1966a) Meteoritic, solar, and terrestrial rare-earth distributions. *Phys. Chem. Earth* **7**, 167–321.

HASKIN L. A., WILDEMAN T. R., FREY F. A., COLLINS K. A., KEEDY C. R. and HASKIN M. A. (1966b) Rare earths in sediments. *J. Geophys. Res.* **71**, 6091–6105.

HASKIN L. A., WILDEMAN T. R. and HASKIN M. A. (1968) An accurate procedure for the determination of the rare earths by neutron activation. *J. Radioanal. Chem.* **1**, 337–348.

HENDERSON J. B. (1972) Sedimentology of Archaean turbidites at Yellowknife, Northwest Territories. *Can. J. Earth Sci.* **9**, 882–902.

HILDRETH W. (1979) The Bishop Tuff: Evidence for the origin of compositional zonation in silicic magma chambers. *Geol. Soc. Amer. Spec. Paper 180*, 43–75.

JACOBS J. W., KOROTEV R. L., BLANCHARD D. P. and HASKIN L. A. (1977) A well-tested procedure for instrumental activation analysis of silicate rocks and minerals. *J. Radioanal. Chem.* **40**, 93–114.

KENNET J. P. (1982) *Marine Geology.* Prentice-Hall, N.J.

KOROTEV R. L., MORRIS R. V. and LAUER H. V., JR. (1984) Stratigraphy and geochemistry of the Stone Mountain core (64001/2). *Proc. Lunar and Planet. Sci. Conf. 15th, J. Geophys. Res.* (in press).

KROGH T. E. (1973) A low-contamination method for hydrothermal decomposition of zircon and extraction of

U and Pb for isotopic age determinations. *Geochim. Cosmochim. Acta* **37**, 485–494.

LINDSTROM D. J. and KOROTEV R. L. (1982) TEABAGS; Computer programs for instrumental neutron activation analysis. *J. Radioanal. Chem.* **70**, 439–458.

LOWE D. R. (1980) Archean sedimentation. *Ann. Rev. Earth Planet. Sci.* **8**, 145–167.

MASUDA A., NAKAMURA N. and TANAKA T. (1973) Fine structures of mutually normalized rare-earth patterns of chondrites. *Geochim. Cosmochim. Acta* **37**, 239–248.

MINAMI E. (1935) Gehalte an seltenen Erden in europaischen und japanishen Tonschiefern. *Nachr. Ges. Wiss. Gottingen, Math-physik Kl.* **IV**, 1, 155–170.

MITTLEFEHLDT D. W. and MILLER C. F. (1983) Geochemistry of the Sweetwater Wash pluton, California: Implications of "anomalous" trace element behavior during differentiation of felsic magmas. *Geochim. Cosmochim. Acta* **47**, 109–124.

MCCULLOCH M. T. and WASSERBURG G. J. (1978) Sm-Nd and Rb-Sr chronology of continental crust formation. *Science* **200**, 1003–1011.

MCLENNAN S. M., TAYLOR S. R. and MCGREGOR V. R. (1984) Geochemistry of Archean metasedimentary rocks from West Greenland. *Geochim. Cosmochim. Acta* **48**, 1–13.

MURALI A. V., PARTHASARATHY R., MAHADEVAN T. M. and SANKAR DAS. M. (1983) Trace element characteristics, REE patterns and partition coefficients of zircon from different geological environments—A case study on Indian zircons. *Geochim. Cosmochim. Acta* **47**, 2047–2052.

NAGASAWA H. (1970) Rare-earth concentrations in zircons and apatites and their host dacites and granites. *Earth Planet. Sci. Lett.* **9**, 359–364.

NANCE W. B. and TAYLOR S. R. (1976) Rare earth patterns and crustal evolution I: Australian post-Archean sedimentary rocks. *Geochim. Cosmochim. Acta* **40**, 1539–1551.

NANCE W. B. and TAYLOR S. R. (1977) Rare earth element patterns and crustal evolution II: Archean sedimentary rocks from Kalgoorlie, Australia. *Geochim. Cosmochim. Acta.* **41**, 225–231.

NESBITT H. W. (1979) Mobility and fractionation of rare earth elements during weathering of a granodiorite. *Nature* **279**, 206–210.

NOYES H. J., FREY F. A. and WONES D. R. (1983) A tale of two plutons: geochemical evidence bearing on the origin and differentiation of the Red Lake and Eagle Peak plutons, central Sierra Nevada, California. *J. Geol.* **91**, 487–509.

PETTIJOHN F. J. (1943) Archean sedimentation. *Bull. Geol. Soc. Amer.* **54**, 925–972.

PETTIJOHN F. J. (1972) The Archean of the Canadian Shield: A resume. *Geol. Soc. Amer. Mem. 135*, 131–149.

PIPER D. Z. (1974) Rare earth elements in the sedimentary cycle: A summary. *Chem. Geol.* **14**, 285–304.

RONOV A. B. and MIGDISOV A. A. (1971) Geochemical history of the crystalline basement and sedimentary cover of the Russian and North American platforms. *Sedimentology* **16**, 137–185.

RONOV A. B., BALASHOV YU. A., GIRIN YU. P., BRATISHKI R. KH. and KAZAKOV G. A. (1974) Regularities of rare-earth element distribution in the sedimentary shell and in the crust of the earth. *Sedimentology* **21**, 171–193.

SIMMONS E. C. and HEDGE C. E. (1978) Minor element and Sr-isotope geochemistry of Tertiary stocks, Colorado Mineral Belt. *Contrib. Mineral. Petrol.* **67**, 379–396.

TAYLOR S. R. (1962) Meteoritic and terrestrial rare earth abundance patterns. *Geochim. Cosmochim. Acta* **26**, 81–88.

TAYLOR S. R. (1977) Island arc models and the composition of the continental crust. *Amer. Geophys. Union, Maurice Ewing Series* **I**, 325–335.

TAYLOR S. R. and MCLENNAN S. M. (1981a) The composition and evolution of the continental crust: rare earth element evidence from sedimentary rocks. *Phil. Trans. Roy. Soc. Lond.* **A301**, 381–399.

TAYLOR S. R. and MCLENNAN S. M. (1981b) The rare earth element evidence in Precambrian sedimentary rocks: implications for crustal evolution. In *Precambrian Plate Tectonics* (ed. A. KRONER) Chapter 21, pp. 527–548, Elsevier.

WILDEMAN T. R. and HASKIN L. A. (1973) Rare earths in Precambrian sediments. *Geochim. Cosmochim. Acta* **37**, 419–438.