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AVERAGE SEDIMENTARY ROCK RARE EARTH ELEMENT PATTERNS AND CRUSTAL EVOLU-TION: SOME OBSERVATIONS AND IMPLICATIONS FROM THE 3800 Ma ISUA SUPRACRUSTAL BELT, WEST GREENLAND. R.F. DYMEK, Dept. of Geol. Sci., Harvard Univ., Cambridge, MA 02138; J.L. BOAK, Arco, P.O. Box 360, Anchorage, AK 99510; L.P. GROMET, Dept. of Geol. Sci., Brown Univ., Providence, RI 02912

<u>INTRODUCTION</u>: The hypotheses that rare earth element (REE) abundances and patterns in clastic sedimentary rocks trace the unidirectional chemical evolution of the upper continental crust, and that the "average" REE pattern of Archaean sediments is fundamentally different from that observed in post-Archaean sediments, have been advanced in recent years (<u>e.g.</u> [1]). If correct, such conclusions indicate substantial differences in the average composition of Archaean crust, and place important constraints on growth <u>vs</u>. no-growth models of continental development (e.g. [2,3]).

These hypotheses rely heavily on three very key assumptions: (a) REE experience no relative fractionation during weathering, erosion, deposition and diagenesis accompanying the transformation of igneous rock into sediment; (b) REE in sediments provide a broad average of available source areas at the time of sedimentation; and (c) sampled units are representative of sediment deposited in the area at the time of formation. Moreover, in the case of <u>meta-</u> sediments, with which one is commonly faced in ancient terranes, it is also assumed that metamorphism (at least through medium grades prior to the onset of melting) does not perturb whole-rock REE patterns. Collectively, these assumptions outline the rationale for linking sediment REE patterns to those in igneous rocks. However, none of these assumptions have been tested extensively, although broad similarities among REE patterns in Phanerozoic sediments (cf. [4]) seem to support the viewpoint that averaging of source area REE does in fact occur, given the diversity of REE patterns in crustal igneous rocks.

We are, however, quite concerned with point (c), <u>i.e.</u>, whether published REE patterns on Archaean sediments are representative of Archaean sediments in general, whether they reflect accidents of preservation, or whether there is an inherent bias in the data base, albeit unintentional. For example, anyone familiar with studies of Archaean geology will recognize the nearly complete absence of data on sediments from high-grade terrains, whereas most data are for graywackes from low-grade greenstone belts, which, as pointed out by Pettijohn [5], bear a strong resemblance to Phanerozoic eugeosynclinal sediment suites.

In this report, we present REE data on a set of clastic metasediments from the 3800 Ma Isua Supracrustal belt, West Greenland. Each of two units from the same sedimentary sequence has a distinctive REE pattern, but the average of these rocks bears a very strong resemblance to the REE pattern for the North American Shale Composite (NASC), and departs considerably from previous estimates of REE patterns in Archaean sediments. We regard the possibility that the source area for the Isua sediments discussed here resembled that of the NASC as highly unlikely. However, REE patterns like that in the NASC may be produced by sedimentary recycling of material yielding patterns such as are found at Isua.

<u>GEOLOGICAL SETTING</u>: The Isua supracrustals are located \sim 140 km northeast of Godthab, central West Greenland, where they crop out in an arcuate belt surrounded and locally intruded by <u>ca</u>. 3700 Ma Amitsoq orthogneiss. Ages on various supracrustal units are in the 3700-3800 Ma range, with the most precise determination being $3769\pm_8^{11}$ Ma by U-Pb methods on single zircons [6]. Of particular significance to the present study is a Sm-Nd whole rock isochron age of 3770±130 Ma [7] on leucoamphibolite ("garbenschiefer" formation), which establishes a minimum age of deposition for the protolith of the Dymek, R.F. <u>et al</u>.

metasediments, as this unit is apparently intrusive into the section.

Several descriptions of Isua geology have been published [10,11], which outlined the presence of metavolcanic and clastic and chemical metasedimentary units. More recent detailed mapping [12] has revealed a coherent stratigraphy. The main supracrustal group - Sequence A - crops out along the entire length of the belt, and contains various amphibolites, quartz-rich chemical metasediment (including carbonate, silicate and magnetite ironstone), calc-silicate gneiss, felsic muscovite-biotite gneiss, and minor garnet-biotite schist. A tectonically separate group - Sequence B - crops out only in the eastern part of the belt, and consists of a lower unit of felsic muscovite-biotite gneiss (MBG) and an upper unit of predominantly garnet-biotite schist (GBS). The contact between the lower and upper units of Sequence B is gradational. MBG have been referred to as "pelitic metagraywackes", whereas GBS represents a series of "ferruginous shales" comprising pelitic to semipelitic to mafic types.

The relationship between Sequences A and B is unclear: Sequence B may be older than or correlate to the lower part of Sequence A, but substantial differences in chemical composition suggest no direct relationship. In this report, we discuss only samples from Sequence B.

<u>RESULTS</u>: REE were analyzed by isotope dilution mass spectrometry; chondrite-normalized data for 12 samples are illustrated on Figure 1.

MBG have REE patterns that are enriched and moderately fractionated with respect to chondrites $(Ce_N/Yb_N=6.8-8.0)$, with highly variable negative Eu anomalies (Eu/Eu *= 0.45-0.96) and a slight flattening in the heavy REE. The similarity in REE pattern shape for these samples, which span a wide range of bulk composition $(e.g., SiO_2=58-76 \text{ wt %})$, suggests that a single component or a relatively constant mixture of components dominates the REE character-istics of MBG. Some Archaean felsic igneous rocks have REE patterns not unlike the MBG [13].

GBS have REE patterns that are less enriched and less fractionated than MBG, and two pattern shapes are discernible. The four samples with lowest REE abundances, which represent pelitic and semipelitic rocks (garn + bio± musc±stl), have fractionated light REE, small Eu anomalies of variable sign, and a slope reversal for the heavy REE (i.e., $Gd_N < Yb_N$). Here again, the similarity in pattern shape suggests a single REE component or mixture of components, although we are unaware of any igneous rocks that have REE pattern shapes like these four GBS samples.

The fractionated light REE suggest a contribution from material not unlike that of the MBG, with which the GBS are locally interlayered. High Cr and Ni contents in GBS (up to 850 and 350 ppm respectively) may indicate a contribution from mafic material. Mixing of REE derived from basaltic rocks (low abundances, unfractionated patterns) with REE derived from felsic rocks (high abundances, fractionated patterns) could explain the lowered light REE abundances in GBS, but we are unable to provide a completely satisfactory explanation for the slope reversal in the heavy REE.

The fifth GBS sample (28-6A), which represents a mafic metasediment (garn +bio+hbl), has relatively unfractionated light REE, a small positive Eu anomaly and only slighlty fractionated heavy REE. The REE pattern shape for this sample strongly resembles that found in Isua amphibolites [8,14], except that it is enriched by a factor of two. This suggests that the REE in this sample were derived almost exclusively from a mafic source.

DISCUSSION: Although the REE patterns for MBG and GBS are clearly different (Figure 1), the fact that these units are interlayered in the field indicates that they were deposited penecontemporaneously and sampled a diverse suite of crustal materials that were in existence at the time of deposition.

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Hence, their REE provide some type of estimate of source area characteristics, but how one constructs an average REE pattern and what that average means, are problematic. Moreover, there is no guarantee that mixing proportions of REE correspond in a direct way to volume proportions of crustal rocks.

The average REE patterns for MBG and GBS are shown in Figure 2. Both convey the general pattern shape of the individual samples in each unit (except for GBS 28-2A as noted above; however, it would be inappropriate to exclude this from the average; were this analysis in fact excluded, it would not change the shape of the average GBS pattern in any significant way). Two average REE patterns for Sequence B are also indicated in Figure 2. The first (left) is simply the arithmetic mean of the twelve analyzed samples, and is shown for illustrative purposes only. The second (right) was calculated by weighting each unit in proportion to its abundance in the field (3 parts MBG: 2 parts GBS). Important features of the Sequence B average metasediment pattern are the enriched and fractionated light REE and the substantial negative Eu anomaly. Also illustrated in Figure 2 (right) are REE patterns for the North American Shale Composite (NASC: [9]) and for average Archaean sediment (AAS: [1]). The similarity in REE pattern shape between the Isua average and NASC is evident, as is the difference between AAS and NASC. These features are emphasized further in Figure 3, where both the Isua Sequence B average and AAS are normalized to the NASC. The relatively flat unfractionated pattern for the Isua average is particularly noteworthy.

CONCLUSIONS: The results reported here lead to the following tentative conclusions. (1) The REE patterns for Isua Seq. B MBG indicate the existence of crustal materials with fractionated REE and negative Eu anomalies at 3800 MA. Processes such as feldspar fractionation in shallow level magma chambers or intracrustal partial melting may have been important in the development of the sediment source rocks. (2) The average Seq. B REE pattern resembles that of the NASC. The methods by which average REE patterns for sediments are determined, and what the significance of such averages is, require further evaluation. (3) If the Seq. B average is truly representative of its crustal sources, then this early crust could have been extensively differentiated. In this regard, a proper understanding of the NASC pattern, and its relationship to post-Archaean crustal REE reservoirs, is (4) The Isua results may represent a "local" effect. Additional essential. study of Archaean sediment REE characteristics, especially those in highgrade terrains, are warranted.

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Figure 1. REE patterns for Isua Seq. B metasediments. The data for 629-7C are revised from those reported previously [8], based on reanalysis using HF bomb dissolution. Reanalysis of selected other samples confirms original patterns.



Figure 2. (left) Average REE patterns for data shown in Fig. 1; "all data" is the arithmetic mean of the 12 analyzed samples. (right) Isua Seq. B weighted average (3 parts MBG: 2 parts GBS) compared to REE patterns for NASC [9] and for average Archaean sediment (AAS) [1].



Figure 3. Comparison of NASCnormalized REE patterns for Isua Sequence B weighted average and "average"Archaean sediment (AAS). Note relatively "unfractionated" pattern for the Isua average, whereas AAS shows light REE "depletion", positive "Eu anomaly", and lowoverall REE concentrations.