A negative Ce anomaly in a peridotite xenolith: Evidence for crustal recycling into the mantle or mantle metasomatism?

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Abstract—The presence of negative cerium anomalies in island arc lavas has been considered enigmatic. Such negative Ce anomalies must be inherent in the source region and can be produced by subducting pelagic sediments + seawater-altered basalts (SWAB) into the mantle. A mantle peridotite from the Mahalula alkaline also contains a negative Ce anomaly, which can be produced by sediment recycling into the upper mantle. However, in spite of the poorly defined effects of cryptic metasomatism and associated /O2 conditions, such a process also seems plausible for the generation of negative Ce anomalies.

In order to define the petrogenesis of this peridotite within the constraints of the present experimental data, we have attempted various mixing models with the end-members: mantle peridotite, Pacific sediment and seawater-altered basalt. In our model, it was assumed that negative Ce anomalies cannot be produced by magmatic or metasomatic processes. Best results were obtained from mixing a maximum of 3 to 5% seawater-altered basalt and 2 to 3% pelagic sediment, with a LREE-enriched mantle precursor. Our model stresses the importance of the contribution that recycled crustal materials can have in the composition of the upper mantle, in particular the recognition of a crustal signature in a mantle regime.

INTRODUCTION

THE RARE EARTH ELEMENTS (REE) have proven to be effective geochemical indicators, since they are sensitive to igneous processes that operate during magma genesis and evolution (e.g. ALLEGRE et al., 1977; ALLEGRE and MINSTER, 1978; HANSON, 1980). The configuration of the 4f electron shell allows Ce and Eu to deviate from the general 3+ valency. These elements may develop anomalies due to reduction (Eu3+ → Eu2+) or oxidation (Ce3+ → Ce4+). It is the vastly different dissociation constants (Kd) of the reduced and oxidized species that produce anomalies in otherwise smooth REE profiles. In igneous systems, the Eu2+ species may already exist at the onset of partial melting, but it is possible that reduction of Eu3+ can occur in magmatic processes. The increased ionic radius of Eu2+ and its compatible charge leads to its preferential incorporation (Kd Eu2+ > Kd Eu3+) into the Ca site of plagioclase (Kd plag Eu2+ > Kd plag Eu3+). As such, negative and positive Eu anomalies have been reported in many igneous rocks including meteorites, lunar samples, as well as terrestrial examples (e.g. WARREN, 1985; HENDERSON, 1984).

The presence of Ce anomalies in igneous rocks is enigmatic. The experimental work of SCHREIBER et al. (1980) demonstrated that Ce4+ is unlikely to occur in a magmatic system due to the reaction

\[ \text{Ce}^{4+} + \text{Fe}^{2+} = \text{Ce}^{3+} + \text{Fe}^{3+}. \]

As Fe2+ will always be in excess of Ce in basaltic magmas, the presence of Ce4+ should never occur in magmatic situations. With Ce present in only one oxidation state in the magma (i.e. only one Kd for Ce ions), no igneous process is available for the production of an anomaly.

Negative Ce anomalies in basaltic island arc lavas have been reported from a variety of locations [e.g. the Solomon Islands (DIXON and BATIZA, 1979; WHITE and PATCHETT, 1984); HEMING and RANKIN (1979) and HOLE et al. (1984)] argued for the negative Ce anomaly to be present in the source region prior to partial melting. However, another hypothesis is that Ce anomalies arise in the mantle through fluid-rock fractionation associated with the slab (WHITE, pers. commun., 1989). Evidence for this comes from areas where arc lavas contain slight negative Ce anomalies, whereas the sediment immediately in front of the arc contains a bulk positive Ce anomaly (WHITE and DUPRE, 1986).

ORIGIN OF NEGATIVE Ce ANOMALIES

The behavior of Ce is largely controlled by its oxidation and reduction chemistry. The oxidation of the soluble Ce4+ to the insoluble Ce4+ species is responsible for the negative Ce anomaly in seawater (e.g. ELDERFIELD and GREAVES, 1982; PALMER, 1983; DEBAAR et al., 1983, 1985). Scavenging of elements by settling Fe-Mn particles facilitates the preferential removal of Ce4+ from the water column and incorporation into Fe-Mn nodules which contain large positive Ce anomalies (ELDERFIELD et al., 1981; FLEET, 1984). The REE contents of pelagic sediments indicate that there is usually a negative Ce anomaly present (e.g. PIPER and GRAEF, 1974; HOLE et al., 1984; WANG et al., 1986), due to interaction with seawater. Furthermore, the magnitude of the Ce anomaly in pelagic sediments appears to vary with age (WANG et al., 1986; KAY and KAY, 1988). A negative Ce anomaly has also been observed in seawater-altered basalts (SWAB) (e.g. MASUDA and NAGASAWA, 1975; MENSZIES et al., 1977; LUDDEN and THOMPSON, 1979), again due to interaction with seawater. Therefore, it is evident that certain areas of the seafloor can exhibit bulk negative Ce anomalies.

Several studies have reported negative Ce anomalies in island arc lavas, but did not comment upon them or considered them a weathering phenomenon or an analytical artifact (e.g. MASUDA, 1968; TAYLOR et al., 1968; JAKES and GILL,
1970; EWART et al., 1973; KAY and HUBBARD, 1978). Later authors proposed that the introduction of pelagic sediment into the source region can produce such anomalies (HEMING and RANKIN, 1979; DIXON and BATIŽA, 1979; WHITE and PATCHETT, 1984; HOLE et al., 1984).

Therefore, it is significant to discover a signature of an inherent negative Ce anomaly in a mantle xenolith from the Malaitan alnomite, Solomon Islands. This implies a significant role for crustal recycling in the evolution of the mantle and generation of magmas. Indeed, BIELSKI-ZYSKIND et al. (1984), in an isotopic study of Malaitan mantle xenoliths, concluded that a crustal component existed in the mantle beneath Malaita. FREY and GREEN (1974) have also reported negative Ce anomalies from three Iherzolite xenoliths entrained in basanite from Victoria, Australia. Even the host basanite has a negative Ce anomaly. However, these authors neglected to comment upon these REE patterns, possibly because of the errors inherent in analysis by INA. OTTONELLO et al. (1979) reported negative Ce anomalies in some Ligurian peridotites from the Alps. These authors considered the Ce anomaly to be a product of peridotite serpentinization, but report only whole-rock data, rather than clinopyroxene separates.

We report the occurrence of a negative Ce anomaly in a mantle peridotite xenolith (CRN211) from the Malaitan alnomite, Solomon Islands. The REE contents of this peridotite form the main thrust of this paper. Major and trace element, and isotope geochemistry of the minerals of this peridotite confirm its mantle origin (NEAL, 1985). The presence of this Ce anomaly has important implications for crustal recycling into the mantle beneath Malaita and generation of Ce-anomalous lavas (cf. JAKES and GILL, 1970; WHITE and PATCHETT, 1984).

GEOLOGICAL SETTING

The Solomon Islands chain delineates the boundary between the Pacific and Indo-Australian plates. The area is dominated by the Ontong Java Plateau (OJP), which is an overthickened portion (up to 42 km) of oceanic crust (COLEMAN, 1976; HUSSONG et al., 1979), abutting the Indo-Australian plate (Fig. 1). The island of Malaita is formed from the obducted leading edge of the OJP. Pipe-like bodies of alnomite (a mica lamprophyre with melilitite in the groundmass) were explosively emplaced in limestones and mudstones which have been folded into NW-SE trending anticlines and synclines (RICKWOOD, 1957). The pipes at Babaru’u and Kwakwai have a core of fine-grained, black alnomite containing megacrysts, surrounded by an autolithic breccia containing peridotite xenoliths, macrocrysts, megacrysts and xenoliths of crustal country rock (NIXON and BOYD, 1979; NEAL, 1985).

RARE EARTH ELEMENTS

Analytical technique

An ultrapure mineral separate of clinopyroxene from CRN211 was prepared by progressive leaching in HCl and HF acids with repeated handpicking. Whole-rock analysis was considered meaningless due to the degree of olivine alteration. The ultrapure clinopyroxene mineral separate was analyzed by isotope dilution mass spectrometry for the REE and was spiked prior to dissolution. The REE were separated on ion exchange columns and measured automatically on a VG Isomass 54E spectrometer, using the method of THIRLWALL (1982). The terms “depleted” and “enriched” are used relative to a flat, chondrite-normalized, bulk Earth REE pattern.

The analytical technique used is critical in the detection of negative Ce anomalies. Such anomalies could result from the dissolution procedure, if Ce was oxidized and precipitated prior to equilibration with the spike (THIRLWALL and GRAHAM, 1984). We feel this is unlikely as the sample was spiked prior to dissolution and care was taken to ensure that all sample was dissolved.

Results

The REE analysis of CRN211 (cpx) is presented in Table 1 and Fig. 2, and a large, negative Ce anomaly is superimposed on a generally LREE-enriched profile ([Ce/Ce*]N = 0.36). The remaining clinopyroxene separate was re-leached and handpicked prior to two further analyses for the REE. Results are within ±1% of the first REE profile. Based on the modal % of clinopyroxene in the peridotite and assuming all the REEs are contained in clinopyroxene, the whole-rock pattern may be calculated (Fig. 2). REE contents of the olivine, orthopyroxene and spinel are typically so low as to not raise these whole-rock estimates appreciably (i.e. <5%).

MODELING

Although there is compelling evidence to suggest the subduction of Ce-anomalous crustal components, there is a lack of experimental evidence to either support or refute the possibility of a metasomatic or fluid-rock interaction for the production of negative Ce anomalies. In our study, we model
the xenolith CRN211 by assuming sediment subduction into the mantle. This is not to suggest this is the only mechanism by which such negative Ce anomalies can be produced, but at present it is the most constrained. Furthermore, negative Ce anomalies in subducted pelagic sediments and SWAB could locally impart a negative Ce anomaly to the mantle, if it survived the subduction processes.

In order to explain the negative Ce anomaly in mantle peridotite CRN211, we have attempted bulk mixing calculations between mantle and subducted components. Similar modeling has been undertaken by Hole et al. (1984) to generate the Ce-anomalous lavas from the Mariana Islands. These authors used a MORB-depleted mantle, Pacific Authigenic Weighted Mean Sediment (PAWMS—an average of Cenozoic sediments) and a small fluid contribution (1%) from the dehydrating slab. The PAWMS component is comprised of 95% average nanofossil ooze and 5% average fergusitic clay from the Nazca plate. They considered that a contribution between 0.3 and 0.5% PAWMS was required in the source to generate the small negative Ce anomalies. The small fluid contribution is required to generate high Rb/Ba ratios.

We have not considered this fluid contribution, as we assume that the generation of the mantle peridotite occurs at a deeper level, at which the slab-derived fluid will be of minimal importance. Our modeling includes: 1) a seawater-altered basalt (SWAB) component; 2) pelagic sediment; and 3) mantle peridotite. The SWAB component is included because this forms a significant proportion of subducted material and can contain a negative Ce anomaly of its own (cf. Ludden and Thompson, 1979).

### End-member components

We assume that the mantle component contains no Ce anomaly and must be LREE-enriched in order to produce the general LREE enrichment of our mantle peridotite. The LREE-enriched Malaitan peridotite PHN4015 is taken as our mantle component (Table 2 and Fig. 3) for the modeling of CRN211. This is representative of the LREE-enriched mantle portion that is present beneath Malaita (Neal, 1985, 1988). Therefore, the sediment-SWAB component must contain a bulk negative Ce anomaly greater than that observed in CRN211.

The modeling components must also predate the age of anehite eruption (34 Ma; Davis, 1977), being at least early Eocene in age. Two sediment compositions, displaying large, negative Ce anomalies, are used (Table 2 and Fig. 3): 1) the...
Cenozoic PAWMS composition of HOLE et al. (1984) ([Ce/Ce*]N = 0.21); and 2) the surface sediment A-29 from the East Pacific Rise of PIPER and GRAEF (1974) ([Ce/Ce*]N = 0.27). These components are chosen in order to demonstrate that the REE profile of CRN211 may be generated by subduction and mixing of SWAB and pelagic sediment with a LREE-enriched mantle.

There is some controversy as to the presence and magnitude of a negative Ce anomaly in pre-Cenozoic Pacific sediments. KAY and KAY (1988) indicate the pre-Cenozoic northern Pacific pelagic sediments contain only small negative Ce anomalies ([Ce/Ce*]N ≈ 0.8). However, LIE et al. (1988) described upper Cretaceous carbonates with large negative Ce anomalies from DSDP Hole 316 ([Ce/Ce*]N ≈ 0.2). In this respect, the PAWMS composition of HOLE et al. (1984) is a feasible component involved in the petrogenesis of our mantle peridotite. The SWAB component 15-2A (Table 2 and Fig. 3) of LUDDEN and THOMPSON (1979) is also used in our modeling. This sample is the weathered outer portion of an Atlantic MOR basalt, and although it is a somewhat extreme composition, it is of the required age (46 Ma) and contains the requisite negative Ce anomaly ([Ce/Ce*]N = 0.38). It is the usual REE signature of CRN211 which suggests that extraordinary and somewhat unique conditions are required for its petrogenesis. Therefore, the crustal components chosen are, by necessity, somewhat extreme.

**Modeling results**

The modeling presented in Fig. 4 and Table 3 is intended to be illustrative rather than absolute. These results demonstrate that our mantle peridotite can be generated by mixing various combinations of subducted components with a LREE-enriched mantle: a) sediment + PHN4015; b) SWAB + PHN4015; or c) both sediment and SWAB + PHN4015. It is difficult to estimate which combination of components is the most realistic, inasmuch as all sediment may be removed by subduction, and the SWAB component may not always exhibit a negative Ce anomaly (e.g. LUDDEN and THOMPSON, 1979). However, the amount of pelagic sediment required is greater than the ~1% postulated for the petrogenesis of island arc volcanics (e.g. HOLE et al., 1984; WHITE and PATCHETT, 1984; KAY and KAY, 1988).

**DISCUSSION**

The pronounced negative Ce anomaly exhibited by mantle peridotite CRN211 suggests pelagic sediment/SWAB input by subduction into the mantle. Such a process has been proposed in order to account for the compositions of some ocean island basalts (e.g. HOFMANN and WHITE, 1982). It is extremely likely that a proportion of pelagic sediment will be subducted, but is it all incorporated into the island arc volcanics? The results of this study suggest not.

It is not clear whether metasomatism could have produced the negative Ce anomaly. Metasomatic fluids are hot, supercritical fluids containing large quantities of Fe during *patent metasomatism* (e.g. DAWSON, 1984; MENZIES and HAWKESWORTH, 1987) which would inhibit the formation of the insoluble Ce**+** species, negating the formation of a negative Ce anomaly by this process. However, the nature of *cryptic metasomatic* fluids is more vague. The general LREE-enriched signature of CRN211 could have been imparted by cryptic metasomatism, but whether such a process produced
the negative Ce anomaly is unclear. Although the experiments of Schreiber et al. (1980) were conducted at 1 atmosphere under anhydrous conditions, $fO_2$ was controlled. Water or pressure will only affect the Ce oxidation state if they affect $fO_2$. Whether high $fO_2$ and low Fe conditions occur during cryptic metamatism remains to be proven.

The presence of subducted basaltic or crustal components (or derivatives thereof) beneath the OJP has been proposed by BIELSKI-ZYSKIND et al. (1984) and NEAL and DAVIDSON (1988). These latter authors have based their conclusions on Sr and Nd isotopic disparities within and between the cpx megacrysts and host amphibole at Malaita, and interpretation of geophysical data (FUROMOTO et al., 1976; HUSSONG et al., 1979). Our present study supports this contention, indicating a proportion of the subducted oceanic material survives to reach the mantle beneath the OJP. The REE signature of the oceanic components has locally survived subduction and been incorporated into the mantle, as indicated by CRN211.

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