

Trace element accessibility in mid-ocean ridge and ocean island basalt: an experimental approach

U. Giese
M. Bau

GeoForschungsZentrum Potsdam, PB 4.3 Lagerstättenbildung,
Telegrafenberg A-50, D-14473 Potsdam, Germany

Introduction

Trace element mobility or immobility is closely related to parameters such as temperature, pH, f_{O_2} and availability of ligands for complexation. Hence, there are situations where a certain element is mobile and others where it is immobile. In any way is the initial availability of trace elements of crucial importance. Certain fractions of the total concentration of a trace element are incorporated into the crystal lattices of minerals or may be loosely bound in interstitial films on grain boundaries. Depending on the element considered and on sample mineralogy and texture, the ratio of these two fractions is variable, resulting in different trace element susceptibilities for mobilisation during fluid-rock interaction. Here we report results of experimental leaching employing the so-called MIG-method (Giese, 1993; Giese *et al.*, 1993) of fresh MORBs and OIBs.

Sample description

The two MORB samples originate from the East Pacific Rise at 21°S. They were sampled from the same basalt pillow and represent the outermost glassy rim and the microcrystalline interior, respectively. The latter comprises olivine, plagioclase and pyroxene microcrystallites in a glassy matrix that is devitrified in places. The chemical

composition of both samples is virtually the same, and they show *LREE*-depleted *REE*_{CN} patterns without any *Eu*_{CN} anomaly, as is typical of N-type MORB. OIBs originate from Mehetia Island (Society hot spot) and from Hawaii. Mehetia Island basalt Me90-05 (discussed in detail by Binard *et al.*, 1993) is an alkalic basalt ($K_2O + Na_2O$: 4.43%), comprising phenocrysts of olivine and clinopyroxene in a matrix that additionally contains plagioclase and titanomagnetite. Its *REE*_{CN} pattern shows strong *LREE* enrichment and no *Eu*_{CN} anomaly (Fig. 1). The OIB from Hawaii is a vesicular tholeiite ($K_2O + Na_2O$: 2.45%) from Kilauea, showing olivine phenocrysts in a matrix of plagioclase, clinopyroxene and glass. Its *REE*_{CN} patterns yield no *Eu*_{CN} anomaly and are less *LREE* enriched than the alkali basalt from Mehetia Island).

Experimental

Four aliquots of 1g of each powdered basalt sample were leached with bi-distilled water at 70°C in the presence of an ion-exchange resin in H^+ form. After 1 h of water-rock interaction pH self-adjusted to pH 3. After leaching times of 2, 5, 20 and 45 h, respectively, the ion-exchange resin was separated from remaining rock powder, and eluted with 4N HNO_3 . Element abundances in the eluates were determined by ICP-AES and ICP-MS. Whole-rock analyses were carried out following sample digestion with HF and HCl in pressure vessels.

The leached fraction of a trace element M is given by $([M]_{\text{eluate}} \times DF) / [M]_{\text{whole-rock}}$ (DF: dilution factor). The leaching of major elements such as Al, Fe or Ca predominantly reflects dissolution of rock-forming minerals and can be used as reference. We define the 'easily accessible trace element fraction' (EAT) as the trace element fraction which is leached at 1% leached Al, i.e. at a low degree of dissolution of rock-forming minerals. $EAT > 1$ indicate higher, $EAT < 1$ lower accessibility compared to the reference element. Here, we chose Al as reference element, because it monitors dissolution of plagioclase and clinopyroxene. Utilising Ca or Fe as reference element gives compatible results.

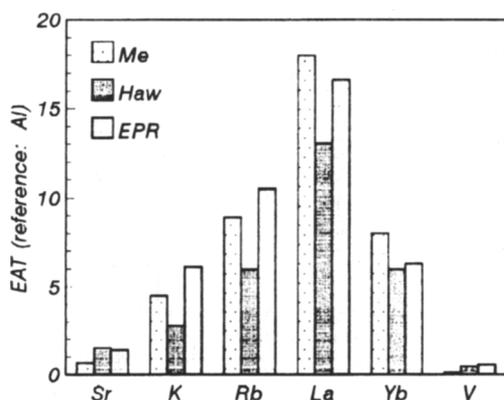


FIG. 1. Values of EAT for Sr, K, Rb, La, Yb and V.

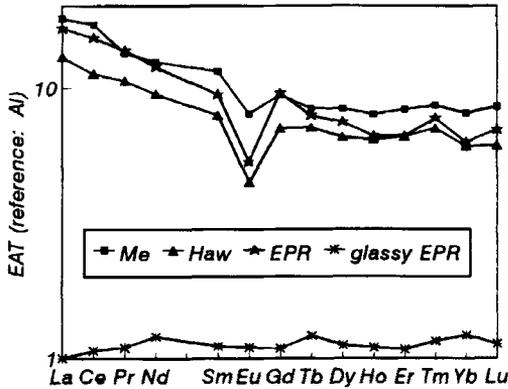


FIG. 2. REE_{EAT} patterns MORBs and OIBs discussed.

Results

Variations between EAT of microcrystalline MORB and OIBs are small for all trace elements considered. Leaching kinetics of compatible (C) elements such as Sr (Fig. 1), Ni, Co and Mn are similar to those of reference elements, resulting in $C_{EAT} \approx 1$, and showing that they are hosted by the rock-forming minerals plagioclase, clinopyroxene and olivine. C_{EAT} and $V_{EAT} < 1$ indicate that Cr and V (Fig. 1) are related to less soluble oxide minerals. Incompatible (I) trace elements such as REEs, K and Rb (Fig. 1, 2), and Cs and U show $I_{EAT} \gg 1$, i.e. significantly higher values.

The unfractionated REE_{EAT} pattern for the MORB glass (Fig. 2) with $REE_{EAT} \approx 1$ indicates homogenous distribution of REEs and Al as should be expected from basaltic glass, and shows that the effects observed for microcrystalline basalts do not represent experimental artifacts. The microcrystalline basalts, irrespective of being MORB or OIB, display similar REE_{EAT} patterns which decrease steadily from La to Dy, are rather horizontal from Dy to Lu, and yield pronounced negative Eu anomalies.

Discussion

Considering that the REEs are commonly regarded (and indeed often are) 'immobile' during seawater-basalt interaction, it is rather surprising that in MORB and OIB the LREEs are considerably more easily accessible to an alteration fluid than LILEs such as Rb, K and Sr. This feature is independent from chemical composition, since N-type MORB, tholeiitic and alkalic OIB show the same characteristics, but appears to be controlled by the mineralogical composition. Sr is predominantly

hosted by plagioclase which is stable under our experimental conditions, and thus, no Sr is leached. In contrast, the REEs do not easily partition into olivine or plagioclase, which therefore show low REE abundances. The rejected REEs accumulate on grainboundaries, and are easily removed during leaching. This is supported by the EAT_{REE} patterns (Fig. 2). Highest partition coefficients between basaltic melts and minerals occurring in significant quantities in our basalts are those for clinopyroxene which is known to preferentially incorporate the HREEs. Crystallisation of a clinopyroxene will deplete the magma in its close vicinity in HREEs, resulting in an increased $LREE/HREE$ ratio on grainboundaries. Plagioclase which preferentially incorporates Eu^{2+} compounds, depletes its surrounding melt in Eu, resulting in a negative Eu anomaly on grainboundaries. Thus, the observed EAT_{REE} patterns are a direct consequence of the mineralogical composition.

The EAT_{REE} patterns suggest that a larger fraction of LREEs compared to HREEs and a smaller fraction of Eu compared to Sm and Gd can be removed during the first stages of basalt alteration. Consequently, a low-temperature alteration fluid may display a source-normalised REE pattern that reflects the EAT_{REE} pattern in Fig. 2. Unfortunately, precipitation of hydrothermal minerals and/or chemical complexation with ligands in solution may modify the REE pattern of this fluid, and thereby obliterate its initial REE characteristic. However, the negative Eu anomaly should be retained, because (i) there are no anomalous differences between complex stabilities of Eu on one side and Sm and Gd on the other, and (ii) Eu can only be decoupled from its neighbours in the REE series, if it is reduced to Eu^{2+} , which at temperatures below $150^{\circ}C$ is not pronounced enough to cause analytically significant Eu anomalies (Sverjensky, 1984). Recently, Michard *et al.* (1993) reported REE abundances in low-temperature ($30^{\circ}C$), acidic ($pH \approx 5.3$), SO_4^{2-} -bearing hydrothermal solutions from Teahitia volcano, Society Islands. These REEs have been mobilised from the basalt, as is shown by similarly positive ϵ_{Nd} values for basalts and fluids (Michard *et al.*, 1993). The source-normalised REE patterns display a significant negative Eu anomaly, being in close agreement with predictions from our leaching experiments. Thus, although our leaching experiments are not intended to simulate natural seawater-basalt interaction, the results obtained tell us about trace element accessibility and may help us to understand some of the characteristics of the trace element distribution in aqueous fluids.