

Characteristics of rare-earth elements extraction from tholeiitic basalt by hydrochloric acid-nitric acid mixture

Polymorphic effect of sesquioxides of lanthanides

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(Communicated by Kazuo YAMASAKI, M. J. A., March 12, 1999)

Abstract: The interesting features that rare-earth elements (REE) exhibit in HCl-HNO₃ acid extraction from powdered tholeiitic basalt are reported here. Cerium which can be oxidized to tetravalent shows the highest extraction percentage. The lower extractability of Eu compared with Sm and Gd is attributed to the high chemical resistance of feldspar in which divalent Eu is preferentially incorporated. Based on the extractability, the stable trivalent rare-earth elements, La, Nd, Sm, Gd, Dy, Er, Yb and Lu are divided into three subgroups; {La, Nd}, {Sm}, and {Gd, Dy, Er, Yb, Lu}. This differentiation of the stable trivalent REE is inferred to be related to the polymorphic crystal structures of A-, B- and C-type sesquioxides of REE. Barium shows an extractability identical with that of La-Nd subgroup.

Key words: Polymorphism; REE; extraction; tholeiitic basalt; hydrochloric acid-nitric acid mixture; crystal structure; sesquioxide; valency.

In course of my basic studies on chemical dissolution or extraction of REE in pulverized silicate rock by a HCl-HNO₃ mixture, it was found that REE show interesting features in extractability. This short communication reports the results of the experiment with some discussions about it.

Experimental. The tholeiitic basalt used came from a core at the Guadalupe site for the Mohole project.¹⁾ It was pulverized in a mortar, and fifteen milliliters of 6N nitric acid and forty-five milliliters of 6N hydrochloric acid were added to forty-seven milligrams of the rock powder in a vessel. The mixture was kept at temperatures a little lower than the boiling point for four hours, with frequent stirring. The insoluble constituents were filtered off, and ten lanthanides plus barium in the solution were determined by the stable isotope dilution²⁾⁻⁴⁾ method. On the other hand, the corresponding abundances⁵⁾ in bulk rock were determined by the same technique after conventional chemical decomposition with a HF-HClO₄ mixture.

Results and discussion. The results are shown

in Table I and Fig. 1. The percentage of extracted (or unextracted) fraction is plotted against atomic number in Fig. 1. Although the resultant extraction pattern may appear complicated, it is rather easy to deal with it simply in terms of the effects of valency, constituent minerals, and structures of oxides as follows.

Disregarding cerium and europium, a simple stepwise curve is obtained. In this connection it seems significant that in addition to the initial normal trivalent state of the lanthanides, cerium and europium may be tetravalent and divalent, respectively, and that the directions of deviations of Ce and Eu from the stepwise smooth curve (Fig. 1) are opposite to each other. The HCl-HNO₃ acid solution apparently further promotes the oxidation of the cerium ions to the tetravalent state, and the formation of a stable chloro complex of Ce (IV) would enhance the solubility of Ce, while europium is preferentially partitioned^{6),7)} into relatively acid-resistant feldspar (aluminosilicates of Na, Ca and K) in which Eu assumes a divalent state^{6),7)} and is subject to protection from oxidation owing to the relatively high stability of aluminosilicate against the prevailing acid digestion.

Warshaw and Roy⁸⁾ mentioned that "the proper understanding of the polymorphic relationships among the rare earth sesquioxides is fundamental to any study involving these compounds and is of special importance

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Table I. Percentages of extracted and unextracted fractions of lanthanides and barium from tholeiitic basalt powder, by treatment with HCl-HNO₃ acid mixture

Element	Extracted (%)	Unextracted (%)
Ba	73	27
La	73	27
Ce	85.6	14.4
Nd	71.7	28.3
Sm	63.3	36.7
Eu	51	49
Gd	55.0	45.0
Dy	54.8	45.2
Er	54.5	45.5
Yb	53.4	46.6
Lu	53.6	46.4

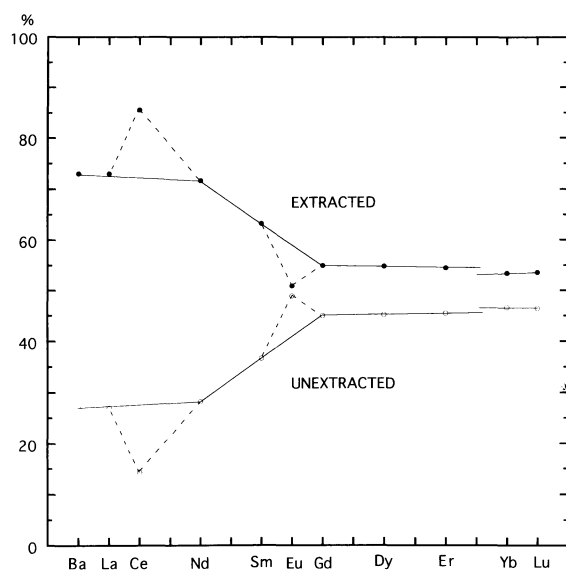


Fig. 1. Percentage of extracted or unextracted fraction as a function of order of atomic number from Ba ($Z = 56$) through Lu ($Z = 71$), in the extraction by HCl-HNO₃ (cf. text).

when one considers the reaction of the rare earth oxides". According to the reference they cited, the first studies of the polymorphism of the rare earth sesquioxides were carried out by Goldschmidt *et al.*, in 1925. These pioneers found that the rare earth sesquioxides could exist in three polymorphic forms, A, B and C, whose structures are hexagonal, probably monoclinic and cubic, respectively.

The careful studies by Warshaw and Roy⁸⁾ using high-purity oxides led them to conclude that Nd₂O₃ does not exhibit any B-type structure and Sm₂O₃ does not exhibit an A-type structure. The sesquioxides of the smallest ions, Y, Ho, Er, Tm, Yb and Lu exist only as the C-type polymorph. The intermediate rare earth oxides, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₂O₃ and Dy₂O₃ exist in both the

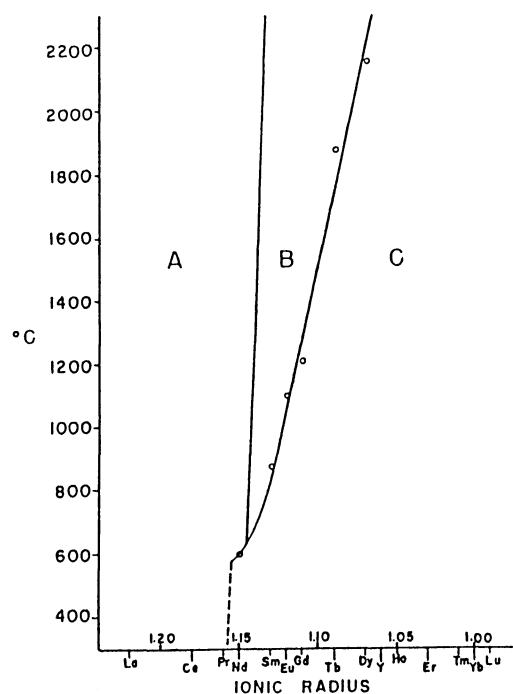


Fig. 2. Temperature stability relationships of the rare earth sesquioxide polymorphs.⁸⁾

B- and C-type polymorphs and these transformations are reversible. It is worthwhile to note that there can be complicated aspects related with metastable states and kinetic rate toward equilibration.

The results of experimental studies by Warshaw and Roy are summarized in Fig. 2. Hoekstra⁹⁾ investigated the pressure effect on the polymorphic forms of rare earth sesquioxides. His data are shown in Fig. 3.

It is known¹⁰⁾ that the temperatures of basaltic magmas near the surface range between 1050–1200°C. If it is assumed that the phase type of REE sesquioxides is decided at about 1000°C and the extraction curve under consideration reflects the polymorphic form of REE sesquioxides, the features shown in Figs. 2 and 3 are consistent with the foregoing assumptions. Although there still remain puzzling problems for the observation reported here, this is the first report suggesting a potential significance of polymorphic forms in relation to the state of REE in natural rocks. The most puzzling process is the mechanism of extraction of REE from the silicate powder by a HCl-HNO₃ mixture. More systematic studies will not only disclose the basic reaction process, but also yield new applications in geochemistry or cosmochemistry of REE. Besides, it merits attention that the extraction of Ba (an alkaline earth metal) is substantially identical with that of La-Nd

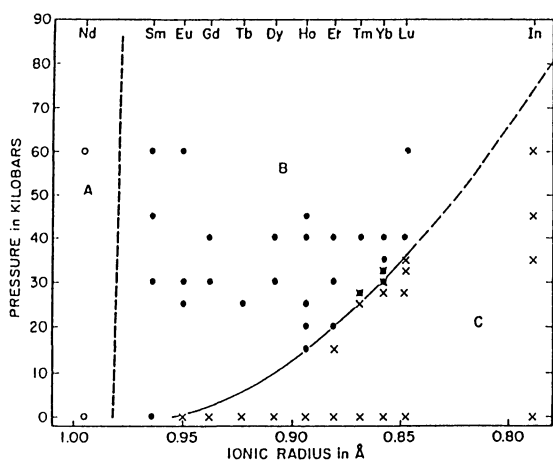


Fig. 3. Rare earth sesquioxides: 1000°C isotherm.⁹⁾ Open circles, closed ones and crosses indicate A-, B- and C-type, respectively, of polymorphism.

subgroup of REE. This will provide a clue to the mechanism of extraction observed in the present experiment. Also, it may be necessary to examine carefully the reality of the very small gap between Er and Yb (Fig. 1 and Table I). The fact that the extraction for Sm falls on a line connecting those for Nd and Gd is considered to reflect the B-type polymorphism, but it is also conceivable that Sm exists as a 1 : 1 metastable mixture of A- and C-types.

In this communication, the term "extraction" is used for convenience sake. In a true sense, however, the

phenomenon responsible for the observed fact would be extraction as well as chemical dissolution. The step-wise features observed may be understood to suggest that the reaction rate of dissolution is directly controlled by the crystal structure (polymorphism) of sesquioxide; the ionic radius affects the structure. From the viewpoints of petrology and elemental partitioning, it would be also significant to check the effect of alteration.

Acknowledgment. Valuable information from Prof. Tsuyoshi Tanaka, Nagoya University, is gratefully acknowledged.

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