Geochemical behaviour of lanthanoid elements in some clays and bauxite

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(Received November 15, 1978)

Semiquantitative eigenvector analysis demonstrates that differentiation of individual lanthanoids occurs in sedimentary environments. By means of eigenvector diagrams the degree of lanthanoid fractionation can be expressed semiquantitatively.

INTRODUCTION

Recent papers have lent support to the idea that under given circumstances the elements of the lanthanoid group (La-Yb) can be differentiated by geological processes (see e.g. ROALDSET, 1978). In analogy with the difference in ion exchange properties described by FIDELIS (1970), and FIDELIS and SIEKERSKI (1965, 1966, 1967), we suggested that orbital splitting and crystal field relations influence the distributions of the lanthanoid elements between minerals under a wide variety of geologic conditions (ROALDSET and CHRISTIE, 1975). It is evident that under those circumstances where water is involved, lanthanoid partition between crystal site and aqueous complex is important for the understanding of lanthanoid element differentiation in nature.

In the present paper eigenvector analysis is used for the study of the behaviour of lanthanoid elements in clays that have been deposited under various conditions, and bauxites.

The data are taken from ROALDSET (1973), and MAKSIMOVIĆ and ROALDSET (1976), and the present work is an effort to extract more information by aid of refined data analysis.

MATERIAL

The material of the present study is three series of samples. Two of them are clays derived from the same geological source area, and they are different mainly by the natural conditions under which they were deposited. The third sample set is bauxite, so rich in hematite that it is nearly also an iron ore of economic value.

It was chosen, because its mode of formation is different from that of the clays.

The selected Quaternary clays are from the lower part of the Numedal river drainage basin, South Norway. The seven varved clay samples (E27-E33 of ROALDSET, 1972, 1973) were deposited in brackish water in the late glacial "Kongsberg fjord", and they belong to the almost unweathered late- and postglacial, immature sediments deposited during the retreat of the Late Weichselian ice sheet about, 9,800 B.P. (ROALDSET, 1973; ROSENOVIST, 1975a, b; SØRENSEN, 1979). The marine clay samples (E42-45, E47-52, E54-63, E67-74, E76, E81, and E83-85 of ROALDSET, 1973) were deposited in ocean water in the same "Kongsberg fjord" and in the present Larvik fjord. They are of Late Pleistocene to Holocene age (11,000 B.P. to Recent (SØRENSEN, 1979)).

The clay samples are mineralogically similar: The clay fraction (< 2μm) is composed mainly of di- and tri-octahedral illite, chlorite and/or vermiculite, and mixed layer minerals. Kaolinite is absent and smectite is present only in traces.

The total lanthanoid contents range from 174 to 700ppm for the varved clays, and within 90 to 530ppm for the fresh marine clays.

The bauxite samples (G1-G7, G10 of MAKSIMOVIĆ and ROALDSET, 1976) are from the Upper Cretaceous karstic deposit at Grebnik, Yugoslavia. They originate from lateritic weathering crusts of ophiolites that have been washed down and deposited in karstic depressions in limestone. The weathering took place in a humid tropical to subtropical climate. Before erosion and redeposition the source
material was weathered mainly to kaolinite. Periodically heavy rain was followed by percolation of large amounts of surface water through the accumulated clayey material. As the pH of the circulating waters in limestones is close to 8.4 (Garrels and Christ, 1965) the different solubility of SiO₂ and Al₂O₃ under such conditions explains the bauxitization process (Maksimović, 1976; Keller, 1957).

The Grebnik samples are rich in aluminium and iron (diopside 46-48%, hematite 24-49%), the kaolinite content is lower than 7.5%, and traces of anatase, chromite and boehmite are present. The overall Ln contents of the bauxite samples range from 300 to 1,200ppm.

**Eigenvector Analysis**

The eigenvector analysis has been made by aid of the program ARTHUR, written by B. R. Kowalski of the University of Washington. It has been demonstrated that plots in the first-to-second, or first-to-second-to-third eigenvector space may be useful to display differences and similarities in sample sets (see e.g. Christie, 1979a, b). In chemometric use, the observation space is usually constructed of property or compositional axes, and the location of a sample point in the observation space is an unambiguous description of the properties of the sample. Thus, relations between samples can be studied in terms of pattern recognition techniques (e.g. Kowalski and Bender, 1972; Wold, 1976).

In the present paper the observation space is constructed of sample axes, and the location of constituent points in that space is studied by aid of eigenvector analysis. By careful study of the factor scores we have made certain that the sample sets make up geochemically homogeneous units.

**Results**

The first-to-second eigenvector diagrams of the present study contain more than 97% of the total variance in the multidimensional constituent space. This type of plots are, therefore, particularly forceful for the study of subtle differences in the chemical behaviour of the sample series. For reasons given below, the analysis was made in two versions, with and without Ce, and the contained and cumulative information along the first and second eigenvector direction for the three sample sets are given in Table 1.

*Brackish water clay and marine clay* These sample sets were chosen to shed light upon the effect of electrolyte concentration and acidity of the water on the distribution of lanthanoid elements between the aqueous phase and clay mineral. The first-to-second eigenvector plots of the lanthanoid elements of these sample sets are given in Figs. 1a and 2a, respectively. The prominent feature of these diagrams is that Ce and Nd are extreme with respect to their geochemical properties. Furthermore, the elements heavier than Eu behave similarly, and Pr is similar to this group.

Because of the extreme properties of Ce in these sample sets, a complementary eigenvector analysis was made on samples without Ce. The results of this analysis are displayed in Figs. 1b and 2b. From these diagrams it is evident that the projected element points of Eu, Tb and Ho coincide, this indicating that they behave similarly in the studied samples.

It is worth to note that the most prominent difference between the brackish water clays and the marine clays is found in the elements Sm, Gd, and Dy. In particular, Gd seems to be geochemically different in the two series.

*Bauxite* This sample set was included in order to investigate what pattern of lanthanoid element points is geochemically general, and what can be assigned to differences in total chemical composition and in differences in the geological environment. Therefore, the diagrams of Figs. 3a and 3b are regarded in relation to the earlier diagrams only.

**Table 1.** Contained and cumulative information in per cent along the first and the second eigenvector direction.

<table>
<thead>
<tr>
<th>Series with Ce included: 1 - brackish water clay; 2 - ocean water clay; 3 - bauxite.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>First eigenvector</td>
<td>95.1</td>
<td>96.1</td>
<td>97.6</td>
<td>95.6</td>
<td>92.1</td>
<td>95.2</td>
</tr>
<tr>
<td>Second eigenvector</td>
<td>4.1</td>
<td>2.6</td>
<td>2.2</td>
<td>3.7</td>
<td>5.7</td>
<td>2.4</td>
</tr>
<tr>
<td>Cumulative</td>
<td>99.2</td>
<td>98.7</td>
<td>99.8</td>
<td>99.3</td>
<td>97.8</td>
<td>97.6</td>
</tr>
</tbody>
</table>
In general, the location pattern is similar in all diagrams, and reflects - presumably and in broad terms - average concentration relations corresponding to the earlier anticipated cosmic abundance. La, Ce, and Nd have the same general location in all the corresponding diagrams, and the same is true for the heavy lanthanoids. In the diagram of Fig. 3b, the elements Pr, Sm, Dy, Yb, and Er seem to form one cluster, and Eu, Tb, Ho, and Lu another one, and Gd plots separately.

CONCLUSIONS

The investigated clays and bauxites represent two extreme geological environments. The glacial and postglacial clays are composed mainly of glacially abraded rock flour admixed with small amounts of preglaciation weathering products, while the karstic bauxites are ultimate products of prolonged chemical weathering in humid tropical climate.

The eigenvector analysis demonstrates that:
- Ce, Nd, and to a lesser extent La, in clays and bauxite differ in their geochemical behaviour from the other lanthanoids.
- Change in electrolyte concentration and pH by passing from brackish to marine water influences the distribution of the polyisotopic elements Gd, Sm, and Dy, which have close to half filled 4f orbitals. In the marine samples Gd is extreme with respect to the other intermediate and heavy lanthanoids. The similarity of Sm and Dy seems to be closer in brackish than in marine environments. Upon encountering sea water the river transported clays are thrust into a chemical environment radically different from that during weathering erosion and transport (e.g. BERNER, 1971), and the observed changes
may be due to halmyrolytic and early diageneric adjustment. For the bauxite samples Pr, Sm, Dy, Er, and Yb seem to cluster in one group, and Eu, Tb, Ho, and Lu in another one. This twofold division supports the assumption of individual fractionation between adjacent (even and odd numbered) lanthanoids during the processes of intense weathering and bauxitization. The eigenvector analysis demonstrates that differentiation of individual lanthanoids may occur in the sedimentary environments. By means of the eigenvector diagrams the degree of lanthanoid fractionation can get a semi-quantitative expression.

REFERENCES


