A NOTE ON THE GEOCHEMISTRY OF ALKALINE ROCKS

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Abstract. Geochemical differences between nepheline syenites of most probable magmatic origin are pointed out and discussed. It is tentatively suggested that concentration of R.E., Zr, Nb and related elements in some nepheline syenites signifies crustal contamination, or derivation, of the magma.

The high Ba and Sr contents together with high K/Rb and K/Cs ratios in many of these rocks may reflect the initial conditions of their parent magma.

Introduction

Work is in progress on the geochemistry of the mildly alkaline plutonic rocks of the Oslo area of Permian age (see for instance Barth, 1945), and a study of the nepheline syenite on Stjernøy, North Norway (Heier, 1961) is completed.[1] This work is the beginning of a study of the geochemistry of the alkaline rocks in general, a study which will also incorporate a comparison of alkaline olivine basalts with other basalt types.

The purpose of this note is to draw attention to two geochemical observations made on nepheline syenite. These two observations are: (i) concentration of rare earths, Zr, Nb and geochemically related elements in some nepheline syenites (especially in those of agpaitic type) as compared with the near absence of these elements in others, and (ii) the very high concentration of Ba and Sr in some nepheline syenites compared with low concentrations of Rb and Cs relative to the concentration of the major alkalies, Na and K, in these rocks.

[1] See the following paper.

A geochemical study of plutonic alkaline rocks is of interest for the following reasons:

(1) Their fractionated rocks, alkali granites and nepheline syenites, are in many cases known to concentrate elements that are normally present in only small amounts in igneous rocks.

(2) Plutonic alkali rock provinces are typically associated with crustal instability and large scale vertical faulting in non-orogenic areas or on the boundaries of orogenic belts. They are rare in orogenic zones. Their geological occurrence may therefore in many cases indicate that they are directly derived from the earth's mantle, and are largely uncontaminated by crustal material.

Petrogenesis of the Nepheline syenites

See SØRENSEN (1960) for a recent discussion of the genesis of agpaitic alkaline rocks. The most popular hypothesis is that a high vapour pressure affected the crystallization trend of their parent magma. Indeed the frequent association of carbonatites with alkaline provinces signifies a high CO_2 pressure. We are not arguing against this mode of formation but the geological evidence of alkaline rocks connected with large scale faulting and crustal instability in non-orogenie areas may be difficult to reconcile with their crystallizing under a high vapour pressure.

The plutonic rocks of the Oslo area are of undoubtedly magmatic origin. However, as intermediate rocks and (nepheline) syenites occupy 90% of the area covered by plutonic rocks, and no evidence exists for the occurrence of large amounts of basic rocks at depth, the origin of the magma is much disputed. BARTH (1954) postulated an *in situ* formation of the Oslo magma produced by energy and hot vapours from below moving upwards and fusing the pre-existing rocks. He related this process to a general degassing of the earth. Very large amounts of heat must be introduced in a rather short time to melt and mobilize the volumes of rocks in question if the regional P.T. conditions are not very close to those of melting. However, the lack of basic members in the Oslo series poses a problem for a direct mantle origin of the magma. [MOORBATH and CZAMANSKE (1962) found a Sr^{87}/Sr^{86} ratio in a granite of this province comparable to the established basaltic ratio.] If Barth's hypothesis is correct the relative differences in concentrations of the elements in the Oslo "prism" as compared with their concentrations in the average pre-Cambrian basement (the pre-existing rocks of the area) could give some indication of element concentrations in the mantle. This calculation is carried out by BARTH (1954) for the major elements and some trace elements. Significantly the relative highest enrichment is found for barium. Work now in progress will give more information about these element abundances. BARTH (1945, 1952, 1954) discusses what he terms "the family tree" of the principal Oslo rock types. Differentiation along one branch of the tree results in an alkali granite (ekerite) characterized by excess silica and deficient alumina giving alkali pyroxenes and amphiboles, but no nepheline, in the end product. The other branch is characterized by both silica and alumina deficiency in the end product (lardalite) resulting in crystallization of nepheline as well as alkali femic minerals.

On Stjernøy a petrographic picture very different from that of the Oslo area is in evidence. There is a great preponderance of gabbros and ultrabasic rocks in the area, and the syenites and nepheline syenites cover a small part of the total area. Carbonatite occurs intimately associated with the latter. However, there may be a considerable time interval and no petrogenetic relations between the emplacement of the gabbros and the younger rocks (nepheline syenite and carbonatite) (HEIER, 1961, p. 147 and p. 152). Of petrographic interest is that the femic minerals in the nepheline syenite and syenite on Stjernøy are diopsidic pyroxenes, common hornblende, and biotite (based on their optics only). There is no sign of the alkali amphiboles and pyroxenes characteristic of the Oslo rocks. Thus the two rock provinces discussed here contain the three groups of alkaline rocks as defined by Shand (see BARTH, 1952, p. 203):

(1) Silica adequate or excessive, alumina deficient (the branch of the Oslo series resulting in the alkali granite, ekerite).
(2) Alumina adequate or excessive, silica deficient (Stjernøy), miaskitic.
(3) Both silica and alumina deficient (branch of Oslo series resulting in nepheline syenite, lardalite), agpaitic.

The Concentrations of Rare Earths, Zr, Nb, and Geochemically Related elements in Nepheline syenites

Work in progress shows that the Oslo rocks are characteristically enriched in the Rare Earths, zirconium, and geochemically related elements. The nepheline syenite pegmatites of the Langesundfjord are especially noted for their richness of minerals concentrating these elements, and the plutonic massifs themselves likewise contain a high concentration of them compared with calcic plutonic rocks. The same elements are characteristically lacking in the Stjernøy province, and elements as La, Nd, Y, and Sc which are not difficult to identify by optical spectrographic methods are less abundant in the Stjernøy nepheline syenites than in normal calcic granites. Likewise the carbonatite and albite-nepheline pegmatites on Stjernøy are characteristically devoid of these elements. The Stjernøy rocks are also very low in U and Th (relative to their K content they are depleted in U and Th by a factor of 10—100 as compared with calcic rocks, HEIER, 1962).

This difference between the two provinces is pointed out because of the common assertion that some of these elements are concentrated in nepheline syenites. Clearly a geochemical difference exists between the Oslo and Stjernøy nepheline syenites both of most probable magmatic derivation.

The basis for the division of nepheline syenites into miaskitic and agpaitic groups was petrographic (sequence of crystallization of their minerals on textural evidence). Agpaitic rocks are often rich in typical residual elements Zr, Ti, Nb, and R.E., and seem to depend for their formation on volatiles moving differentially within the magma (SØRENSEN, 1960).

Miaskitic rocks frequently form through assimilation of limestone by subalkaline magmas.

The geochemical differences between the Oslo and Stjernøy alkaline rocks may be related to this difference in petrogenesis, or they reflect primary differences in the composition of the parental magma.

All the elements mentioned here are very strongly lithophile and they should therefore be expected to be largely concentrated in the crust of the earth. During the exogenic differentiation the trivalent rare earths and the pentavalent Nb and Ta are characteristically concentrated in hydrolyzate sediments. Hence their geochemical coherence in some magmatic alkaline rocks is explained if their parent magma formed through fusion of crustal rocks. Zirconium on the other hand is characteristically concentrated in the resistates but any zirconium present in the weathering solutions will become precipitated in the hydrolyzate sediments (RANKAMA and SAHAMA, 1950). Zr is especially high in most of the Oslo rocks compared with calcic rock series.

The concentration of these elements in the Oslo rocks may be an indication of crustal derivation, or strong crustal contamination, of the parent magma. As mentioned, this origin is strongly advocated by BARTH (1954). The tendency for these elements to hydrolyze may possibly be in favour of the rocks forming from a vapour rich magma where the elements are selectively concentrated in the vapour phase. However, the impression is that the Oslo province on the whole is enriched in these elements compared with calcic rock series, but this is not yet established. It appears from the Russian literature (c.f. SHEINMANN *et al.*, 1961) that rare element mineralization (Zr, Hf, Nb, Ta, R.E.) in alkaline complexes often are related to a late stage Na-metasomatism (albitization). The authors are not aware of any such relations in the Oslo rocks.

The near exclusion of the same elements in the Stjernøy province may signify a different origin of the magma.

The Distribution of Ba, Sr, Rb and Cs in Nepheline syenites

The work now in progress shows the rocks from both the Oslo and Stjernøy provinces to be enriched in Ba and Sr, and depleted in Rb, Cs (relative to K*), Pb and Tl as compared with crustal averages. These relations are most pronounced in the nepheline syenite on Stjernøy. As the geologic situation is strongly indicative of a magmatic formation of the rocks it is interesting to consider what are the processes that can result in such element distributions in what must be considered

* It must be emphasized that the absolute concentrations of Rb (and possibly of Cs) are higher in the Oslo series than in the same volume of pre-existing crustal rocks. It is only relative to K that Rb (and Cs) is depleted.

as the most fractionated of the rocks. From the scattered data available in the literature it appears that such element distributions are often found in alkaline provinces. The nepheline syenite (lardalite) and alkali granite (ekerite) in the Oslo area are not high in Ba and Sr but they tend to have higher than average K/Rb ratios. Ba and Sr in this province is concentrated in intermediate rocks (larvikite) and the Oslo province as such is enriched in these elements compared with a similar volume of average crustal material. Some reconnaissance work done on a restricted number of samples from the nepheline syenite at Blue Mountain, Ontario indicates that rock to be low in Ba and Sr. A metasomatic origin of the nepheline syenites in that area has been advocated but is not considered likely by HEWITT (1961). However, the rock has definitely a complex metamorphic history (HEWITT, 1961, p. 145).

It is important to note the common geologic association of carbonatites with alkaline rocks. The high Ba and Sr contents of the calcite in carbonatites relative to metalimestones are well established and probably diagnostic.

A magmatic fractionation process that results in an end product concentrated in Ba and Sr, and depleted in Rb and Cs relative to K and Na is unknown. [K/Rb ratio in the Stjernøy nepheline syenite is about 400 and Cs is undetected (1 p.p.m.) in rocks containing between 5 and 6% *K*]. In normal magmatic fractionation Rb and Cs are concentrated with K, and enriched relative to that element in the most fractionated rocks. Ba and Sr are to some extent related to K but they tend to be concentrated in the early K-minerals. It is possible that a selective concentration of certain elements in a gas phase coexisting with the magma can lead to this result but the process is yet unknown. It will be very interesting to see if the current work by WYLLIE and coworkers (1960, 1963) can shed some light on this problem.

Assimilation of crustal material in a magma should rather be expected to result in the opposite as Rb and Cs should be expected to be more concentrated in the crust than Ba and Sr.

The authors propose that these unusual element abundances may reflect the primary composition of the parent magma, i.e., rocks of the Stjernøy type crystallize from magma characterized by high Ba and Sr, and low Rb and Cs contents. It is relevant to point out here that high Ba and Sr contents seem to be characteristic of kimberlites which most certainly have a deepseated, though possibly complex, origin.

Acknowledgements

Dr. A. E. Ringwood has read the manuscript and given constructive criticism.

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Accepted for publication October 1963.
Printed June 1964.