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Zr-Y-U stratigraphy of the kakortokite-lujavrite sequence, southern Ilímaussaq intrusion

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The kakortokite-lujavrite sequence in the southern part of the Ilímaussag intrusion has been subdivided on a number of field and hand-specimen criteria (Bohse & Andersen, 1981). The sequence is thought to represent a single pulse of magma except for the final, volumetrically insignificant intrusion of M-C lujavrite.

In the present work, Zr, Y and U data on the kakortokite-lujavrite sequence are presented. The primary aim of the geochemical survey was to see if the field divisions could be confirmed. To this end, we analysed about 200 representative samples by reconnaissance X-ray fluorescence (XRF) techniques for the elements Zr, Y, Rb, Sr, Pb, Zn, Mn, Fe, La, Ce and Nd. Preliminary interpretation suggested that ratios such as Zr/Y and Zr/La showed a progressive variation through the sequence. We subsequently re-analysed the samples by precise XRF techniques for Zr, Y and U and it is these values which are now presented and discussed. A limited number of lujavrites from the northwestern corner of the Ilímaussaq intrusion (Kvanefjeld) were also studied for comparison with the southern sequence.

Bohse *et al.* (1974) and Steenfelt & Bohse (1975) outlined the evolution of U in the kakortokite-lujavrite sequence using fission track analysis of eudialyte. They reported U values from the unaltered cores of eudialyte crystals and showed that contents increased through the sequence. Altered areas along margins and cracks were found to be enriched in U and this effect was attributed to the influence of late magmatic or hydrothermal fluids rich in U.

Analytical techniques

Zr, Y and U were analysed by conventional XRF techniques using powder pellets. Matrix effects were controlled by measuring the Compton scatter peak from the Mo tube in an offpeak position to avoid the serious interference from Nb and Y lines. The precision for Zr, Y and U at typical concentration levels is close to ±1.0, ±1.5 and ±2.5% relative, respectively. Determined (and recommended) values ppm for the international lujavrite standard NIM-L are: Zr 10 600 (11 000), Y 20.1 (?25), U 13.7 (14). Agreement between U values obtained by XRF and delayed neutron counting is good (generally within 5% relative).

Results and discussion

Table 1 presents median values for Zr, Y and U in the main rock units of the kakortokite-lujavrite sequence and fig. 1 plots Zr versus Y and U for the sequence in southern Ilímaussaq.

It is apparent from fig. 1 that Zr-U and Zr-Y show a high degree of correlation in several of the rock units. This correlation can be equated with the varying abundance of cumulus

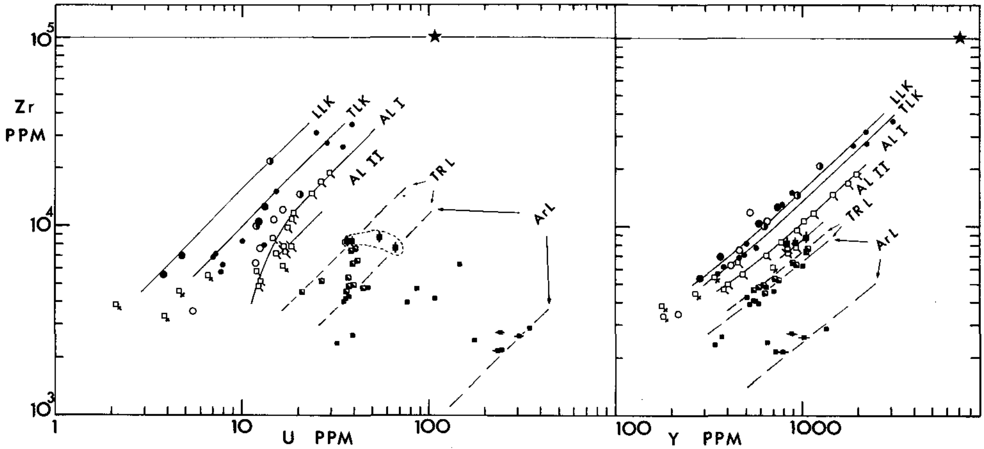

Fig. 1. Zr versus U and Y in the kakortokite-lujavrite sequence, southern Ilímaussaq. ● black, ◑ red, ○ white LLK lower layered kakortokite; • TLK transitional layered kakortokite; ⌑ AL I aegirine lujavrite I; ⌑ aegirine lujavrite I (5 samples from a different locality, not considered further); ⌑ AL II aegirine lujavrite II; ◪ TR L transition zone lujavrites; ■ arfvedsonite lujavrite; ■ Nj L naujakasite lujavrite; ■ M-C L medium- to coarse-grained lujavrite. ★ eudialyte, aegirine lujavrite I.

eudialyte. By extrapolating these eudialyte control lines to 10% Zr (the Zr content of eudialyte), the Y and U values for eudialyte can be calculated. For the kakortokites, eudialyte values are calculated more reliably when only the data for black kakortokite are used (see below).

Although 5–10 samples may be needed to reliably establish a single U content by extrapolation, this value will then be valid for all 5–10 samples. In this way, the XRF whole-rock technique quickly analyses the eudialyte in a great many samples. The technique is not limited to Y and U, but can reveal the contents of all elements dominantly held by eudialyte

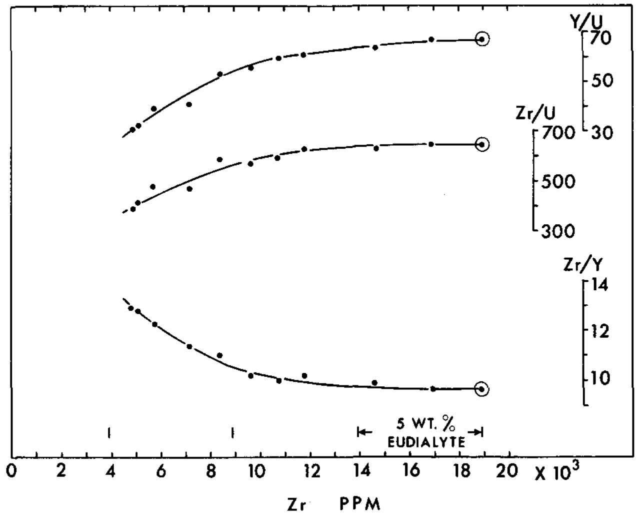

Fig. 2. Zr versus Y/U, Zr/U and Zr/Y across a single eudialyte cumulate horizon, bore hole 7, aegirine lujavrite I.

Table 1. Median Zr, Y and U contents and ratios in the kakortokite-lujavrite rocks, Ilímaussaq intrusion

Rock unit	No. of samples	Zr	Y	U	Zr/Y*	Y/U*	Zr/U*
SOUTHERN ILÍMAUSSAQ							
Lower layered kakortokite	12	8400	507	12.0	16.7	42.6	741
- white	5	7570	460	12.4	16.5	37.1	645
- red	3	14700	938	13.8	15.8	51.2	809
- black	4	8640	480	8.6	18.2	65.8	1200
Transitional layered kakortokite	12	9410	633	11.0	15.5	50.4	797
- white	3	7760	507	10.0	15.9	45.8	740
- red	7	26600	1900	25.2	14.0	62.8	977
- black	2	6930	471	7.1	14.7	66.5	976
Aegirine lujavrite I	11	9640	944	17.1	10.2	55.2	564
Aegirine lujavrite II	3	7660	844	17.0	8.8	49.6	437
Transition zone lujavrites	14	4890	633	38.8	7.4	16.6	126
Arfvedsonite lujavrite	9	3340	627	97.5	6.6	7.4	48
Naujakasite lujavrite	3	2600	890	250	2.8	3.3	9.2
M-C lujavrite	4	8320	900	47.0	8.8	20.1	187
KVANEFJELD							
Arfvedsonite lujavrite	12	2640	788	215	2.9	3.8	11
Naujakasite lujavrite	12	746	1380	344	0.56	3.7	2.3
M-C lujavrite	13	1880	558	180	3.8	3.2	12
MINERALS (SOUTHERN ILÍMAUSSAQ)							
Eudialyte (aegirine lujavrite I)	2	100000	7000	104	14.4	68.5	990
Steenstrupine (late veins, Agpat)	2	6410	12700	4530	0.52	2.9	1.5

* Calculated independently using individual ratio values.

(Hf, REE and Nb, Ta, W and Th in some rock types). It does depend, however, on the collection of samples with a range of Zr contents, preferably high Zr contents. In our samples, there is thus some bias towards samples with high Zr, Y and U contents. This is apparent when median values given in this paper are compared with median values obtained on more representative samples (Bailey *et al.*, 1981a).

In detail, the very careful sampling in aegirine lujavrite I (bore hole 7) revealed that here, at least, the eudialyte control lines are, in fact, gently curved. This feature is brought out more clearly by plotting ratios against Zr (fig. 2). It is seen that ratios tend to a constant value, applicable to eudialyte, only at the highest Zr levels. Other phases generate significant deviations at lower Zr contents.

The U values for eudialyte obtained by extrapolating mineral control lines or curves are in reasonable agreement with values obtained (a) by XRF analysis of separated eudialytes (Table 1) and (b) by fission track analysis. In detail, the extrapolated values tend to be higher, and this suggests that analysis of whole-rock samples includes additional U beyond that deposited in primary eudialyte. This U may have been deposited from U-rich intercumulus liquids and/or late magmatic or hydrothermal solutions. Some of it may be represented by the altered areas in eudialyte reported by Steenfelt & Bohse (1975). The presence of well-defined Zr-U curves and lines through a series of whole-rock samples indicates that U was not introduced randomly into these samples by outside solutions; the U probably has an 'internal, closed-system' origin. Thus, precipitation of U in altered areas of eudialyte could be a closed-system autometasomatic phenomenon. On this basis, whole-rock chemistry is equivalent to the primary chemistry even though the rock shows alteration under the microscope and during fission track analysis.

Fig. 3 reveals that variations in Zr/U and Zr/Y can be used to establish a geochemical stratigraphy for the kakortokite-lujavrite sequence in southern Ilímaussaq and to characterise each rock unit. Zr/U ratios fall from 1200 in the earliest black kakortokites to 9.2 in the final naujakasite lujavrites (Table 1). Zr/Y ratios change by a factor of 6.5 from 18.2 in the early black kakortokites to 2.8 in the naujakasite lujavrites.

The Zr/U and Zr/Y ratios fall along two trends; they begin to evolve more rapidly at the boundary between kakortokite and aegirine lujavrite I. The speed of evolution is more or less constant on this logarithmic diagram both between the various lujavrite units and within the main mass of arfvedsonite lujavrite (see below for discussion).

Two deviations from these regular trends for Zr/U and Zr/Y require attention. Firstly, the Zr/U ratio, and to a lesser extent the Zr/Y ratio, for kakortokites is not a constant. In the lower layered kakortokite, median values decrease from 1200 in black kakortokite to 809 in red kakortokite to 645 in white kakortokite. Only the eudialyte control line for the black kakortokites extrapolates to the measured Zr/U ratio of cumulus eudialyte grains. (The eudialyte contains about 40 ppm U, Zr/U equals 2500; Steenfelt & Bohse, 1975). We attribute the lower Zr/U ratios of the red and white kakortokites to the presence of a higher amount of low-Zr/U magma trapped between the cumulus phases. This magma has crystallised forming adgrowths to the cumulus phases (including eudialyte) and also forming new interstitial phases such as minor Li-mica and rinkite (a Nb silicate with a low Zr/U ratio).

Secondly, on the basis of geological and textural evidence, the M-C lujavrite has been regarded as crystallising from the final, volatile-rich fraction of the lujavrite magmas. However, the relatively high Zr/U and Zr/Y ratios point to a more primitive geochemical character. Bailey *et al.* (1981b) attribute the relatively low U contents in Kvanefjeld M-C lujavrite to loss of U-bearing solutions. However, it is difficult to see how this could explain the relatively high Zr and Zr/Y values. It is possible that the M-C lujavrite was isolated from the main lujavrite magma chamber at a relatively early stage and largely avoided fractionation before its final-stage emplacement.

Given these irregularities, it is found that the progressive decrease of Zr/U and Zr/Y through the kakortokite-lujavrite sequence agrees with the sequence of formation deduced from field evidence. We anticipate that isolated bodies of lujavrite in the Ilímaussaq intrusion can be assigned to their correct position in this sequence using the above geochemical parameters.

The *naujakasite lujavrite* has the most evolved levels and ratios of Zr, Y and U of all the lujavrites in southern Ilímaussaq and is known to occur at the highest stratigraphic level of the lujavrite sequence. It can thus be regarded as the most evolved of the lujavrite magmas.

Kvanefjeld lujavrites

The geological relations of the various Kvanefjeld lujavrites have been studied in surface exposures and drill cores (Sørensen *et al.*, 1969, 1974). While their relative ages are well established, no attempt have been made to establish a cumulate stratigraphy.

The Kvanefjeld lujavrites follow the geochemical trends found in the southern Ilímaussaq sequence but absolute contents differ (Table 1, figs 3 and 4). Judged from their Zr/U and Zr/Y ratios, the 'most primitive' arfvedsonite lujavrites at Kvanefjeld correspond roughly to

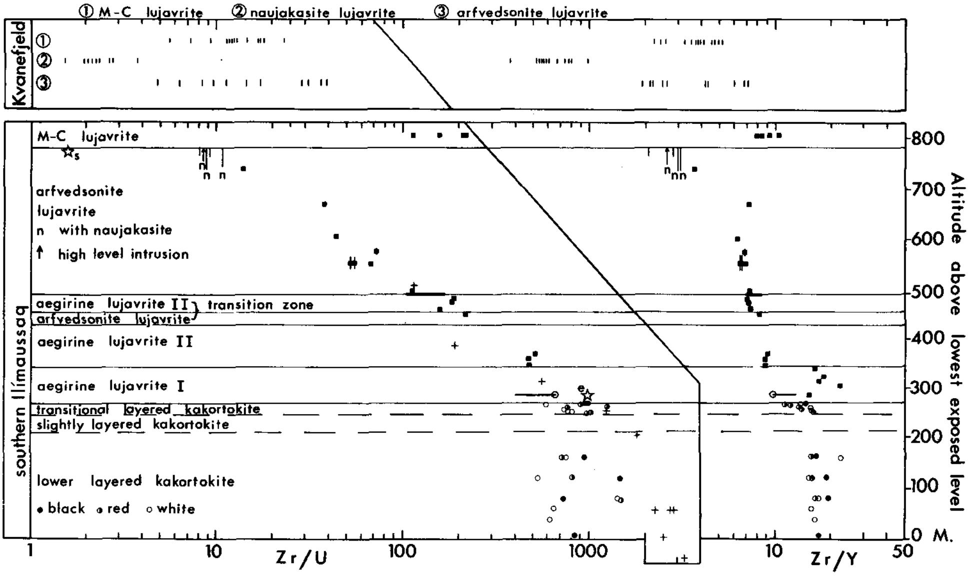

Fig. 3. Zr/U and Zr/Y stratigraphy in the kakortokite-lujavrite sequence, southern Ilímaussaq; and comparison with Kvanefjeld lujavrites. ● black, ◑ red, ○ white kakortokites, ■ lujavrites (vertical bar indicates the uncertainty in stratigraphic height). + Zr/U based on fission track analyses of eudialyte (Steenfelt & Bohse, 1975). ✫ e, s analyses of separated eudialyte (aegirine lujavrite I) and steenstrupine (late veins). –⊖ values from fig. 2.

the 100 m stratigraphic level with the arfvedsonite lujavrite sequence from southern Ilímaussaq (fig. 4). They evolve beyond the highest, 290 m, level of the southern sequence. The naujakasite lujavrites have the lowest Zr/U and Zr/Y ratios among the Kvanefjeld lujavrites and, by analogy with the southern sequence, may represent the most fractionated of the Kvanefjeld lujavrites. The M-C lujavrite, as in the southern sequence, is characterised by relatively high Zr, Zr/U and Zr/Y values (see above).

These features suggest that the Kvanefjeld lujavrites underwent an independent, more prolonged, fractionation in an isolated magma chamber. The fractionation mechanism, however, was similar in the two chambers.

Origin of Zr/U and Zr/Y stratigraphic trends

Fig. 3 indicates that the stratigraphic trend for Zr/U, and to a lesser extent for Zr/Y, can be divided into two parts. The earliest part of the sequence shows little change but there is a steady decrease in the later part. The changeover cannot be located exactly at the moment but could well be at the boundary between kakortokite and lujavrite.

This boundary correlates with a number of geologic and petrologic features. The kakortokites formed under relatively quiet, regular conditions probably across the whole floor of the intrusion. Excellent gravity sorting of cumulus phases points to sinking through a wide vertical interval. In contrast, even the earliest lujavrites can be in contact with the overlying roof rocks and contain a high percentage of roof and wall xenoliths. There are local intrusive and flowage features, fracturing and bending of crystals and late to post-magmatic shearing.

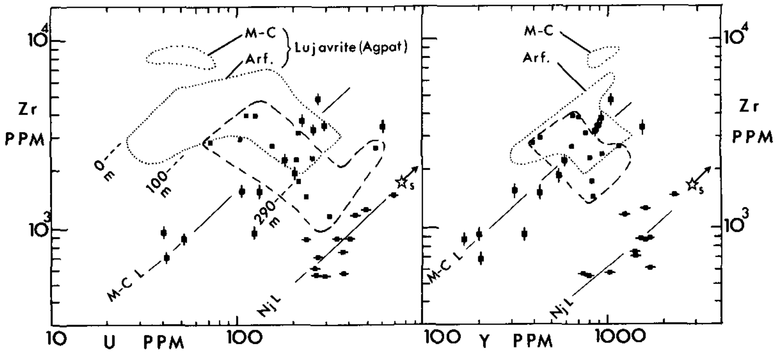

Fig. 4. Zr versus U and Y in Kvanefjeld lujavrites. Symbols as in fig. 1. The star with arrow points towards the composition of steenstrupine. Stratigraphic levels within arfvedsonite lujavrite from southern Ilímaussaq are indicated.

The lujavrites are thought to be poorly sorted mushes and partial cumulates which closely approach liquid compositions at higher levels. Cumulus aegirine suggests low H_2O–HF activity but high oxygen activity. Grain sizes decrease upwards throughout the kakortokite-lujavrite sequence.

These features suggest that the appearance of lujavrite is related to a major roof subsidence and fragmentation and to the development of sub-chambers with a small vertical interval. Some magma may have flown out from the margins of the main, conformably crystallising chambers and intruded adjacent rocks. More open, oxidising conditions with a decrease in the activity of H_2O and HF, and accelerated cooling of these small chambers, may have occurred.

The kakortokite-lujavrite boundary thus marks a major change in the physical conditions of crystallization. Is this physical change also responsible for the changes in Zr/U and Zr/Y stratigraphic trends?

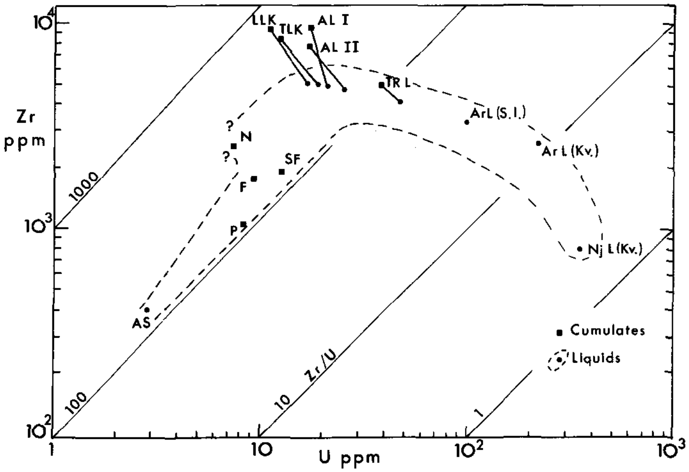

Fig. 5. Theoretical Zr-U evolution for Ilímaussaq cumulates and liquids. Source of data: Gerasimovsky (1969), Bailey *et al.* (1978; this volume a, b) and this paper. AS augite syenite, P pulaskite, F foyaite, SF sodalite foyaite, N naujaite. Lujavrite abbreviations as in fig. 1 (S.I. southern Ilímaussaq, Kv. Kvanefjeld).

(1) *Changes in partition coefficients.* During fractionation of kakortokite and lujavrite, the bulk partition coefficients for Zr and U are largely determined by eudialyte. D^{Zr}_{eud} increases as the Zr contents of the magma decrease (fig. 5). D^{U}_{eud} also appears to increase: U contents of eudialytes from lower layered kakortokite to arfvedsonite lujavrite increase more rapidly (× 22) than U contents in whole-rocks (× 8) or postulated magmas (× 4) (fig. 5). (Increasing D^{U}_{eud} may reflect break-up of complex U ions in the melt and the greater availability of free U ions which can enter eudialyte). We estimate that $D^{Zr/U}_{eud}$ probably decreases from about 2.0 to 1.2 and bulk partition coefficients show a similar trend. These estimates suggest that residual magmas and derivative (cumulate) rocks will show a decrease in Zr/U ratios but that the ratio will decrease more slowly in the later stages. This is opposite to the observed trend.

(2) *Diminished volume of magma chambers.* If the appearance of lujavrite is related to roof subsidence and the development of smaller, possibly isolated, magma chambers then subsequent fractionation will proceed at a more rapid rate. If the volume diminished enough (e.g. 50% or more), this effect could override the trend discussed in (1).

(3) *Changing character of analysed whole-rocks.* In the kakortokites, efficient separation of cumulus phases (high Zr/U ratios) from coexisting magma (lower Zr/U ratios) produced cumulate rocks with high Zr/U ratios. In the overlying lujavrites, however, the decreased vertical interval for crystal settling and the mush-like character of the magmas lead to an inefficient separation of cumulus phases and the formation of partial cumulates which more closely approached the relatively low Zr/U ratio of the magma. The approach becomes very close in the highest level arfvedsonite and naujakasite lujavrites which are probably similar in composition to their parent liquids.

We conclude that mechanisms (2) and (3) prevailed over mechanism (1) and that the postulated change in physical conditions is capable of explaining the observed chemical changes. Thus, the diminished volume and vertical dimension of the lujavrite magma chamber lead to a more rapid fractionation and to the appearance of poorly sorted partial cumulates.

Zr-U evolution of Ilímaussaq liquids

In fig. 5 we schematically and speculatively present the evolution of Zr and U in the cumulate rocks and coexisting magmas of the Ilímaussaq intrusion. The control points for this diagram are limited:

(1) The augite syenite and the earliest roof rocks of the internal, layered sequence (pulaskite, foyaite and sodalite foyaite) show a steady increase of Zr and U which is consistent with the process of fractional crystallization. At this stage virtually no Zr or U is removed in the fractionating phases.

(2) The sodalite-rich roof cumulates (naujaite) show unusually low U and high Zr/U values. See Steenfelt & Bohse (1975).

(3) Magma coexisting with kakortokite has a lower Zr, higher U and lower Zr/U ratio than the bulk kakortokite separate. A suggested magma composition is marked in fig. 5. Supporting this suggestion is the analysis of a 'microkakortokite' dyke (Zr 4850 ppm, U 19.5 ppm;

Larsen & Steenfelt, 1974) which has been regarded as close to an Ilímaussaq liquid in composition.

(4) The final lujavrites (arfvedsonite and naujakasite lujavrites from southern Ilímaussaq and Kvanefjeld) are considered to be close to liquids in composition.

(5) Between controls (3) and (4) we envisage a series of liquids with steadily decreasing Zr and Zr/U and rising U values.

Fig. 5 essentially reveals a steady increase in U but a rise and fall in Zr contents. This can be integrated with the appearance of Zr-rich eudialyte in the 'intermediate' kakortokite stage of the evolution and the steady exhaustion of the succeeding melts in Zr. U only enters eudialyte in limited amounts and continued to concentrate into the final economic lujavrites at Kvanefjeld.

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