

## SECONDARY ALTERATION IN ECLOGITES FROM KIMBERLITE PIPES

G. W. BERG, *Geochemistry Department, University of Cape Town,  
Rondebosch, C. P., South Africa.*

### ABSTRACT

An analcime-type zeolite has been found in eclogite xenoliths from the Roberts Victor kimberlite pipe. Analytical data obtained for the primary pyroxene (omphacite) and secondary minerals (mica, analcime, clay) indicate that the xenoliths have been contaminated by K, Rb and Cs, which are important for the study of the origin of eclogites. Metasomatic alteration of an eclogite during the intrusion of the kimberlite may be followed by further contamination of the eclogite by the migration of elements during the weathering of the kimberlite. For many elements abundance data must be determined on separated primary eclogite minerals and data obtained on whole-rocks should be treated with some circumspection.

### INTRODUCTION

A number of geochemists have recently commented on the possible secondary contamination of eclogites, particularly those from kimberlite pipes. Heier (1963) for example, discussed the possible introduction of K in eclogites with the formation of secondary phlogopite. (See also Lovering and Morgan 1963, Tilton and Reed 1965 and Haskin *et al.* 1966.)

Gurney, Berg and Ahrens (1966) found remarkably high concentrations of Cs in relation to K in a number of eclogites from the Roberts Victor mine 50 miles E.N.E. of Kimberley; K/Cs ratios ranging from 7370 to 158, with an average of 1817, were estimated for 16 eclogites from this pipe and the specimen AA3 believed, but not confirmed, to have come from the same occurrence. On the other hand, Rb did not show enrichment in these eclogites compared to the commonly encountered K/Rb ratio of 230; the 17 eclogites studied by Gurney *et al.* (1966) showed K/Rb ratios ranging from 257 to 534 with an average of 367. Six specimens of fresh Roberts Victor kimberlite were found to have K/Rb ratios in a narrow range with an average of 246, and K/Cs ratios ranging from 4000 to 7100.

Petrographic descriptions of some typical whole eclogites analyzed by Gurney *et al.* (1966) are given by Williams (1932, Vol. I. Ch. XI). Among the secondary minerals described, Williams notes an unidentified turbid white alteration of the pyroxene in certain eclogites. I found, after separating the minerals of the specimen RV372, that this turbid alteration product was the host for Cs in the rock, and that it gave the xray diffraction pattern of analcime (Gurney *et al.* (1966)).

The present communication reports further investigations into the

relationship between the mineralogy of eclogites and their alkali-metal abundances. Attention is drawn to the manner in which secondary minerals may obscure the primary abundances of elements in eclogites, particularly in the case of the alkali-metals, and possibly other elements.

#### EXPERIMENTAL

*Mineral Separation.* Minerals were separated from powder passing 120 mesh using appropriate combinations of magnetic separation and methylene iodide diluted with acetone. Operations were repeated until the clear pyroxene was obtained where possible (see descriptions). Even with repeated operations and fine grinding the alteration products could not be isolated completely from the clinopyroxene.

*X-ray Diffraction.* The diffraction lines of the alteration products were identified by diffractograms (Fig. 1) of perfectly pure pyroxene, somewhat altered pyroxene, and the purest available alteration product, so that lines could be directly allocated to the respective minerals. The minerals were mounted on glass slides as acetone smears. Following Loughnan (1966), who identified zeolite peaks as those destroyed after acid treatment of whole rock powder, the RV 378 pyroxene alteration product was boiled for 40 minutes in 2N HCl and the residue diffracted after filtering, washing and drying.

Diffractometer traces were made of 27 whole-rock eclogite powders mounted in a Philips holder, to detect zeolite alteration. Localities and numbers of whole-rock samples diffracted were as follows: Roberts Victor mine, Orange Free State, South Africa, 17 (including AA3); Jagersfontein, Orange Free State, South Africa, 2; Crown mine, district Kroonstad, Orange Free State, South Africa, 1; Dodoma, Tanzania, 2; Visser's Pipe, Shinyanga District, Tanzania, 1; Almklovdalen, Norway, 3; Grytingevag, Norway, 1. An example showing the clear zeolite peaks at 5.57 Å and 3.42 Å on some whole-rock diffractograms is illustrated in Figure 1. (A microscopic description of this rock is given by Williams (1932) and is quoted by Heier (1963).) A Philips PW1050/30 diffractometer was used at scanning speed of 1.2θ/min with Ni-filtered Cu radiation and a Geiger counter detector. Samples showing zeolite peaks were subsequently mounted in the Philips holder again and the 5.57 Å analcime peak scanned 11 times at ¼° 2θ/min for each specimen using Fe-filtered Co radiation. The averaged 5.57 Å peak height of each rock was used as an estimate of the relative volume of zeolite in the respective specimens. The range in the 11 peak heights measured on any one sample varied from 23 to 41 percent of the mean peak height recorded for the sample. To obtain an indication of the reproducibility of the mounting technique one sample was mounted four times and scanned as described above; average peak heights of 1.20, 1.22, 1.25 and 1.30 inches were recorded.

*Analytical.* Sodium and potassium were determined in three pyroxenes and three alteration products from the same rocks using an EEL flame photometer. K was determined by the same technique in a further six separated pyroxenes to investigate in more detail the K contributions of the pyroxenes to the whole-rocks. Rb and Cs were determined in the three alteration products using a spectrographic technique adapted from the method referred to by Gurney *et al.* (1966). Any values assigned to the pure alteration products must be considered semiquantitative since they are based on an arbitrary estimate of the purity of the material analysed.

#### DESCRIPTION OF MATERIAL ANALYZED

*RV372 Pyroxene Alteration.* Turbid white to grey grains show occasional relicts of unaltered pyroxene under the microscope, the presence of which is confirmed on the diffractogram.

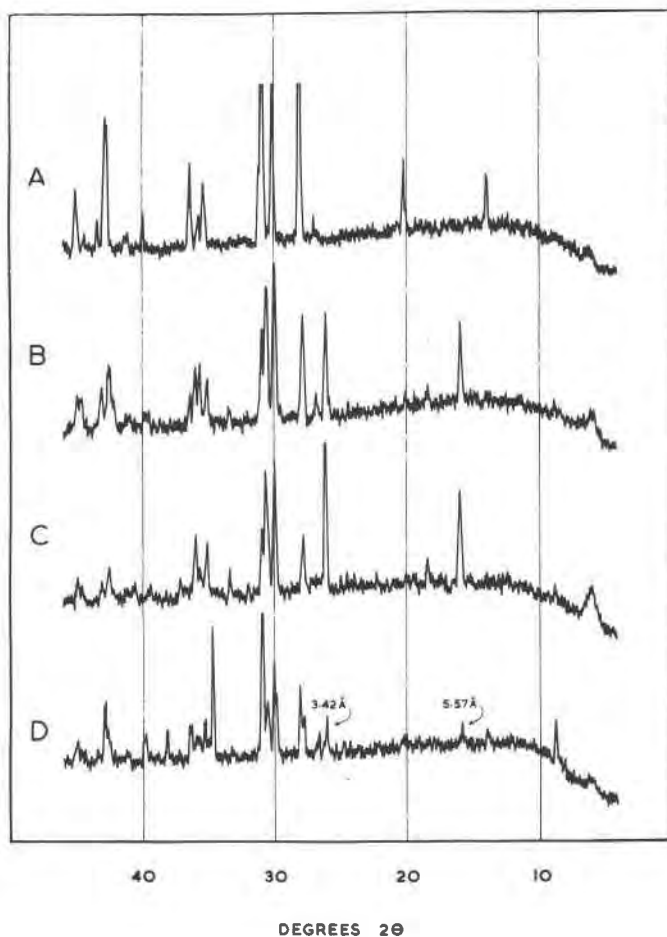


FIG. 1. Diffractograms of: A. Unaltered pyroxene RV378; B. Altered pyroxene RV378; C. Purest available alteration product of pyroxene RV378; D. RV378 whole-rock illustrating zeolite peaks. (CuK radiation.)

From X-ray diffraction data the alteration is identified as a zeolite based on the analcime structure. The  $d$  spacings of the alteration product, and relative intensities, are as follows (b=broad) (peaks ( $<10$ ) not recorded): 5.57(55); 4.84(20); 4.65(20); 3.78(12); 3.43(100); 3.32(15b); 3.03 calcite? (35); 2.92(75); 2.686(25); 2.488(25); 2.275(12b); 2.113(15); 1.903(15); 1.742(20).

*RV378 Pyroxene Alteration.* Under the microscope the specimen appears as black grains of highly altered pyroxene showing occasional relicts of the original mineral. Diffraction data show the alteration product to have an analcime-type structure. The analcime peaks were destroyed by boiling the specimen in 2N HCl. In addition to the pyroxene alteration, the

specimen contains small quantities of clay and mica, probably vermiculite and phlogopite or biotite, as indicated by the peaks at 14.50 Å and 10.04 Å. The spacings of the pyroxene alteration, clay and mica are: 14.50 clay (25); 10.04 mica (10); 5.57(60); 4.83(20); 3.42(100); 2.92(70); 2.797(10); 2.682(20); 2.420(10).

*KRV4 Secondary Material from Eclogite.* Brown mica is identified under the microscope together with brown to black grains secondary after pyroxene, some unaltered relicts of which remain. The diffractogram shows the sample to consist mainly of a mixture of phlogopite or biotite and a 14 Å clay, probably vermiculite; the presence of a small amount of analcime is suggested by weak reflections at 5.57 Å and 3.42 Å.

At present insufficient data is available to test the possibility that the zeolite in the three specimens may be an intermediate member of the analcime-wairakite series reported by Surdam (1965).<sup>1</sup> It may be noted, however, that the splitting of the 3.42 Å peak characteristic of wairakite was not observed for the zeolite separated from the eclogites. The data given in Tables 1 and 2 indicate a lower Na content for the zeolite than for the pri-

TABLE 1. Na, K, Rb AND Cs IN PUREST AVAILABLE ALTERATION PRODUCTS

	Na percent	K percent	Rb ppm	Cs ppm	K/Rb	K/Cs
RV378 pyroxene alteration (Est. 75% zeolite)	3.51	0.51	14	75	364	68
RV372 pyroxene alteration (Est. 40% zeolite)	3.29	0.27	3.4	18	794	150
KRV4 secondary alteration (Est. 10% zeolite)	1.78	1.0	27	12	370	833

The K data in Table 1 show that the unaltered pyroxene present in the samples makes a negligible contribution to the K concentrations reported above.

mary pyroxenes; however, owing to the incomplete separation obtained, no further details of the zeolite composition are available.

*Separated Pyroxenes.* Specimens 501, 372, 351, 381 and 378 are optically clear under the microscope. Numbers 377, 374 and 503 show a very slight cloudiness in approximately 30 percent of the grains. KRV4 has occasional definite signs of alteration. Diffraction data for RV378 agrees closely with that given by Warner (1964) for omphacite from a Norwegian eclogite. RV372 shows a similar pattern but systematically smaller spacings. Further study of the pyroxenes is in progress.

## RESULTS AND DISCUSSION

*The K-Rb-Cs Relationship.* K, Rb and Cs concentrations in eclogite alteration products are given in Table 1, and K and Na in pyroxenes in

<sup>1</sup> In the present communication "analcime" is used to indicate a zeolite having the analcime structure but not necessarily the Na end member.

TABLE 2. Na AND K IN ECLOGITES AND THEIR SEPARATED PYROXENES

Sample <sup>a</sup>	Pyroxene		Whole rock	
	Na (%)	K <sup>b</sup> (%)	Na(%)	K <sup>c</sup> (%)
RV377		0.03		0.46
RV374		0.11		0.66
Tan501		0.03		0.12
Tan503		0.04		0.05
RV372	4.44	<0.05	3.16	0.16
Jag351		0.02		0.09
RV381		0.10		0.16
RV378	3.93	0.12	2.39	0.26
KRV4	3.65	0.11	2.19	0.22

<sup>a</sup> RV, KRV=Roberts Victor, Tan=Dodoma, Tanzania, Jag=Jagersfontein.

<sup>b</sup> The instrument was set to give a deflection of 30 for the solution of a mineral containing 0.1 percent K, maximum deflection being 100.

<sup>c</sup> From Gurney *et al.* (1966).

Table 2. Cs was not detected in the pyroxenes. An attempt was made to estimate Rb in the RV378 pyroxene, which has the highest K content of the pyroxenes examined, but no Rb line was recorded. The Rb detection limit of the analytical method applied is 0.5 ppm or less, indicating a K/Rb ratio of greater than 2,000 for the pyroxene. Rb was nevertheless readily detected in a specimen of very slightly altered RV378 pyroxene containing 0.13 percent K, emphasizing the extreme care required in mineral separation if meaningful data is to be obtained.

Data obtained in the present study (Table 1) show that the zeolite alteration of Roberts Victor eclogites has a generally higher K/Rb ratio than the value of 230 commonly encountered in crustal rocks; the latter value was also found for the Roberts Victor kimberlite (Gurney *et al.* 1966). The zeolite contributes significantly to the trend in the K/Rb ratios reported by Gurney *et al.* (1966) for the Roberts Victor eclogites.

As shown by Table 1, Cs in the eclogites is accommodated in analcime and it is instructive to consider the crystallo-chemical properties of this zeolite. The structure and chemistry of analcime is described by Deer, Howie and Zussman (1963) (Vol. 4) who refer to numerous investigators. It is noteworthy that the analcime structure is stable over a wide range of chemical compositions.

The complete range of solid solution found for the Na and Cs end members of the analcime structure (Barrer, Baynham and McCallum (1953)) is of particular significance to the present study. The analcime and pollucite aluminosilicate framework structures are in fact virtually





the secondary phlogopite may be expected to have a K-Rb-Cs relationship analogous to that of the fresh host kimberlite. No data on fresh phlogopite from the eclogites are available, however; further study is in progress.

Two possible modes of formation for the secondary analcime-mineral in the eclogites will be considered. The zeolite alteration in Roberts Victor eclogites could have formed during a late hydrothermal phase of kimberlite emplacement, analogously to the alteration of tuffs in the active thermal region of Wairakei. Steiner (1953) reports zeolites, including possibly analcime, below 240 ft. in this region, while the same author (1955) found wairakite in drill cores from 600 to 2,890 feet.

I incline to an alternative explanation that the zeolite in eclogites formed during deep weathering of the host kimberlite. Melvill (1910) states that yellow-ground occurred to a depth of approximately 140 feet at the Roberts Victor mine, deeper than in any other kimberlite with which he was familiar. Melvill's data indicate that half or more of the kimberlite mined at Roberts Victor, from which the eclogites studied here were recovered, was this yellow surface-weathered product. Even at 300 feet the kimberlite appears to have been considerably altered. It seems most unlikely that a high-pressure mineral like the omphacite of the xenolithic eclogites would remain unaffected by this weathering; the formation of the secondary zeolite in Roberts Victor eclogites could be attributed to this phase. The discussion of Bradley (1929) suggests the possibility of analcime formation under near-surface conditions. (See also Deffeyes, 1959.)<sup>1</sup>

Gurney *et al.* (1966) analyzed five specimens of fresh kimberlite collected near an old shaft on the Roberts Victor property, and found from 1.67 to 3.37 percent K, 73 to 135 ppm Rb and 4 to 8 ppm Cs. I analyzed two samples of yellow-ground, assumed to have weathered from a kimberlite originally chemically similar to the fresh material analysed, and found 0.2 percent K. The Rb and Cs, which may be inferred to have been leached together with K during the weathering of the original kimberlite to yellow-ground, would have been available for incorporation in secondary zeolite if this formed in the eclogite xenoliths during the same weathering process.

The occurrence in some eclogites of 14 Å clay, which must be the alteration product of phlogopite or biotite formed earlier, is a further indi-

<sup>1</sup> When considering the possible depth of burial of eclogites during either hydrothermal or deep weathering alteration it should be borne in mind that since the time of kimberlite emplacement in the Kimberley region, the original land surface has been lowered considerably by erosion (Du Toit 1956; Williams, 1932, Vol. 1, p. 274) approximately 3000 feet suggested by Hamilton and Cooke (1960, p. 275).



cation of the low-temperature alteration processes to which the eclogites were subjected. Vermiculite is a common constituent of yellow-ground, having formed similarly from the phlogopite of fresh kimberlite. (See for example Nixon *et al.*, 1963.)

The extent of zeolite alteration in a particular eclogite may also depend on the crystallo-chemical properties of its pyroxene. My data suggest that pyroxenes of relatively high Na content are especially susceptible to alteration to zeolite, but no conclusive evidence is available. Further work in progress at present may clarify this aspect. Replacement of jadeite by analcime has been reported by Tilley (1956, in Deer *et al.* (1963) vol. 2, p. 107), but as far as I am aware, no further instances of alteration of pyroxene to analcime are on record.

*Summary of the K-Rb-Cs Relationship.* The two primary silicate minerals in the eclogites are garnet and pyroxene; only the pyroxene may be expected to contribute significantly to the Na, K and Rb of the whole rock.

Table 2 indicates that while the sodium determined in eclogite whole rocks is predominantly primary, the whole rock K is almost completely secondary. Potassium is accommodated principally in secondary phlogopite with a K-Rb-Cs relationship probably comparable to that of the host kimberlite. Zeolite, which may form at a later stage, accommodates relatively high concentrations of Cs as well as some K and Rb. The zeolite may have a higher K/Rb ratio than the phlogopite, but has a very much lower K/Cs ratio. The absence of K/Cs coherence in Roberts Victor eclogites reported by Gurney *et al.* (1966) is a consequence of the accommodation of K predominantly in phlogopite and Cs predominantly in zeolite, two minerals which form independently of one another at different times. The overall alkali abundance relationship for individual kimberlitic eclogites depends on the varying proportions of minerals present, representing a primary and two secondary geochemical phases. Cases of extreme alteration are not considered here since such specimens would be rejected for purposes of estimating the abundances of elements in eclogites.

#### CONCLUSIONS

This study re-emphasizes the need for revision of certain data for eclogites. Data pertaining to whole-rock kimberlitic eclogite for any of the so-called late-differentiated elements which are relatively abundant in kimberlites, should be considered with some scepticism. This applies particularly to K and geochemically related elements, and probably also to others such as Sr and the rare earth group. These considerations are especially important for the Roberts Victor eclogites which, because of

their quite exceptional abundance in the kimberlite of this mine, have been distributed to numerous laboratories.

## ACKNOWLEDGEMENTS

The writer is indebted to the following: Mr. C. D. Hallam of Anglo American Corporation for arranging a visit to the Roberts Victor mine; Dr. A. O. Fuller for fruitful discussion on X-ray diffraction; J. J. Gurney and A. J. Erlank for helpful discussion on the spectrographic method, and Professor L. H. Ahrens, Dr. H. S. Yoder and Dr. J. B. Dawson for critical reading of the manuscript. M. A. Berg drafted the diagrams. Financial assistance from the C.S.I.R., Pretoria, is gratefully acknowledged.

## REFERENCES

- BARRER, R. M., J. W. BAYNHAM AND N. MCCALLUM (1953) Hydrochemical chemistry of silicates Part V Compounds structurally related to analcite. *J. Chem. Soc.*, 4035-4041.
- BEATTIE, I. R. (1954) The structure of analcite and ion exchanged forms of analcite. *Acta Crystallogr.* **7**, 357-359.
- BRADLEY, W. H. (1929) The occurrence and origin of analcite and meerschaum beds in the Green River formation of Utah, Colorado, and Wyoming. *U.S. Geol. Surv. Prof. Pap.* **158-A**, 1-8.
- DAWSON, J. B. (1962) Basutoland kimberlites. *Geol. Soc. Amer., Bull.* **73**, 545-559.
- DEER, W. A., R. A. HOWIE AND J. ZUSSMAN (1963) *The Rock-forming Minerals*. Longmans Green, London.
- DEFFEYES, K. S. (1959) Zeolites in sedimentary rocks. *J. Sediment. Petrology*, **29**, 602-609.
- DU TOIT, A. L. (1956) *Geology of South Africa*. Oliver and Boyd, Edinburgh.
- FORNASERI, M., AND A. PENTA (1960) Elementi alcalini minori negli analcimi e loro comportamento nel processo di analcimizzazione della leucite. *Period. Mineral.*, **29**, 85-102.
- GURNEY, J. J., G. W. BERG AND L. H. AHRENS (1966) Observations on caesium enrichment and the potassium/rubidium/caesium relationship in eclogites from the Roberts Victor Mine, South Africa. *Nature*, **210**, 1025-1027.
- HAMILTON, G. N. G. AND H. B. S. COOKE (1960) *Geology for South African Students*. 4th Edition, Central News Agency, South Africa.
- HASKIN, L. A., F. A. FREY, R. A. SCHMITT AND R. H. SMITH, Meteorites, solar, and terrestrial rare-earth distributions, in Ahrens, L. H. *et al.* (eds.) *Phys. Chem. Earth*, **7**, Pergamon Press, London, p. 167-321.
- HEIER, K. S. (1963) Uranium, thorium and potassium in eclogitic rocks. *Geochim. Cosmochim. Acta*, **27**, 849-860.
- LOUGHNAN, F. C. (1966) Analcite in the Newcastle coal measure sediments of the Sydney Basin, Australia. *Amer. Mineral.*, **51**, 486-498.
- LOVERING, J. F. AND J. W. MORGAN (1963) Uranium and thorium abundances in possible upper mantle materials. *Nature*, **197**, 138-140.
- MELVILL, E. H. V. (1910) Note on the Roberts Victor mine. *Trans. Geol. Soc. S.A.*, **12**, 205-212.
- NIXON, P. H., O. VON KNORRING AND J. M. ROOKE (1963) Kimberlites and associated inclusions of Basutoland: a mineralogical and geochemical study. *Amer. Mineral.*, **48**, 1090-1132.
- STEINER, A. (1953) Hydrothermal rock alteration at Wairakei, New Zealand. *Econ. Geol.*, **48**, 1-13.

- (1955) Wairakite, the calcium analogue of analcime, a new zeolite mineral. *Mineral. Mag.*, **30**, 691–698.
- SURDAM, R. C. (1966) Analcime wairakite mineral series (abstr.) *Geol. Soc. Amer., Spec. Pap.*, **87**, 169–170.
- TILLEY, C. E. (1956) Nephelene associations. *Kon. Ned. Geol.-Mijn. Gen., Geol. Sci., Brouwer vol.*, 403.
- TILTON, G. R. AND G. W. REED (1963) Radioactive heat production in eclogite and some ultramafic rocks. In J. Geiss and E. D. Goldberg (eds.) *Earth Science and Meteoritics*. North Holland Publishing Co., Amsterdam, p. 31–43.
- WARNER, J. (1964) X-ray crystallography of omphacite. *Amer. Mineral.*, **49**, 1461–1467.
- WILKINSON, J. F. G. (1959) The geochemistry of a differentiated teschenite sill near Gunnedah, New South Wales. *Geochim. Cosmochim. Acta*, **16**, 123–150.
- WILLIAMS, A. F. (1932) *The Genesis of the Diamond*. Ernest Benn, London.

*Manuscript received, August 10, 1966; accepted for publication, October 13, 1966.*