UR1980_27

/0

1980/27. Barium-bearing heulandite from DDH 55, Fingal

D.C. Green

Abstract

A thin vein of red zeolite in a core from DDH 55 in the Fingal district has been identified as a barium-bearing heulandite with the average oxide formula:

$$[(Ba)_{0.3}\ (Na)_{0.7}\ (K)_{0.3}\ Ca_{2.6}{}^{+}]\ O_4 \cdot (Al_{7.8}\ Fe_{0.2})\ O_{12} \cdot Si_{28}O_{56} \cdot \sim 24H_2O$$

Heulandite forms at low temperatures and is precipitated from groundwaters enriched in alkalies following the breakdown of vitric tuff components in the Triassic sediments.

INTRODUCTION

In March 1980, a sample of dull coal/carbonaceous mudstone containing a cross-cutting vein 1 mm thick of a bright red mineral was cored at a depth of 164.22 m in DDH 55. The sample was submitted to the Fuel Geoscience Unit of CSIRO for identification and a description of the coal petrology of the enclosing rocks, as a dolerite plug was suspected (R.H. Castleden *pers. comm.*) to occur in the vicinity of the drill hole.

The red mineral was identified by X-ray diffraction as "clinoptilolite, one of the mordenite group of the zeolites". A chemical analysis, based on the XRD identification (J.C.P.D.S. card 22-1236) was given.

As both clinoptilolite and the closely related heulandite are formed by direct or indirect breakdown of silicic glass shards in sediments of volcanic derivation, additional work was carried out to further identify the red mineral.

OPTICAL PROPERTIES

In thin section, the red colouration is seen to be due to minute flecks of haematite that vary in abundance and are zoned parallel to the essentially rectangular crystal outline. Individual zeolite crystals are prismatic, well formed, from 0.02 to 0.1 mm wide, and up to 0.6 mm in length. Optical properties are: low negative relief; $n_\gamma \approx 1.5$; optically +ve with low-moderate 2V, estimate $2V_z = 25°$; and prismatic crystals length fast with extinction parallel to cleavage. Insufficient material was available for a powder photograph.

CHEMISTRY

The results of electron probe microanalysis using mineral standards and the Jeol-Edax system at the Central Science Laboratory, University of Tasmania are given in Table 1.

DISCUSSION

Classification of zeolites is somewhat arbitrary and in the case of heulandite and clinoptilolite, confusing. Although the structures of the two minerals are apparently isomorphous, solid solution between them is said to be incomplete. Thus clinoptilolite is a valid species, generally of higher SiO_2 content ($\gtrsim$ 65% SiO_2) than heulandite. Other authors suggest that the difference lies in the cation content, *i.e.* (Na + K) > Ca in the case of clinoptilolite. The most useful parameters (Hay, 1977) are:

	Heulandite	*Clinoptilolite*
$Si/Al + Fe^{3+}$	2.9 - 4	4 - 5.1
Ca/(Na + K)	Generally > 1	Generally < 1
K/Na	" < 1	" > 1
Typical oxide formula	$4[CaO.Al_2O_3.7SiO_2.6H_2O]$	$(Na_2,K_2)O.Al_2O_3.10SiO_2.8H_2O$
	K, Na also present	CaO also present

Table 1. ANALYSIS OF BARIUM-BEARING HEULANDITE, DDH 55, FINGAL

	1	2	3	4	5
Na_2O	0.84	0.93	0.69	0.61	0.81
Al_2O_3	13.03	15.50	15.02	15.40	13.97
SiO_2	62.93	62.32	62.03	63.58	63.95
K_2O	0.53	0.51	0.42	0.42	0.52
CaO	4.79	5.36	5.51	5.56	5.06
BaO	0.79	1.60	1.46	1.49	1.00
ΣFe as Fe_2O_3	1.37	- *	-	-	1.65
$H_2O\pm$ (by difference)	15.58	13.33	14.34	12.78	13.07
Total	99.86	99.55	99.47	99.85	100.03
	* - = less than 0.2%				
Si	28.76	27.74	27.87	28.30	28.64
Al	7.02	8.13	7.95	8.08	7.37
Fe^{3+}	0.24	-	-	-	0.28
Na	0.75	0.80	0.60	0.52	0.70
Ca	2.35	2.56	2.65	2.65	2.43
Ba	0.14	0.28	0.26	0.26	0.18
K	0.31	0.29	0.24	0.24	0.30
H_2O	24.8	21.2	22.8	20.3	20.8
$Si/Al + Fe^{3+}$	3.96	3.41	3.51	3.50	3.74

The chemical analyses by electron microprobe (Table 1) supports the classification of this mineral as a heulandite, but is somewhat unusual with its barium content of over 1%.

Five zeolites commonly occur in sedimentary rocks: analcime, clinoptilolite, heulandite, laumontite and phillipsite. Whether a clay mineral or zeolite forms depends on the physical environment and on the activities of dissolved species such as H^+, alkali and alkali-earth cations and H_4SiO_4. The species of zeolite that forms depends on temperature, pressure, the activity of various ions and the activity or partial pressure of water. In this case, the cross-cutting nature of the veinlet and euhedral form of the crystals suggests an open hydrologic system.

Zeolite alteration takes place when percolating groundwater is chemically modified by hydrolysis or dissolution of vitric components. With increasing cation/H^+ ratio, zeolite formation is favoured at the expense of clay minerals. The composition of the parent volcanic rocks exercises an important control (*e.g.* Boles and Coombs, 1977; Hokonui Hills, New Zealand). Zeolites such as heulandite can form at essentially N.T.P. conditions and no estimate of depth of burial can be made from this limited occurrence. The absence of laumontite implies a temperature of less than 50°C. There is no evidence in the mineralogy of additional heat as a consequence of the dolerite intrusion some 60 m stratigraphically above this horizon.

The origin of the barium content is intriguing. A barium-bearing heulandite is described from Baltimore (Shannon, 1925). Average shales contain ∿ 0.05% BaO and felsic volcanic rocks up to 0.2%. The most likely reason is that clay minerals with K in 12-fold co-ordination discriminate against Ba strongly in most cases, so it is to be expected that the divalent barium ion with large ionic radius (1.34 Å) can proxy for either Ca^{2+} or K^+ in the exchangeable cation positions in the zeolite structure.

The recognition of zeolites as widespread authigenic silicates in sedimentary rocks derived from volcanic tuffs has led to a remarkable interest in their economic use because of the distinctive molecular sieve properties. The chief applications are in the field of pollution control, sewage treatment, coal gasification, soil conditioning and animal nutrition. Clinoptilolite, with its property of absorbing the ammonia molecule, is the most important zeolite for these purposes. Should any substantial amounts of zeolite be found in the Mesozoic sediments, commercial exploitation in the fields above could be expected as an addition to the well known but limited deposits of zeolites in Tasmanian Tertiary basalt. Further work on zeolites (particularly stilbite, laumontite) in the Triassic sediments that are affected by dolerite intrusions is in hand and will be the subject of a separate report.

REFERENCES

BOLES, J.R.; COOMBS, D.S. 1977. Zeolite facies alteration of sandstones, Southland Syncline, New Zealand. *Am.J.Sci.* 277:982-1012.

MUMPTON, F.A. (ed.) 1977. *Mineralogy and geology of natural zeolites.* Mineral Society of America. Short Course Notes (Vol. 4) November, 1977. Southern Printing Co. : Blacksburg, Virginia.

SHANNON, E.V. 1925. A reexamination of beaumontite from Baltimore. *Am. Mineralogist* 10:31-34.

[22 August 1980]