

## Harmotome from the Tokatoka district, New Zealand

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**SUMMARY.** Harmotome, associated with analcime, is described from andesite dykes at Rehia and Maungarahu in the Tokatoka district, New Zealand. The Maungarahu harmotome has the composition:  $(\text{Na}_{1.03}\text{K}_{0.23})(\text{Ba}_{1.54}\text{Ca}_{0.18})\text{Al}_{4.66}\text{Si}_{11.31} 12.39 \text{ H}_2\text{O}$ ; physical properties:  $\alpha 1.498$ ,  $\beta 1.503$ ,  $\gamma 1.506$ ,  $2V_\gamma 75-82^\circ$ ,  $\beta: [001] 28^\circ$ ,  $D 2.378$ ; and cell constants:  $a 9.906 \pm 0.006$ ,  $b 14.119 \pm 0.003$ ,  $c 8.712 \pm 0.007 \text{ \AA}$ ,  $\beta 124^\circ 57' \pm 3'$ . The harmotome is Ba-poor, and 2  $\text{Na}^+$  has substituted for  $\text{Ba}^{2+}$  on a valency basis. Analcime associated with the Maungarahu harmotome has chemical composition:  $(\text{Na}_{15.16}\text{K}_{0.08}\text{Ca}_{0.09})\text{Al}_{15.52}\text{Si}_{32.47} 15.93 \text{ H}_2\text{O}$  and physical properties:  $n = 1.483$ ,  $D = 2.257$ ,  $a = 13.708 \text{ \AA}$ .

The zeolites are believed to have crystallized from Na and Ba-rich alkaline solutions at approximately 200 °C. The source of the Ba is barite concretions in adjacent limestones.

ZEOLITES are widespread in the Tertiary volcanic rocks of Northland, New Zealand, but they have attracted little attention and there are few records of identifications of individual species.

Most of the zeolites are apparently sodium and calcium varieties, but a barium-rich zeolite (harmotome) has been found at Maungarahu in the Tokatoka district (Black, 1964). Following this discovery the writer's interest was drawn to rare abnormally high barium values in some published analyses of igneous rocks in the area (Mason, 1957; Black, 1967) as possible indications of other occurrences of barium-rich species.

Dr. Brian Mason kindly provided a thin-section and sample of the andesite from Rehia, near Tokatoka, with the highest recorded barium value (1.26 % BaO) in the district (Mason, 1957). Crushed samples of this rock were centrifuged in bromoform-acetone mixtures and sufficient zeolite was concentrated to positively identify harmotome. Thin-sections of the other barium-rich andesites and basalts show small areas of zeolite and although no attempt was made to separate the zeolite fractions harmotome may be present in these rocks also.

*Description of harmotome localities.* Large well-formed crystals of harmotome, sometimes exceeding 2 cm in length, are found with analcime in joints along the contact between a 20-m andesite dyke and limestone country rocks at Maungarahu. Harmotome and analcime are not confined to joints, and thin sections of the andesite show these minerals pervading the rock as small veins and in large irregular areas replacing felsic groundmass minerals and the cores of plagioclase phenocrysts. In some thin sections zeolites constitute 15 % of the rock.

At Rehia, harmotome has been seen only in thin section, where it occurs with analcime and apophyllite as irregular patches replacing the groundmass of a small

(3-m wide) andesite dyke. Apophyllite and calcite have been found in druses at this locality.

Limestone in contact with the Maungarahu dyke has been baked but no metamorphic calc-silicate minerals have been developed. However, limestones in contact with the smaller Rehia dyke have been decarbonated and recrystallized into larnite-bearing assemblages (Mason, 1957). Although zeolites occur in joints along the immediate contact, the zeolites are confined to the igneous rocks and have not been found in the limestones.

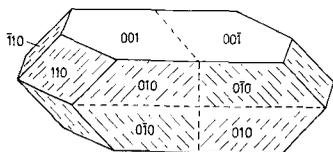


FIG. 1. Habit of Maungarahu harmotome showing simple penetration twinning.

*Description of harmotome.* Harmotome from both localities shows penetration twinning.

The habit of the Maungarahu harmotome is shown in fig. 1. Except for the absence of  $\{100\}$  faces on all crystals examined the twins are simple penetration twins similar to those of the morvenite twin type (Černý, 1960). Since the Rehia harmotome has been found only in irregular areas within the andesite, no study of its crystal habit could be made.

X-ray data for the Tokatoka harmotomes agree closely with those for harmotome from Andreasberg (N.M.N.H. R 10767), although when other physical properties (density and refractive indices) are compared the properties of the Maungarahu harmotome fall outside the range normally considered to be characteristic of harmotome (Sekanina *et al.*, 1937; Černý *et al.*, 1965). The low density of the Maungarahu harmotome suggests a barium deficiency:

Andreasberg	$\alpha$ 1.504	$\beta$ 1.507	$\gamma$ 1.509	$2V_{\gamma}$ 80°	$\beta:[001]$ 30°	D 2.436 $\pm$ 0.002
Rehia	1.505	1.508	1.510	75–80	30	2.458 $\pm$ 0.002
Maungarahu	1.498	1.503	1.506	75–82	28	2.378 $\pm$ 0.002

The refractive indices are all  $\pm 0.001$ .

There seems little reason to doubt that natural harmotomes are monoclinic with space group  $P2_1$  (Sadanaga *et al.*, 1961; Sahama *et al.*, 1967) and probably wellsite and most natural phillipsites also have this symmetry (Černý, 1964). Using cell constants given by Sadanaga *et al.* (1961) the powder data for the Maungarahu harmotome were indexed and Dr. D. E. Appleman of the U.S. Geological Survey kindly refined the cell constants using his least-squares refinement computer program. Cell constants for the Maungarahu harmotome are:  $a$  9.906 $\pm$ 0.006,  $b$  14.119 $\pm$ 0.003,  $c$  8.712 $\pm$ 0.007 Å,  $\beta$  124° 57'  $\pm$  3'.

Single crystals of the Maungarahu harmotome were crushed for analysis (table I).

The Maungarahu harmotome is low in barium and relatively high in sodium. Recalculation of the analysis into ions per unit cell on the basis of 32 oxygen shows a deficit in  $Ba^{2+}$  and a considerable excess of monovalent cations over that required to satisfy the idealized harmotome formula:  $(Na,K)_x Ba_2 Al_{4+x} Si_{12-x} O_{32} 12H_2O$ .

Although it was unlikely that analcime impurities were present, since the analysis is not abnormally high in  $SiO_2$  or  $Al_2O_3$  and optical and X-ray examination of the

sample before analysis failed to reveal the presence of analcime, single crystals of harmotome were analysed with an A.R.L. electron microprobe to check for the presence of intergrown analcime.

No analcime was detected. The high sodium values of the wet chemical analysis were confirmed by the electron-microprobe analyses although sodium counts were variable. The average of 95 analyses gave a value of 2.26 % Na<sub>2</sub>O with a minimum value of 1.20 % and a maximum of 3.92 %. The crystals are apparently zoned with relatively Na-rich and Ba-poor outer margins. Analyses of the other elements failed to show any consistent systematic variation with respect to either Ba content or to position in the crystal.

TABLE I. *Chemical composition of harmotome and analcime*

	1	2	3	4	Ions per unit cell on the basis of 32 O for harmotome and 96 O for analcime				
					1	2	3	4	
SiO <sub>2</sub>	47.22	47.53	45.21	55.75					
Al <sub>2</sub> O <sub>3</sub>	16.52	15.93	15.26	22.60					
Fe <sub>2</sub> O <sub>3</sub>	tr.	—	0.74	—	Si	11.31	11.47	11.05	32.47
MgO	—	—	0.48	—	Al	4.66	4.53	4.39	15.52
CaO	0.70	0.55	0.09	0.14	Fe <sup>3+</sup>	—	—	0.14	—
Na <sub>2</sub> O	2.22	0.54	1.81	13.41	Mg	—	—	0.17	—
K <sub>2</sub> O	0.77	1.43	0.24	0.04	Ca	0.18	0.14	0.02	0.09
BaO	16.44	18.66	20.66	tr.	Na	1.03	0.25	0.86	15.16
SrO	n.d.	0.02	0.01	n.d.	K	0.23	0.44	0.07	0.03
H <sub>2</sub> O+	14.92	10.97	15.57	8.20	Ba	1.54	1.76	1.98	—
H <sub>2</sub> O—	0.60	4.37	0.27	—	H <sub>2</sub> O	12.39	12.34	12.69	15.93
Total	99.39	100.00	100.34	100.14					

1. Harmotome, Maungarahu (Anal. P. M. Black).
2. Harmotome, Moravia (Černý *et al.*, 1965). Analysis recalculated to 100 % after deducting 1.68 % stevensite and 0.58 % limonite.
3. Harmotome, Finland (Sahama *et al.*, 1967).
4. Analcime, Maungarahu (Anal. P. M. Black). Physical properties:  $n$  1.483 ± 0.001,  $D$  2.257 ± 0.002,  $a$  13.708 ± 0.002 Å.

The microprobe analyses indicate that monovalent cations, or more specifically Na<sup>+</sup>, have substituted for Ba<sup>2+</sup>. When the monovalent cations are proportioned with 0.56(Na,K) assigned to compensate for the deficiency of 0.28(Ba,Ca) the remaining 0.71(Na,K) shows only a slight excess over that required to balance Al<sup>3+</sup> substitution for Si<sup>4+</sup>.

It is unlikely that the relatively small Na ion would enter the larger Ba site. The Na<sup>+</sup> ions are probably distributed throughout the second smaller alkali site in the structure proposed by Sadanaga *et al.* (1961).

Introduction of alkalis into the harmotome structure may result from Si<sup>4+</sup> ⇌ (Na<sup>+</sup>,K<sup>+</sup>) + Al<sup>3+</sup> and Ba<sup>2+</sup> ⇌ 2(Na<sup>+</sup>,K<sup>+</sup>) substitutions. Of the two, the former is the most common and accounts for the majority of high alkali harmotomes. The high alkalis in the harmotome described by Sahama *et al.* (1967) (analysis 3, table I) are

entirely due to  $\text{Si}^{4+} \rightleftharpoons (\text{Na}^+, \text{K}^+) + \text{Al}^{3+}$  substitutions since the Ba site is completely filled with  $\text{Ba}^{2+} + \text{Ca}^{2+}$ .

Substitution of the second type is apparently rare in nature and most harmotomes approximate to the formula  $(\text{Na}, \text{K})_x \text{Ba}_2 \text{Al}_{4+x} \text{Si}_{12-x} \text{O}_{32} 12\text{H}_2\text{O}$  with minor substitution of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  for  $\text{Ba}^{2+}$ . However,  $\text{Ba}^{2+} \rightleftharpoons 2(\text{Na}^+, \text{K}^+)$  substitutions have been studied experimentally and cation exchange data for natural low-symmetry harmotome and phillipsite (designated '*H*-zeolites' by Taylor and Roy, 1964) indicate complete solid solution between Na,K- and Ba-*H*, and between Na,K-, and Ca-*H* zeolites, but limited solid solution between Ba- and Ca-*H* forms. Sodium-exchanged harmotome together with other cation exchanged forms have been prepared from natural Ba-*H* harmotome by Barrer *et al.* (1959) and Hoss and Roy (1960). Both groups of authors record that  $2\text{Na}^+ \rightleftharpoons \text{Ba}^{2+}$  replacement has little effect on the harmotome structure and that X-ray powder diffraction patterns of Na-rich forms are similar to those of natural Ba-*H* harmotome.

The Maungarahu harmotome with 0.56(Na,K) substituting for  $\text{Ba}^{2+}$  is the most Ba-poor, alkali-rich member of the  $\text{Ba}^{2+} \rightleftharpoons 2(\text{Na}^+, \text{K}^+)$  solid solution series yet recorded and its discovery suggests that other members may exist in nature. The Moravian harmotome (table I, analysis 2) described by Černý *et al.* (1965), with 0.20(Na,K) required to satisfy the barium deficiency is the most Ba-poor member previously recorded.

An analysis of the analcime (table I, analysis 4) associated with the Maungarahu harmotome shows relatively little substitution of calcium and potassium for sodium. The trace of barium may be due to harmotome impurities, although no harmotome was detected in optical or X-ray examination of the analysed powder. The Maungarahu analcime is chemically similar to 'sedimentary' analcimes formed by the reaction of saline waters with volcanic material in the presence of quartz (Coombs and Whettan, 1967).

It is interesting to note that during the co-precipitation of an *H*-zeolite and analcime the analcime phase is relatively pure and the  $\text{Ba}^{2+}$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  are apparently concentrated in the *H*-zeolite structure.

*Discussion.* The association of analcime and harmotome indicates that harmotome crystallized from sodium-saturated, barium-rich, alkaline brine solutions.

No work has been carried out on phase relations in the system  $\text{BaO}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ . Experimental work by Barrer *et al.* (1959) suggests that at low temperatures the high-symmetry Na- and Ba-*P* zeolites would be most likely to crystallize although these zeolites are not known in nature. However, Taylor and Roy (1964) have shown that under hydrothermal conditions synthetic Ba-*P* zeolites readily convert to well crystallized lower symmetry Ba-*H* phases and that Na,Ba-*P* zeolites convert to Ba-*H*+analcime, both reactions occurring at temperatures of less than 200 °C. According to the data of Hoss and Roy (1960) the upper stability limit of harmotome under hydrothermal conditions is approximately 320 °C, although the introduction of  $\text{Na}^+$  into the structure apparently decreases its stability field. Harmotome has also been found in deep sea sediments (Morganstein, 1967) indicating that it can crystallize at

low temperatures under favourable conditions. The optimum condition for hydrothermal crystallization of harmotome–analcime assemblages is probably about 200 °C.

The restricted occurrence of harmotome in Northland suggests that the concentrations of barium were due to abnormal local conditions. High barium values are not characteristic of basic to intermediate igneous rocks nor of limestones, which form the country rock of the Tokatoka district. The only other barium mineral known in Northland is baryte, which is found in rare concretionary horizons in the Northland limestones (Ferrar, 1934).

A careful search of limestones adjacent to the Maungarahu and Rehia dykes revealed a 10-cm thick lens of coarsely crystalline baryte and calcite in scawtite-rock 1½ metres from the contact with the Rehia dyke. This baryte lens was undoubtedly originally a concretion. The association of baryte concretions in limestones adjacent to a dyke containing harmotome can hardly be fortuitous and the concretions were probably the source of barium in both localities. Baryte is relatively insoluble at low temperatures, but its solubility increases with temperature and is markedly increased by the presence of NaCl (Holland, 1967). The solubility of calcite on the other hand decreases with temperature and is strongly dependent on  $P_{\text{CO}_2}$ .

Although igneous intrusions may have supplied both heat and alkaline solutions to the local groundwaters, it is not necessary to postulate a strictly magmatic origin for the sodium-rich brine solutions since Ellis *et al.* (1964) have convincingly shown that groundwaters in contact with basalts and andesites preferentially leach out silica, soda, and halogens. In both Tokatoka harmotome localities zeolites penetrate and replace the felsic groundmass of the andesites. This feature indicates that zeolitization took place after consolidation of the andesites but does not necessarily indicate that it occurred after all magmatic activity had ceased.

Saline groundwaters, locally heated by the intrusion of an igneous body, would selectively dissolve baryte from adjacent concretionary limestone bands and concentrate barium ions in solution. These hot barium-rich waters percolating through and leaching silicon and sodium from the andesite would be expected to result in the localized formation within the andesite of barium and sodium-rich alkaline brines favourable to the crystallization of harmotome and analcime. At Rehia where  $P_{\text{CO}_2}$  may have been abnormally high, due to decarbonation reactions associated with the formation of larnite and other high temperature calcsilicates, sufficient calcite was dissolved to increase the concentration of calcium ions in solution to a level which allowed the crystallization of a calcium-rich phase, apophyllite.

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