

*Wairakite, the calcium analogue of analcime,  
a new zeolite mineral.*

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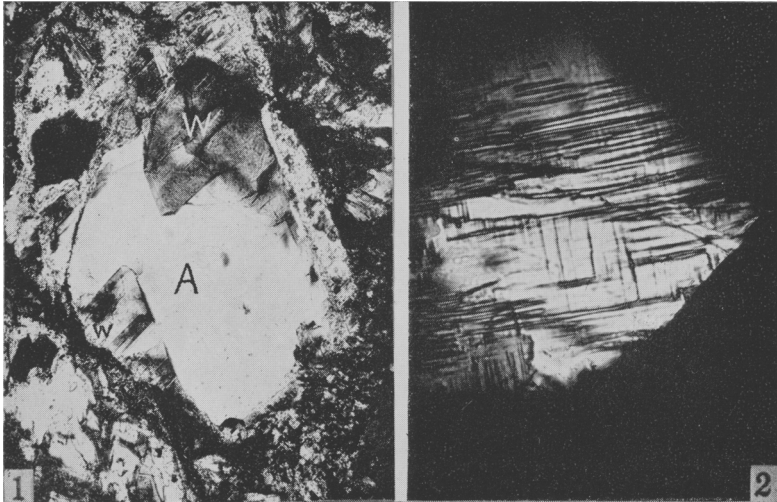
INTRODUCTION.

**D**URING the study of hydrothermal alteration of cores recovered from holes drilled at Wairakei during the exploration for geothermal steam, an unusual zeolite mineral was found. Optical, chemical, and X-ray data indicate that this zeolite is a new mineral, the calcium analogue of analcime. The name wairakite is given to the new mineral after the locality Wairakei in New Zealand. Wairakei is situated in the central part of the North Island, approximately 4 miles north-north-east from Lake Taupo, in an active volcanic region. The material was submitted to Dr. D. S. Coombs, Department of Geology, University of Otago, Dunedin, for an investigation of its X-ray crystallography. The results of his study are given in a paper published in the present number of this magazine. I take this opportunity of thanking Dr. Coombs for his ready co-operation.

GEOLOGICAL OCCURRENCE.

Wairakite occurs in tuffaceous sandstones and breccias, vitric tuffs and ignimbrite which originally had a similar chemical composition, i.e. of a plagioclase-rhyolite. All these rocks, Pliocene to Pleistocene in age, have been and are still being altered by hydrothermal fluids (Steiner, 1953). The new mineral has been found in drill cores obtained from levels ranging from 600 to 2890 feet and in rocks ejected by steam from some of the drill holes. In drill cores it is generally of microscopic grain-size, and its amount varies approximately from 2 to 15 %. It replaces andesine phenocrysts (fig. 1) and fills pores, cavities, and veinlets. In one core only, from hole 19 at a depth of 2890 feet, a white incrustation made up of wairakite has been noted. On the other hand, rock fragments ejected by steam from drill hole 19 (May 1954) often contain megascopic veinlets and fractures, 0.5–25 mm. thick, which are lined with drusy subhedral crystals or completely filled with massive

aggregates of wairakite. One of these ejected fragments (P 13871)<sup>1</sup> is made up of exceptionally large subhedral crystals of wairakite, 15 mm. across, implanted on a base consisting of calcite and aragonite (fig. 3). Some of the larger crystals show occasionally octahedral- or icositetrahedral-like faces.



Photomicrographs of wairakite, New Zealand.

FIG. 1. Primary andesine (A) partly replaced by wairakite (W) in rhyolitic breccia at 1855 feet (drill hole no. 18). Crossed nicols.  $\times 73$ .

FIG. 2. Grain of wairakite showing two sets of twin lamellae at right angles. Crossed nicols.  $\times 150$ .

#### PHYSICAL PROPERTIES.

In hand-specimen wairakite is colourless to white, and has a vitreous lustre, grading to almost dull. In transmitted light it is always colourless. The streak is white, and the mineral is brittle. Other physical properties and the corresponding values for analcime are as follows:

		Wairakite.	Analcime.
Specific gravity ...	...	2.26	2.22-2.29
Fusibility ...	...	$2\frac{1}{2}$	$2\frac{1}{2}$
Hardness ...	...	$5\frac{1}{2}$ -6	5- $5\frac{1}{2}$

Although wairakite filling microscopic pores does not show any cleavage, two cleavage-like lines probably parting, intersecting at right

<sup>1</sup> The number refers to specimens and microscopic sections in the New Zealand Geological Survey, Wellington.

angles and parallel to two sets of twinning lamellae (fig. 2), can be occasionally observed on powdered material obtained by crushing a megascopic crystal. Moreover, Dr. Coombs observed in an orientated section cut parallel to (100) a cleavage bisecting the angles between mutually perpendicular sets of twin lamellae.

Essential optical properties of wairakite are:  $\alpha$   $1.498 \pm 0.001$ ,  $\gamma$   $1.502 \pm 0.001$ ,  $\gamma - \alpha = 0.004$ ,  $2V\gamma$  (apparently on single lamellae) variable  $70-105^\circ$ , average near  $90^\circ$ , weak  $r > v$  about  $\gamma$ .

The indices of refraction have been determined with sodium-light and standard immersion liquids. The mineral is distinctly birefringent, no isotropic patches have been observed in contrast with birefringent analcime from Låven, Norway (Klein, 1897), and Loch Borolan, Scotland (Stewart, 1941). Polysynthetic twinning lamellae, commonly spindle shaped, are a conspicuous diagnostic property, and two sets of twinning lamellae, enclosing an angle of  $90^\circ$ , can often be observed (fig. 2). In studying thin sections no crystal outlines have been found. For this reason, the two sets of twinning lamellae in fig. 4 are orientated to hypothetical crystal faces, two of them being parallel to the twinning planes.

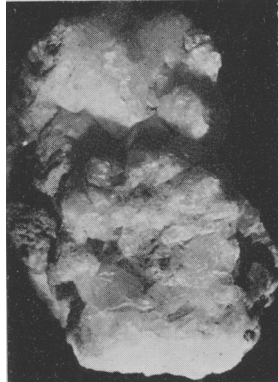


FIG. 3. Drusy subhedral crystals of wairakite, ejected from drill hole no. 19.  $\times 2$ .

The amount of water given up at various temperatures as determined by J. A. Ritchie is as follows:

Temperature.	Loss of water in % by weight.
Between 110 and 380° C. ...	4.23
,, 380 and 800° ...	4.09
Above 800° ... ..	0.03
Total	8.35

These data suggest a continuous dehydration curve characteristic of zeolites.

#### CHEMICAL PROPERTIES.

Wairakite gelatinizes with hydrochloric acid, and this decomposition is increased by heating. For chemical analysis a subhedral crystal was

crushed and powdered. A sample of the powdered material was examined under the microscope for its purity. Because no other mineral was noticed the analysed sample is considered to be of high purity. The chemical composition is given in table I, which also shows that the calculated formula is very close to  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ .

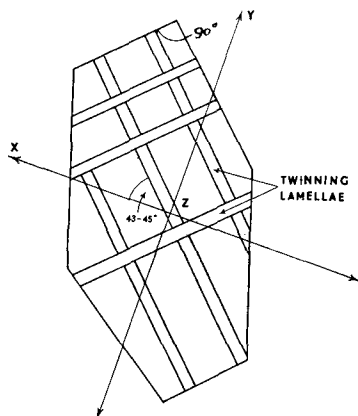


FIG. 4. Optical orientation in relation (at  $43-45^\circ$ ) to two perpendicular sets of twin lamellae in wairakite. (Crystal outline assumed.)

TABLE I. Chemical analysis and molecular ratios of wairakite.

(Analyst, J. A. Ritchie, Dominion Laboratory, Wellington.)

$\text{SiO}_2$	...	55.9	0.932	932	4.08
$\text{Al}_2\text{O}_3$	...	23.0	0.225	225	0.98
$\text{CaO}$	...	11.7	0.209	} 228	} 1.00
$\text{SrO}$	...	0.05	0.0005		
$\text{Na}_2\text{O}$	...	1.06	0.017		
$\text{K}_2\text{O}$	...	0.16	0.002		
$\text{Cs}_2\text{O}$	...	0.017	—	—	—
$\text{Rb}_2\text{O}$	...	0.0003	—	—	—
$\text{H}_2\text{O}+$	...	8.35	0.472	472	2.07
$\text{H}_2\text{O}-$	...	0.15	—	—	—
		<u>100.39</u>			

According to the theory advanced by Winchell (1925) zeolites are characterized as follows:

- (a) Ratio  $\text{Al}_2\text{O}_3 : \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O} = 1 : 1$ .
- (b) Ratio  $\text{Al} + \text{Si} : \text{O} = 1 : 2$ .
- (c) Replacement of sodium by calcium occurs in the way that  $\text{NaSi}$  is substituted by  $\text{CaAl}$ ; substitution under control of valency takes place only to a minor extent.

From table I it can be seen that the corresponding ratios (*a* and *b*) are in agreement with this theory. However, when the formulae of analcime and wairakite are compared, it is evident that in wairakite sodium is replaced by calcium under valency control only, the ratio Al:Si being constant in contrast with Winchell's theory (*c*).

#### FORMATION OF WAIKAKITE.

As wairakite invariably occurs in hydrothermally altered rocks which are still being affected by hydrothermal fluids, its hydrothermal origin can hardly be doubted. The temperature measured in the vertical range in which wairakite has been observed ranges from 200 to 250° C., and the calculated hydrostatic pressure from 55 to 265 atmospheres. The alkaline character of hydrothermal waters in the drill holes at Wairakei as established by S. H. Wilson,<sup>1</sup> Dominion Laboratory, Wellington, indicates that wairakite, similarly to other zeolites, forms in an alkaline environment, but the prevailing pH is not known. Because the ratio of CaO to SiO<sub>2</sub> is comparatively high, hydrothermal solutions with excess of lime and deficient in silica can be postulated as being responsible for the formation of wairakite. There is no clue as to when the hydrothermal activity commenced.

From the rare occurrence of wairakite in nature it can be inferred that this mineral requires for its formation a definite set of chemical and physical conditions of a rather restricted range. At Wairakei the occurrence of this mineral suggests that the comparatively high temperature (200–250° C.) prevailing at a relatively shallow depth (600–2890 feet) is the controlling factor, other conditions being equal.

Microscopic investigation indicates that wairakite forms by: (*a*) Hydrothermal replacement and recrystallization of andesine; in this case the required constituents are available in a reactive state, partly in the andesine, and partly in hydrothermal waters. (*b*) Crystallization from hydrothermal solutions, filling pores and cavities; hydrothermal solutions provide all the necessary constituents.

There is no suggestion of its being formed by ion-exchange. In this connexion it is interesting to compare the formation in nature with the attempted syntheses of calcium-analcime, chemically analogous to wairakite. Two kinds of hydrothermal synthesis have been attempted: (*a*) synthesis by ion-exchange; (*b*) crystallization from reactive components. The synthesis of calcium-analcime by ion-exchange from analcime

<sup>1</sup> Personal communication.

(Barrer, 1950) succeeded to a limited extent only; it is not relevant to the formation of wairakite, though of importance from a structural point of view. On the other hand, hydrothermal crystallization of calcium-analcime attempted by Noll (1936, *a*, *b*) and of analcime, successfully carried out by both Barrer (1949) and Noll (1936*a*), is imitative of the formation of wairakite in nature. Noll used, for the attempted synthesis of calcium-analcime, hydrated alumina, silica gel, and a solution of  $\text{Ca}(\text{OH})_2$ , the ratio  $\text{CaO}:\text{Al}_2\text{O}_3:\text{SiO}_2$  being 1:1:4. The experiment was conducted at a temperature of  $300^\circ\text{C}$ . with a corresponding saturated vapour pressure of 87 atmospheres. The reaction time was between 15 and 24 hours. Unfortunately it is not known whether Noll really succeeded in his synthesis of calcium-analcime, as he states (1936*a*, p. 136) that the phase formed could not yet be identified. However, from his experiments it can be seen that the temperature and pressure applied approximate the conditions characteristic of the formation of wairakite in nature. It is also noteworthy that the molecular ratio of the reactive components  $\text{CaO}:\text{Al}_2\text{O}_3:\text{SiO}_2$  was 1:1:4, thus corresponding to the composition of wairakite. No data are given concerning pH which, according to Barrer (1948), can be as important in hydrothermal reactions as temperature or composition. Judging by the set of physical and chemical conditions used by Noll, one would expect that, unless the reaction time was too short or the concentration of CaO too low, he succeeded in his synthesis of calcium-analcime. But it should be noted that he used the same set of conditions and material for his successful synthesis of analcime except that  $\text{Ca}(\text{OH})_2$  was, of course, replaced by NaOH. The importance of Noll's attempt to synthesize calcium-analcime by hydrothermal crystallization is much enhanced by the discovery of wairakite. Therefore, the suggestion is made that this synthesis should be attempted anew.

#### RELATIONSHIP BETWEEN WAIRAKITE AND ANALCIME.

It is obvious that wairakite ( $\text{CaO}.\text{Al}_2\text{O}_3.4\text{SiO}_2.2\text{H}_2\text{O}$ ) and analcime ( $\text{Na}_2\text{O}.\text{Al}_2\text{O}_3.4\text{SiO}_2.2\text{H}_2\text{O}$ ) have analogous formulas. This analogy raises the question whether and to what extent an isomorphous substitution takes place between the two. The possible existence of such an isomorphous series is examined by means of a triangular diagram (fig. 5). It shows the variation in content of soda, lime, and potash of 30 analcimes in relation to wairakite. In discussing this relationship the present writer is aware of the probable differences in the temperature of

formation of the specimens taken into consideration. The diagram brings out clearly that:

1. The extent of isomorphous substitution between analcime and wairakite is very limited, with only few scattered intermediate members.
2. Most of the points, 18 in number, are clustered near the  $\text{Na}_2\text{O}$  vertex.
3. The tendency for soda being substituted by lime and potash is restricted to the field between 50 and 100%  $\text{Na}_2\text{O}$ .

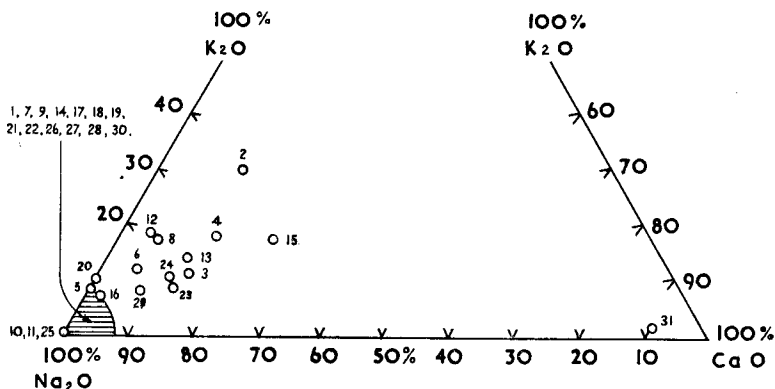


Fig. 5. Plot of chemical analyses of analcime (nos. 1-30) and wairakite (no. 31), showing lack of intermediate members.

References to analyses in fig. 5.

1. Morcinov (Kašpar, 1939). [M.A. 10-35.]	20. Heldburg (ibid.).
2, 3, 4. Montana (Larsen and Buie, 1938). [M.A. 7-448.]	21. Los Islands (Roques, 1947). [M.A. 10-294.]
5, 6. Arizona (Ross, 1928).	22. Eritrea (Morgante, 1945). [M.A. 11-292.]
7. Loch Borolan (Stewart, 1941).	23, 24. Cyclopean Is. (Grassi-Cristaldi and Scafile, 1929). [M.A. 5-83.]
8. Oregon (Hewett et al., 1928). [M.A. 4-324.]	25. Faeroe Is. (Tiselius, 1935). [M.A. 6-524.]
9. Foya (Klein, 1897).	26. Bohemia (Kratochvíl, 1933). [M.A. 6-129.]
10. Låven (new analysis).	27. Hungary (Reichert and Erdélyi, 1935). [M.A. 6-130.]
11. Kyogle (Hodge-Smith, 1929). [M.A. 4-323.]	28. Timan (Zeberg, 1915). [M.A. 2-58.]
12. Texas (Lonsdale, 1928). [M.A. 4-96.]	29. Caucasus (Smirnov, 1924). [M.A. 2-527.]
13. Etna (Dana, Min., 1892, p. 597).	30. Cyclopean Is. (Di Franco, 1926). [M.A. 4-375.]
14, 15. Blagodatsk (ibid.).	31. Wairakite (new analysis).
16. Wiesenthal (ibid.).	
17. Fassathal (ibid.).	
18. Kuchelbad (ibid.).	
19. Mte. Catini (ibid.).	

Thus, it can be concluded that, unless the intermediate members are stable only under conditions which are not common in nature, analcime and wairakite are isomorphously not related, though the atomic radii Na (0.98) and Ca (1.06) are approximately equal. The difference in valency and ionic charge appears to deter isomorphic replacement of analcime and wairakite.

However, isomorphous substitution of analcime and wairakite depends greatly on similarity of the crystal structure of these two minerals. A slight departure from the analcime structure is shown by wairakite according to the results of Dr. Coombs' X-ray investigation. If this structural difference is significant then analcime and wairakite can hardly be expected to form an isomorphous series at atmospheric temperatures.

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