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JOURNAL OF THE GEOLOGICAL SOCIETY OF JAPAN, Vol. 77, No. 1, p. 1-8, January 1971

SOME PHYSICAL PROPERTIES OF ANALCIME-WAIRAKITE SOLID SOLUTIONS

YOTARO SEKI*

(Received July 31, 1970)

Introduction

Analcime is common as a secondary mineral in hydrothermally altered rocks or as a diagenetic mineral in some sedimentary rocks. Also analcime occurs as a primary or late-stage constituent of some igneous rocks.

Recently the occurrence of wairakite, the Ca-analogue of analcime, has been reported from many places of the world. It now seems clear that wairakite is an important mineral in the petrogenesis of metamorphic rocks, especially rocks metamorphosed under a relatively high geothermal gradient.

In this paper, the present writer will summarize data accumulated for the last half century on chemical compositions and some physical properties of analcimes, wairakites and minerals having the intermediate chemical compositions.

Ionic substitutions in analcime-wairakite solid solutions

SAHA (1959, 1961) synthesized analcimes having a wide range of composition from $NaAlSi_{1.5}O_5 \cdot 0.75\ H_2O$ through $NaAlSi_2O_6 \cdot H_2O$ (*i.e.*, ideal analcime) to $NaAlSi_3O_8 \cdot 1.5\ H_2O$. He showed in the same papers that natural analcimes also have a wide range of chemical compositions from stoichiometric analcime to a composition very close to $NaAlSi_3O_8 \cdot 1.5\ H_2O$.

A wide range of chemical composition for natural analcimes was also demonstrated by ROSS (1928, 1941), WILKINSON (1963), WILKINSON and WHETTEN (1964), HASHIMOTO (1964), COOMBS and WHETTEN (1967), CROOK (1967), and SEKI and OKI (1970). These studies have demonstrated that natural analcimes form a complete solid solution series from $Na_{19.2}Al_{19.2}Si_{28.8}O_{96} \cdot mH_2O$ to $Na_{12}Al_{12}Si_{36}O_{96} \cdot nH_2O$.

PETERS and others (1966), WILKINSON (1968) and IIJIMA and HAY (1968) indicate a maximum K_2O content of about 2 weight % in the analcime solid solutions. FUDALI (1963) also found in his experimental work that the maximum content of K_2O in the analcime solid solutions is 1.7 weight %. The limited substitution in analcimes of Na by K may be due to too large ionic radii of K to be accomodated in the position normally occupied by Na (WILKINSON, 1968).

Figure 1 shows the frequency distribution of K_2O weight % in 49 natural analcimes from the literature. The "potassium-rich analcimes" which have been reported by LARSEN and BUIE (1938) (K_2O=4.48%), were omitted from Figure 1, because these analcimes may have included potassium silicates such as K-feldspar, hyallophane or leucite as impurities.

Wairakite is a calcium-analogue of analcime and has the chemical composition of $Ca_8Al_{16}Si_{32}O_{96} \cdot 16H_2O$. Analcimes have cubic or pseudocubic symmetry. However, wairakite is a monoclinic mineral. BARRER (1950), STEINER (1955), COOMBS (1955), AMES and SAND (1958) and AMES (1966) have said that if an analcime-wairakite solid solution series exists the isomorphous sub-

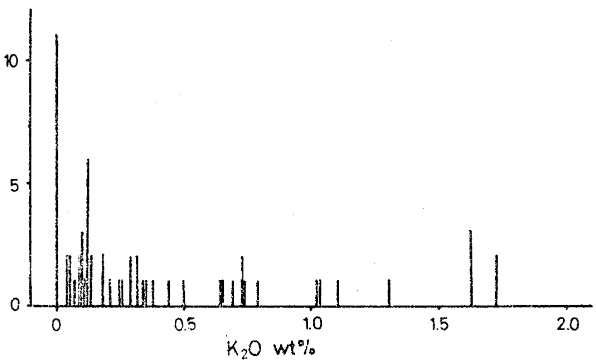

Fig. 1. Frequency of K_2O content in analysed analcimes and wairakites.

* Department of Foundation Engineering, Saitama University Urawa, Japan

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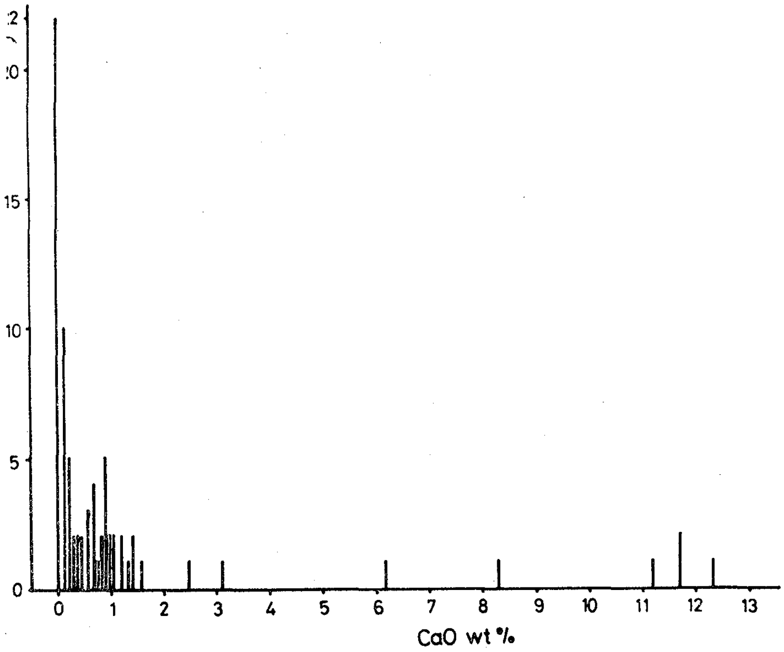

Fig. 2. Frequency of CaO content in analysed analcimes and wairakites.

stitution of calcium for sodium must be very limited due to the structural difference in these two end-members. In 1959, however, COOMBS and others showed that there is evidence from refractive indices that a complete range of synthetic analcimes from sodium to calcium end-members may be formed in the laboratory.

Recently SURDUM (1966) and SEKI and OKI (1970) have found minerals of intermediate chemical compositions between analcime and wairakite from Vancouver Island and the Tanzawa Mountains respectively. Physical properties such as index of refraction, density and unit-cell dimensions of these intermediate minerals are also intermediate between those of analcime and wairakite. Figure 2 shows the frequency distribution of CaO wt.% for natural analcimes and wairakites.

The maximum K_2O content in reported wairakites is 0.79 wt%. The substitution of K for Ca in wairakite may be more limited than the case of substitution of Na by K in analcime because of the larger ratio of ionic radii of K/ ionic radii of Ca compared to the ratio of the ionic radii of K/ ionic radii of Na.

Probably, analcime and wairakite form a continuous chemical series on the basis of substitution of Ca⇌2Na, although there may be some vacant fields in the system of $Na_{19.2}Al_{19.2}Si_{28.8}O_{96}\cdot mH_2O$–$Na_{12}Al_{12}Si_{36}O_{96}\cdot nH_2O$–$Ca_8Al_{16}Si_{32}O_{96}\cdot H_2O$ system (SEKI and OKI, 1970).

Nat′-Ab′-Wa ratio of natural analcime-wairakite solid solution

As have been noted in a previous section, natural analcime-wairakite solid solutions are believed to be chiefly composed of the following three end members:

$Na_{19.2}Al_{19.2}Si_{28.8}O_{96}\cdot mH_2O$ .... Nat′
$Na_{12}Al_{12}Si_{36}O_{96}\cdot nH_2O$ .... Ab′
$Ca_8Al_{16}Si_{32}O_{96}\cdot pH_2O$ .... Wa

A part of Na and Ca in these end members can be occupied by K.

Table 1. Calculation of Nat′ : Ab′ : Wa ratio of an analcime from Takakusayama, Japan (TIBA, 1966).

A		B		C	D	E	F
SiO_2	52.81	O	96.00	12.12	83.88	33.55	50.33
Al_2O_3	23.38	Si	31.57	4.04	27.53	12.58	15.10
Fe_2O_3	0.37					27.68	
CaO	1.58	(Al+ Fe′′′)	16.66	2.02	14.64	4.19	10.07
Na_2O	12.48					14.26	
K_2O	0.00	Ca	1.01	1.01			
H_2O+	8.86	(Na+ K)	14.47		14.47	4.19	10.07
H_2O	0.21					14.26	
Total	99.69						

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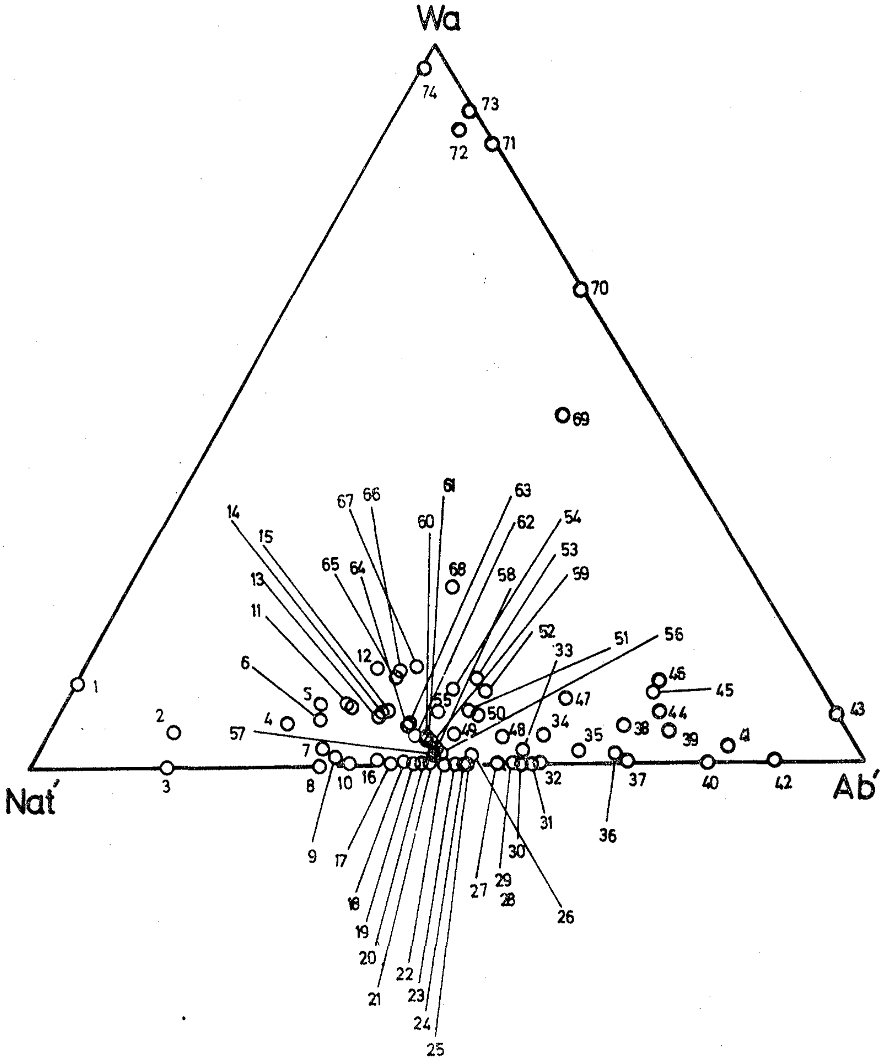

Fig. 3. **Plot** of analysed wairakite-analcime solid solution minerals on $Ca_8Al_{16}Si_{32}O_{96}$ (Wa)-$Na_{19.2}Al_{19.2}Si_{28.8}O_{96}$(Nat′)-$Na_{12}Al_{12}Si_{36}O_{96}$(Ab) system.

Number	Literature
57	BAUER, 1960
21, 24, 25, 42, 45	CROOK, 1967
8, 10, 13, 16, 17, 18, 20, 22, 23, 28, 29, 34, 37, 50, 55, 59, 61, 64	DANA, 1914
7, 31	DEER and others, 1963
62	Di FRANCO, 1926
53, 65, 66, 67	GRASSI and other, 1929
4, 47, 49	HARADA, 1936
68	HARADA and SAKURAI, 1967
40	HASHIMOTO, 1964
19	HODGE, 1929
52	IWKIN, 1955
44, 48	KANO and other, 1966
36	KASPER, 1939
33	KRATOCHVIL, 1933

Number	Literature
26	MORGANTE, 1945
9	REICHERT and other, 1935
38	ROSS and other, 1924
74	SEKI, 1966
71	SEKI, TAKEYASU and others, 1968
72	SEKI, ONUKI and others, 1969
46, 69, 70	SEKI and other, 1970
54	SMIRNOV, 1924
73	STEINER, 1955
5, 12, 15, 58, 63	TIBA, 1963
1, 2, 3, 6, 11, 14, 56, 60	WILKINSON, 1963, 1968
39	WILKINSON and other, 1964
27, 32, 51	YAGI, 1953
30, 35	YODER and other, 1960
41, 43	ZEBERG, 1915

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The present writer calculated the Nat′-Ab′-Wa ratio on the anhydrous basis of natural analcime-wairakite series minerals by the following procedure (Table 1):

(1) The atomic numbers are calculated from the analysis on the anhydrous basis of O=96. The atomic numbers are grouped together as follows: (Al+Fe′′′) and (Na+K). The atomic proportions of Fe′′, Mg and Mn are usually so small that they can be neglected. Then all the atomic numbers are arranged in the order of O, Si, (Al+Fe′′′), Ca and (Na+K) (Column B in Table 1).

(2) Calculate atomic numbers of O, Si and (Al+Fe′′′) which must form the Wa end member from the atomic proportion of Ca as follows:

O=Ca×12
Si=Ca×4
(Al+Fe′′′)=Ca×2 (Column C in Table 1)

(3) Subtract thus calculated atomic proportions from the original atomic proportions (Column D in Table 1)

(4) Calculate the molecular ratio of Nat′ to Ab′ from the Al/Si ratio of Column D in Table 1. Al/Si ratios of Nat′ and Ab′ molecules are 0.666 and 0.333 respectively.

(5) Divide the atomic proportion of O under Column D of Table 1 into Nat′ and Ab′ end members (Column E and Column F in Table 1). Atomic proportions of Si, (Al+Fe′′′) and (Na+K) calculated from thus divided atomic proportions of O and the following ratios are usually very close to those represented under Column D in Table 1 as shown by underlined values in Column E and Column F of Table 1:

	Nat′	Ab′
Si/O	0.300	0.375
(Al+Fe′′′)/O	0.200	0.125
(Na+K)/O	0.200	0.125

(6) Calculate the molecular ratio Nat′:Ab′:Wa from oxygen proportions distributed under Columns C, E and F in Table 1.

The Nat′:Ab′:Wa ratio of an analcime from Takakusayama, Japan (TIBA, 1966) calculated by this procedure is 52.5 : 34.9 : 12.6.

Nat′ : Ab′ : Wa ratios of analcime-wairakite solid solutions collected from the literature were calculated as shown in Figure 3.

Index of refraction of analcime-wairakite solid solutions

Indices of refraction, N_{max}, for analcime-wairakite solid solutions were plotted on a Nat′-Ab′-Wa

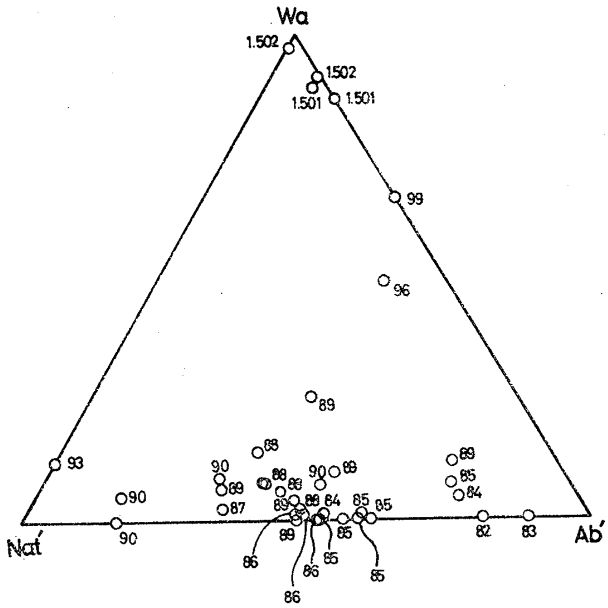

Fig. 4. Maximum index of refractions of wairakite-analcime solid solutions. Abbreviations are as follows:

82 : 1.482	85 : 1.485	88 : 1.488
83 : 1.483	86 : 1.486	89 : 1.489
84 : 1.484	87 : 1.487	90 : 1.490

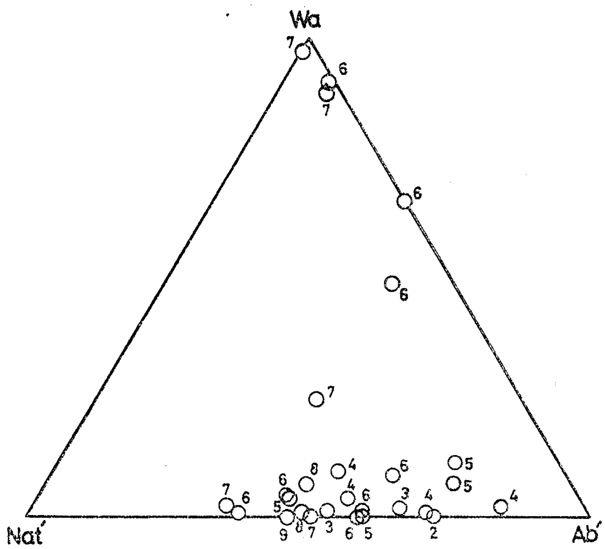

Fig. 5. Directly measured densities of wairakite-analcime solid solutions. Abbreviations are as follows:

2 : 2.22	5 : 2.25	8 : 2.28
3 : 2.23	6 : 2.26	9 : 2.29
4 : 2.24	7 : 2.27	

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triangular diagram in Figure 4.

The refractive index, N_{max}, of analcime-wairakites series minerals generally increases with increasing Nat′ and Wa components and decreases with increasing Ab′ component.

Density variation of analcime-wairakite solid solutions

Directly measured density values of analcime-wairakite solid solutions were plotted in a Nat′-Ab′-Wa diagram (Figure 5). Figure 6 shows the density values calculated from the chemical compositions and unit-cell dimensions by the present writer.

The accurate direct measurement of mineral density is usually rather difficult and the calculated density values are not always close to those directly measured. However, from Figures 5 and 6, it can be said that density of analcime-wairakite solid solutions generally increases with increasing Nat′ and Wa components and decreases with increasing Ab′ component.

Unit-cell dimensions of cubic or pseudocubic analcime minerals

Analcimes chiefly composed of Nat′ and Ab′

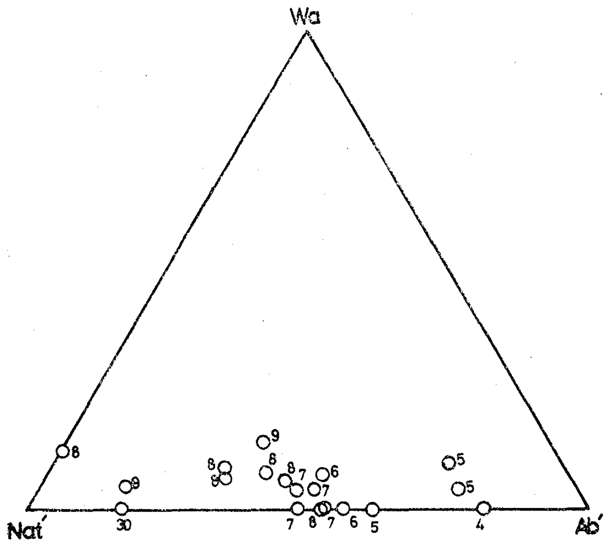

Fig. 6. Densities calculated from chemical compositions and unit-cell dimentions of wairakite-analcime solid solutions. Abbreviations are as follows:

4 : 2.24 7 : 2.27 9 : 2.29
5 : 2.25 8 : 2.28 30 : 2.30
6 : 2.26

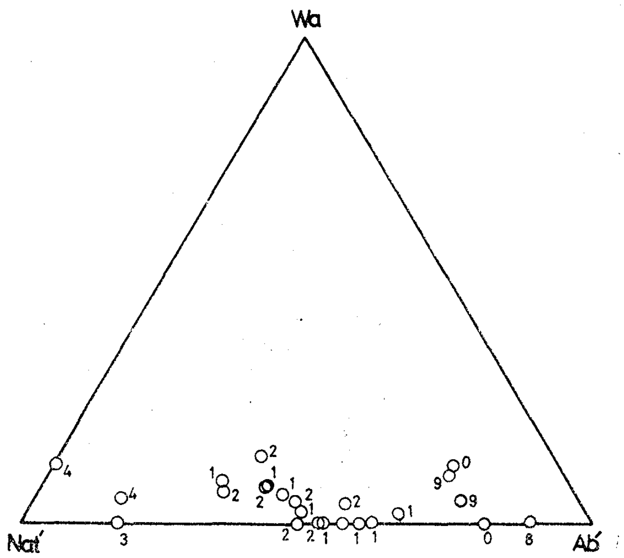

Fig. 7. Unit-cell dimension *a* (in Å) of analcimes. Abbreviations are as follows:

8 : 13.68 1 : 13.71 3 : 13.73
9 : 13.69 2 : 13.72 4 : 13.74
0 : 13.70

molecules are mostly cubic and sometimes pseudocubic. Their unit-cell dimension *a* varies from 13.68 Å to 13.74 Å.

Figure 7 indicates unit-cell dimension *a* of analcimes plotted in the Nat′-Ab′-Wa diagram. The unit-cell dimension generally increases with increasing Nat′ end member and decreasing Ab′ end member, as already noted by SAHA (1959), WILKINSON (1963) and COOMBS and WHETTEN (1967). From Figure 7 it can be said that with increasing Wa end member in analcimes their unit-cell dimension *a* generally becomes larger.

Double refraction of analcime-wairakite solid solutions

Analcime is ideally cubic and accordingly must be isotropic. Some analcimes, however, exhibit faint double refraction (usually$\leqslant$0.001) which may be due to strain or to ordering of the (Si, Al) atoms in the structure.

Wairakite which is monoclinic always has distinct double refraction (equal to or greater than 0.004).

Figure 8 shows the relation of the order of double refraction to chemical composition in analcime-wairakite solid solutions. Most isotropic analcimes have compositions near $Na_{16}Al_{16}Si_{32}O_{96}$ on the anhydrous basis (ideal analcime).

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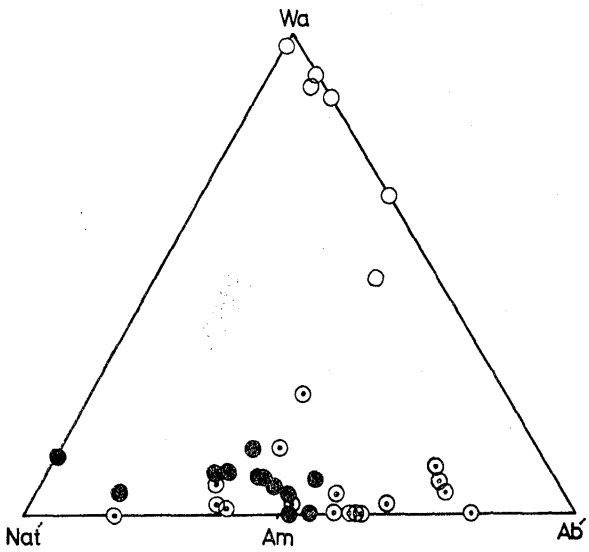

Fig. 8. Order of double refraction in wairakite-analcime solid solutions.
Solid circle : no double refraction
Circle with a dot : weak double refraction ~0.001
Open circle : distinct double refraction ⩾0.004

Variation of index of refraction and density in analcime-wairakite solid solutions

The index of refraction, N_{max}, and the density in analcime-wairakite solid solutions must vary with variation of their chemical compositions as indicated by broken lines and chains in Figure 9

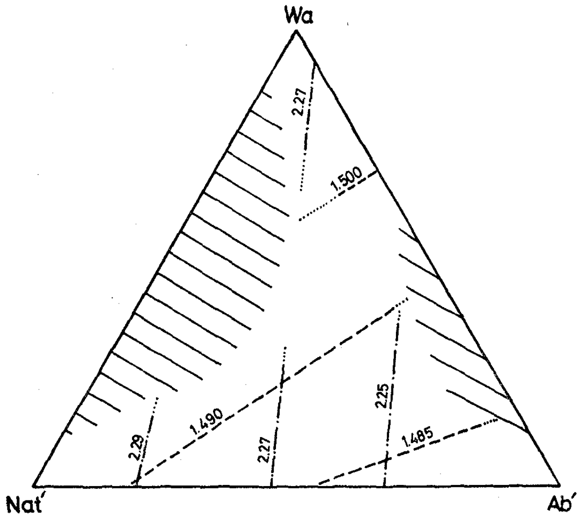

Fig. 9. Probable vacant fields in wairakite-analcime solid solution.
Chains and broken lines show the variations of density and maximum index of refraction respectively.

respectively. These two kinds of physical properties should be useful to estimate the chemical composition of analcime-wairakite solid solutions.

Probable vacant fields in analcime-wairakite solid solutions

From data presented in Figure 3, the presence of two vacant fields in the system of Nat′-Ab′-Wa can be estimated as shown in Figure 9. Unless we have coexisting pairs of wairakite-analcime of $NaAlSi_3O_8$ composition and wairakite-analcime of $NaAlSi_{1.5}O_5$ composition, however, such vacant fields may be due to bulk compositions or mineral associations of the investigated rocks and not to a solvus relationship. Further experimental and petrographic investigations will be necessary to solve this problem.

Acknowledgements

The present writer thanks W. G. ERNST and J. G. LIOU of the Department of Geology, University of California, Los Angeles for their helpful advice and critical reading of this manuscript.

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アナルサイム-ワイラカイト系鉱物の物理的性質

関　陽太郎

(要　旨)

アナルサイム-ワイラカイト系鉱物は H_2O を除外して計算すると $Na_{19.2}Al_{19.2}Si_{28.8}O_{96}$ (ナトロライト成分), $Na_{12}Al_{12}Si_{36}O_{96}$ (アルバイト成分) および $Ca_8Al_{16}S_{32}O_{96}$ (ワイラカイト成分) の三成分系で表現される. 現在まで報告された信頼するに足る資料をまとめると, この三成分系のフィールドは, 一部の空域を除くとほぼうまるようであり, 特に, ワイラカイトとアナルサイム固溶体 (ナトロライト成分-アルバイト成分) との間は $Ca \rightleftharpoons 2Na$ の置換による連続固溶体関係であるらしい. 屈折率, 格子恒数, 比重, 複屈折がこの三成分系でどのように変わるかということを示した.

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