WAIRAKITE-ANALCIME SOLID SOLUTIONS FROM LOW-GRADE METAMORPHIC ROCKS OF THE TANZAWA MOUNTAINS, CENTRAL JAPAN

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ABSTRACT

Minerals of intermediate chemical composition between analcime and wairakite are described. They were found in the highest metamorphosed part of the laumontite and mix-layer chlorite zone of the metamorphosed area in the Tanzawa Mountains, central Japan. Chemical analyses and X-ray diffraction studies were carried out on these materials. The results plotted in the $W\text{-}Na\text{-}Ab'$ diagram indicate that the compositional variation is more extensive than reported in the past. Possible distribution of vacant fields in the diagram is also discussed.

Introduction

Surdam (1966) noted that wairakites formed in low-grade metamorphic rocks of the Triassic group of Vancouver Island range in their chemical compositions from $NaAlSi_2O_6 \cdot H_2O$ to $CaAl_2Si_4O_{12} \cdot 2H_2O$ as determined by electron microprobe analyses.

Somewhat analogous minerals of intermediate chemical composition between analcime and wairakite from metamorphosed Tertiary volcanic rocks of the Tanzawa Mountains, central Japan, will be described in some detail in this paper.

Petrography of some rocks carrying minerals of wairakite-analcime series in the Tanzawa Mountains, Japan

Rocks of the early—middle Miocene Tanzawa group and late Miocene—early Pliocene Ashigara group of the Tanzawa Mountains have been recrystallized under P-T conditions of metamorphism ranging from the zeolite facies through the pumpellyite-prehnite and the actinolite-greenschist facies to the amphibolite facies. This metamorphism occurred by down-sinking of a thick (>10,000 meters) pile of submarine volcanic and clastic materials and the intrusion of quartz diorite magma accompanied with lateral migration of the geosynclinal basin during early Miocene to early Pliocene (Seki *et al.*, 1969). The metamorphosed area of the Tanzawa Mountains can be divided into the following five zones based on the occurrence of some metamorphic minerals :

Zone I : Stilbite and vermiculite zone

Zone II : Laumontite and mixed-layer chlorite zone

Zone III : Pumpellyite, prehnite and chlorite zone

Zone IV : Actinolite-greenschist zone

Zone V : Amphibolite zone

Metamorphic rocks containing wairakite or minerals of intermediate chemical composition between wairakite and analcime are found in the highest grade part of Zone II. Petrographical characters of three rocks from which wairakite-analcime series minerals were separated are summarized in Table 1.

Chemical compositions of minerals of the Tanzawa wairakite-analcime series

Three zeolites from the Tanzawa Mountains having intermediate chemical compositions between wairakite and analcime were carefully separated by means of "three-layers heavy-liquid method" (Oki, 1969). As far as observed under the microscope, these separated specimens are completely pure and homogeneous. These three

Table 1. Petrographical characters of Tanzawa metamorphic rocks bearing minerals of wairakite-analcime series

	T-1 (KOH65081511a)	T-2 (KOH65081515a)	T-3 (KOH65081604)
Original rocks	Basaltic tuff breccia	Basaltic tuff breccia	Andesitic fine-grained tuff
Phenocrysts of original rocks	Augite (partly replaced by chlorite and leucoxene) Plagioclase (partly replaced by albite, prehnite and sericite)	Augite (partly replaced by chlorite and leucoxene) Plagioclase (partly replaced by wairakite)	Plagioclase (partly replaced by laumontite)
Matrix and Druse	Matrix (augite, plagioclase, magnetite and glass): wholly replaced by chlorite, wairakite, leucoxene and small amounts of prehnite and epidote Druse: filled with chlorite and wairakite	Matrix (augite, plagioclase, magnetite and glass): partly replaced by chlorite, wairakite, quartz and leucoxene Druse: filled with chlorite, quartz and wairakite	Matrix (plagioclase, augite (?), magnetite and glass): wholly replaced by calcite, chlorite, laumontite, analcime and very small amounts of quartz and leucoxene

specimens were chemically analysed by a wet method based on an ion-exchange technique (Oki *et al.*, 1962). The analytical results are shown in Table 2 with atomic proportions in terms of anhydrous basis of O=96. Molecular ratios of $\text{Ca}_8\text{Al}_{16}\text{Si}_{32}\text{O}_{96}$ (Wa), $\text{Na}_{19.2}\text{Al}_{19.2}\text{Si}_{28.8}\text{O}_{96}$ (Nat), and $\text{Na}_{12}\text{Al}_{12}\text{Si}_{36}\text{O}_{96}$ (Ab') of these three minerals are

Table 2. Chemical compositions, atomic ratios and molecular ratios of minerals of wairakite-analcime series from the Tanzawa Mountains, central Japan (Analyst, Y. Oki).

	T-1 (KOH65081511a)	T-2 (KOH65081515a)	T-3 (KOH65081604)
SiO_2	57.07	56.27	57.41
TiO_2	0.00	tr.	0.00
Al_2O_3	20.64	21.32	20.11
Fe_2O_3	0.48	n.d.	n.d.
FeO	tr.	n.d.	n.d.
MnO	n.d.	n.d.	0.00
MgO	0.04	0.43	0.70
CaO	8.30	6.17	1.42
Na_2O	4.14	6.57	10.79
K_2O	0.14	0.17	0.07
H_2O^+	9.20	8.88	8.87
H_2O^-	0.23	0.06	0.17
Total	100.24	99.87	99.54
O	96.00	96.00	96.00
Si	33.33	32.87	33.64
Al	14.40	14.79	14.01
Fe'''	0.20	—	—
Mg	0.04	0.38	0.62
Ca	5.26	3.89	0.90
Na	4.75	7.50	12.36
K	0.11	0.13	0.05
H_2O	18.18	17.44	17.50
$\text{Ca}_8\text{Al}_{16}\text{Si}_{32}\text{O}_{96}$ (Wa)	66	49	11
$\text{Na}_{19.2}\text{Al}_{19.2}\text{Si}_{28.8}\text{O}_{96}$ (Nat)	0	11	19
$\text{Na}_{12}\text{Al}_{12}\text{Si}_{36}\text{O}_{96}$ (Ab')	34	40	70

Table 3. X-ray powder diffraction data, optical properties

<i>hkl</i>	A		B (T-1)	
	2θ (CuK α)	<i>I</i>	2θ (CuK α)	<i>I</i>
200	13.0°	37	13.0°	10
211	15.9	100	15.9	50
220	18.4	30	18.4	21
321	24.46	23	24.45	10
400	26.10	100	26.10	100
004	26.27	100	26.22	100
332	30.80	33	30.77	52
422	32.20	9	32.17	7
431	33.46	16	33.46	18
521	36.08	17	36.05	16
440	37.23	11	37.23	16
611	40.70	13	40.70	10
543	47.10	4	47.02	4
640	48.06	10	48.00	11
552	49.06	9	48.97	9
732	52.80	17	52.76	17
800	53.69	6	53.69	5
831	58.07	7	58.06	8
Paired peaks of 332, 332: 431, 431: 521, 521	clearly observed		observed	
Refractive indices	$\alpha=1.498\pm0.001$ $\beta=1.502\pm0.001$		$n_{\max}=1.499\pm0.001$	
Double refraction	anisotropic		anisotropic	
Crossed lamellar twin	clearly observed		clearly observed	
Unit-cell dimensions	$a=13.65 \text{ \AA}$ $b=13.66$ $c=13.56$ $\beta=90^\circ 23'$		$a=13.66 \text{ \AA}$ $b=13.66$ $c=13.58$ $\beta=90^\circ 20'$	
Density	2.26 _g		2.26 ₀	

A: Wairakite from Katayama geothermal area, Onikobe, Japan.
Bore-hole core GO-7, 397.64 m (Seki *et al.*, 1969).

B: Wairakite from Tanzawa Mountains. T-1.

and densities of minerals of wairakite-analcime series.

C (T-2)		D (T-3)		E	
2θ (CuK α)	I	2θ (CuK α)	I	2θ (CuK α)	I
13.0°	10	—	—	—	—
15.9	55	15.9	80	15.9	74
18.4	19	18.4	31	18.3	18
24.43	9	24.35	7	24.22	8
26.10	100	26.05	100	26.01	100
—	—	—	—	—	—
30.71	51	30.62	50	30.61	66
32.12	6	32.01	9	31.94	8
33.43	12	33.37	25	33.33	21
35.99	18	35.94	10	35.91	15
37.22	9	37.15	6	37.11	18
40.68	8	40.62	6	40.57	11
46.99	3	—	—	—	—
47.98	10	47.91	6	47.88	12
48.92	7	48.90	5	48.85	8
52.64	15	52.60	16	52.57	21
53.64	5	53.47	5	53.45	5
57.96	6	57.90	5	57.85	7
weakly observed		not observed		not observed	
$n_{\max} = 1.496 \pm 0.001$		$n_{\max} = 1.489 \pm 0.001$		$n = 1.482 \pm 0.002$	
anisotropic		anisotropic		isotropic	
weakly observed		not observed		not observed	
$a = 13.66 \text{ \AA}$ $b = 13.66$ $c = 13.65$ $\beta = 90^\circ 20'$		$a = 13.70 \text{ \AA}$		$a = 13.71 \text{ \AA}$	
2.25 ₆		2.25 ₃		2.24 ₄	

C: Wairakite from Tanzawa Mountains. T-2.

D: Analcime from Tanzawa Mountains. T-3.

E: Analcime from Kasukabe, Japan (Hashimoto, 1964).

also shown in Table 2.

X-ray powder data, unit-cell dimensions, optical properties and densities

Table 3 summarizes X-ray powder diffraction data, unit-cell dimensions calculated therefrom, optical properties and densities of the minerals of wairakite-analcime series from the Tanzawa Mountains, a wairakite from the Onikobe geothermal area and an analcime from Kasukabe, Japan.

From Table 3, it is clear that the investigated Tanzawa minerals are intermediate with regard to X-ray diffraction, unit-cell dimensions and optical properties between wairakite and analcime. T-1 is clearly monoclinic, but the c dimension of T-2 is practically the same as a and b of the same mineral and separation of the $\bar{3}32$ peak from 332 is indistinct. Probably the mineral T-2 is monoclinic but its monoclinicity obviously is very small.

As far as observed from X-ray powder data and optical properties the mineral T-3 must be cubic or pseudocubic, but not monoclinic.

Refringence and density decrease in the order of T-1, T-2 and T-3, correlating with the decrease of the Wa end member in these materials.

Considerations

Starting with glasses, Saha (1959, 1961) synthesized analcimes having a wide composition range from $\text{NaAlSi}_{1.5}\text{O}_6 \cdot 0.75\text{H}_2\text{O}$ through $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ (ideal form of analcime) to $\text{NaAlSi}_3\text{O}_8 \cdot 1.5\text{H}_2\text{O}$. He showed that the variation of water contents and unit-cell constants are linear functions of the silica contents of the analcimes. Natural analcimes also have a wide range of chemical compositions from stoichiometric analcime to a composition very close to $\text{NaAlSi}_3\text{O}_8 \cdot 1.5\text{H}_2\text{O}$. Saha also found that the difference $2\theta_{\text{Analcime (639)}} - 2\theta_{\text{Silicon (331)}}$ ($\text{CuK}\alpha$ radiation) can be used to determine the substitution of NaAl for Si in analcime solid solutions.

Ross (1928, 1941), Wilkinson (1963) and Wilkinson and Whetten (1964) have demonstrated a wide range of chemical composition for analcimes formed in a basaltic lava sequence and in pyroclastic and sedimentary piles. Recently Coombs and Whetten (1967), from data for unit-cell sizes of analcimes, showed that analcimes from sedimentary and burial metamorphic rocks range in chemical composition from $\text{Na}_{16}\text{Al}_{16}\text{Si}_{32}\text{O}_{96} \cdot 16\text{H}_2\text{O}$ to $\text{Na}_{13}\text{Al}_{13}\text{Si}_{35}\text{O}_{96} \cdot n\text{H}_2\text{O}$.

Steiner (1955) and Coombs (1955) who first reported the occurrence and mineralogical properties of wairakite suggested that isomorphous substitution between analcime and wairakite is very limited due to structural differences between these two end members.

The compositions of wairakites described in this paper and those of wairakites and analcimes from the literature are plotted in Fig. 1. Evidently $\text{Na}_{19.2}\text{Al}_{19.2}\text{Si}_{28.8}\text{O}_{96} \cdot m\text{H}_2\text{O}$ (Nat in Fig. 1) and $\text{Na}_{12}\text{Al}_{12}\text{Si}_{36}\text{O}_{96} \cdot n\text{H}_2\text{O}$ (Ab' in Fig. 1) form a continuous solid solution nature.

Fig. 1. Plot of wairakites and analcimes in a $\text{Ca}_8\text{Al}_{16}\text{Si}_{32}\text{O}_{96} \cdot p\text{H}_2\text{O}$ (Wa) - $\text{Na}_{19.2}\text{Al}_{19.2}\text{Si}_{28.8}\text{O}_{96} \cdot m\text{H}_2\text{O}$ (Nat) - $\text{Na}_{12}\text{Al}_{12}\text{Si}_{36}\text{O}_{96} \cdot n\text{H}_2\text{O}$ (Ab') diagram. Open circles are minerals described in this paper, and black circles from literatures.

We have no conclusive data, however, to indicate the presence of complete solid solution between $\text{Ca}_8\text{Al}_{16}\text{Si}_{32}\text{O}_{96} \cdot p\text{H}_2\text{O}$ (Wa in Fig. 1) and the other two end members. Notes presented by Coombs and others (1959) and by Surdam (1966) are incomplete to demonstrate complete solid solution between Nat and Wa, Ab' and Wa, and $\text{Na}_{16}\text{Al}_{16}\text{Si}_{32}\text{O}_{96} \cdot q\text{H}_2\text{O}$ (Am in Fig. 1) and Wa.

From the data presented in Fig. 1, two types of vacant field in the system of Wa-Nat-Ab' can be anticipated as shown in Fig. 2.

Fig. 2. Probable vacant fields (hatched areas) in the Wa-Nat-Ab' system.

If Fig. 2a is correct, minerals which lie within field A are monoclinic but those having compositions within field B are cubic or pseudocubic. Monoclinicity of minerals in field A generally becomes less conspicuous with the decrease of the Wa component and the increase of the Ab' and/or Nat compositions. However, if Fig. 2b is accepted, the cubic or pseudocubic symmetry of Nat-Ab' solid solution must be gradually distorted into a monoclinic one with the increase of the Wa molecule. In either case of Figs. 2a and 2b, there will be a wide vacant immiscibility area between the wairakite composition and $\text{Na}_{16}\text{Al}_{16}\text{Si}_{32}\text{O}_{96} \cdot q\text{H}_2\text{O}$ (ideal composition of analcime, Am).

Three new analyses in

this paper indicate the compositional variation is more extensive than reported in the past. However, unless we can demonstrate equilibrium between a sodic wairakite and a calcic analcime which coexist, the presence of a solvus in the Wa-Ab'-Nat system as shown in Fig. 2a can not be completely proved. Further study of natural minerals of wairakite-analcime series as well as more detailed experimental work of the Wa-Ab'-Nat system are necessary to throw more light on this problem.

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REFERENCES

- Coombs, D.S. (1955). *Min. Mag.*, 30, 699.
Coombs, D.S., Ellis, A.J., Fyfe, W.S. & Taylor, A.M. (1959). *Geoch. et Cosmoch. Acta*, 17, 53.
Coombs, D.S. & Whetten, J.T. (1967). *Geol. Soc. Amer. Bull.*, 78, 269.
Hashimoto, M. (1964). *J. Geol. Soc. Japan*, 70, 227.
Oki, Y. (1969). In preparation.
Oki, Y., Oki, S. & Shibata, H. (1962). *Bull. Chem. Soc. Jap.*, 35, 273.
Ross, C.S. (1928). *Amer. Min.*, 13, 195.
Ross, C.S. (1941). *Amer. Min.*, 26, 627.
Saha, P. (1959). *Amer. Min.*, 44, 300.
Saha, P. (1961). *Amer. Min.*, 46, 859.
Seki, Y., Oki, Y., Matsuda, T., Mikami, K. & Okumura, K. (1969). *Journ. Assoc. Jap. Min. Petr. Economic Geol.*, 61, 1 & 50.
Steiner, A. (1955). *Min. Mag.*, 30, 691.
Surdam, R.C. (1966). *Geol. Soc. Amer. Special Paper*, 87, 169.
Wilkinson, J.F.G. (1963). *Min. Mag.*, 33, 498.
Wilkinson, J.F.G. & Whetten, J.T. (1964). *J. Sed. Petr.* 34, 543.

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