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Abstract

A mordenite was found as in-fillings of amygdales of Pliocene hornblende andesite in Aira area, Kagoshima prefecture. The mineraligical properties of the mordenite were examined by X-ray powder diffraction (XRD), chemical analysis, thermal analysis, infrared absorption analysis, and scanning electron microscopy (SEM). SEM shows that the mordenite crystals exhibit fibrous form with $< 1\ \mu$m in width and $> 100\ \mu$m in length. The unit cell parameters calculated from XRD data are a = 18.12(2), b = 20.46(2), and c = 7.535(4) Å. The structural formula calculated is $(Mg_{0.07}Ca_{0.74}Na_{1.26}K_{0.40})\ (Al_{4.06}Fe^{3+}_{0.08})(Si_{20.05}Ti_{0.02})O_{48} \cdot 13.47H_2O$. This fibrous mordenite was formed by low grade hydrothermal alteration.

Key words: Mordenite, Hydrothermal alteration, Mineralogical properties, Altered andesite

Introduction

Mordenite is a relatively common and widespread variety of zeolite occurring as diagenetic alteration products of tuffaceous sediments (Sudo *et al.*, 1963; Utada, 1970, 1971; Iijima and Utada, 1972), and as authigenic crystals in amygdales and in fillings of cavities in silicic rocks (Tomita *et al.*, 1970; Yoshimura and Wakabayashi, 1977). In southern Kyushu, Neogene greenish andesitic rocks and tuffaceous sediments that contain various clay minerals and zeolites such as clinoptilolite (Minato and Utada, 1968), mordenite (Tomita *et al.*, 1970), and laumontite (Tomita *et al.*, 1979) are widely distributed. In Aira area, Kagoshima Prefecture in particular, mordenite is found to occur in altered hornblende andesite. The present study reports the mode of occurrence and mineralogical properties of this mordenite in the altered andesite of Aira area, Kagoshima Prefecture.

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Experimental methods

The mordenite collected by hand picking was pulverized in an agate mortar. The powdered sample was examined by means of X-ray powder diffraction (XRD), thermal analysis, infrared absorption (IR), chemical analysis, and scanning electron microscopy (SEM).

XRD was undertaken with the use of the Rigaku diffractometer (30kV, 100mA) equipped with a graphite monochromater, 1/2° divergence and scattering slits, using a scanning speed of 0.5° 2θ /min. Thermal analysis was also carried out using the Rigaku differential thermal and thermogravimetric analysis (DTA-TGA) apparatus by which temperature measurements were made from room temperature to 1100℃ with a heating rate of 10℃/min using about 25mg powdered sample. IR analysis was made utilizing the Nihonbunko infrared absorption spectrophotometer. The IR spectrum was recorded by KBr method. Chemical analysis followed the gravimetric method for SiO_2, $H_2O(+)$, and $H_2O(-)$, colorimetric procedures for TiO_2 and atomic absorption spectrometry for other elements. SEM observation was carried out using the JEOL JSM-25SII scanning electron microscope.

Mode of occurrence

The hydrothermally altered andesites and andesitic tuff of Miocene to Pliocene age widely distributed in southern Kyushu generally exhibit greenish color and contain quartz or cristobalite and ferromagnesian clay minerals such as saponite, corrensite, or chlorite as major

Fig. 1 Map showing the sample locality and distribution of Neogene greenish rocks in Kagoshima Prefecture.

alteration products (Kawano and Tomita, unpublished data). The andesitic rocks also contain zeolites such as clinoptilolite, mordenite, and laumontite. In Aira area, the mordenite occurs as white color in-fillings of amygdales in the hydrothermally altered hornblende andesite (Fig. 1). The amygdales show irregular orientations with lengths measuring less than 15cm. The altered hornblende andesite contains Fe-rich saponite, cristobalite, and very small amounts of mordenite. The Fe-rich saponite occurs mainly as replacements of mafic phenocrysts and groundmass.

Results

XRD data of mordenite and its unit cell parameters calculated using the program LCLSQ (Burnham, 1991) are listed in Table 1, together with data of mordenites from three other localities: Scotland (Harris and Brindley, 1954), Yoshida, Kagoshima Prefecture (Tomita *et al.*, 1970), and Shirasawa, Miyagi Prefecture (Negishi, 1972). The indices proposed by Nakajima (1973) were adopted in this study. The recalculated unit cell parameters of Scotland, Yoshida, and Shirasawa mordenites showed slightly larger values compared with those reported in the original articles. Because the original cell parameters were obtained using the indices previously given by Harris and Brindley (1954) (see Table 1).

The chemical analyses and numbers of cations based on 48 oxygens are presented in Table 2, together with those of Scotland, Yoshida, and Shirasawa mordenites. The ideal formula of mordenite is:

$$(Ca_1, Na_2, K_2)_2Al_4Si_{20}O_{48} \cdot 14H_2O.$$

The structural formula of the Aira sample is:

$$(Mg_{0.07}Ca_{0.74}Na_{1.26}K_{0.40})\,(Al_{4.06}Fe^{3+}_{0.08})\,(Si_{20.05}Ti_{0.02})\,O_{48} \cdot 13.47H_2O.$$

Relatively, this Aira mordenite is reasonably close to the ideal formula, with almost similar characteristic feature of natural mordenite as previously reported. Ca and Na are the dominant exchangeable cations in both samples (Fig. 2).

The DTA curve shows a single broad endothermic peak at 152℃ due to dehydration. The TGA curve displays gradual weight loss of 14.5% up to about 500℃ and remains constant at higher temperatures (Fig. 3).

The IR spectrum of the Aira mordenite is shown in Fig. 4. The absorption bands at 3600, 3425, and 1640cm^{-1} are due to OH vibration of water molecules contained in mordenite structure as zeolitic water, 1225 and 1050cm^{-1} are due to Si-O stretching vibration, and absorptions at 800-400cm^{-1} are mainly caused by Si-O linkage of tectosilicate structure (Oinuma and Hayashi, 1967).

Fig. 5 shows the SEM photograph of the Aira mordenite. The sample exhibits fibrous habit. The most of the fibrous crystals are generally $<1\,\mu$m in width and $>100\,\mu$m in length.

Table 1 X-ray powder diffraction data and unit cell parameters of mordenites.

		1		2		3		4	
hkl	$d_{cal.}$(Å)	$d_{obs.}$(Å)	I	$d_{obs.}$(Å)	I	$d_{obs.}$(Å)	I	$d_{obs.}$(Å)	I
110	13.568	13.57	35	13.7	6	13.7	20	13.777	1
200	9.063	9.06	100	9.10	9	9.12	43	9.158	3
111	6.587	6.58	10	6.60	8	6.60	7	6.607	3
130	6.383	6.38	21	6.39	5	6.41	60	6.411	1
021	6.067	6.06	4	6.09	2	6.09	2	6.108	1
310(201)	5.794	5.79	32	5.80	5	5.82	20	5.828	1
330	4.522	4.518	55	4.535	8	4.529	44	4.534	4
420	4.143	4.141	12			4.152	10	4.149	1
150	3.991	3.992	93	4.008	9	3.990	100	4.003	6
241	3.834	3.832	7	3.854	4	3.840	7	3.840	1
002	3.767	3.758	3	3.778	4	3.770	4	3.768	1
421(112)	3.630	3.628	3			3.640	3		
510	3.569	3.567	4			3.576	4		
202	3.479	3.471	18	3.486	10	3.480	20	3.479	10
350(060)	3.388	3.385	69	3.398	9	3.394	64	3.393	6
222				3.315	1	3.290	2	3.289	1
530	3.201	3.198	46	3.224	9	3.209	40	3.230	6
441	3.093	3.100	3			3.100	3		
261(531)	2.938	2.938	4			2.950	4	2.939	1
402	2.897	2.893	11	2.899	7	2.903	40	2.897	2
152				2.746	1	2.740	2		
621	2.704	2.698	4	2.706	1	2.706	6		
370	2.631	2.630	3			2.636	4		
080(461)	2.557	2.558	10	2.569	3	2.560	15	2.561	1
532(442)	2.439	2.517	6	2.534	5	2.522	7	2.519	1
a(Å)		18.12(2)		18.32(13)		18.25(8)		18.23(2)	
b(Å)		20.46(2)		20.53(16)		20.47(10)		20.48(3)	
c(Å)		7.535(4)		7.59(2)		7.58(1)		7.524(4)	

1, Mordenite from Aira, Kagoshima Prefecture; 2, Mordenite from Scotland (Harris and Brindley, 1954); 3, Mordenite from Yoshida, Kagoshima Prefecture (Tomita *et al.*, 1970); 4, Mordenite from Shirasawa, Miyagi Prefecture (Negishi, 1972). The indices are driven from Nakajima (1973). ( ), Indices reported by Harris and Brindley (1954).

Table 2 Chemical analyses and numbers of cations based on 48 oxygens.

	1	2	3	4
SiO_2	68.43	68.24	66.68	67.68
TiO_2	0.11	0.11	0.20	0.16
Al_2O_3	11.76	11.04	11.85	12.23
Fe_2O_3	0.38	1.74	1.23	0.49
MgO	0.17	0.23	0.57	–
CaO	2.36	1.31	2.97	3.13
Na_2O	2.21	3.19	1.84	2.00
K_2O	1.08	2.45	1.30	1.65
$H_2O(+)$	8.85	6.59	8.71	7.75
$H_2O(-)$	4.93	5.02	4.78	5.14
Total (%)	100.28	99.92	99.93*	100.23
Si	20.05	19.91	19.65	19.79
Ti	0.02	0.02	0.04	0.04
Al	4.06	3.80	4.14	4.22
Fe^{3+}	0.08	0.38	0.27	0.11
Mg	0.07	0.10	0.25	–
Ca	0.74	0.41	0.94	0.98
Na	1.26	1.80	1.06	1.13
K	0.40	0.91	0.49	0.62
H_2O	13.47	11.31	13.32	12.58

1, Mordenite from Aira Kagoshima Prefecture; 2, Mordenite from Scotland (Harris and Brindley, 1954); 3, Mordenite from Yoshida, Kagoshima Prefecture (Tomita, *et al.*, 1970) 4, Mordenite from Shirasawa, Miyagi Prefecture (Negishi, 1972). *including 0.15% MnO and 0.01% P_2O_5.

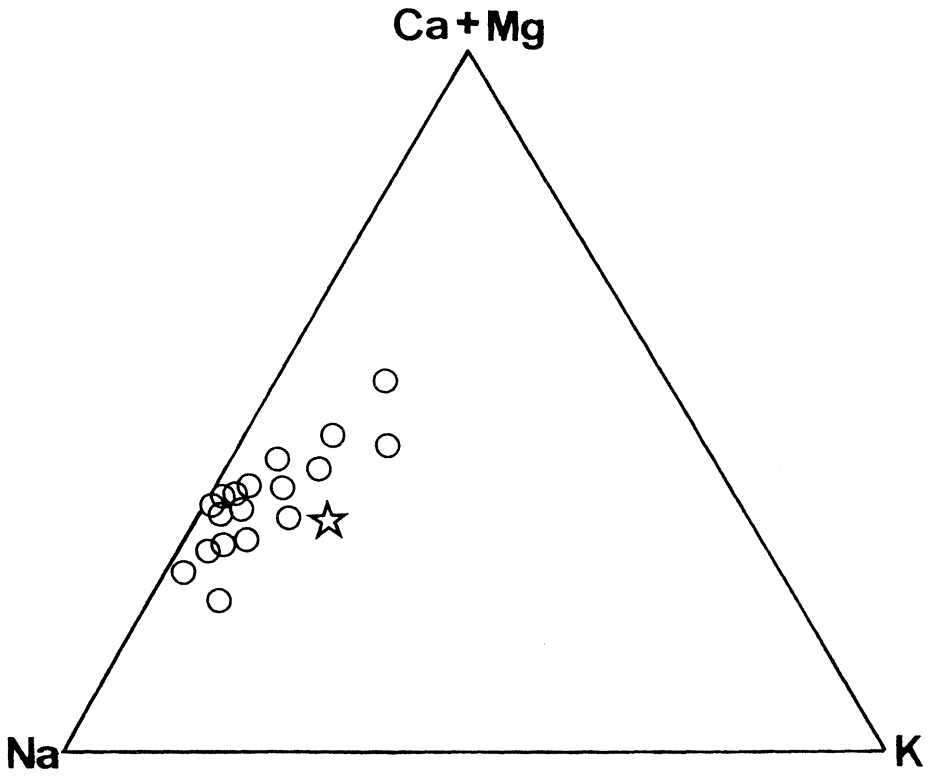

Fig. 2 Exchangeable cations plotted in (Ca + Mg) − Na − K diagram. Open star, Mordenite from Aira; Open circles, Mordenites reported previously (Passaglia, 1975).

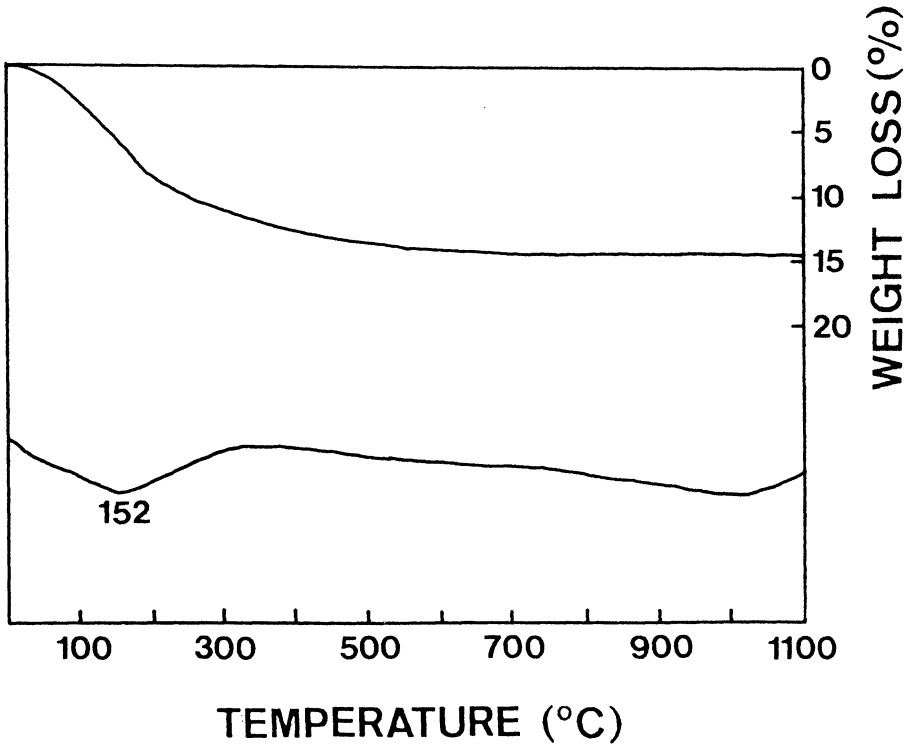

Fig. 3 DTA-TGA curves of mordenite from Aira.

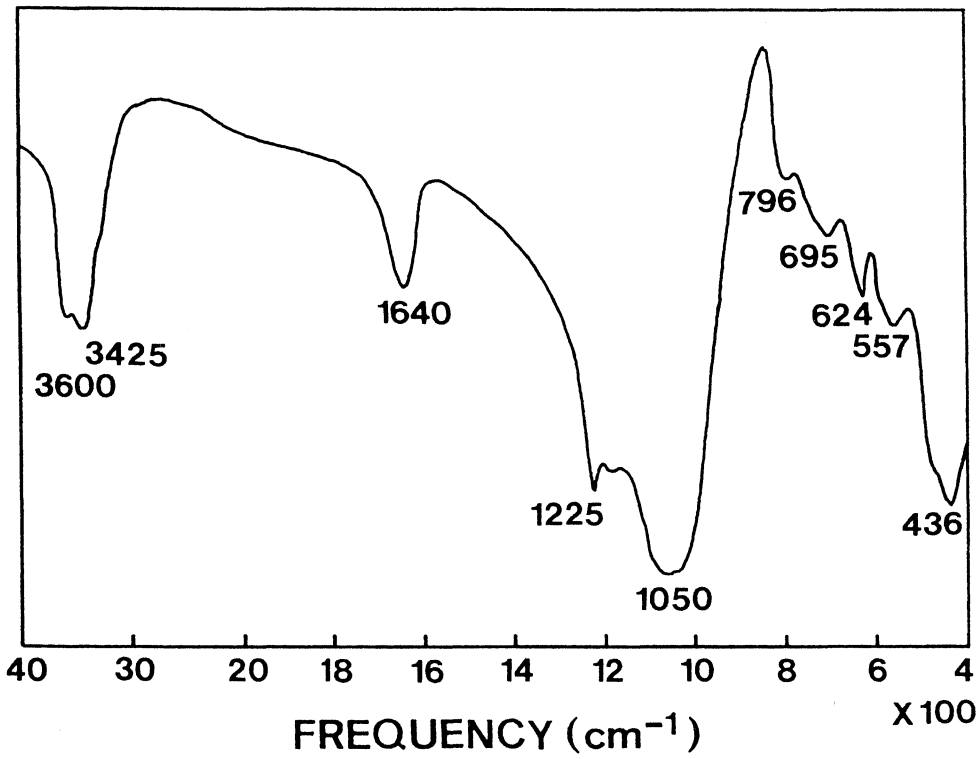

Fig. 4 IR spectrum of mordenite from Aira.

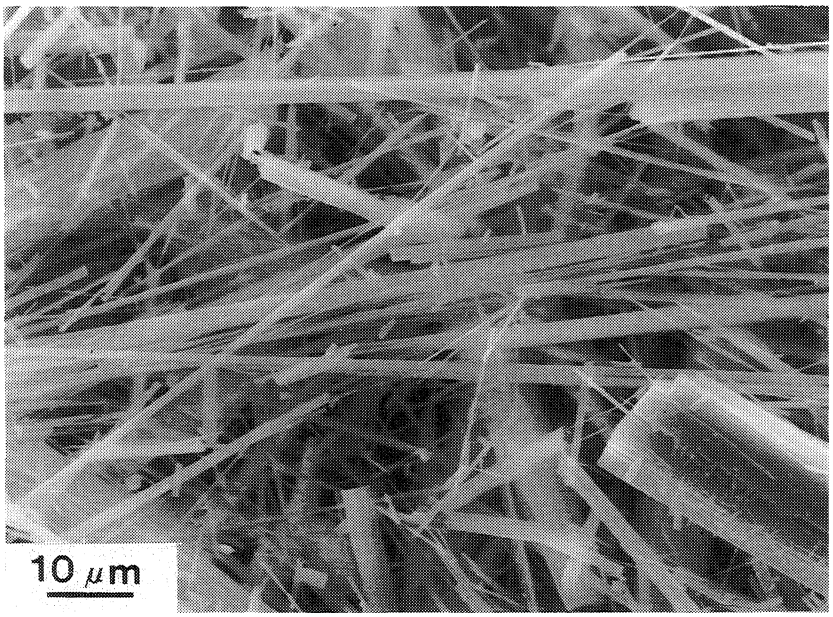

Fig. 5 SEM photograph of mordenite from Aira.

Conclusion

Neogene greenish andesitic rocks distributed widely in southern Kyushu contain various hydrothermally altered minerals as mentioned above. In Aira area, fibrous mordenite and small amounts of mordenite occur as replacements of feldspar phenocrysts or groundmass of andesitic rocks containing Fe-saponite. These mordenites were probably formed by hydrothermal alteration associated with formation of the Fe-saponite. Zeolites are used for indicator of degree of diagenetic alteration in northeastern Japan. The distribution of zeolite with increasing burial depth is; clinoptilolite + mordenite → analcime + heulandite → laumontite (Utada, 1965). This suggests that the mordenite was formed under relatively low temperature condition. Furthermore, there are many reports which indicate that mordenite occurs in the most low grade alteration part in zeolitization zone (Nakajima and Tanaka, 1967; etc.). Fe-saponites also occur relatively low grade diagenetic alteration area in northeastern Japan (Kimbara, 1975). Based on these facts, the mordenite and Fe-saponite distributed in the Aira area must be formed by low grade hydrothermal alteration. Minato and Utada (1968) likewise noted that the Neogene formation distributed in southern Kyushu has similar alteration characteristics to "Green tuff" in northeastern Japan. However, many problems such as mode of occurrence and distribution of alteration minerals in this Neogene formation remain unclear to warrant comparison. The present study of the occurrence of mordenite accompanied with Fe-saponite in the andesite in Aira will therefore give important interests for further study of hydrothermal alteration of the Neogene formation in southern Kyushu.

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