Mordenite tuff from the Itaoroshi zeolite deposit, Miyagicho, Miyagi Prefecture

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Fourteen specimens of mordenite tuff from the Itaoroshi zeolite deposit, Miyagi-cho, Miyagi Prefecture, were investigated by means of cation exchange, carbon dioxide gas adsorption, X-ray diffraction, chemical analyses and Hunter's whiteness measurement. The specimens were collected from a column of the Shirasawa formation at the vicinity of the zeolite deposit. The bulk chemical composition of them is fairly homogeneous, and ranges in Si/Al ratio from 4.28 to 5.63, averaging 4.81. Equivalent content of Ca^{2+} surpasses those of Na^+ , K^+ and Mg^{2+} . The content of calcium has good correlation with that of mordenite. Also the significant correlations were recognized among mordenite content, carbon dioxide amount adsorbed, cation exchange capacity (CEC) and total value of cations leached by NH_4^+ . The upper part of the column which is highly mordenitized bed is about 80 meters in thickness. While in the lower part, the mordenite content decreases as the depth increases. Average mineral composition of the 8 specimens collected from the highly mordenitized bed is as follows: mordenite=65.8 wt.%, quartz=5.8 wt.%, α -cristobalite=1.6 wt.%, feldspar=3.3 wt.% and amorphous materials=23.5 wt.%. Their average CEC is 140.3 meq./100 g.

Introduction

Mordenite tuffs which were produced from volcanic glass by hydrothermal alteration is widely distributed in the Shirasawa caldera at the western vicinity of Sendai, Miyagi Prefecture (Sudo *et al.*, 1963; Negishi, 1972). The Itaoroshi zeolite deposit is located at a central hill of the Shirasawa caldera near Itaoroshi-toge as shown in Fig. 1. Since 1965, zeolite rocks of the Itaoroshi zeolite deposit have been produced for industrial and agricultural uses by Sintohoku Chemical Industry Company. The zeolite rocks are embedded in the upper part of

the Shirasawa formation which is late Miocene in age. Recently Utada (1986) reported that

Fig. 1. Location of the Itaoroshi zeolite deposit.

zeolites of the deposit were formed from vitric materials in caldera filling lacustrine sediments by the alteration under the condition of high geothermal gradient. The amount of zeolite rocks in the Itaoroshi deposit is estimated around 90 million tons. At present, the products of about 6,000 tons/year are utilized for pet toilet sand, catalyst, adsorbents, soil improver and others. The mineralogical and physico-chemical properties of those mordenite tuff specimens will be discussed here.

Specimens

The detail of geology will be given in another paper (Utada, in preparation). Fourteen samples were collected along a road from the top of a hill to downwards as their sampling points shown in Fig. 2. Their depth and rock-type are listed in Table 1. The depth of sampling points corresponds to the distance which was measured on the perpendicular from the cardinal points of 300 meters above the sea level. Specimens No. 20, No. 26A, and No. 38A are pumice tuffs and the rest are fine or medium tuffites. The bulk chemical compositions of mordenitized tuffs are shown in Table 2.

Table 1. Specimens studied

Specimen No.	Depth (m)	Rock type
4E	1.0	m-tuffite
8A	4.0	f-tuffite
12	9.2	m-tuffite
14B	11.0	m-tuffite
17A	13.9	f-tuffite
20	16.0	pumice tuff
22A	17.3	m-tuffite
24	28.0	m-tuffite
26A	37.5	pumice tuff
29	43.7	laminated m-tuffite
31	47.8	laminated f-tuffite
38A	75.4	pumice tuff
36	81.4	m-tuffite
41	84.0	m-tuffite

Experimental

Carbon dioxide gas adsorption measurement

The powder samples were dehydrated at 400°C in the vacuum for 1 h. After activation, amounts of carbon dioxide adsorbed on the specimens at 25°C and 1 atm. were measured by the volumetric method.

CEC and total leached cations measurement

The cation exchange capacities of the specimens were obtained by the Shollenberger's method. The Na⁺, K⁺, Ca²⁺ and Mg²⁺ leached by the NH₄⁺ exchange were also analyzed.

Fig. 2. Sampling points of specimens at Itaoroshi zeolite deposit.

Table 2. Bulk chemical compositions of Itaoroshi mordenite tuffs

Component	No. 12	No. 17A	No. 38A	14 specimens	
				Average	Range
SiO ₂ (wt.%)	68.58	68.84	70.33	69.21	66.33 - 72.76
TiO ₂	0.18	0.18	0.17	0.18	0.17 - 0.21
Al ₂ O ₃	12.06	12.19	12.27	12.22	10.74 - 13.23
Fe ₂ O ₃	1.06	0.58	0.39	0.75	0.25 - 1.20
MnO	0.00	0.01	Tr	0.00	0.00 - 0.01
MgO	0.07	0.05	0.13	0.06	0.00 - 0.14
CaO	2.29	2.11	1.90	1.99	0.56 - 2.61
Na ₂ O	1.43	1.48	2.56	1.65	1.05 - 2.56
K ₂ O	1.41	1.65	1.24	1.64	1.24 - 2.45
P ₂ O ₅	0.01	0.01	0.01	0.01	Tr - 0.01
H ₂ O	13.07	12.16	11.12	12.11	7.70 - 14.55
Total	100.16	99.71	100.12	99.82	
Si/Al	4.82	4.79	4.86	4.81	4.28 - 5.63

Chemical analysis

The chemical analyses of the specimens were made by the X-ray fluorescent spectroscopy using the glass beads composed of 90 wt.% lithium borate and 10 wt.% specimens heated at 1,000°C.

Whiteness measurement

The Hunter's whiteness for the powder specimens was measured by a color and color difference meter (Nihon Denshoku Industry Co., Ltd.).

Mineral composition analysis

Constituent minerals of the specimens were identified by a X-ray powder diffractometry (Rigaku RAD-IIB) and examined by a JEOL JSM35C scanning electron microscopy.

Mordenite content was calculated from the amount of carbon dioxide adsorbed at 25°C and 1 atm. or from CEC based on the values for the pure mordenite; CO₂ 86.0 ml/g, CEC 218.5 meq./100 g (Torii *et al.*, 1979b). The contents of quartz, α -cristobalite and feldspar were determined by the standard binary mixture method in X-ray analysis (Torii *et al.*, 1979a). The amount of amorphous materials in the tuffs

were assumed by subtracting the total percent values of mordenite, quartz, α -cristobalite and feldspar from 100.

Results and Discussion

Physico-chemical properties

Several properties of the 14 specimens are shown in Table 3. The high Hunter's whiteness indicates that these tuffs are fairly whitish in color. Except specimens No. 36 and No. 41, collected from lower parts of the bed, tuff specimens show high mordenite content ranging from 52.2 wt.% to 70.9 wt.%. These mordenite tuffs indicate high adsorption capacities and good gas separation properties (Torii *et al.*, 1969a, 1969b, 1971a, 1971b, 1973; Asaka *et al.*, 1979).

Mineral composition

The mineral composition analyses for the 14 specimens are indicated in Table 4. The mordenite ranges in content from 17.2 wt.% to 70.9 wt.%, averaging 58.2 wt.%. The content of quartz ranges from 3.3 wt.% to 21.6 wt.%, while that of α -cristobalite falls in the narrow range of 0.2-3.1 wt.%. Feldspar shows a content range of 0.0-17.1 wt.%, and the amorphous

Table 3. Several properties of Itaoroshi mordenite tuffs

Specimen No.	CO ₂ adsorbed (ml/g)	CEC (m.equi./100g)	Mordenite content (wt.%)	Si/Al	Hunter's whiteness
4E	54.6	146.9	63.5	4.62	86.2
8A	—	138.4	63.3*	4.69	88.3
12	61.0	147.4	70.9	4.82	85.8
14B	58.9	145.5	68.5	5.63	89.0
17A	—	150.5	68.9*	4.79	87.8
20	50.1	111.4	58.3	4.89	80.6
22A	55.6	141.6	64.7	4.58	89.6
24	58.6	140.3	68.1	4.35	89.5
26A	—	118.5	54.2*	5.14	87.6
29	—	129.7	59.4*	5.23	88.0
31	56.8	141.1	66.0	4.28	89.4
38A	—	113.9	52.2*	4.86	81.5
36	34.3	92.9	39.9	4.96	84.3
41	14.8	55.0	17.2	4.67	79.5

* Mordenite contents estimated from the CEC values.

Table 4. Mineral compositions of Itaoroshi mordenite tuffs

Specimen	Mor	Q	C	Feld	AM
4E	63.5	6.0	2.2	1.0	27.3
8A	63.3	8.1	2.6	0.8	25.2
12	70.9	4.9	1.4	0.0	22.8
14B	68.5	5.5	3.1	3.2	19.7
17A	68.9	7.8	0.8	6.2	16.3
20	58.3	4.5	0.6	1.9	34.7
22A	64.7	4.0	1.3	4.9	25.1
24	68.1	5.8	0.8	3.1	22.2
26A	54.2	9.0	0.4	2.4	34.0
29	59.4	3.3	0.6	0.0	36.7
31	66.0	7.2	0.2	4.1	22.5
38A	52.2	3.3	0.2	17.1	27.2
36	39.9	21.6	1.0	16.5	21.0
41	17.2	21.6	2.1	14.5	44.6
Average	58.2	8.0	1.3	5.4	27.1

Mor, Mordenite; Q, Quartz; C, α -cristobalite; Feld, Feldspar; AM, Amorphous materials.

materials content varies from 16.3 wt.% to 44.6 wt.%.

Fig. 3 shows relations among the depth of sampling points, the contents of mordenite, quartz and feldspar, and CEC for the 14 specimens. Variation of mordenite content is almost proportional to that of CEC. The mordenitization occurred fairly homogeneously in the upper part of the columnar section and fibrous mordenite crystals, which were observed by scanning electromicrography, are found in the micro druse (Fig. 4A). Below

Fig. 3. Relations among the depth of columnar section, mineral compositions and cation exchange capacity for Itaoroshi zeolite tuff.

about 75 meters, the mordenite content decreases drastically whereas vitric materials and feldspar increase as becoming deep (Fig. 4B). The highly mordenitized beds attains to about 80 meters in thickness. The degree of mordenitization in the pumice tuffs is a little inferior to that in tuffites.

The actual working place of the mordenite

Fig. 4. Scanning electron micrographs of specimens No. 12 (A) and No. 36 (B).

Fig. 6. Change of chemical compositions with the columnar section depth at Itaoroshi zeolite deposit.

Table 5. Comparison between cation compositions leached by NH_4^+ and those in the original mordenite tuffs (meq./100 g)

Specimen No.	Cation leached by NH_4^+				CEC	
	(Cation in the original tuff)					
	Na^+	K^+	Ca^{2+}	Mg^{2+}		Total
4E	40.2 (33.9)	32.3 (48.9)	73.5 (74.1)	4.9 (4.0)	150.9 (160.9)	146.9
8A	37.7 (43.4)	14.4 (28.5)	80.2 (77.4)	4.4 (4.0)	136.7 (153.3)	138.4
12	43.1 (46.3)	17.6 (30.1)	77.6 (81.8)	4.4 (3.0)	142.7 (161.6)	147.4
14B	44.6 (45.2)	15.3 (27.9)	62.8 (79.0)	3.8 (0.4)	126.5 (153.0)	145.5
17A	44.2 (47.9)	19.1 (34.9)	72.7 (75.4)	6.3 (2.4)	142.3 (160.6)	150.5
20	32.9 (57.0)	20.1 (28.9)	46.2 (92.9)	1.7 (0.0)	100.9 (178.8)	111.4
22A	42.2 (45.3)	20.9 (30.7)	71.0 (85.1)	3.5 (0.0)	137.6 (161.1)	141.6
24	37.5 (56.8)	29.6 (39.0)	65.2 (78.2)	3.4 (0.4)	135.7 (174.4)	140.3
26A	44.0 (67.9)	19.2 (33.7)	26.0 (70.7)	3.0 (4.0)	92.2 (176.3)	118.5
29	44.1 (52.7)	18.1 (27.5)	43.6 (77.8)	2.9 (0.0)	108.7 (158.0)	129.7
31	39.9 (39.4)	21.5 (33.5)	63.3 (74.1)	3.8 (4.4)	128.5 (151.4)	141.1
38A	50.7 (82.4)	11.9 (26.5)	20.8 (67.7)	9.2 (6.5)	92.6 (183.1)	113.9
36	35.0 (63.6)	8.1 (45.3)	32.7 (39.6)	8.4 (7.1)	84.2 (155.6)	92.9
41	18.0 (62.6)	7.1 (52.1)	22.5 (19.8)	4.6 (2.0)	52.2 (136.5)	55.0

alkali and alkaline earth ions in the specimens are shown in Table 5. In the original composition of specimens from No. 4E to No. 31 (from 1 m to 47.8 m in depth), equivalent content of

Ca^{2+} surpasses those of Na^+ , K^+ and Mg^{2+} . The Na^+ almost all predominates over the K^+ . On the whole, total cation equivalent value has a tendency to surpass the CEC, which is proportional to the mordenite content.

The cation compositions leached by NH_4^+ exchange for mordenite-bearing tuff specimens are assumed to be directly reflective to those for mordenite mineral in the specimens. In the specimens with high mordenite content such as No. 4E, No. 12, No. 17A, etc., the equivalent contents of leached Ca^{2+} and Na^+ tend to be almost consistent with those in the original tuffs. In the specimens of this type, the Ca^{2+} is dominant over the Na^+ and K^+ . On the contrary, in the specimens of relatively low mordenite content such as No. 26A and No. 38A, there is a difference between the equivalent contents of Ca^{2+} and Na^+ leached by NH_4^+ exchange and those in the original rocks. And, the leached Na^+ is dominant over the Ca^{2+} and K^+ . Typical mordenite compositions of the above two type are estimated as follows:

It is assumed that the disparities between CEC and total amount of leaching cations are attributed to other cations such as H^+ .

Nakajima and Tanaka (1967) and Seki (1973) reported that calcium rich mordenite is found in the rocks of relatively higher grade alteration part of the zeolite facies. These results coincide with the synthetic data that mordenite stability increases as increasing of $\text{CaO}/(\text{Na}_2\text{O} + \text{CaO})$ ratio. The maximum temperature of mordenite stability is about 380°C at the composition of $\text{CaO}/(\text{Na}_2\text{O} + \text{CaO}) = 0.7$. The (Na, Ca)-mordenite changes immediately into plagioclase + quartz + H_2O assemblages above the temperature of stability limits (Naka-

Table 6. Correlation matrix among some physico-chemical properties for the mordenite tuffs from the Itaoroshi deposit

	Mor	CEC	TLC	TCT	Number
SiO ₂	-0.719	-0.705	-0.750	-0.297	14
Al ₂ O ₃	-0.292	-0.255	-0.045	-0.214	14
CaO	0.902	0.825	0.735	0.541	14
Na ₂ O	-0.543	-0.620	-0.747	0.461	14
K ₂ O	-0.594	-0.495	-0.296	-0.433	14
H ₂ O	0.911	0.899	0.834	0.281	14
CO ₂	1.000	0.976	0.935	0.607	9
Mor	1.000	0.977	0.908	0.358	14
CEC	—	1.000	0.951	0.241	14
TLC	—	—	1.000	0.108	14

Mor, Mordenite content; CEC, Cation exchange capacity; TLC, Total leached cation by NH₄⁺ exchange; TCT, Total cation in the tuff by chemical analyses; CO₂, Carbon dioxide amount adsorbed.

jima, 1973). In the Itaoroshi upper bed between 1 and 28 meters in the columnar section, the CaO/(Na₂O+CaO) ratio ranges from 0.58 to 0.74, averaging 0.63. This suggests that the formation temperature of mordenite in the Itaoroshi deposit was rather higher. Because the contents of quartz and feldspar increase as the content of mordenite decreases in the lower horizons, it is assumed that mordenite decomposed at the deep area.

Relationships among some properties

The correlation matrix among some variables is given in Table 6. Apart from other chemical components, CaO and H₂O contents indicate major correlations with mordenite content, CEC and total value of leached cations. This may mean that the formation of mordenite in the Itaoroshi deposit depended upon the CaO content in the original rocks. Also the significant correlations are recognized among mordenite content, carbon dioxide amount adsorbed, CEC and total value of leached cations as reported by Torii *et al.* (1979b). On the other hand, the total cation value in the original tuff correlates slightly with other properties

such as mordenite content.

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宮城県宮城町板風鉾産モルデン沸石凝灰岩

鳥居 一雄・岩崎 孝志・鈴木 啓三・歌田 実

宮城県宮城町上愛子の板風鉾山で採取した14個のモルデン沸石凝灰岩試料について陽イオン交換、炭酸ガス吸着、X線回折、化学分析、およびハンター白色度の測定を行った。試料はゼオライト鉾床を胚胎する白沢層の異なる層準で採取した。モルデン沸石凝灰岩の化学組成はほぼ均質で、Si/Al比は4.28~5.63で、その平均値は4.81である。Ca²⁺量はNa⁺, K⁺およびMg²⁺量より多く、CaO含有量はモルデン沸石含有量と強い相関を示す。また、モルデン沸石含有量は炭酸ガス吸着量、陽イオン交換容量およびNH₄⁺交換で溶出した全陽イオン量とも強い相関を示す。モルデン沸石を多量に含む部分の層厚は約80mであり、これ以下の層準では深さが増すにつれモルデン沸石含有量は低下している。現在稼行中の強くモルデン沸石化した地層から採取した8試料の平均鉾物組成は以下の通りである：モルデン沸石；60.8 wt.%, 石英；5.8 wt.%, α-クリストパル石；1.6 wt.%, 長石；3.3 wt.%, 非晶質物質；23.5 wt.%。また、その平均陽イオン交換容量は140.3 meq./100 gである。