

# THE MORDENITE-PTILOLITE GROUP; CLINOPTILOLITE, A NEW SPECIES

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## INTRODUCTION

The preceding description of ptilolite from Utah, confirms previous determinations of its orthorhombic character and shows its formula to be  $10\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{RO} \cdot 7\text{H}_2\text{O}$ . The analyses of mordenite, as given in the literature, show a very similar composition, but optical examination shows its fibers to have a small but definite inclined extinction. Grouping all the available analyses of mordenite, ptilolite, and related minerals (flokite), as far as possible, into two groups, depending on whether the material has parallel or inclined extinction, has shown that there are three distinct minerals, very similar in their properties.

Conflicting statements as to their relationships have been published; thus Bøggild<sup>1</sup> has urged the identity of flokite (shown to be mordenite) with ptilolite, and Walker the identity of ptilolite with mordenite. By correlating the published data as to composition, crystallography, and optical properties, supplemented by new determinations, it is shown that three distinct species are represented by these high-silica, acid-insoluble, zeolite-resembling minerals:

1. Mordenite (How, 1864),  $9\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot (\text{Ca}, \text{K}_2, \text{Na}_2) \text{O} \cdot 6\text{H}_2\text{O}$ . Monoclinic or triclinic, with inclined extinction of about  $5^\circ$ .

2. Ptilolite (Cross and Eakins, 1886),  $10\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot (\text{Ca}, \text{K}_2, \text{Na}_2) \text{O} \cdot 7\text{H}_2\text{O}$ . Orthorhombic, with parallel extinction.

3. Clinoptilolite. The mineral from Wyoming described by Pirsson in 1890 and accepted by Dana (6th ed.) as crystallized mordenite. It is evidently a dimorphous form of ptilolite,  $10\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot (\text{Ca}, \text{K}_2, \text{Na}_2) \text{O} \cdot 7\text{H}_2\text{O}$ , but is monoclinic, tabular and not fibrous, with large extinction angles. It is proposed to rename this mineral from Wyoming, *clinoptilolite*, referring to its inclined extinction but agreement in chemical composition with ptilolite.<sup>2</sup>

Thugutt arrived at similar conclusions, regarding ptilolite with parallel extinction as having a 10:1 silica-alumina ratio, with the formula  $10\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot (\text{Ca}, \text{Na}_2, \text{K}_2) \text{O} \cdot 6 \frac{2}{3} \text{H}_2\text{O}$ , the formula given in Dana for mordenite. He also recognized that mordenite, with a similar formula, had inclined extinction.

<sup>1</sup> See bibliography at end of paper for references.

<sup>2</sup> These conclusions have been reported in *The American Mineralogist*, vol. 8, pp. 93-94, 1923.

DISCUSSION OF ANALYSES

If the analyses of mordenite and of ptilolite, as given in the literature, be grouped into one of two classes, depending on whether the mineral has parallel or inclined extinction, and the ratios calculated from the analyses, it will be found that those having inclined extinction agree with the formula  $9\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{RO} \cdot 6\text{H}_2\text{O}$  (mordenite), and those with parallel extinction agree with the formula  $10\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{RO} \cdot 7\text{H}_2\text{O}$  (ptilolite), with the exception of the mineral from Wyoming, described by Pirsson, and here called clinoptilolite.

Grouping all the analyses, according to their ratios, under one or the other of the two formulas given, the analyses of mordenite are as follows:

ANALYSES OF MORDENITE

Number	1	2	3	4	5	6	7	8	9
Locality	Nova Scotia	Tyrol	Iceland	Nova Scotia	Nova Scotia	Idaho			
Biblio. ref.	How 1	Thugutt 9	Callisen 10	Walker & Parsons 14	Walker & Parsons 15	Ross & Shannon 16			
SiO <sub>2</sub> .....	68.40	66.86	67.69	67.08	67.18	64.84	65.88	67.24	66.25
Al <sub>2</sub> O <sub>3</sub> .....	12.77	12.13	12.43	11.85	12.36	12.07	12.40	12.94	11.88
CaO.....	3.46	3.86	2.65	1.56	3.42	3.08	3.52	2.72	2.75
Na <sub>2</sub> O.....	2.19	2.41	4.36	4.74	3.34	3.80	3.52	4.08	4.05
K <sub>2</sub> O.....	0.16	0.67	.....	2.08	0.47	0.38	0.56	0.36	0.69
H <sub>2</sub> O.....	13.02	13.87	13.35	12.84	13.23	14.79	13.40	13.44	13.85
Fe <sub>2</sub> O <sub>3</sub> .....	.....	0.03	.....	0.31	0.24	.....	.....	.....	.....
MgO.....	.....	0.17	0.09	.....	.....	0.26	0.48	0.28	0.44
Total.....	100.00	100.00	100.57	100.46	100.24	99.22	99.76	101.06	99.91
Extinction..	Small <sup>a</sup>	7°-8°	5°	Small <sup>a</sup>	—	3°40'	Small	—	—

<sup>a</sup> Determined by the writer.

The second analysis given by Walker and Parsons (Biblio. 14) is omitted as the sample contained "small spherical radiations of some other zeolite."

The ratios calculated from these analyses are given below, combining CaO, Na<sub>2</sub>O, and K<sub>2</sub>O into RO. In obtaining the figures, a weighted average is taken for each analysis, instead of arbitrarily taking any constituent as unity. A glance at the figures reveals not only a very close similarity for each constituent in the different analyses but shows very close agreement with the formula  $9\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{RO} \cdot 6\text{H}_2\text{O}$ .

## RATIOS OF ANALYSES OF MORDENITE

Number	1	2	3	4	5	6	7	8	9	Av.
SiO <sub>2</sub> .....	9.30 9×1.03	8.87 9×0.99	9.06 9×1.01	9.11 9×1.01	9.06 9×1.01	8.53 9×0.95	8.86 9×0.98	8.96 9×1.00	8.83 9×0.98	8.95 9×0.99
Al <sub>2</sub> O <sub>3</sub> .....	1.02	0.95	0.98	0.95	0.98	0.94	0.98	1.02	0.93	0.97
RO.....	0.81	0.95	0.96	1.03	0.98	1.00	1.12	1.01	1.07	0.99
H <sub>2</sub> O.....	5.93 6×0.99	6.17 6×1.03	5.98 6×1.00	5.85 6×0.97	5.98 6×1.00	6.52 6×1.09	6.03 6×1.01	6.00 6×1.00	6.17 6×1.03	6.07 6×1.01

The analyses of ptilolite, with a 10:1 ratio of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub>, are as follows:

## ANALYSES OF PTILOLITE

Number	10	11	12	13	14	15	16	17	18
Locality	Custer County, Colorado	Jefferson County, Colorado	Crown Prince Rudolph Island	Elba	Iceland	Faroer Islands	Faroer Islands	Guadalcanar	Utah
Biblio. ref.	Cross and Eakins 2	Cross and Eakins 4	Colomba 6	D'Achiaridi 7	Lindström 8	Thugutt 9	Thugutt 9	Tschermak 12	Schaller 17
SiO <sub>2</sub> .....	67.83	70.35	67.52	65.21	67.15	78.70	74.34	67.23	67.35
Al <sub>2</sub> O <sub>3</sub> .....	11.44	11.90	10.76	11.20	11.63	7.22	8.84	10.92	11.49
CaO.....	3.30	3.87	3.31	3.77	2.33	1.99	2.18	1.83	3.87
Na <sub>2</sub> O.....	2.63	0.77	1.19	6.07 14.22	4.46	2.08	2.74	3.92	2.63
K <sub>2</sub> O.....	0.64	2.83	1.69		0.72	0.30	0.43	0.58	0.11
H <sub>2</sub> O.....	13.44	10.18 <sup>b</sup>	14.43	13.98	9.71	12.05	14.91	13.95	
Fe <sub>2</sub> O <sub>3</sub> .....	.....	.....	.....	0.09	.....	tr.	.....	0.29	.....
MgO.....	.....	.....	.....	tr.	tr.	.....	.....	0.34	.....
Total.....	99.28	99.90	98.90	100.47	100.36	100.00	100.58	100.02	99.40
Extinction.	0°	0° <sup>b</sup>	0°	0°	0° <sup>b</sup>	.....	.....	.....	0°

<sup>a</sup> See footnote under table showing ratios.

<sup>b</sup> Determined by the writer.

The ratios calculated for these analyses are as follows:

RATIOS OF ANALYSES OF PTILOLITE

	10	11	12	13	14	15	16	17	18	Av.
SiO <sub>2</sub>	10.23 10×1.02	10.06 10×1.01	10.00 10×1.00	9.83 10×0.98	9.95 10×1.00	( <sup>a</sup> )	( <sup>a</sup> )	9.78 10×0.98	10.04 10×1.00	9.98 10×1.00
Al <sub>2</sub> O <sub>3</sub>	1.02	1.00	0.94	1.00	1.02	0.93	0.91	0.94	1.01	0.97
RO	0.98	0.97	0.86	....	1.09	0.95	0.94	0.96	1.01	0.97
H <sub>2</sub> O	6.79 7×0.97	4.88 <sup>b</sup>	7.16 7×1.02	7.18 7×1.03	6.94 7×0.99	7.11 7×1.02	7.12 7×1.02	7.26 7×1.04	6.94 7×0.99	7.06 7×1.01

<sup>a</sup> Ratios not given as sample analyzed was mixed with silica.

<sup>b</sup> The ratio of the water is low. The authors state that "The mineral began to lose water at a very low temperature and even on drying in the air bath at 100°C. there was a noticeable loss; the amount thus lost, however, was found to be regained upon exposure to the air, and before the analysis was made the material was allowed to remain loosely covered for several days." The sample was analyzed in the "very dry" climate of Denver. The authors suggest that the Denver climate "may have had sufficient desiccating power to remove part of the water from the mineral analyzed there."

The ratios are in very close agreement with the formula 10SiO<sub>2</sub>·Al<sub>2</sub>O<sub>3</sub>·(Ca, Na<sub>2</sub>, K<sub>2</sub>)O·7H<sub>2</sub>O.

The distribution of the CaO, Na<sub>2</sub>O, K<sub>2</sub>O, and MgO, as given in the analyses, which have been grouped together as RO, on the basis of ratio percentages, is as follows, given with decreasing CaO.

The table shows that there is no distinction in the distribution of the RO bases between mordenite and ptilolite. CaO is 50 per cent or over in 3 mordenites and 4 ptilolites; Na<sub>2</sub>O is 50 per cent or over in 4 mordenites and 2 ptilolites. In both of these minerals, CaO and Na<sub>2</sub>O seem to be mutually replaceable to almost any extent. In no analysis, is K<sub>2</sub>O over 33½ per cent. In the single analysis of clinoptilolite, the CaO, Na<sub>2</sub>O, and K<sub>2</sub>O are present in the ratio of 1:1:1.

## PERCENTAGE OF BASES GROUPED AS RO, WITH DECREASING CaO

Analysis						
No.	Mordenite	Ptilolite	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	MgO
11	..	P	62	11	27	..
12	..	P	62	20	18	..
1	M	..	62	35	3	0
18	..	P	61	38	1	..
2	M	..	58	33	6	3
10	..	P	55	39	6	..
5	M	..	51	45	4	..
15	..	P	49	47	4	..
7	M	..	46	41	4	9
6	M	..	44	48	3	5
16	..	P	44	51	5	..
3	M	..	40	58	..	2
8	M	..	39	52	3	6
9	M	..	37	50	5	8
14	..	P	35	59	6	..
<sup>a</sup> 19	<sup>a</sup>	<sup>a</sup>	31	32	33	4
17	..	P	30	58	5	7
4	M	..	22	60	18	..

<sup>a</sup> Clinoptilolite from Wyoming.

## CLINOPTILOLITE

The clinoptilolite from Wyoming, described as mordenite, is entirely different in habit, forming thin tabular crystals, like those of heulandite. Pirsson's analysis agrees closely with the formula for ptilolite, the ratios of SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>:(Ca, Na<sub>2</sub>, K<sub>2</sub>)O:H<sub>2</sub>O being 10.10:1.04:1.05:6.78. The refractive indices, determined on part of the original material, kindly supplied by Professor W. E. Ford from the Brush collection, are given below.

## OPTICAL PROPERTIES

The determinations of the optical properties of mordenite, and ptilolite, as given in the literature, may be brought together in the following two tables, extending the data given by Ross and Shannon.

OPTICAL PROPERTIES OF MORDENITE

Locality	$\alpha$	$\beta$	$\gamma$	Sign	Extinction
Idaho	1.475	1.477	1.478	.....	.....
Idaho (1)	1.470	1.475	1.475	—	$X \wedge c = 3^\circ 40'$ , $Z = b$
Idaho (2)	1.472	1.475	1.476	.....	Small
Idaho (3)	.....	1.473	.....	.....	.....
Idaho (4)	.....	1.473	.....	.....	.....
Nova Scotia (How)	.....	1.473	.....	.....	Small
Nova Scotia (Walker and Parsons)	1.471	.....	1.475	.....	Small
Iceland	1.472	.....	1.474	—	5°
Average	1.472	1.474	1.476	.....	About 5°

OPTICAL PROPERTIES OF PTILOLITE

Locality	$\alpha$	$\beta$	$\gamma$	Sign	Extinction
Colorado	1.476	1.480	1.480	—	0°
Utah	1.473	1.475	1.478	.....	0°
Elba	1.480	.....	1.482	—	0°
Iceland	.....	.....	1.480	.....	0°
Average	1.474	1.478	1.480	.....	0°

Clinoptilolite is optically negative.  $Z$  to  $a$ -axis is  $15^\circ$ , whence  $Y$  to  $c$ -axis =  $16\frac{1}{2}^\circ$ , according to Pirsson. Crushed fragments show extinction angles of about  $34^\circ$ . Larsen determined  $\alpha$  as 1.476 and  $\gamma$  as 1.479;  $2V$  very small, dispersion  $\rho < \nu$  strong. Cleavage  $b(010)$ , nearly  $\perp Y$ .

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