

MORDENITE AS AN ALTERATION PRODUCT OF A PITCHSTONE GLASS

P. G. HARRIS* AND G. W. BRINDLEY†

ABSTRACT

A hydration product formed from the glass of a pitchstone (Judd's No. 1 dike, Isle of Arran, Scotland) is identified by *x*-ray analysis as the zeolite mordenite. Chemical analysis shows some removal of alkalis in the change from the original glass to the final product.

INTRODUCTION (P.G.H.)

In the course of an investigation by one of us (P.G.H.) of the composition of co-existing phases from glassy rocks, a pitchstone, labelled as Judd's No. 1 dike, Tomore Shore, Arran, Scotland, in the collections of the Geology Department of the University of Leeds, was separated with heavy liquids into its components. A fraction lighter than the glassy groundmass and derived from it by hydration, is shown by *x*-ray analysis to be the zeolite mordenite.

Although alteration of volcanic glasses generally results in the formation of clay minerals such as montmorillonite (Hauser and Reynolds, 1939), nontronite (Allen and Scheid, 1946) and sericite (Norton, 1941), other products have been described, notably zeolites. Coombs (1952) describes the alteration of the more acid glasses in a series of andesite tuffs to laumontite, with some evidence of an intermediate stage of alteration to heulandite or analcime. Analcime of similar origin has been described by Ross (1941).

OCCURRENCE (P.G.H.)

The parent material is a quartz-fayalite pitchstone occurring as a dike in the shore at Tomore, Arran, Scotland (see Tyrrell, 1928). The glassy groundmass is more abundant than usual (96% of the volume of the rock) and is comparatively free from crystallites which form long green needles. The alteration product (about 1% of the rock) is not identifiable in thin section. As a powder, it is readily distinguished from the clear glass, being of a buff yellow color, due perhaps to ferric oxide. Between crossed nicols the yellow color masks any optical characteristics. Most of the separated grains contain both glass and the alteration product, while the crystallites occur in both phases.

* Formerly Geology Department, University of Leeds, England; now at Dominion Laboratory, Wellington, New Zealand.

† Formerly Physics Department, University of Leeds, England; now Research Professor of Mineral Sciences, Pennsylvania State University, Pa., U.S.A.

CHEMICAL ANALYSES (P.G.H.)

Chemical analyses of the pure glass and of the alteration product are given in Table 1.

TABLE 1. CHEMICAL ANALYSES OF A PITCHSTONE GLASS AND OF ITS HYDRATION PRODUCT

	1	2
SiO ₂	73.41	68.24
TiO ₂	0.14	0.11
Al ₂ O ₃	11.65	11.04
Fe ₂ O ₃	0.28	1.74
FeO	1.09	n.d.
MnO	0.03	n.d.
MgO	0.02	0.23
CaO	0.75	1.31
Na ₂ O	3.63	3.19
K ₂ O	3.63	2.45
H ₂ O+	4.76	6.59
H ₂ O-	0.10	5.02
P ₂ O ₅	0.03	n.d.
Others	0.28*	n.d.*
	99.80	99.92

1. Glass from pitchstone, Judd's No. 1 Dike, Tomore, Arran. Analyst, P.G.H.

2. Alteration product of glass. Analyst P.G.H.

* In analysis 1, this item represents the difference between H₂O± by the Penfield method and the total loss on ignition corrected for oxidation of FeO. It may be due to other volatiles in the glass, such as non-carbonate CO₂. In analysis 2, any such component is included in H₂O+, which is based on the loss on ignition.

The analysis of the mordenite fraction may be recalculated in conformity with the theoretical mordenite structure (Ca,Na₂,K₂)₄Al₈Si₄₀O₉₆·28H₂O.

Disregarding the titanium and iron oxide contents, the analysis gives a formula (Mg_{0.2}Ca_{0.8}Na_{3.7}K_{1.8})Al_{7.7}Si_{40.3}O₉₆·22.9H₂O, which is reasonably close when the possible presence of unaltered glass is considered.

The analyses show that the main changes are small removals of alkalis and a considerable increase of water content. These resemble the changes accompanying palagonitization (cf. Hoppe, 1941). The latter, however, differ in several respects.

- (a) The alteration products of palagonitization are amorphous and give no *x*-ray powder diagram.
- (b) Palagonitization is accompanied by a greater decrease in alkalis and in CaO content.

(c) Palagonite forms from basaltic glass. More acid glasses seem to result in zeolites or clays.

(d) The water content is significantly different.

Palagonite, even after washing with acetone, during its separation, still retains more than 10% of H₂O— (unpublished analysis), while analyses by Hoppe and others have H₂O— contents as high as 14%. This content of H₂O— may be as diagnostic a feature of a true palagonite as the amorphous character shown by *x*-rays.

X-RAY EXAMINATION (G.W.B.)

X-ray powder diagrams of the alteration product were taken with 19 cm. and 20 cm. diameter cameras and filtered CoK_α radiation ($\lambda = 1.79020$ Å). The material is well crystallized and gives fifty or more easily measurable lines. Diagrams taken with a stationary powder specimen show smooth and continuous diffraction lines without obvious broadening; the crystal size is, therefore, estimated to be about 1–5 μ . The high order reflections do not resolve the K_α doublet.

The occurrence of a long spacing, about 13.7 Å, is noteworthy but the material is clearly not a clay mineral of any known type. Data for a number of zeolites in the *A.S.T.M.* index show some similarities with the observed results, but no satisfactory agreement was obtained. A search through crystallographic literature showed that Waymouth, Thornely and Taylor (1938) had measured the cell dimensions of a mordenite from Aros, Isle of Mull, Scotland (British Museum Cat. No. 47614) which were consistent with a (110) spacing of 13.6 Å, but no powder data are given in their paper. Powder data for natural and synthetic mordenites have been recorded by Barrer (1948) which confirm the long spacing of about 13.5 Å and show general agreement with the present data.

To confirm the identification of the alteration product as mordenite, a specimen from the same sample of Mull mordenite which Taylor and his colleagues had previously studied was obtained from the British Museum with the assistance of Dr. G. F. Claringbull. Its powder diagram is more clearly defined than that of the alteration product and many weak lines are recorded which are not measureable from the alteration product, but in all essential respects the diagrams are identical. While the powder diagrams of the zeolites as a group tend to have certain similarities, which in fact were sufficient to suggest that the alteration product was probably a zeolite, the differences between them are such that no doubt attaches to the identification of the alteration product as mordenite.

Table 2 compares the powder data for the Mull mordenite (B.M. 47614), for the alteration product from Arran, and a natural mordenite examined by Barrer; the intensities listed by Barrer are transcribed to a numerical basis as follows *s*,10; *ms*,8; *m*,6; *mw*,4; *w*,2; *vw*,1; *vw*, $\frac{1}{2}$.

TABLE 2. X-RAY POWDER DATA FOR MORDENITE

1				2		3	
<i>d</i> _{obs.}	<i>I</i>	<i>d</i> _{calc.}	<i>hkl</i>	<i>d</i> _{obs.}	<i>I</i>	<i>d</i> _{obs.}	<i>I</i>
13.7	5	13.58	110	13.7	6	13.5	10
9.10	9	9.080	200	9.10	9	8.66	10
6.61	9	6.592	111	6.60	8	6.54	10
6.38	4	6.383	130	6.39	5	—	—
6.10	5	6.070	021	6.09	2	—	—
5.79	5	5.801	201	5.80	5	5.72	6
5.03	1	5.046	221	—	—	—	—
4.871	2	4.872	131	—	—	—	—
4.525	8	4.527	330	4.535	8	4.50	10
4.143	3	4.150	420	—	—	—	—
3.999	9	3.991	150	4.008	9	3.99	10
3.842	6	3.836	241	3.854	4	—	—
3.763	2	3.770	002	3.778	4	—	—
3.624	1	3.633	112	—	—	—	—
3.563	1	3.576	510	—	—	—	—
3.483	10	3.482	202	3.486	10	—	—
3.393	9	3.409	060	3.398	9	3.40	10
3.308	1	3.296	222	3.315	1	—	—
3.222	10	3.206	530	3.224	9	3.15	10
3.103	2	3.096	441	—	—	—	—
2.946	2	2.950	531	—	—	—	—
2.896	6	2.900	402	2.899	7	2.90	8
2.743	1	2.741	152	2.746	1	—	—
2.700	3	2.709	621	2.707	1	2.70	1
2.639	1	2.632	370	—	—	—	—
2.560	4	2.564	461	2.569	3	—	—
2.522	5	2.523	442	2.534	5	2.50	6
2.465	2	—	—	2.469	1	—	—
2.437	2	—	—	2.440	1	2.43	2
2.343	2	—	—	—	—	—	—
2.299	1	—	—	—	—	—	—
2.275	1	—	—	—	—	—	—
2.228	2	—	—	2.234	$\frac{1}{2}$	—	—
2.162	2	—	—	2.165	$\frac{1}{2}$	—	—
2.123	1	—	—	2.124	$\frac{1}{2}$	—	—
2.047	4	—	—	2.051	3	2.02	4
2.019	4	—	—	2.019	$\frac{1}{2}$	—	—
1.998	4	—	—	2.001	$\frac{1}{2}$	—	—
1.953	4	—	—	1.955	4	1.94	4
1.936	1	—	—	—	—	—	—
1.917	2	—	—	1.922	1	—	—
1.883	4	—	—	1.884	4	—	—
1.865	1	—	—	1.857	2	1.855	4
1.850	1	—	—	—	—	—	—
1.813	3	—	—	—	—	—	—
1.795	3	—	—	1.795	2	1.785	4
1.765	1	—	—	—	—	—	—
1.738	1	—	—	1.746	$\frac{1}{2}$ ²	—	—
1.720	2	—	—	1.722	$\frac{1}{2}$	—	—
1.698	1	—	—	1.697	$\frac{1}{2}$	1.687	$\frac{1}{2}$
1.686	2	—	—	—	—	—	—
1.665	2	—	—	—	—	—	—
1.647	1	—	—	—	—	1.646	$\frac{1}{2}$
1.622	2	—	—	1.621	$\frac{1}{2}$	—	—
1.597	3	—	—	1.597	1	1.585	1
1.546	2	—	—	1.548	1	—	—
1.527	3	—	—	1.528	2	1.527	2

TABLE 2 (Cont'd)

1				2		3	
$d_{\text{obs.}}$	I	$d_{\text{calc.}}$	hkl	$d_{\text{obs.}}$	I	$d_{\text{obs.}}$	I
1.508	1			—	—	—	
1.492	$\frac{1}{2}$			—	—	—	
1.478	1			1.479	$\frac{1}{2}$	1.477	2
1.445	3			1.447	2	1.439	6
1.426	2			1.427	$\frac{1}{2}$	—	
1.412	3			1.413	$\frac{1}{2}$	1.415	$\frac{1}{2}$
1.401	2			1.401	$\frac{1}{2}$	—	
1.386	3			1.387	1	—	
1.375	3			1.376	$\frac{1}{2}$	1.376	1
1.354	1			—	—	—	
1.334	1			—	—	—	
1.318	1			—	—	1.311	$\frac{1}{2}$
1.300	2 b			1.301	$\frac{1}{2}$	1.291	1
1.278	1			1.281	$\frac{1}{2}$	—	
1.266	2			1.267	1	1.262	1
1.245	2			1.245	$\frac{1}{2}$	1.238	1
1.228	1			1.228	$\frac{1}{2}$	—	
1.217	1			1.216	1	1.211	$\frac{1}{2}$
1.209	$\frac{1}{2}$			—	—	—	
1.1955	$\frac{1}{2}$			—	—	—	
1.1856	1			1.1858	$\frac{1}{2}$	1.180	$\frac{1}{2}$
1.1731	$\frac{1}{2}$			—	—	—	
1.1568	$\frac{1}{2}$			1.1587	$\frac{1}{2}$	1.154	$\frac{1}{2}$
1.1445	1			1.1447	$\frac{1}{2}$	—	
1.1285	2			1.1285	$\frac{1}{2}$	1.125	$\frac{1}{2}$
1.1061	$\frac{1}{2}$			—	—	1.095	$\frac{1}{2}$
1.0642	$\frac{1}{2}$						
1.0217	$\frac{1}{2}$						
0.9802	$\frac{1}{2}$						
0.9580	$\frac{1}{2}$						
0.9386	$\frac{1}{2}$						
0.9324	$\frac{1}{2}$						
0.9288	$\frac{1}{2}$						
0.9192	$\frac{1}{2}$						
0.9171	$\frac{1}{2}$						
9.9128	$\frac{1}{2}$						
0.9098	$\frac{1}{2}$						
0.9047	$\frac{1}{2}$						

1.ordenite from Aros, Isle of Mull, Scotland (B.M. Cat. No. 47614).

2. Alteration product from Tomore, Isle of Arran, Scotland.

3. Natural mordenite, examined by Barrer (1948).

b signifies broad line.

The powder data have been indexed for the lower order reflections and the orthorhombic cell dimensions derived therefrom are given in Table 3 where they are compared with those given by Taylor and his colleagues.

CONCLUSIONS

The chemical and x -ray data combine to show that the alteration product is the zeolite mordenite. The close similarity in chemical composition of the original glass and the resultant zeolite suggests that the nature

TABLE 3. UNIT CELL DIMENSIONS OF MORDENITE

	1	2
<i>a</i>	18.25 ± 0.1 Å	18.16 ± 0.10 Å
<i>b</i>	20.35 ± 0.1	20.45 ± 0.10
<i>c</i>	7.50 ± 0.05	7.54 ± 0.05

1. Data by Waymouth, Thornely and Taylor (1938).

2. Present data: camera diameter 19 cm. filtered CoK_α radiation, λ = 1.79020 Å.

of the zeolites which form by alteration of glasses, depends largely on the composition of the original material.

Zeolites, as intermediate products in the breakdown of volcanic material, may be more common than is thought.

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