ZEOLITIC ALTERATION OF PYROCLASTICS

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Abstract

The frequent alteration of vitric pyroclastics to clay materials, of which montmorillonite is the most abundant, has been well established and bentonite is recognized as a rock name for such material. This paper points out that the mineral clinoptilolite, which may be included with the zeolites, is also a common alteration product of pyroclastics where the alteration is less complete. This mineral seems to be an intermediate product in the process of alteration of the volcanic glass, with the clay mineral an end product of the process.

A zeolitic mineral identified as clinoptilolite was observed very commonly in a number of samples of altered pyroclastics from the Miocene of California. The abundance of this mineral and its mode of occurrence seemed significant enough to make an exact mineral determination advisable. The results obtained in the examination of altered pyroclastics from this and other regions suggest that the features here presented may characterize many occurrences.

Many of the beds of pyroclastics in the Monterey group of California, especially in the upper part of the section, are nearly unaltered vitric volcanic ash, the isotropic glass having an index of refraction close to 1.50. Other beds occurring lower in the section show an alteration of the vitric tuffs to a clay mineral with the optical characters of montmorillonite, and some of these retain in part their original vitroclastic texture, as seen in thin section. In other beds the original tuff seems less completely altered, and in thin section the original texture is well preserved with the larger shards appearing nearly isotropic, and only the finer-grained material and groundmass are composed largely of the birefringent clay mineral. In addition there are grains and crystals of a mineral of lower refringence and birefringence than the clay mineral. In certain areas, particularly in bubble cavities, this mineral develops a good crystal form.

On washing down such a sample to eliminate the fine clay mineral, the residue is composed of relict shards retaining many of the characteristic shapes of the original volcanic glass fragments

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and many minute crystals which in part appear penetrating the shards. In this washed residue the thickness of grains is greater than in thin section and thus shows that the shards are also weakly birefringent, and of the same index of refraction as the crystals. Both the shards of microcrystalline aggregates and the anhedral crystals on heating to less than 200° Centigrade, show a marked increase in birefringence and decrease in refringence.

The mineral where showing a good euhedral crystal form has a tabular habit with development of crystal faces similar to those of heulandite, and also to those of clinoptilolite from Wyoming, originally described as mordenite, and reproduced in Dana's System of Mineralogy on page 573. Penetration twinning is frequent and undulatory extinction is general. The mean index of refraction seems somewhat variable but is near 1.480. The axial angle is large, and measurement of the bisectrix angle emerging normal to the flat lying plates seemed considerably above 90°, indicating the obtuse bisectrix. As this bisectrix is Z, the mineral would be

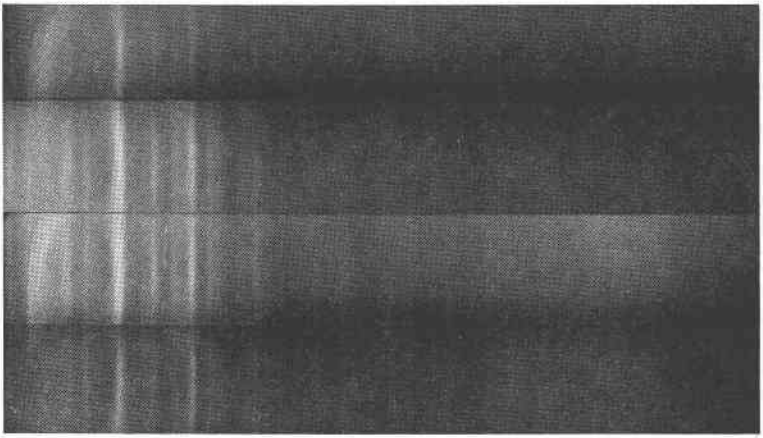

FIG. 1

1. Crystals from Miocene bentonite at Highland Monocline, San Luis Obispo County, California.
2. Clinoptilolite from Wyoming. Type material from original occurrence in Wyoming (described by Pirsson as mordenite).
3. Residue of shard fragments from bentonite, Dome, Arizona (sample analyzed).
4. Heulandite, West Paterson, New Jersey.

negative in optical sign. The mineral is not attacked by warm hydrochloric acid and fuses with difficulty. These properties seem to indicate clinoptilolite, recently named and described by Schaller.[1]

The anhedral aggregates composing the shards show these same properties. *X*-ray examinations by the powder method were made to ascertain whether the euhedral crystals and the microscopic aggregates of the shards were actually identical and further whether this material corresponds to the mineral clinoptilolite. The results showed complete identity of this crystalline alteration product with clinoptilolite. Some typical spectrograms are reproduced (Fig. 1), and a spectrogram of heulandite is included. Comparison of the diffraction patterns of clinoptilolite and of heulandite shows that they are practically indistinguishable. In view of differences in their optical characteristics and chemical composition, as well as possibly some variability in the latter, the most probable assumption for the present seems to be that the two minerals represent members of a series of solid solutions. This, however, is a separate problem which will require further study. It may only be added in this connection that a sample of mordenite, which was supposed to be a part of the type specimen, gave a very different diffraction pattern, and therefore does not seem to belong to the heulandite group of minerals.

The occurrence of clinoptilolite is so common in the altered pyroclastics in the California Miocene that it seemed desirable to determine whether it is of more general occurrence. A sample of bentonite from Dome, Arizona, that was not completely altered to the clay mineral and showed in thin section many relict shards of apparently isotropic glass, was examined. The washed residue, consisting largely of these characteristic shard forms, showed the same optical characters as the mineral from California, and the *X*-ray pattern confirmed the identity. This is one of the samples shown in the spectrogram figure. As this sample was most easily separated and purified, a sample of the clinoptilolite was obtained by washing out of the clay mineral and eliminating the feldspar, etc., by liquid flotation. This sample was analyzed in the chemical laboratory of the United States Geological Survey, by J. G. Fairchild, with the following results:

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[1] Schaller, Waldemar T., The mordenite-ptilolite group; Clinoptilolite, a new species: *Am. Mineral.*, **17**, 128, 1932.

Analysis of clinoptilolite from Dome, Arizona

SiO_2	64.30
Al_2O_3	12.78
Fe_2O_3 (total Fe)	.82
CaO	2.42
Na_2O	3.96
K_2O	1.36
MgO	.62
H_2O-	4.78
H_2O+	9.50
	100.54

In regard to this analysis, Dr. Schaller states: "The analysis of the sample of clinoptilolite, as given, yields the ratios: 8.56 SiO_2: 1.00 Al_2O_3: 1.09 RO(RO=CaO, Na_2O, K_2O, MgO): 6.35 H_2O. While considerably different from the normal formula of heulandite, these ratios are not very close to the formula ($10SiO_2 \cdot 1Al_2O_3 \cdot 1RO \cdot 7H_2O$) of clinoptilolite. However the sample analyzed contained about 5 per cent of clay mineral and if allowance be made for this impurity, the ratios come closer to those of clinoptilolite. The *X*-ray pattern shows that the mineral can not be mordenite."

A sample from Pedro, Wyoming, from the thick bentonite in the basal part of the Pierre shale of the Black Hills region, seemed less completely altered than most of the bentonites of this area, and in thin section shows many of the larger shards as apparently isotropic relict glass fragments in a finer groundmass of montmorillonite. On a similar examination of the washed residue, these shards appeared to be the same mineral though in finer cryptocrystalline aggregates, and *X*-ray patterns (not reproduced here) confirmed this material as clinoptilolite. In this sample from the Pierre shale, the crystal phenocrysts consist of an andesine-labradorite plagioclase and euhedral crystals of biotite and apatite and some magnetite, but with no quartz or orthoclase. In the other samples examined the phenocrysts are less abundant but consist of a sodic plagioclase, orthoclase, quartz and minor amounts of zircon. This suggests that the Pierre bentonite was derived from a somewhat more calcic glass, though it gave the same alteration products.

Alteration of volcanic rocks resulting in the formation of a zeolite has been described by various writers, and an occurrence in the Green River formation, described by Bradley,[2] has some features in common with the results here presented, though the resulting zeolite was analcite with some apophyllite. It now appears from the results of this investigation that an alteration of pyroclastics to clinoptilolite is very widespread, though the recognition and positive identification of the mineral offers difficulties.

The relations strongly suggest that this clinoptilolite is an intermediate stage in the process of alteration that finally results in a typical bentonite composed of a clay mineral, though it is not implied that all bentonites have gone through such an intermediate stage. The chemical composition of the mineral is close to that of an alkalic volcanic glass, whereas the composition of a bentonite composed of montmorillonite shows a distinct loss in silica and alkali, with a relative increase in alumina and magnesia. These chemical relations would seem to support the view that the zeolite is an intermediate product and the clay mineral a later stage of more complete alteration.

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[2] Bradley, Wilmot H., The occurrence and origin of analcite and meerschaum beds in the Green River formation of Utah, Colorado, and Wyoming: *U. S. Geol. Survey, Prof. Paper* **158,** pp. 1–7, 1929.