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New occurrence of faujasite in southeastern California

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Abstract

Faujasite occurs with phillipsite in a palagonitized cinder cone in the southern half of section 16, R. 11 E., T. 16 N., Halloran Spring Quadrangle, San Bernardino County, California. Faujasite forms water-clear, millimeter-sized octahedra, commonly twinned on the spinel law. Averaged electron microprobe analyses yield the composition $Ca_{0.95}Mg_{0.22}Na_{1.04}K_{0.02}[Al_{3.40}Si_{8.60}O_{24}]\cdot 16H_2O$. Measured density is 1.93(1) g/cm^3; the refractive index is 1.466(2); and the unit cell edge of 24.638(3)Å.

Geologic relations of the deposit require that the components for the zeolites be derived from the basaltic glass during the hydration forming the palagonite. Faujasite formed where solutions were the most dilute, and phillipsite formed later from presumably more concentrated solutions.

A review of faujasite compositions from all known localities, including new analyses from three localities in Hessen, West Germany, reveals compositional variations within narrow limits. Si/Al commonly varies only from 2.14 to 2.70, but there is somewhat more variation in Ca/(Ca+Mg). The composition of natural faujasite can be expressed by the formula $(Ca, Na_2, Mg)_{3.5}[Al_7Si_{17}O_{48}]\cdot 32H_2O$, where Z = 8.

Introduction

Faujasite, first described by Damour in 1842 (Doelter, 1921) from its occurrence at Sasbach, Kaiserstuhl, West Germany, has proven to be a rare zeolite. Several localities are mentioned in the early literature, such as Annerod and Grossen-Buseck in Hessen, West Germany (Hintze, 1893), in the eastern Aar Massif, Switzerland (Parker, 1923), and in Ottawa County, Quebec, Canada (Doelter, 1921). However, until recently the only material to be studied by modern analytical methods was that from Sasbach (Rinaldi *et al.,* 1975) and Oahu (Iijima and Harada, 1969).

A new locality has been discovered in southeastern California where faujasite occurs in relative abundance. Faujasite and phillipsite form millimeter-sized crystals in the cavities of a palagonitized tuff on the slopes of a Pliocene volcano in the southern half of section 16, R. 11 E., T. 16 N., Halloran Spring Quardrangle (15′ series), San Bernardino County, California (this cone will hereafter be referred to as the section 16 volcano). This paper describes this occurrence, gives the properties of the faujasite, and shows that components necessary for its formation were released directly from the glass in the forming of the palagonite.

Faujasite has recently been collected from two old localities—Annerod and Grossen-Buseck, and from a recent core drilled at Hasselborn near Ilbeshausen. All three localities are in the basaltic rocks of the Vogelsberg, Hessen, West Germany. Descriptions of these localities and minerals are given by Hentschel (1980 and in preparation).

Description of the California deposit and zeolites

The volcano with the faujasite-bearing tuffs is the northernmost in the Pliocene to Recent lava field that lies on the western flank of the Cima Dome, a large geomorphic feature in the eastern Mojave Desert, San Bernardino County, California. Vents in the lava field are characterized by cinder cones. The older cones are substantially eroded, leaving necks and ill-defined rings and radial dikes.

The section 16 volcano apparently erupted in a major drainage, where more than 100 m of cinders, consisting of basaltic glass, were deposited on granitic gravels. Water saturated the lower two-thirds of this accumulation, converting the basaltic glass to palagonite. The upper third was partially altered to clay and hematite, coloring the pile red (Fig. 1). The zeolites occur in vesicles in the palagonitized

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tephra and as very thin crusts at the base of the reddened tephra.

Faujasite and phillipsite occur sparingly in the cavities of the tephra, filling less than 25% of the void volume. Faujasite is most abundant near the top of the palagonitized section (Fig. 1), but is present sparingly throughout. In contrast to most zeolite occurrences these were not preceded by clay minerals. Many bombs with diameters greater than 10 cm remain unaltered and contain zeolites only in surface cavities. The total volume of faujasite is probably not greater than 10% of the volume of phillipsite. This type of occurrence is very similar to that described by Iijima and Harada (1969) on Oahu, Hawaii.

The zeolites

Faujasite occurs as water clear octahedra as much as 0.75 mm in diameter. The crystals are commonly intergrown and twinned on the spinel law (Fig. 2). The compositionally homogeneous crystals yielded particularly consistent physical properties. The refractive index is 1.466(2), and the density, measured by the flotation method in acetone-diluted bromoform, is 1.93(1) g/cm^3. The cell edge, 24.638(3)Å, was refined from X-ray powder data, standardized with synthetic CaF_2 (a = 5.459(1)Å) using Cu$K\alpha$ X-radiation (λ = 1.5418Å). The X-ray powder pattern is listed in Table 1. All of these values are very similar to those determined from the faujasites from Sasbach and Hessen.

Phillipsite occurs as radiating, twinned prisms in clusters as much as 1 mm in diameter. Where it is in contact with faujasite, the phillipsite can be shown to have grown later, a relationship also observed at Sasbach (Rinaldi *et al.*, 1975), and the Hessen localities. At each of the localities in Germany faujasite is associated with offretite, which was not found at the California locality. Faujasite is a minor associate of herschellite and phillipsite from Aci Reala, Sicily, where it again was the first to form.

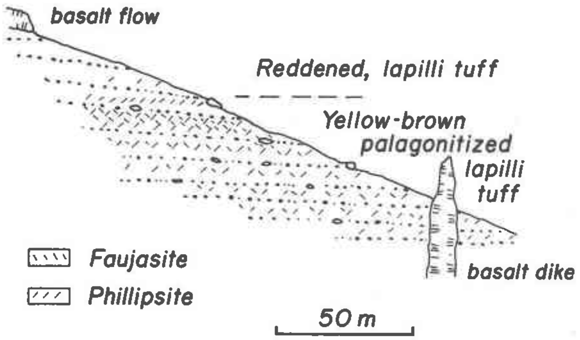

Fig. 1. Sketch of the spatial relations of palagonitized cinders and the occurrence of zeolite in the cinder cone in section 16, R. 11 E., T. 16 N., near Halloran Summit, San Bernardino County, California

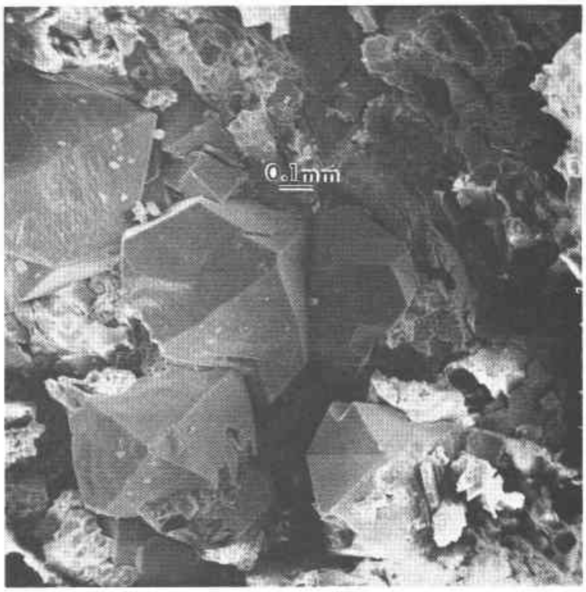

Fig. 2. Scanning electron photograph of faujasite octahedra and twinned octahedra (spinel law) on a matrix of palagonite from near Halloran Summit, San Bernardino County, California.

Chemical composition

The faujasite, phillipsite, and palagonite were analyzed with an ARL electron microprobe.

Table 1. X-ray powder data for faujasite from southeastern California

hkl	d(obs)	d(calc)	I/I_o	hkl	d(obs)	d(calc)	I/I_o
111	14.21	14.22	95	844	2.513	2.515	4
220	8.67	8.71	18	755	2.481	2.476	4
311	7.41	7.43	11	773	2.380	2.381	8
222	7.11	7.11	3	666	2.373	2.371	36
331	5.64	5.65	83	775	2.224	2.222	5
333	4.74	5.65	39	880	2.179	2.178	12
440	4.355	4.355	52	955	2.152	2.153	7
442	4.110	4.106	5	866	2.113	2.113	2
620	3.895	3.896	14	973	2.089	2.090	10
533	3.757	3.757	100	884	2.053	2.053	11
444	3.552	3.555	9	11 5 3	1.979	1.979	3
551	3.449	3.450	20	886	1.924	1.924	4
642	3.292	3.292	64	10 8 2	1.901	1.901	5
731	3.207	3.208	16	11 7 3	1.841	1.842	5
733	3.010	3.010	23	995	1.801	1.802	10
822	2.903	2.904	36	11 7 5	1.765	1.764	6
840	2.754	2.755	28	10 8 6	1.742	1.742	13
753	2.704	2.704	11	11 9 3	1.696	1.696	15
664	2.628	2.626	33	12 8 4	1.647	1.646	3
931	2.582	2.582	12	14 6 2	1.604	1.604	3
				999	1.580	1.580	11

X-ray powder data obtained from a diffractometer, using Cu$K\alpha$ X-radiation (λ = 1.5418 Å), standardized with synthetic CaF_2 (a = 5.459 Å) and scan speed of 1/2° per minute.

Groups of crystals and palagonite were embedded in epoxy and ground to expose the centers of crystals. These mounts were polished and coated with approximately 200Å of carbon. An accelerating voltage of 15 kV was used for all elements with a sample current of 10 nanoamps. Common silicate standards were used, and the emission data were reduced with a slightly modified verison of the computer program EMPADR 7 (Rucklidge and Gasparrinni, 1969). In order to overcome some difficulties in analyzing zeolites by EMX methods, large beam diameters (20 μm) were used. To minimize errors from the ion migration effect, the counting rate for sodium and potassium was projected to time zero. The unaltered basalt was analyzed by standard X-ray fluorescence and atomic absorption methods.

Approximately 30 faujasite crystals from four different specimens (all from the faujasite zone of Fig. 1) and five from each of the Hessen localities were analyzed with the electron microprobe. Ten high quality analyses (judged by the difference between the cation charge and the amount of Al being less than 5%) were obtained. The faujasites are comparatively homogeneous; columns 1 and 2 in Table 2 are representative analyses of the cores and rims of several crystals so analyzed. All such analyses show that the rims are slightly enriched in Na and Si. In a general sense the Mojave faujasites are similar to those from Germany, but there are some consistent differences (Fig. 3). The Si/Al ratios vary between 2.50 and 2.60 compared with 2.58 to 2.67 at Sasbach, 2.28 at Annerod and Grossen-Buseck, and 2.14 at Hasselborn. The Ca/(Ca+Mg) ratios are substantially higher in the California and Hessen faujasites (0.79 to 0.82) compared with 0.55 at Sasbach. Both faujasite and phillipsite from the California locality are richer in Na than any of the corresponding zeolites from the German localities (Fig. 3). Considering the wide range of framework compositions that it is possible to achieve with synthetic sodium faujasites (zeolites X and Y, where Si/Al varies from 1 to 1.5 and 1.5 to 3.0, respectively), the compositions of these natural faujasites have a much smaller range of variation.

Table 2. Electron microprobe analyses of faujasites

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
SiO_2	48.22	48.27	48.59	53.90	46.80	46.82	45.72
Al_2O_3	16.35	16.18	15.97	19.20	17.42	17.42	18.12
Fe_2O_3	nd	.09	nd	.07	.03	.02	nd
MgO	.79	.94	.79	.04	1.29	.76	.96
CaO	4.93	5.03	4.93	3.46	6.00	6.55	6.85
SrO	nd	nd	nd	nd	.13	.15	nd
BaO	nd	nd	nd	.22	nd	nd	nd
Na_2O	3.11	2.92	3.02	3.61	1.66	1.46	1.61
K_2O	.09	.08	.16	5.38	.17	.30	.16
Cell Contents, based on 24 Oxygens							
Si	8.58	8.59	8.65	8.48	8.35	8.37	8.19
Al	3.43	3.39	3.35	3.56	3.66	3.67	3.83
Fe	--	.01	--	.01	--	--	--
Mg	.21	.25	.21	.01	.34	.20	.26
Ca	.94	.96	.94	.58	1.15	1.26	1.32
Sr	--	--	--	--	.02	.02	--
Ba	--	--	--	.02	--	--	--
Na	1.07	1.01	1.04	1.10	.58	.51	.56
K	.02	.02	.04	1.08	.04	.07	.04
Si/Al	2.50	2.53	2.58	2.38	2.28	2.28	2.14

(1) Faujasite, San Bernardino County, California, outer edge of crystal
(2) Faujasite, San Bernardino County, California, core of same crystal
(3) Faujasite, San Bernardino County, California, average of 15 analyses
(4) Phillipsite, San Bernardino County, California, average of 4 analyses
(5) Faujasite, Annerod, Hessen, Germany, average of 3 analyses
(6) Faujasite, Grossen-Buseck, Germany, average of 4 analyses
(7) Faujasite, drill core at Hasselborn near Ilbeshausen, Vogelsberg, Hessen, Germany, average of 3 analyses

An exception to these consistencies is the sodium-rich faujasite from Aci Reale, Sicily. A single analysis suggests a composition near $Na_{1.76}Ca_{1.22}Mg_{0.09}K_{0.18}[Al_{4.37}Si_{7.59}O_{24}]\cdot 16H_2O$. Here the Si/Al ratio is 1.74, and composition is substantially more sodic than that of other known faujasites. It is associated with both phillipsite and herschellite

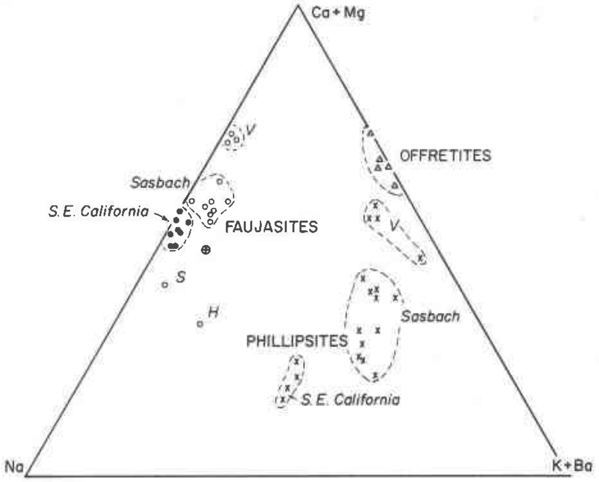

Fig. 3. Triangular plot of Ca+Mg, Na, and K+Ba contents of known faujasites and associated phillipsites and offretites. Analyses labelled with letters are: V—the three Vogelsberg localities—Annerod, Grossen-Buseck, and Hasselborn; S—Aci Reala, Sicily; and H—Salt Lake Crater, Oahu, Hawaii. The ⊕ is the composition of elements released from the cinders during palagonitization (Table 3).

(Si/Al in each is 1.85 and both are sodium-rich). Minerals from this locality warrant further study.

Origin

The faujasite in the palagonitized tuffs grew directly on the walls of vesicles with no precursor clay and was followed by phillipsite. At Sasbach there is also a scarcity of clay in the vesicles and fractures in the host limburgite, and the faujasite preceded offretite and phillipsite.

The field relations illustrated in Figure 1 show a zonation similar to that in tephra cones on Oahu (Hay and Iijima, 1968), where sideromelane was converted to palagonite by percolating ground water. The distribution of faujasite can be interpreted as having crystallized early while the water was most dilute. Phillipsite crystallized later and deeper in the pile where salinities were greater.

The alkali and alkaline earth cations occur in zeolites in channels and cavities bonded to the framework near the tetrahedra occupied by Al. Commonly these cations are in 6-fold coordination with framework oxygens and water molecules in the cavity or channel. The ratio of water molecules to cations in such zeolites is low (between 1 and 4). For example in analcime, $NaAlSi_2O_6 \cdot H_2O$, the ratio is 1. However, certain other zeolites contain cations that are held within large cavities and are completely surrounded by water molecules, forming a fully hydrated cation, just as if it were in an aqueous solution. The cations and water molecules in faujasite have this arrangement (Baur, 1964). In such zeolites the ratio of water molecules to cations is between 5 and 7.

If the framework grows around cations in a template mechanism (Breck, 1974, p. 340), then we might expect zeolites like faujasite to grow from dilute solutions, in which the cations exist most commonly as hydrated complexes rather than bonded to fragments of alumino-silicate complexes as in gels. This supposition is supported by growth of synthetic faujasite. The synthetic phase with the faujasite structure and a composition close to the natural phases, Zeolite Y, grows from solutions with very high H_2O/Al_2O_3 ratios (Breck, 1974, Table 4.6).

Comparison of the compositions of the palagonitic glass with that of an unaltered bomb (Table 3), shows that the alkali and alkaline earth metals were released to the pore solution in the same proportions as they are in the faujasite (Fig. 2). Crystallization of phillipsite, however, fractionates K from the solution, while keeping a constant Na/Ca ratio. Although Al and Si must be released to the solution, the composition comparisons do not allow an accurate appraisal of the amounts or mechanisms of release of these elements.

Table 3. Compositional changes during the palagonitization of the basaltic glass

	unaltered bomb		palagonite		compositional
	weight %	mole%	weight %	mole %*	change in moles
SiO_2	49.0	45.3	42.6	39.7	-5.6
TiO_2	3.2	2.2	3.1	2.2	0
Al_2O_3	16.0	17.4	9.35	10.3	-7.1
Fe_2O_3	3.25				
FeO	8.85	9.0	12.8	9.0	0
MnO	0.2	0.2	0.2	0.2	0
MgO	5.0	6.9	4.7	6.6	-0.3
CaO	8.0	7.9	1.72	1.7	-6.2
Na_2O	4.6	8.2	0.44	0.8	-7.4
K_2O	1.6	1.9	0.96	0.6	-1.3
P_2O_5	0.5	0.4			
H_2O	0.1	0.6			
total	100.30	100.0			

the number of moles in this column was adjusted to make the change in iron and titanium equal to zero.

Acknowledgments

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