

HIGH- AND LOW-SILICA FAUJASITES:
A SUBSTITUTIONAL SERIES

ALAN C. WRIGHT, *Baroid Division National Lead Company, Houston, Texas*; AND J. PAUL RUPERT AND W. T. GRANQUIST,¹
Mellon Institute, Carnegie-Mellon University, Pittsburgh, Pennsylvania.

ABSTRACT

For synthetic faujasites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratios from 2.44 to 4.93, the unit-cell parameter, a , and the positions of certain infrared bands varied linearly with mole fraction of AlO_2^- . Natural faujasite from limburgite from the Kaiserstuhl in southwestern Germany was near the high-silica end member of the series, although the lattice constant and one of the infrared bands deviated slightly from the linear relationship of the synthetics. This deviation can be explained by the likely presence of a small amount of amorphous silica in the synthetic samples. A uniform nomenclature is proposed, for example faujasite, sodium (2.44), which identifies the structure, exchange cation and position in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ stability range.

INTRODUCTION

Knop (1892) states that the mineral faujasite was first discovered in 1844, in vesicles in limburgite from "der Kaiserstuhl im Breisgau," by deDrèe and Adam (see Knop, p. 120) and named by Damour (1844) after the French geologist, B. Faujas de Saint Fond. Damour's (1848) analysis of the mineral has been used in the recent literature, for example, by Barrer (1956, 1959) and Baur (1964).

Synthetic zeolites with the faujasite structure have been prepared by Milton (1959), designated Zeolite X, and by Breck (1964a), Zeolite Y.² The work of Bergerhoff and co-workers (1956, 1958), Broussard and Shoemaker (1960), and W. H. Baur (1964) established the structures of these synthetics to be the same as natural faujasite, within the limits of some uncertainty regarding the positions of water and exchangeable cations. Therefore, the differences existing between these substances are compositional (see Breck, 1964b, Table I): Zeolite X, $\text{Na}_{88}[\text{AlO}_2]_{86}(\text{SiO}_2)_{106} \cdot 264 \text{H}_2\text{O}$; faujasite, $(\text{Na}, \frac{1}{2} \text{Ca}, \frac{1}{2} \text{Mg})_{60}[\text{AlO}_2]_{60}(\text{SiO}_2)_{132} \cdot 260 \text{H}_2\text{O}$; Zeolite Y, $\text{Na}_{56}[\text{AlO}_2]_{56}(\text{SiO}_2)_{136} \cdot 264 \text{H}_2\text{O}$.

Breck (1964a) pointed out that a for the cubic unit-cell changes with the silica/alumina ratio, and stated that measurement of a could serve to

¹ To whom correspondence and reprint requests should be directed.

² Interestingly, the use of letter designations for zeolites has a historical precedent in the work of Koenigsberger and Müller, *Neues Jahrbuch für Mineralogie, Geologie, und Paläontologie, Beilageband, 44, 402 (1921)*, who discussed materials designated as Zeolites A, X, Y, and Z. Their zeolites were not the same as the Breck and Milton materials of the same letter designation.

determine the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. His patent claims a range of $\text{SiO}_2/\text{Al}_2\text{O}_3$ from 3 to about 6, and we infer that a should vary continuously over this range. The Milton patent claims $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios from 2 to 3, but makes no statement about the change of a over this compositional range. Zhdanov and co-workers (1964) studied the infrared spectra, including the lattice vibration region, of synthetic faujasites ranging in $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio from 2.22 to 5.10. The smooth variation of their spectra with composition demonstrated no reason to separate materials in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ range of 2 to 3 from those occurring between 3 and 6. The probability that Zeolite X, Y and natural faujasite were all members of a substitutional series prompted us to undertake the synthesis of synthetic faujasites of varying composition and to study the properties of these synthetics together with a sample of the natural mineral.

EXPERIMENTAL

Natural faujasite (104 mg) was handpicked from the crystalline material lining the vacuoles in limburgite from the Kaiserstuhl, Germany. Our sample and that analyzed by Damour (1848) were from the same locality. The selected crystals of faujasite were identified by their octahedral appearance. The crystals were ground to a fine powder and washed repeatedly with NaCl solution (10% w/w) and distilled water to convert the mineral to the sodium form. Removal of Ca^{2+} was followed by X-ray fluorescence scans at several stages of the ion exchange procedure.

An X-ray diffractometer trace with CuK_α radiation and $2^\circ 2\theta/\text{min}$ scanning rate demonstrated that our sample of the natural mineral was free of accessory phases. In Figure 1 this diffractometer trace is compared to a trace, obtained under the same instrumental conditions, of commercial Zeolite Y (Grade SK40) obtained from Union Carbide. Because of the small size of the natural faujasite sample, a small holder ($11 \text{ mm} \times 11 \text{ mm} \times \frac{1}{2} \text{ mm}$) was used for the two traces in Figure 1. As a result, the low angle peaks are attenuated because the sample intercepts only part of the beam; as the angle increases the peaks gradually approach their proper intensity. Therefore, relative intensities determined from Figure 1 would be in error. Comparison of the two patterns is valid, however, and establishes the structural similarity of the two materials.

Synthetic¹ faujasite was prepared by dissolving the required amounts of NaOH and NaAlO_2 in water, adding with stirring the proper amount of SiO_2 , allowing the resultant mixture to stand overnight at room temperature, and finally heating this "digested" slurry at reflux, with minimal stirring, for 24–48 hours. The silica source and the starting composition

¹ The synthesis technique was adapted from Barrer (1959) and the Milton (1959) and Breck (1964) patents.

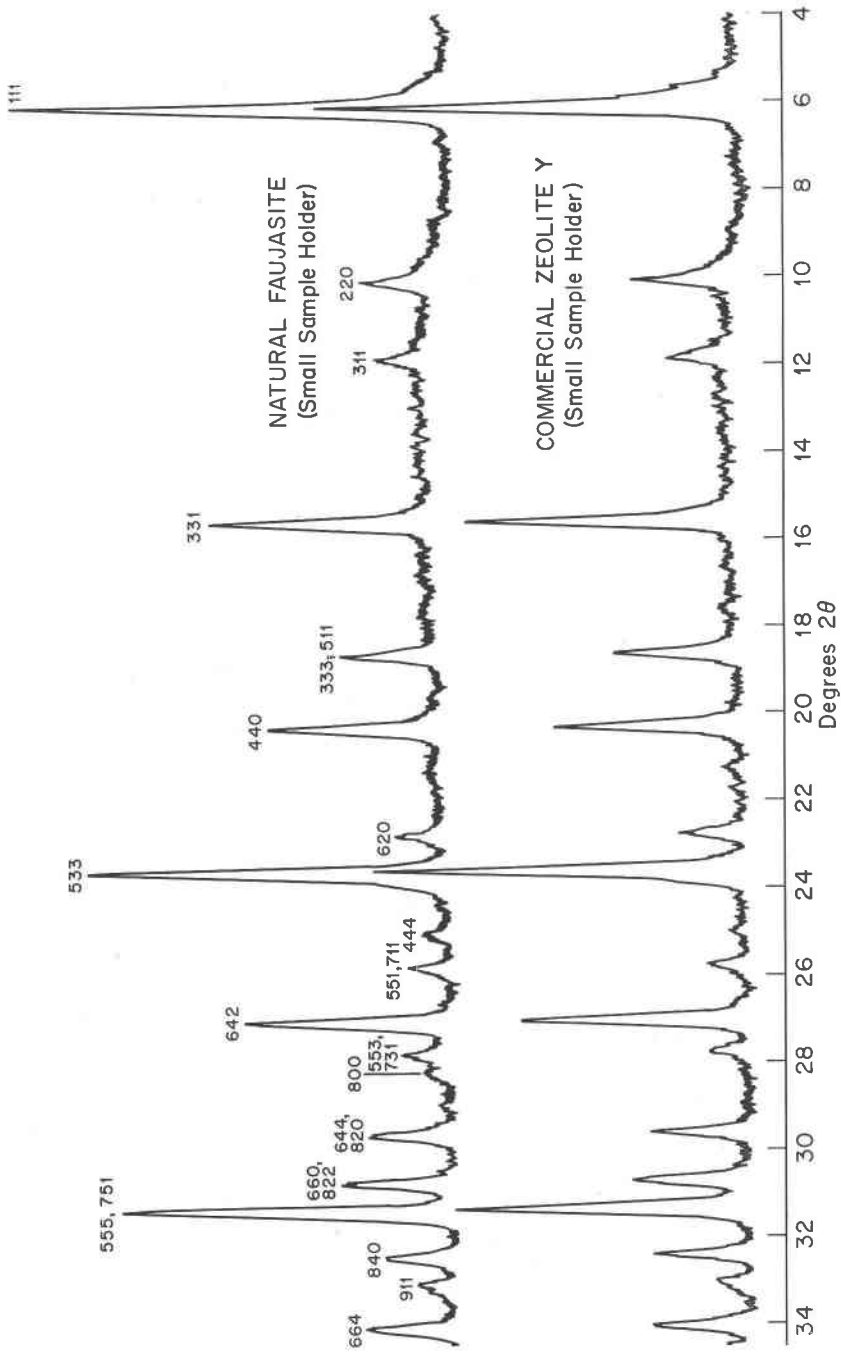


Fig. 1. Diffractometer traces for natural and synthetic faujasite. $\text{CuK}\alpha$ radiation.

proved to be extremely important to the crystallization of the very open faujasite structure. For $\text{SiO}_2/\text{Al}_2\text{O}_3$ product ratios above 3.5, we used a commercial high-solids silica sol, Ludox, sold by E. I. duPont de Nemours and Company. Product phases were identified by means of an X-ray diffractometer, with CuK_α radiation and $2^\circ 2\theta/\text{min}$ scans.

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratios of the sodium form of natural faujasite and the synthetic samples were determined by X-ray fluorescence using faujasite standards of known composition, determined by wet analysis. The compositional data are summarized in Table 1. Infrared transmission

TABLE 1. EXPERIMENTAL DATA FOR SYNTHETIC FAUJASITES

Silica Source	Starting Composition		Product Composition		<i>a</i> , Å
	Na ₂ O	SiO ₂	SiO ₂	X(AlO ₂ ⁻) ^a	
	SiO ₂	Al ₂ O ₃	Al ₂ O ₃		
Silica Gel	1.43	3.70	2.67	0.428	N.S.
Silica Gel	1.55	12.6	2.94	0.405	N.S.
Silica Gel	1.42	13.3	3.00	0.400	24.88
Silica Gel	1.42	13.3	3.12	0.391	N.S.
Silica Gel	1.58	12.5	3.14	0.389	N.S.
Ludox	.53	16.6	3.66	0.353	24.78
Ludox	.44	15.5	4.34	0.315	24.71
Ludox	.44	15.5	4.93	0.289	N.S.
Commercial zeolite X			2.44	0.450	24.97
Commercial zeolite Y			4.87	0.291	24.67
Natural faujasite			4.51	0.307	24.65

^a Mole fraction of alumina tetrahedra.

N.S. = not studied.

spectra over the range 400–4000 cm^{-1} were obtained for all samples through the use of either KBr pellets or Nujol mulls and either a Beckman IR-9 or IR-12 infrared spectrophotometer.

Five synthetic samples, including commercial Zeolites X and Y from Union Carbide, were selected on the basis of freedom from accessory phases and equivalent crystallinity (approximately equal intensities and widths at half height of corresponding reflections). These samples and the sodium form of natural faujasite were then studied in more detail. Portions of the samples were mixed with NaCl and the mixtures scanned on the diffractometer at $\frac{1}{8}^\circ 2\theta/\text{min}$ over the faujasite 555 and the NaCl 200 reflections. The displacement of the 555 from the NaCl 200, $\Delta 2\theta$, was

measured and, by the appropriate correction to the known θ of the NaCl 200, used to obtain θ for the faujasite 555. This Bragg angle was converted to a for the cubic faujasite structure, and the mole fraction of alumina tetrahedra calculated from the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (Table 1). We estimate that the values of a have a probable error of $\pm 0.01 \text{ \AA}$ and the mole fraction of AlO_2^- a probable error of ± 0.005 .

Absorption spectra were obtained on the same six samples under the following experimental conditions: Beckman IR-12; Nujol mulls with a concentration of 0.07 g of sample per ml; scanning speed of $20 \text{ cm}^{-1}/\text{min}$ from $350\text{--}400 \text{ cm}^{-1}$; $40 \text{ cm}^{-1}/\text{min}$ from $400\text{--}530 \text{ cm}^{-1}$; and $80 \text{ cm}^{-1}/\text{min}$ from $530\text{--}1300 \text{ cm}^{-1}$; period, 2 sec; demountable KBr cells with 0.01 mm spacers in both sample and reference beams, wavelength accuracy, $\pm 2\text{-cm}^{-1}$.

RESULTS AND DISCUSSION

Damour (1848) found natural faujasite to contain 43.35 percent SiO_2 and 15.80 percent Al_2O_3 ; corrected to a 100 percent basis, these values became 46.12 and 16.81 percent, respectively. Thus, on the basis of this work from 120 years ago, natural faujasite has an $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 4.66 and a mole fraction of AlO_2^- tetrahedra of 0.301. Our values, determined by X-ray fluorescence on the sample described earlier in this paper, were $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.52$ and $X_{\text{AlO}_2^-} = 0.307 \pm 0.005$. Dependent on one's point of view, this close correspondence is a tribute either to Damour's skill as an analyst or to the validity of the X-ray fluorescence technique. Barrer (1959) reported the lattice constant of natural faujasite to be 24.65 \AA ; our value is $24.65 \pm 0.01 \text{ \AA}$.

In Figure 2 we plot the lattice constant against the mole fraction of AlO_2^- tetrahedra.¹ The straight line was drawn on the basis of the five synthetic samples mentioned above. Three points from data taken from the literature also appear in Figure 2. Two of the points represent synthetic samples studied by Barrer (1959), and the third point corresponds to a synthetic faujasite studied by Broussard and Shoemaker (1960). We consider the experimental line and these literature points to be in good agreement.

The point for natural faujasite falls somewhat below the line; this deviation can be explained by assuming the presence of a small, relatively constant, amount of amorphous silica in the synthetic samples. That is, if one extrapolates the line to $a = 24.65 \text{ \AA}$, the lattice constant for the natural mineral, and notes the corresponding value of the mole

¹ Mole fraction of AlO_2^- is used as the independent variable in Figures 2 and 4 because of the linearity thus obtained. The dependent variables are not linear with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio, the more common compositional parameter.

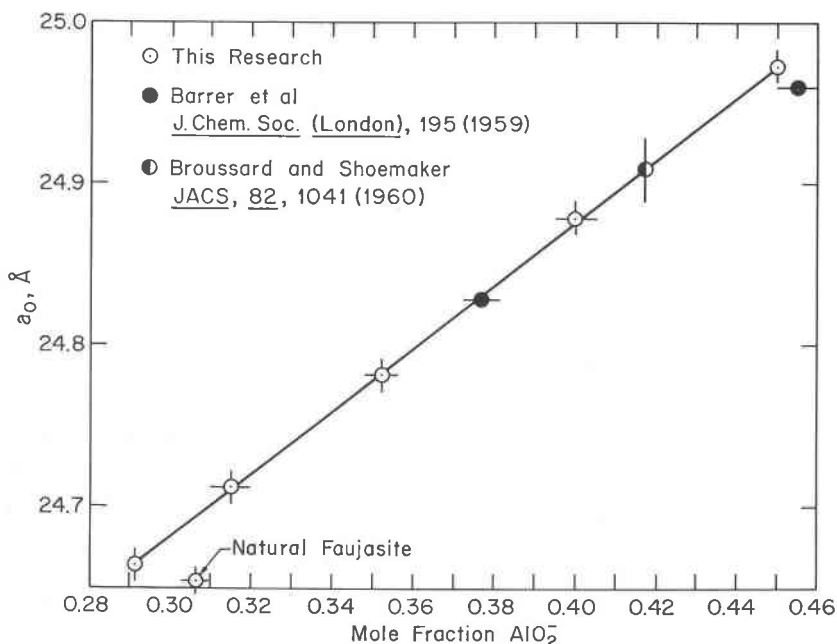


Fig. 2. The effect of Al^{3+} for Si^{4+} replacement on the lattice constant a . The vertical and horizontal lines through each point are estimates of the probable error. For the two synthetic end-members of the series, compositional error is not shown because these samples, determined by wet analysis, served as standards.

fraction of AlO_2^- , the difference between this extrapolated value and the measured $X_{\text{AlO}_2^-} = 0.307$ can be used to calculate the necessary amount of non-crystalline phase. Such a calculation demonstrates that an amount of amorphous silica no larger than 10–11 percent of the total weight of silica in the sample would be sufficient to explain the deviation shown. The assumptions underlying the calculation are: (1) quantitative transfer of alumina from the feed gel to the crystal, *i.e.*, the amorphous phase is only silica; (2) a relatively constant content of amorphous silica, an assumption which is reasonable since the samples were chosen on the basis of equivalent crystallinity as defined earlier; (3) no amorphous silica in the natural faujasite.

Since the sample studied by Broussard (1960) and one of the two faujasite samples synthesized and studied by Barrer (1959) fall on our experimental line, we must extend this assumption of a relatively constant small amount of amorphous silica to these samples as well. At first glance, this extension seems to weaken the hypothesis; more detailed consideration leads to the opposite view. Broussard's sample was a com-

mercial Zeolite X of lower alumina content ($X_{\text{AlO}_2^-} = 0.418$) than the sample of Zeolite X ($X_{\text{AlO}_2^-} = 0.450$) studied by us. One would expect the crystallinity of the two samples to be equivalent and the method of synthesis the same. If one assumes that actual commercial practice follows the teachings of Milton (1959) and Breck (1964), then the three commercial samples (our X and Y and Broussard's X) and our synthetic samples were all prepared by minor variations of the same procedure, which involves as a fundamental requirement crystallization from a silica-rich environment.

Of Barrer's two faujasite samples, the one ($X_{\text{AlO}_2^-} = 0.378$) which falls on the experimental line was crystallized from a silica-rich environment by a synthesis procedure very similar to that described in this paper, even to the selection of starting materials. Barrer's other faujasite was crystallized by the same technique, but the starting $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio was 1, the product mole ratio was 2.4, and alumina had to be eliminated. It is significant that this sample ($X_{\text{AlO}_2^-} = 0.455$), crystallized from an alumina-rich environment, falls below the experimental line. Thus, while we have no proof of the existence of the amorphous silica postulated above, the hypothesis does provide a likely explanation of the deviation of the natural faujasite from the experimental line.

Infrared absorption spectra of the five synthetic samples¹ appear in Figure 3. The positions of the peaks marked (A), (C) and the half-height (B), are dependent on the mole fraction of alumina tetrahedra. In Figure 4, we plot the position in cm^{-1} for these three features for the five synthetics and natural faujasite as a function of mole fraction of AlO_2^- and find a linear dependency. For the natural faujasite spectrum, the positions of peaks (B) and (C) fit the line; for peak (A), however, the point is displaced upwards. That is, the actual peak position occurs at too high a value of $X_{\text{AlO}_2^-}$. Extrapolation of the straight line, drawn on the basis of the synthetic samples, to the natural faujasite peak position would give a lower value of $X_{\text{AlO}_2^-}$ than observed. Since this peak, in the following argument, is attributed to Si-O-Si and Si-O-Al, the reasoning used above for the X-ray data would also apply here.²

We were able to make empirical assignments for some of these bands.

¹ The absorption spectrum for the sodium form of natural faujasite has not been included in Figure 3 to prevent further confusion in an already overcrowded figure. The curve is the same as those shown; the positions of the peaks (A), (B), (C) are indicated in Figure 4. We would be willing to furnish copies of this natural faujasite spectrum, on request.

² It should be noted that for pure SiO_2 (*i.e.*, only Si-O-Si) this peak occurs at 1120 cm^{-1} for amorphous silica and 1100 cm^{-1} for α -quartz. Both of these measurements were made at the concentrations and instrumental conditions used in the zeolite study. The effect is more complicated for the IR results because both the band position and $X_{\text{AlO}_2^-}$ would shift with added silica.

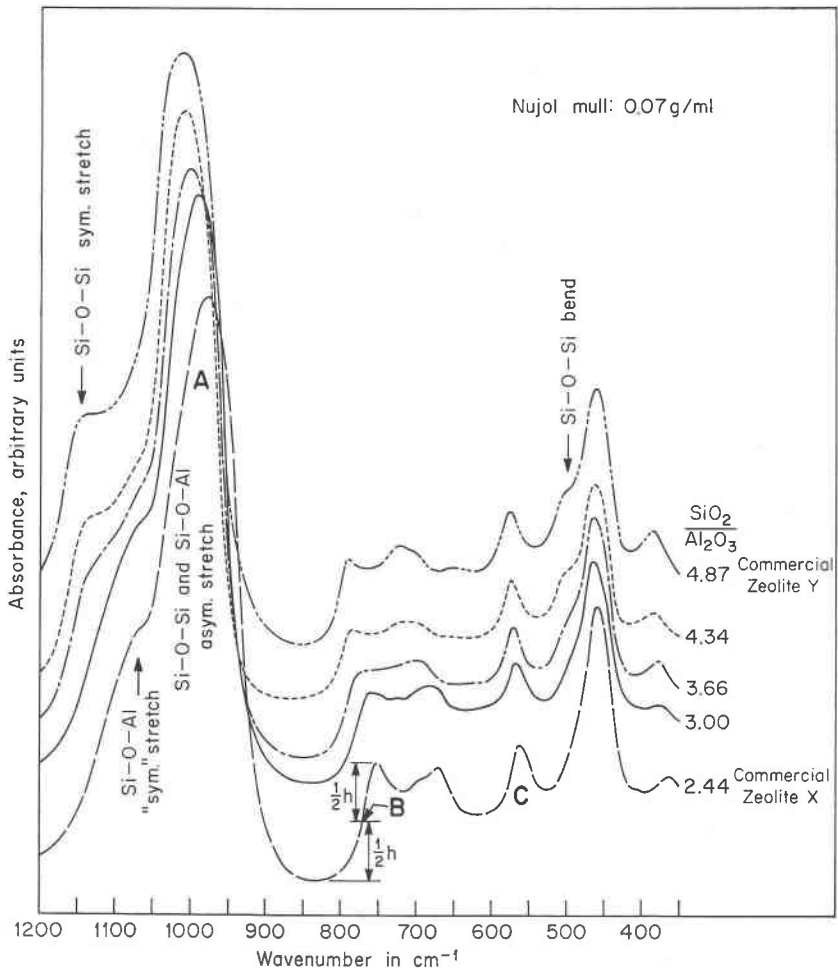


FIG. 3. Infrared absorption spectra for several synthetic faujasites.

If we assume no Al-O-Al linkages, the samples range from virtually no Si-O-Si to approximately equal numbers of Si-O-Si and Si-O-Al. Thus, we can identify the bands present in the spectra of the sample containing the most silica, but absent in the sample with the least silica, as due to Si-O-Si vibrations. Such bands are the shoulder at 1140 cm^{-1} (symmetric Si-O-Si stretching mode) and the shoulder at 505 cm^{-1} (Si-O-Si out-of-plane bending mode). Using these assignments as guides, we can tentatively identify the shoulder at 1075 cm^{-1} (most clearly seen in the sample with the least silica) as the Si-O-Al "symmetric" stretch. The strongest

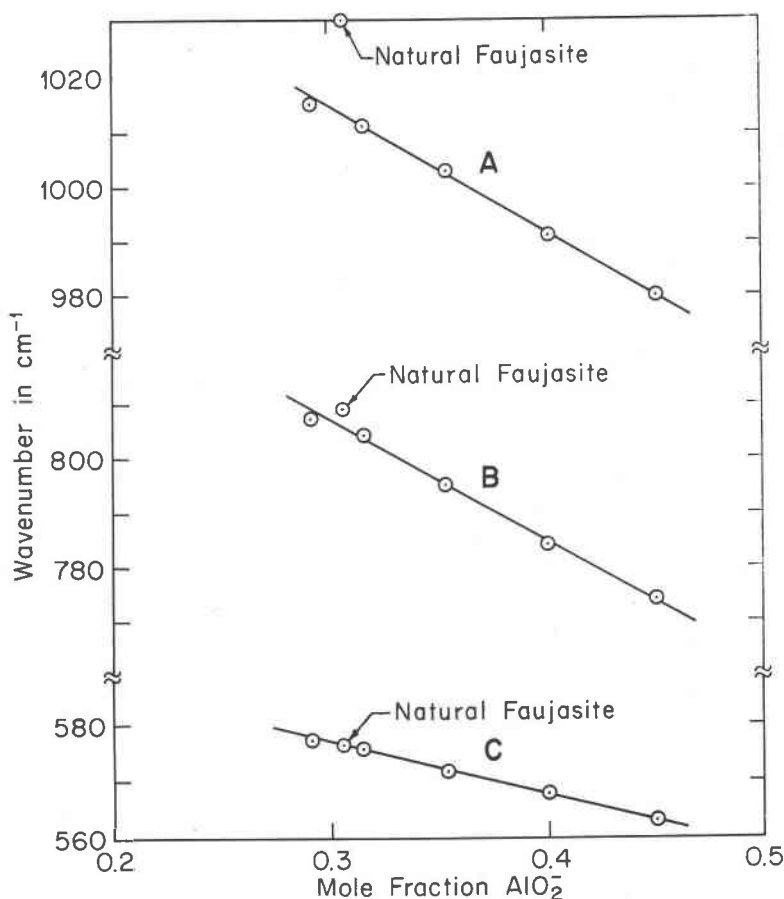


FIG. 4. The effect of Al^{3+} for Si^{4+} replacement on the position of various infrared bands.

band at about 1000 cm^{-1} is probably due to Si-O-Si and Si-O-Al asymmetric stretching modes. The gradual shift of this band with increase in the mole fraction of AlO_2^- , accompanied by little change in half-width, indicates that adjacent groups are strongly coupled so that one observes an averaging effect rather than the presence of discrete bands. Such discrete bands for Si-O-Si and Si-O-Al symmetric stretches are an indication of weak coupling. Probably the remainder of the bands in the region $800\text{--}350\text{ cm}^{-1}$ can be attributed to various more or less strongly coupled bending modes.

Our interpretation of the foregoing information is that the faujasite structure has stability limits that range at least from a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole

ratio of 2.44 to 4.93, with an even wider range possible.¹ Within these stability limits, a changes linearly with the mole fraction of alumina tetrahedra, as does the position of certain infrared absorption maxima in the lattice vibration region. We see no reason to divide this composition range at a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 3.0 and assign structures with ratios less than this value to Zeolite X, structures with ratios greater than 3.0 to Zeolite Y, and then suppose that natural faujasite is something else again.

We therefore would like to suggest a uniform nomenclature for this structural series. By virtue of priority, the name faujasite is proposed for the structure over the entire stability range. We can identify the exchangeable cation in the usual way, such as faujasite, sodium, for example. We then specify the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in parentheses after the exchange cation, such as for example, faujasite, sodium (2.5), and in this way locate the structure in the stability range. Thus, the correspondence between this proposal and the particular samples of Zeolites X and Y used in this study are as follows:

Zeolite X: faujasite, Na (2.44)

Zeolite Y: faujasite, Na (4.87)

In this proposal, we assume that the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ mole ratio is always unity, although it is recognized that in the high alumina end of the series, the ratio is frequently slightly less than unity, presumably because of hydrolysis.

ACKNOWLEDGMENTS

The authors thank Baroid Division National Lead Company for their support of this work and permission to publish it.

Dr. S. S. Pollack, Mellon Institute, instructed us in the microscopic identification of faujasite and furnished us with the X-ray traces in Figure 1. Mr. Hugh O'Donnell, also of Mellon Institute, had the patience to work at the microscope and select the 104 mg of faujasite crystals. Mr. D. H. Larsen, Los Angeles, called our attention to the book by Knop and the work of Koenigsberger and Müller. We are indebted to these men for their contributions.

The paper, without the natural faujasite data, was presented at the 1967 Spring Symposium of the Pittsburgh Catalysis Society.

REFERENCES

- BARRER, R. M., W. BUSER, AND W. F. GRÜTTER (1956) Synthetischer "Faujasit." I. Eigenschaften und Ionenaustauschcharakter. *Helv. Chim. Acta*, **39**, 518-530.
- , J. W. BAYNHAM, F. W. BULTITUDE, AND W. M. MEIER (1959) Hydrothermal Chemistry of the Silicates. VIII. Low-temperature crystal growth of aluminosilicates, and of some gallium and germanium analogues. *J. Chem. Soc. (London)*, 195-208.

¹ In this work, we make no attempt to establish the limits of the stability range.

- BAUR, W. H. (1964) On the cation and water positions in faujasite. *Amer. Mineral.*, **49**, 697-704.
- BERGERHOFF, G., H. KOYAMA, AND W. NOWACKI (1956) Zur Kristallstruktur der Mineralien der Chabasit—und der Faujasitgruppe. *Experientia*, **12**, 418-419.
- , W. H. BAUR, AND W. NOWACKI (1958) Über die Kristallstruktur des Faujasites. *Neues Jahrb. Mineral. Monatsh.*, 193-200.
- BRECK, D. W. (1964a), Crystalline Zeolite Y, U.S. Patent 3,130,007, April 21, 1964. (1964b), Crystalline molecular sieves. *J. Chem. Ed.*, **41**, 678-689.
- BROUSSARD, L., AND D. P. SHOEMAKER (1960) The structures of synthetic molecular sieves. *J. Amer. Chem. Soc.*, **82**, 1041-1051.
- DAMOUR, A. (1844), Der Faujasite, eine neue Mineral-Gattung. *Jahrb. Mineral.*, 72-73.
- (1848), Nouvelle analyse de la Faujasite. *Ann. Mines, Ser. 4*, **14**, 67-68.
- KNOP, A. (1892), *Der Kaiserstuhl im Breisgau*. Engelmann, Leipzig.
- MILTON, R. M. (1959) Molecular sieve adsorbents. *U. S. Pat.* 2,882,244, April 14, 1959.
- ZHDANOV, S. P., A. V. KISELEV, V. I. LYGIN, AND T. I. TITOVA (1964) Infrared spectra of synthetic faujasites varying in composition and of their adsorbed water. *Zhurn. Fiz. Khim.*, **38**, 2408-2414. [Transl. in *Russian J. Phys. Chem.*, **38**, 1299-1303.]

Manuscript received, October 30, 1967; accepted for publication, April 8, 1968.