We have now determined accurate angles of the zeolite crystal using a two-cycle goniometer as shown in the corrected Figure 1. Full determination of the morphology of yugawaralite from the Shimoda, Japan (a new locality) has been reported by Sameshima (1969).

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HIGH- AND LOW-SILICA FAUJASITES: AN ADDENDUM

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Concern has been expressed regarding a conflict between the conclusions and proposals contained in the paper "High- and Low-Silica Faujasites: A Substitutional Series" by A. C. Wright, J. P. Rupert and W. T. Granquist (1968), hereafter referred to as WRG; and some composition-dependent properties of the faujasite group reported in a paper by Breck and Flanigen (1968), referred to after this as BF. In particular, Professor J. V. Smith, in a private communication, has: (1) questioned the presence of the small ($<10\%$ of the total silica present) amount of amorphous silica proposed by WRG to account for the displacement of the sodium form of natural faujasite from the linear relationship (cell-dimension *vs* mole fraction of AlO_2^-) displayed by a series of synthetic sodium faujasites; (2) suggested Al, Si ordering in the natural faujasite as a more likely explanation of this deviation; (3) cited the BF results on triethylamine adsorption and on cell-dimension *vs* number of Al atoms/unit cell for Ca-exchanged synthetic faujasites as evidence of a discontinuity in the faujasite series at $Si/Al=1.5$, and the conductivity results of Freeman and Stamires (1961) as providing a major distinction between X and Y Zeolites; and 4) objected to the WRG nomenclature proposal because it ignores this discontinuity. Point 3 is significant because the discontinuity forms the basis for division by BF of the faujasite series

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into the so-called Zeolite X and Zeolite Y composition ranges. It is the contention of WRG that the faujasite series is continuous over the stability range (*i.e.*, from the high-alumina end of the Zeolite X range to the high-silica end of the Zeolite Y) and that no justification exists for the two sub-ranges.

It is the purpose of this addendum to delineate this conflict, discuss the discontinuities described by BF, and set the stage for further contributions directed towards these questions. We thank Professor Smith for raising these issues and providing us with his point of view.

AMORPHOUS SILICA AND/OR AL, SI ORDERING

The deviation of sodium-exchanged natural faujasite from the linear relationship (cell-dimension *vs* composition) exhibited by the synthetic sodium faujasites can be due to incorrect mole fractions of AlO_2^- for the synthetic series arising from the presence of amorphous silica, or to Si, Al ordering in the natural mineral which reduces the cell-dimension of the natural mineral below that of the synthetic analog (same mole fraction of AlO_2^-).

WRG do not present evidence for the existence of amorphous silica. However, some support for this postulate exists in infrared work reported by Angell and Schaffer (1965) and Hattori and Shiba (1968). Both studies propose as one possible explanation of the 3750 cm^{-1} band the presence of siliceous impurity in the zeolite. The presence of the small ($<5\%$ of the anhydrous sample weight) amounts of silica proposed by WRG is difficult to establish or refute by X-ray techniques; perhaps definitive evidence could be obtained by a suitable modification of these infrared procedures.

In the original WRG manuscript, ordering in the natural faujasite was proposed as an alternative explanation. This suggestion was discarded during the reviewing process because the decrease in cell-dimension seemed too large to be due to ordering. Recently, Iijgima and Harada (1969), in a discussion of authigenic zeolites from Oahu, Hawaii, described faujasite with $a = 24.69 \pm 0.02$ Å and a Si/(Al+Fe) = 2.33 (0.48% Fe_2O_3 was found in the crystals), corresponding (counting Fe as Al) to $X_{AlO_2^-} = 0.300$ or 57.6 Al/unit cell. This natural faujasite contains *less* Al (based on WRG; the same amount based on Damour, 1848) than the Kaiserstuhl samples, but has a *larger* cell dimension (exchange cations: Kaiserstuhl, Na, Ca, Mg; Oahu, Na, Ca, K) and falls, perhaps fortuitously, on the WRG a vs. $X_{AlO_2^-}$ line for the synthetic sodium faujasites. If a sample can be obtained, it will be converted to the sodium form and studied under the conditions used by WRG. The two natural and the synthetic samples can then be compared in the same exchanged form and the same hydration conditions.

Smith's discussion, coupled with the existence of specimens of natural faujasite with *a* differing by 0.04 Å, prompts us to advance this ordering explanation once again. Perhaps both explanations are valid and each contributes part of the observed deviation.

TRIETHYLAMINE ADSORPTION

Our work on the faujasite group has continued with a study of the properties of the series as functions of the mole fraction of AlO_2^-. Adsorption of various gases and vapors, among them triethylamine, is now under study by our colleague, J. V. Kennedy. We reserve the detailed results to a paper under preparation, but here respond to the BF discontinuity with two figures.

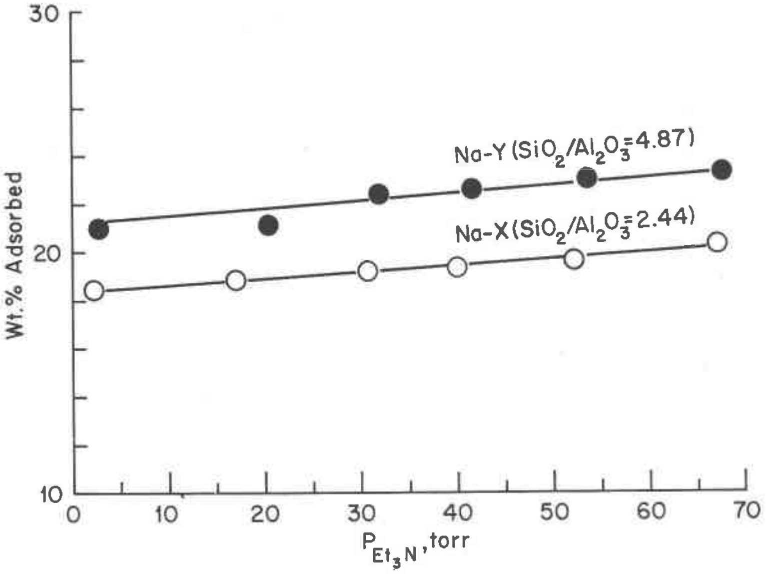

FIG. 1. Equilibrium adsorption of triethylamine on two synthetic faujasites. Conditions: Quartz helix balance; samples outgassed at 350°C and 10^{-6} torr overnight; balance case at 36°C; Et_3N source at various T to produce stated P; sample at 26°C.

Figure 1 presents equilibrium sorption data for triethylamine on sodium X and Y faujasites (and here we use "X" and "Y" to mean specific compositions, not ranges; see WRG), compositions which correspond to points on both sides of the BF discontinuity. The data were obtained at various vapor pressures of the amine, ranging from ca. 2–70 torr. Both of the curves in Figure 1 must, of course, go to 0 percent sorption at 0 torr, and it is one of the unique features of the faujasite structure that such remarkable sorption can occur at very low vapor pressures. We maintain that the small difference in sorption capacity between X and Y

(19.4% *vs* 22.4% at 10 torr) can be explained without recourse to a discontinuity.

Since the cell dimension increases with mole fraction of AlO_2^-, one would expect a corresponding increase in the volume of the cages, and the normal expectation would be that X would sorb more than Y; the reverse situation is observed. However, the X unit cell contains 86 monovalent charge-balancing cations, while the Y cell contains, in only slightly less volume, 56 such ions. Without here considering distribution over S_I, S_{II}, etc., cation sites, we suggest that the increase in the number of such cations blocks access by triethylamine to more of the X network of cages than the Y.

In Figure 2, we have replotted the data from BF Figure 9 as wt.% sorbed *vs* mole fraction of AlO_2^-. To prevent increasing the scatter because of uncertainty in position, we have taken the points from a figure, drawn on graph paper, which appears in the file history of the prosecution

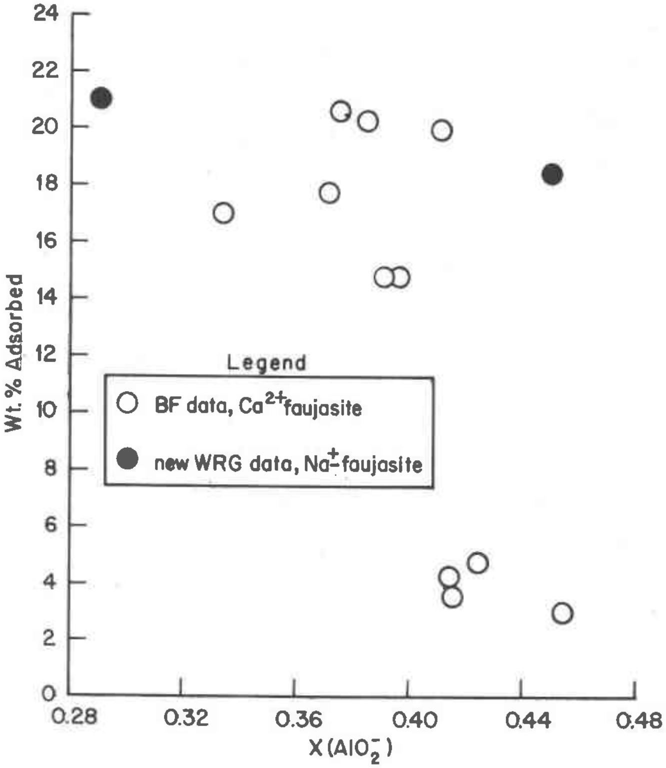

FIG. 2. Triethylamine adsorption as a function of mole fraction of AlO_2^- tetrahedra. Open circles are the Breck (1964) and BF data on Ca-exchanged faujasites; solid circles are new data on sodium faujasites (commercial X and Y).

of the Breck (1964) U. S. Patent. The figure appears as part of an affidavit, dated February 27, 1963, filed by Breck in the course of the prosecution. Comparison of this graph with the BF Figure 9 shows both to be based on the same experimental data.

Two points cross-plotted from our Figure 1 at $P = 3.0$ torr also appear in Figure 2. In comparing these results one should remember that the BF samples are primarily Ca-faujasites (the caption for BF Fig. 9 states that "the degree of calcium exchange is greater than 85 mole% for all zeolite samples"), while our two points were obtained for the sodium forms. The BF adsorption was measured at 2.2 torr for a time stated by BF as 4 hours, but by the Breck affidavit as 1.2 hours. Our data were taken at equilibrium, which demanded times up to eight hours at the lowest triethylamine vapor pressures. We do not attempt to draw the best curve through this collection of points, but leave this process to the reader's imagination. We submit that the extreme scatter shown is probably the result of insufficient equilibration time for the adsorption process, and that the supposed discontinuity is the result of such insufficiency.

CELL-DIMENSION A CONTINUOUS OR DISCONTINUOUS FUNCTION OF COMPOSITION

The data of WRG and BF are in agreement concerning the continuous variation of cell dimension with composition for the sodium forms of synthetic faujasites synthesized from sodium-bearing systems. However, BF (Fig. 10) find discontinuities in a plot of cell constant *vs* composition for *dehydrated calcium* forms prepared from these sodium faujasites by an ion-exchange process, followed by heating in air at 400°C for 16 hours. BF differentiate between the so-called X and Y regions on the basis of one such discontinuity.

It might be more logical to attribute these irregularities, and, in fact, the scatter of all these points, to a nonconstant level of calcium exchange. We are particularly disturbed by the statement in the caption of BF, Fig. 10: "the degree of calcium exchange is greater than 85 mole % for all zeolite samples." In view of the increase in cell dimension caused by calcium exchange (compare the Ca and Na forms at constant Al content), it seems important to use in such a study homoionic Ca-samples of equivalent crystallinity, or at least a series of samples of constant Ca^{2+}/Na^{+} ionic ratio. On the basis of the statement quoted above, a variability in the extent of calcium exchange probably exists and this variability might well be enough to explain the Ca results. However, consider the work reported below.

More important to this question of the continuity of cell dimension with composition is the recent paper by Dempsey, Kühl, and Olson

(1969), referred to below as DKO. They presented cell dimensions and compositions (as Al/unit cell) for some 17 *hydrated* synthetic *sodium* faujasites over the composition range 52–96 Al/unit cell. Their results differ markedly from WRG and BF in that DKO show two distinct breaks at Si:Al near 1.4:1 and 2:1. These breaks, for which the paper presents a plausible explanation, separate the compositional range into three regions and are similar to those which occur in the BF *dehydrated* synthetic *calcium* faujasites.

The DKO results further differ from both BF and WRG in that DKO consistently show a larger cell dimension at any given composition over the entire compositional range. For example, at 59 Al/unit cell: the Na form of Kaiserstuhl faujasite (WRG) has a cell dimension of 24.65 Å; the WRG (and BF) line gives $a = 24.70$ Å; and the DKO line corresponds to $a = 24.74$ Å. If the compositions are correct (*i.e.*, all Al and Si is present as crystalline faujasite), one would conclude that the (Al, Si) ordering is such that Kaiserstuhl >WRG>DKO, where the DKO is the least ordered.

DKO do not give details of the synthesis of these samples. It is important to a critical comparison of WRG and DKO to know if the syntheses differed in any detail and particularly if a different method of synthesis was used in each of the three ranges. Obviously, much more work is required with emphasis on the regions of the DKO breaks.

CONDUCTIVITY

In our opinion, the excellent work of Freeman and Stamires (1961) does not establish a difference between the X and Y composition ranges, which is meaningful for the issue treated here. The data demonstrate an increase in ΔH for the conduction process as the number of Al for Si replacements decreases. The mechanism of the process must be a jump of a charge-balancing cation (particularly when such a cation is monovalent) from a position near the site of negative charge density at an Al/Si replacement to another such site. It seems reasonable as a first approximation that ΔH for this process should increase as both the number of charge carriers and negative charge density sites decrease. It is not clear that an explanation of the conductivity data requires two energetically-discrete types of site. There are several different crystallographic positions [see, for example, Breck (1964b)] for the charge-balancing cations in the hydrated faujasite structure, and the binding energies of cation to site must differ in these different positions. It may be that the conduction process involves only the least tightly bound cation type (Type III), which is depleted in numbers as the composition changes toward high-silica, or perhaps as such depletion occurs more tightly bound cations become involved in the conduction process. In either case, ΔH should increase with depletion. The S-shape of Freeman and Stamires' curve (ΔH *vs* composition) supports the latter suggestion. However, the curve does not show any evidence of a discontinuity, but does demonstrate a smooth increase which occurs over the Y range.

CONCLUSIONS

We conclude that:

1. The deviation of the sodium-exchanged form of natural faujasite from the linear relationship (cell-dimension *vs* mole fraction of AlO_2^-) displayed by a series of synthetic sodium faujasites ranging in $X(AlO_2^-)$ from 0.291 to 0.400 can be attributed to the presence of small amounts ($<5\%$ of total sample weight) of amorphous silica, or to the existence of a higher degree of ordering in the natural mineral, or to both.
2. The discontinuity in the Et_3N adsorption of Ca-exchanged forms of a series of synthetic faujasites rests upon uncertain experimental evidence and, in fact, may be an experimental artifact.
3. Rather than justifying separation of this substitutional series into the so-called Zeolite X and Y ranges, the experimental evidence now available supports either the continuous variation of cell dimension with composition or separation into three discrete compositional ranges.
4. A nomenclature based upon the use of the word "faujasite" as a group name with designation of charge-balancing cation and composition (in terms of SiO_2/Al_2O_3, Si/Al, $X_{AlO_2^-}$, or number of Al atoms/unit cell) makes more sense than the use of the terms Zeolite X and Y for other than specific compositions.

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