MATTERS ARISING

Si, Al ordering
in Linde A zeolite

ALTHOUGH we congratulate Bursill *et al.*¹ on their excellent high-resolution images of zeolite Linde A, we wish to question some of their interpretation—in particular the evidence on Si, Al ordering.

For a Linde A zeolite with Si/Al ratio of exactly 1, regular alternation of Si and Al leads inexorably to a super-cell with $a = 2.4$ nm and space group $Fm\bar{3}c$ from the pseudo-cell with $a = 1.2$ nm and space group $Pm\bar{3}m$ for fully disordered Si and Al. Although many structure determinations have been made with the pseudo-cell, the superstructure diffractions are easily observable on long-exposure X-ray photographs. Gramlich and Meier² obtained a satisfactory refinement of the superstructure of Zeolite A in which alternate tetrahedra had dimensions appropriate for occupancy at least mainly by Si and by Al. Recent refinements of dehydrated K-exchanged zeolite A (ref. 3) and dehydrated zeolite A (ref. 4) (the as-synthesized Na variety) were made to test the concept of zero-coordination, and satisfactory refinements were obtained of the superstructure. All these X-ray diffraction data, and much unpublished data, cannot be explained by the ordering model proposed by Engelhardt *et al.*⁵ on the basis of high-resolution magic-angle spinning ^{29}Si NMR measurement. This model yields a unit cell with $a = 1.2$ nm and space group $Pm\bar{3}$, and can be ruled out immediately by the X-ray diffraction data which require a cell with $a = 2.4$ nm. In the following, note that zeolite A has strong alternation of Si and Al on the tetrahedral nodes of the framework, and that only a small percentage of nodes are not surrounded by four atoms of the opposite type.

Pluth and Smith³ found evidence from detailed electron microprobe analyses of A crystals made by Charnell's method that the Si/Al ratio is >1 (~ 1.03). This was supported by population estimates from published^{3,4} and unpublished X-ray measurements which indicated less than 12 exchangeable monovalent cations in the pseudo-cell (for example 11.5 Na atoms in dehydrated zeolite A (ref. 4)). Such deviation from the ideal value must cause some Si atoms to be surrounded by less than four Al atoms. Silica-rich regions might have a different stability than regions with Si/Al equal to unity, and Bursill *et al.* might find it useful to measure the Si/Al ratio of their crystals.

Although Pluth and Smith refined their structures with the 2.4-nm cell and space group $Fm\bar{3}c$, they and earlier workers found several observed diffractions which violated the c glide plane. Further measurements are now in progress to dis-

Fig. 1 Three ordering schemes for zeolite A. *a*, Complete disorder of tetrahedrally coordinated cations would give a 1.2-nm cell repeat with space group $Pm\bar{3}m$. *b*, Regular alternation of Si and Al requires 2.4 nm and $Fm\bar{3}c$. *c*, The isometric cell for the model of Engelhardt *et al.*⁵ has a 1.2-nm repeat and $Pm\bar{3}$; note the absence of a mirror plane in (110) directions.

cover the source of these violations. Note that these diffractions are weak and might result from the exchangeable cations and not from the Si and Al atoms. In the dehydrated K-exchanged- and Na-A varieties, some exchangeable cations have a low occupancy of sites on the walls of cavities, and local distortions of the framework can be expected. Such distortions must be considered as a potential cause of space group violations.

The ^{29}Si NMR results were interpreted by Engelhardt *et al.*⁵ in terms of an ordering scheme in which each Si is surrounded by three Al and one Si, and each Al by three Si and one Al (Fig. 1). This ordering scheme gives an isometric cell with $a = 1.2$ nm and space group $Pm\bar{3}$, in contrast with 1.2 nm ($Pm\bar{3}m$) for complete disorder and 2.4 nm ($Fm\bar{3}c$) for regular alternation of Si and Al. The 3:1 ordering scheme is not compatible with the 2.4-nm cell repeat found consistently in long-exposure X-ray photographs, and can be ruled out except for small regions. Simple comparison of NMR data from one zeolite with another is obviously unreliable, and further interpretation is needed of the

data in ref. 5. The observation by Bursill *et al.* of hkl (all odd) reflections with $h + l = 2n$ does not confirm "the recent criticism of space group $Fm\bar{3}c$ ". This class of diffractions obeys the F centred lattice deduced by the X-ray crystallographers. Violations of the condition for the c glide plane (l must be even in hhl and $0kl$) are needed to cast doubt on $Fm\bar{3}c$ (for example, observation of 111; 3,3,17; 7,7,23; 13,13,11; 15,15,15 for dehydrated A ref. 4).

We suggest that Linde A zeolite has strong alternation of Si and Al atoms, and that only local regions deviate therefrom. The new refinement of dehydrated A zeolite⁴ could be used to make a computer-simulated image for comparison with Fig. 1 of ref. 1: qualitatively a good match is likely, thereby indicating extraction of water by the pre-pumping procedure¹. We look forward to more important observations of zeolites by electron microscopy, and suggest that existing X-ray diffraction data can provide a fundamental basis for interpretation.

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BURSILL ET AL. REPLY—We thank Smith and Pluth for their comments but we are not convinced by their arguments. Recent experimental results reaffirm that Na-A zeolites possess an aluminosilicate ordering scheme, in which each Si ion is connected through oxygen bridges to three Al ions and one Si ion, and each Al ion to three Si and one Al; that is 3:1, rather than 4:0, ordering prevails.

Our reasons for disputing the accepted space group $Fm\bar{3}c$ rests partly on some of the X-ray results of Smith and Pluth^{1,2} but chiefly on results from three other, independent techniques: electron diffraction^{3–5}, high-resolution magic-angle spinning ^{29}Si NMR^{6–8}, and neutron diffraction⁹. Weak superlattice reflections appear readily in electron diffraction patterns, requiring exposure times of ~ 1 s. enabling many hundreds of crystals