

alternative pathways of differentiation⁶. Ammonia can do this because it is a permeant weak base, but DIF, they suggest, acts by blocking a cell-surface proton pump. This is supported by, among other things, the exciting new finding that low concentrations of diethylstilbestrol, a potent inhibitor of proton pumps in fungi, can efficiently induce stalk formation. It remains to be demonstrated however that such pumps exist in *Dictyostelium* and are modulated by DIF levels; furthermore it will be necessary to determine the structure of DIF, and to find out how (and indeed whether) DIF and ammonia concentrations can carry positional information. But to be able to formulate such specific questions at all is a unique achievement in the field of pattern formation.

Recent evidence from several groups complicates any straight-forward morphogenetic gradient explanation of slime mould pattern formation. Two years ago, Sternfeld and David¹³ discovered a third minority cell type in *D. discoideum* slugs which shares staining and ultrastructural properties with prestalk cells. These cells, the 'anterior-like' cells, are dispersed throughout the posterior (prespore) zone. Anterior-like cells sort out to form a new tip when the prestalk zone is removed; this is presumably prevented in normal slugs by a diffusible inhibitor released by prestalk cells. Some of the remaining prespore cells quickly redifferentiate to replenish the supply of anterior-like cells, and in fact the new prestalk zone is made up partly of redifferentiated prespore cells¹⁴.

Since pattern regulation, in prespore isolates at least, seems to involve sorting out of randomly dispersed cell types, it seems possible, by analogy, that the original pattern is formed by random differentiation followed by sorting out. This idea, first promulgated by Takeuchi¹⁵, has received some support from the finding that prespore cells are first found to be intermingled with non-prespore cells during the late aggregate stage^{16,17}. Unfortunately, it is not yet possible to distinguish between prestalk cells and undifferentiated

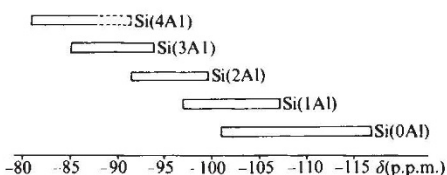
cells in such aggregates, and it would be necessary to demonstrate actual intermingling of both cell types as they differentiate to rule out positionally specified differentiation. Prestalk cells do make specific proteins¹⁸, so it is hoped that monoclonal antibodies will soon provide the tools necessary to settle this question. But even in the case of such salt and pepper patterns, diffusible substances would still be a plausible basis for the control of cell proportions: only the effective range of the morphogens would be shorter.

Zeolites

Bond angles and chemical shifts

from Lovat Rees

ZEOLITES are porous tectosilicates of immense importance as catalysts and molecular sieves in the petroleum industry. Recently much interest has been focused on the short-range Si-Al order in the zeolite framework, since this appears to be fundamental to the catalytic and other chemical properties. Thermal stability, important for industrial applications, is known generally to increase with increasing Si/Al ratio, and to this end aluminium can be removed from the framework either by treatment with SiCl_4 or by heat treatment of the ammonium-exchanged zeolite, without disrupting the original topology and crystallinity of the parent material.



Overlapping shift ranges of different aluminosilicate networks, $\text{Si}(n\text{Al})$, where $n = 0-4$.

The latter process is widely used to produce 'ultrastable' faujasite — the catalyst used by all major oil companies for cracking and hydrocracking reactions in petroleum refining.

Since the first study of zeolites by high-resolution solid-state ^{29}Si nuclear magnetic resonance (NMR), described in 1979 (ref.1), considerable progress has been made in elucidating the structure of both natural and synthetic zeolites using the technique. In the study of Si-Al structure the method gives distinct chemical shifts for SiO_4 tetrahedra, depending on how many AlO_4 tetrahedra they are linked to via oxygen bridges. It is also possible to estimate the relative numbers of the various $\text{Si}(n\text{Al})$ (where $n = 0-4$) links from signal intensities.

However recent studies of some thirty natural and synthetic zeolites² have shown that as well as the number of neighbouring aluminium atoms, other structural features, such as bond angle, cation type

and position, may induce fairly large shift contributions. Therefore, the shift ranges of $\text{Si}(n\text{Al})$ units with different values of n may overlap significantly for different types of aluminosilicate network (see the figure) and the assignment of n from chemical shifts alone may lead to erroneous conclusions^{3,4}.

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In this issue of *Nature*, Smith and Blackwell (p.223) have tested empirical correlations between the chemical shift for aluminium-free silicates (that is, $\text{Si}(n\text{Al})$ with $n = 0$) and several geometrical parameters in a number of silica polymorphs. They find strong correlations between chemical shift and mean Si-Si bond length and with mean Si-O-Si bond angle, and a weak correlation with mean Si-O bond distance. These results suggest that we are now closer to a more exact understanding of the reasons for the spread of chemical shifts, and confirm an earlier suggestion by Thomas *et al.*⁵ that a qualitative correlation should exist between chemical shifts and T-O-T bond angles (where T = Si or Al) in zeolite frameworks.

With a knowledge of atomic coordinates of a zeolite structure, unambiguous assignments of n may become possible even for those zeolites that show only a single NMR resonance. For example, the recently published ^{29}Si NMR spectrum of calcined silicalite containing nine different chemical shifts⁶ has been confirmed by Smith and Blackwell. But because the atomic coordinates were not known with sufficient accuracy Smith and Blackwell could not assign the lines to specific SiO_4 tetrahedra.

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