

form of presentation would, of course, put the presenting cell at risk of being killed by class I-restricted cytotoxic T lymphocytes but, guarding against this, induced actively cytotoxic cells may move into the blood and lymph rather than stay in the central lymphoid organs. Are there two forms of presentation of exogenous antigen, one the endocytic pathway for soluble antigen

operative in all cells but immunologically relevant only in cells which express class II molecules, and another performed only by phagocytic cells? Time will tell. □

Michael J. Bevan is in the Department of Immunology, Research Institute of Scripps Clinic, 10666 North Torrey Pines Road, La Jolla, California 92037, USA.

Structure determination

Solid-state NMR comes of age

Colin A. Fyfe

HIGH-RESOLUTION nuclear magnetic resonance spectroscopy (NMR) of liquids and solutions has developed into the most widely used analytical technique for the determination of the structures of unknown chemical compounds. It has recently become possible to obtain similar information from solids which, when used together with the information from traditional X-ray diffraction techniques, yields a complete picture of the structure of many materials. Elsewhere in this issue Kirkpatrick and co-workers (*Nature* **325**, 236; 1987) describe work on plagioclase feldspars that represents the state-of-the-art in this area, particularly because the complementary nature of the NMR and diffraction techniques is fully exploited.

In high-resolution solution NMR, signals are observed whose frequencies (chemical shifts) are diagnostic of the local magnetic (chemical) environment and, most importantly, whose relative intensities reflect the numbers of nuclei in the different environments. These two elements are critical in the determination of unknown chemical structures. However, NMR experiments on protons in solid materials yield only broad, featureless absorptions as the direct dipole-dipole interactions between the abundant ^1H nuclei are orders of magnitude greater than the chemical shifts from which structural information is obtained.

By working with dilute nuclei such as ^{13}C and ^{29}Si , and using high-power decoupling to remove dipolar interactions from the protons, 'magic-angle' spinning spectroscopy of the sample (Andrew, E.R. *et al.* *Nature* **182**, 1659; 1959 and Lowe, I.J. *Phys. Rev. Lett.* **22**, 285; 1959) to produce the isotropic chemical shifts and cross-polarization (Pines, A., Gibby, M.G. & Waugh, J.S. *J. chem. Phys.* **56**, 1776; 1972) to enhance the signal-to-noise ratio, J. Schaefer and E. Stejskal of Monsanto were able to obtain spectra of good resolution from completely solid samples (*J. Am. Chem. Soc.* **98**, 1031; 1976). In the case of many inorganic materials such as glasses, zeolites, minerals and clays, the interactions of protons are not important and the experiment is the very simple one

of magic-angle spectroscopy alone.

Suddenly, these experiments opened up the possibility of obtaining structural and chemical information on a range of materials and catalysed an upsurge of interest in many aspects of solid-state chemistry. The emphasis in most of these early studies was in extending the techniques and in applying them to different systems. Now, however, it is possible to see in more general terms how the early work fits in with the data provided by the more traditional diffraction investigations of solid systems.

In the case of amorphous materials such as surfaces, polymers and glasses, the NMR data are particularly important because diffraction studies yield extremely limited information as there is no long-range order in amorphous solids. Even in cases where single crystals are available, problems can arise where the structure is dynamic and/or disordered in nature or where individual atoms are difficult to distinguish (such as silicon and aluminium in minerals and synthetic zeolites) and the combination of the two techniques yields a more complete description of the structure. Because the NMR experiments provide the same information (isotropic shifts) in both phases, they can provide a bridge between phases, for example, the structure that exists in a single crystal as determined by X-ray diffraction techniques and the one that exists in solution.

The investigation of zeolites and minerals is a good example of the development of the combined use of NMR and diffraction data. The two techniques are complementary as NMR monitors the local environment (geometry of the atom, nature of the attached groups and local ordering) whereas diffraction data monitor long-range periodicity and lattice networks. Together, the two methods provide a complete description of the structure. Zeolites, open framework aluminosilicate structures, are widely used as catalysts, sorbents and molecular sieves in industry (Breck, D.W. *Zeolite Molecular Sieves* Wiley, New York, 1974). They are microcrystalline in nature and only limited powder diffraction data are available.

Because silicon and aluminium are adjacent in the periodic table, they have almost identical scattering factors, which makes it difficult to distinguish between them. In most systems, the atoms are disordered throughout the lattice. This distribution of local environments is exactly the kind of information which NMR can provide. E. Lippmaa *et al.* (*J. Am. Chem. Soc.* **103**, 4992; 1981) showed that the ^{29}Si magic-angle NMR spectra of these systems exhibit to a first approximation five peaks corresponding to the five local environments $\text{Si}[\text{}^4\text{Al}]$, $\text{Si}[\text{}^3\text{Al}, \text{Si}]$, $\text{Si}[\text{}^2\text{Al}, \text{}^2\text{Si}]$, $\text{Si}[\text{Al}, \text{}^3\text{Si}]$ and $\text{Si}[\text{}^4\text{Si}]$ describing the average distribution of silicon and aluminium throughout the lattice, and this has been confirmed and extended by others (Fyfe, C.A. *et al.* *Angew. Chem. Int. Edn* **22**, 259; 1983). There is a constant and additive effect on the shift for each aluminium atom added to the local environment. In addition, for highly siliceous systems where all environments are $\text{Si}[\text{}^4\text{Si}]$, signals are observed because of each of the crystallographically inequivalent sites in the unit cell (Fyfe, C.A. *et al.* *Chem. Lett.* **10**, 1547; 1983), and these shifts can be related to the local geometries of the atoms (see Smith, J.V. *et al.* *Nature* **303**, 223; 1983 and Thomas, J.M. *et al.* *Chem. Phys. Lett.* **102**, 158; 1983) and the effect of disorder can be described (Fyfe, C.A. *et al.* *J. Am. Chem. Soc.* **106**, 4435; 1984).

From these and related studies a clear set of general rules have emerged that can be used in extensions of the techniques to investigations of other aluminosilicate structures, most importantly minerals. The plagioclase feldspars described by Kirkpatrick *et al.* in this issue are the most abundant aluminosilicate minerals of the Earth's crust, but their detailed structures exhibit very complex and subtle variations and are quite imperfectly described, as is the distribution of silicon and aluminium atoms in all phases. The authors used ^{29}Si magic-angle NMR to investigate a series across the solid solution from ordered albite ($\text{NaAlSi}_3\text{O}_8$) to anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) at the two extrema. In the case of highly ordered albite, it is possible to assign the local environments related to the three peaks in the spectrum as is the case for these in the spectrum of a very special highly ordered anorthite. From these data it is possible to assign the peaks and interpret the distribution of local environments of the intermediate phases and to combine this information with that already available from diffraction data to propose mechanisms for the structural variations of the intermediate phases. Experiments of this type on disordered minerals and ceramics are currently under way in several laboratories. □

Colin A. Fyfe is in the Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada.