

major element chemistry and uranium and thorium contents can now be tentatively extended to the rare earth elements, yttrium and scandium.

J. W. MORGAN  
J. F. LOVERING

Department of Geophysics and Geochemistry,  
Institute of Advanced Studies,  
Australian National University,  
Canberra.

<sup>1</sup> Lovering, J. F., *Trans. Amer. Geophys. Union*, **39**, 947 (1958).

<sup>2</sup> Morgan, J. W. (unpublished thesis).

<sup>3</sup> Lovering, J. F., *J. Geophys. Res.*, **64**, 1073 (1959).

<sup>4</sup> Schmitt, R. A., Smith, R. H., and Olchy, D. A., *Geochim. Cosmochim. Acta*, **28**, 67 (1964).

## CHEMISTRY

### Cation Sites in Synthetic Zeolites

SYNTHETIC zeolites<sup>1</sup>, especially those with the same structure as natural faujasite, have recently come into prominence as industrial catalysts. Pickert, Rabo, Dempsey, Schomaker and references<sup>2</sup> have convincingly demonstrated the importance of the positions of the exchangeable cations which compensate for the effective negative charge of aluminium atoms in the aluminosilicate framework. 'Linde' 13X normally has Na<sup>+</sup> in all the cation positions. Very little attention has been given to the effect of dehydration of the zeolites on the position of the cations, or the position of individual ions when more than one type of cation is present.

We have examined the electron spin resonance spectrum of Mn<sup>2+</sup> at a concentration of 1 equivalent per cent of exchangeable cations in 'Linde' 13X pre-exchanged with a variety of other ions. The Mn<sup>2+</sup> ions can occupy different sites; their position depends on which other cations are present and the extent of dehydration. Fig. 1 shows the spectrum of Mn<sup>2+</sup> in the hexagonal prisms which connect the sodalite cages of the faujasite framework. In these sites the cations are in distorted octahedral co-ordination. This spectrum occurs for hydrated 13X extensively pre-exchanged with Zn<sup>2+</sup>, Mg<sup>2+</sup> or Li<sup>+</sup>. It is noteworthy that these ions are smaller than Mn<sup>2+</sup> and have a high charge to radius ratio. They evidently prefer other sites to the hexagonal prisms. The spectra of Mn<sup>2+</sup> in hydrated 13X pre-exchanged with other ions, (Na<sup>+</sup>), K<sup>+</sup>, Cd<sup>2+</sup>, La<sup>3+</sup>, Ca<sup>2+</sup> show six peaks but no fine structure (Fig. 2). Pre-exchange with Cs<sup>+</sup>, which cannot enter the hexagonal prisms or the sodalite cages, causes a little Mn<sup>2+</sup> to enter the prisms, but most seems to remain in the cages while Na<sup>+</sup> fills the prisms.

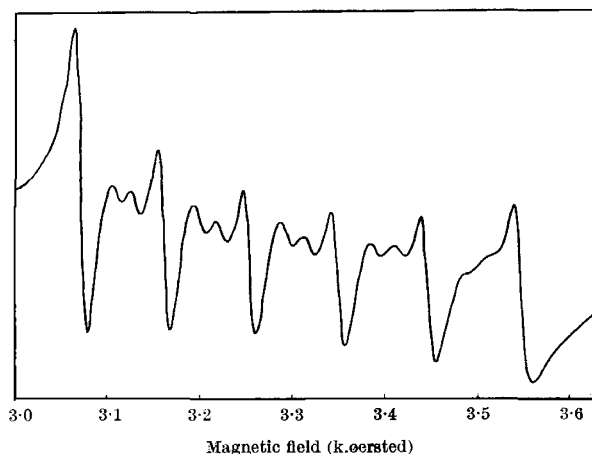


Fig. 1. The first derivative electron spin resonance absorption spectrum of hydrated 13X approximately 72 per cent exchanged with Zn<sup>2+</sup> ions and 1 per cent Mn<sup>2+</sup> ions, measured at 3,270 Mc/s

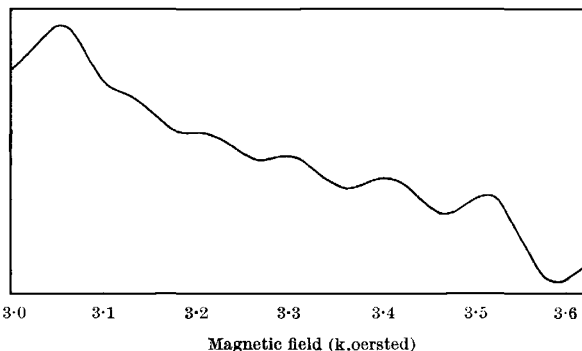


Fig. 2. The electron spin resonance spectrum of 13X treated with sodium acetate/acetic acid buffer, pH 5.5, and 1 per cent exchanged with Mn<sup>2+</sup> ions, measured at 9,270 Mc/s

During dehydration of 13X exchanged with Zn<sup>2+</sup> the spectrum of Fig. 1 remains unchanged, indicating that the Mn<sup>2+</sup> remains in the hexagonal prisms but, in 13X pre-exchanged with Li<sup>+</sup>, Mn<sup>2+</sup> leaves the prisms. Mg<sup>2+</sup> gives an intermediate result. On the other hand, when 13X is pre-exchanged with Ca<sup>2+</sup>, Mn<sup>2+</sup> enters the prisms only after dehydration at 200° C, while further dehydration at 400° C progressively releases the Mn<sup>2+</sup> probably to the sodalite cages.

In our observations only the transitions between the + $\frac{1}{2}$  and - $\frac{1}{2}$  electron spin levels of Mn<sup>2+</sup> can be resolved; the basic six line spectrum is due to coupling with the <sup>55</sup>Mn nucleus, spin  $\frac{5}{2}$ . The fine structure of Fig. 1 arises from transitions in which the nuclear spin also changes. The fine structure must disappear when the Mn<sup>2+</sup> or its environment is in rapid motion. Thus Fig. 2 suggests that Mn<sup>2+</sup> in hydrated 13X exchanged with large ions is at least partly co-ordinated to water. The proof that it is Mn<sup>2+</sup> in hexagonal prisms which generates the spectrum of Fig. 1 comes both from theoretical examination and from the fact that the spectrum does not change with dehydration. The hexagonal prisms are the only sites not associated with water.

T. I. BARRY  
L. A. LAY

Division of Molecular Science,  
National Physical Laboratory,  
Teddington.

<sup>1</sup> Breck, D. W., *J. Chem. Educ.*, **41**, 678 (1964). Broussard, L., and Shoemaker, D. P., *J. Amer. Chem. Soc.*, **82**, 1041 (1960).

<sup>2</sup> Pickert, P. E., Rabo, J. A., Dempsey, E., and Schomaker, V., *Proc. Third Intern. Cong. Catalysis*, Amsterdam 1964 (North Holland Publishing Co., Amsterdam).

### Quantitative Chromatographic Analysis of Organic Acids by Tritiating Methylation

IN fatty-acid analysis, thin-layer chromatography is a valuable technique for the separation of complex mixtures into specific groups and for separations of *cis* and *trans* isomers and certain positional isomers of unsaturated fatty acids, which cannot easily be achieved by gas-liquid chromatography.

Isotope derivative methods may be a valuable tool for quantitative evaluation of thin-layer chromatograms. Esterification with <sup>14</sup>C-diazomethane<sup>1</sup> has been applied for this purpose, but the preparation of the reagent is rather complicated and expensive. We therefore applied a method according to which samples of organic acids are esterified with inactive diazomethane after exchange with tritiated water. This 'tritiated methylation', developed by Melander<sup>2</sup> and Verly *et al.*<sup>3</sup> for the preparation of labelled methanol, was used before for the analysis of gibberellins by Baumgartner *et al.*<sup>4</sup>

An ethereal solution (0.2 ml.) of tritiated water, containing 6.67  $\mu$ c. in 1  $\mu$ l. water per ml. dry diethyl ether,