

the accretion disk. A more delicate analysis of the eclipse light curves should sharpen the observational constraints on the distribution of superhump light on the face of the accretion disk.

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Differentiation between ^{27}Al nuclei in alums by Fourier transform pure nuclear quadrupole resonance

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Aluminium is the most abundant metal in the Earth's lithosphere and is present in many commercially important materials. Recent studies on its role in zeolites¹ and proposed solar energy storage schemes involving aluminium salts² have led to renewed interest in analytical methods capable of identifying and characterizing specific crystalline sites. In particular, new techniques are necessary which do not require single crystals. One such technique is Fourier transform nuclear quadrupole resonance (NQR) with pulsed field cycling^{3,4}, and we report here on its application to the determination of specific ^{27}Al sites in model aluminium compounds, the alums.

In crystalline compounds, aluminium occurs most often with either four or six nearest neighbours. Tetrahedrally coordinated aluminium is the catalytically active centre in zeolites, where each ^{27}Al atom is believed to be surrounded by four O-Si linkages. The octahedral form, as characteristically found in the alum family, surrounds each ^{27}Al site by six bonds (often to H_2O molecules). Much work has gone into characterizing these sites. In powder samples, the NMR spectra are very broad and the methods used to obtain information have been two-dimensional solid state NMR⁵ and magic angle sample spinning (MASS) NMR⁶. Although the latter technique has proved useful in studies of ^{29}Si in zeolites^{7,8}, its applicability to aluminium is limited because of the small dispersion in ^{27}Al chemical shifts and the line broadening arising from quadrupolar effects, with the result that it generally reveals only the difference between tetrahedral or octahedral sites^{9,10}, except in rare cases of resolution between tetrahedral sites¹¹. As an example, Fig. 1 shows MASS spectra of ^{27}Al in two closely related materials, the ammonium and potassium alums ($\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$). This technique reveals no difference between these two samples.

In contrast to high field NMR techniques, magnetic resonance should readily differentiate between signals from similar sites in a zero applied magnetic field; we rely in this instance on the inherent chemical sensitivity of the nuclear quadrupole interaction to resolve structural differences. The quadrupolar interaction arises from the coupling of a non-spherical nuclear charge distribution (characteristic of any nucleus where I , the nuclear angular momentum operator, is less than $\frac{3}{2}$) to molecular and crystalline electric field gradients. In ^{27}Al sites of high symmetry,

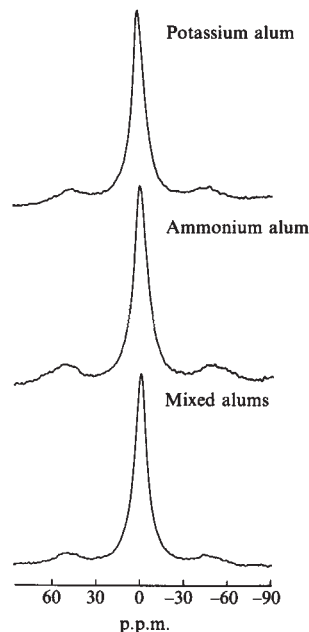


Fig. 1 ^{27}Al magic angle spinning spectra of representative alums. Spectra are observed at 78.2 MHz at a spinning rate of 4 kHz. Chemical shifts are referenced to $\text{Al}(\text{H}_2\text{O})_6^{3+}$. The mixed alum sample is 56 mol% potassium alum, 44 mol% ammonium alum.

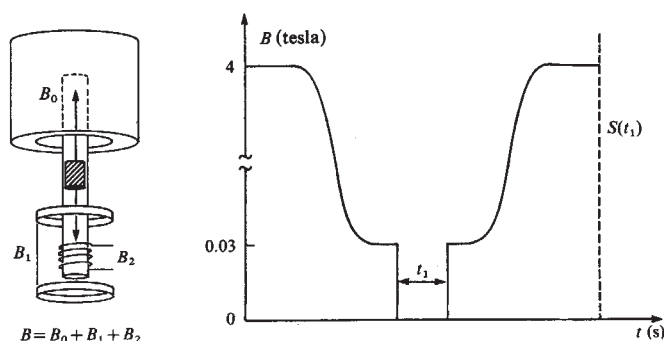


Fig. 2 Schematic diagram showing the effective field at the sample as a function of time. The sample is pneumatically transported from the bore of superconducting magnet B_0 to a point where B_1 accurately compensates for the fringe field. Coil B_2 (0.03 T) is switched off for a time t_1 during which pure quadrupolar evolution occurs. After returning the sample to B_0 , the high field magnetization, $S(t_1)$, is measured. The cycle is repeated for equally spaced points in t_1 until no further change in magnetization is observed. Fourier transformation of the magnetization as a function of t_1 results in the zero field spectrum.

the magnitude of the field gradient term is small. Direct detection of the pure NQR transitions is thus difficult (as the energy splittings are small¹²).

We instead used the chemical sensitivity of pure NQR, in combination with the high signal-to-noise ratio associated with observation of NMR in large applied magnetic fields. This is done by cycling the magnetic field between a large value and zero, and is accomplished in two steps (see Fig. 2): first, the sample is mechanically transported from the bore of a superconducting magnet and then the residual field is pulsed to zero with electronically switched coils. If the second stage occurs quickly relative to the quadrupolar frequencies, the spin system in zero field oscillates at frequencies characteristic of the pure quadrupolar coupling. This oscillation is interrupted at time t_1 by reapplying the field. The sample is then returned to high field where the signal amplitude is monitored. This field cycle is

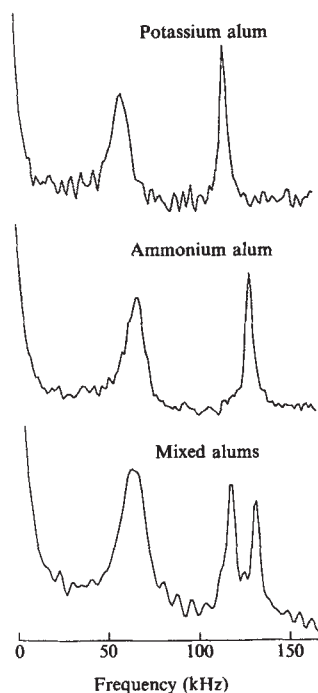


Fig. 3 ^{27}Al Fourier transform pure nuclear quadrupole resonance spectra of representative alums. Each site contributes two lines to the zero field spectrum. η , asymmetry parameter in the quadrupole tensor, was calculated to be 0.17 for potassium alum and ammonium alum. Respective values of 391 and 438 kHz were obtained for the quadrupole coupling constant, $(e^2qQ)/h$, where eQ is the nuclear quadrupole moment, eq is the electric field gradient, and h is Planck's constant. The pair of high frequency lines in the mixed sample (56 mol% potassium alum, 44 mol% ammonium alum) clearly indicate the existence of two distinct ^{27}Al sites.

repeated with different, equally spaced values of t_1 , to give an interferogram which describes the evolution of the spin system in zero field and which, on Fourier transformation, yields the zero field spectrum.

For a spin- $\frac{5}{2}$ nucleus such as ^{27}Al , we expect to observe a pair of lines for each crystalline site. (In aluminium compounds where the crystal symmetry is low, a third line of low intensity may be observed.) Figure 3 illustrates the results for the two alums whose MASS spectra are shown in Fig. 1. Despite nearly identical crystal structures and high field NMR spectra, the zero field nuclear quadrupole experiment clearly differentiates between the two types of aluminium nuclei. We expect that even more sensitive differentiation will be possible between ^{27}Al sites in other systems such as zeolites.

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Direct determination of strontium enrichment on grain boundaries in a garnet lherzolite xenolith by proton microprobe analysis

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The mechanisms by which trace and radiogenic elements are held and transported in the Earth's mantle are of prime importance in studies of basalt petrogenesis and the chemical processing of the mantle. While such mechanisms include the migration of melts and the convective physical admixture of differentiated material¹, the role of fluids as transport agents has attracted much interest, especially, in regions affected by kimberlitic activity²⁻⁴, continental basaltic volcanism^{5,6}, and in areas of subduction-related magmatic activity^{7,8}. The observation that many incompatible elements are readily leached from garnet lherzolites by dilute acid treatment³ has led to the assumption that a proportion of these elements is located on grain boundaries, rather than in solution in the various minerals present. This indirect evidence is reinforced by comparison of the compositions of mineral separates with their bulk parental material^{4-8,11}. Although careful electron microprobe analyses have made it possible to detect minor and trace elements within grains¹², the low concentrations involved, together with the high X-ray background of the electron microprobe, have made it impossible to investigate the supposed distribution of incompatible trace elements on grain boundaries. We have measured directly, using a high-resolution proton microprobe^{9,10}, the distribution of Sr and other elements in a garnet lherzolite xenolith. The analyses demonstrate that, in this sample, Sr is preferentially concentrated along grain boundaries.

An inherent limitation in the use of the electron microprobe to analyse very, small concentrations of elements lies in the substantial non-characteristic X-ray background caused by electron *bremstrahlung*. This is very much reduced when a proton beam is used to excite X rays in a sample because the enormously increased mass of the proton minimizes the amount of deceleration near the target. In the present experiments, the specimens were analysed by using a 4.0-MeV proton beam to excite characteristic X rays in the samples. The beam was focused electromagnetically to a spot diameter of 2 μm and was rastered over an area of up to 4 mm \times 4 mm. The samples were prepared as 30- μm thin sections and the X rays generated were detected and analysed using a Link Si(Li) detector system. As the penetration of a proton beam is much greater than that of a beam of electrons in an electron microprobe, the sections were mounted on glass slides using Lakeside 70 thermoplastic resin as a mounting medium. The sections were then removed from the glass slides by gentle heating and remounted over 1-cm holes machined in aluminium target holders to remove any possibility of X-ray generation in the specimen backing. The resulting targets were finally washed carefully in acetone to remove any traces of resin. Samples were irradiated for ~ 10 h using a 50 μm Al filter to cut out the low-energy X-ray background, and maps of the distribution of X rays from major and trace elements in the samples were built up as 256 \times 256 pixel images. As the proton beam penetrated right through the thin samples used, the transmitted beam current was also continuously measured for each pixel so that the effects of any fluctuations in beam current could be corrected. A detailed description of the Oxford proton microprobe system is given elsewhere^{9,10}.

Figure 1 shows elemental maps for the distribution of Ni, Mn, Cr and Sr in a 4 mm \times 4 mm area of a granular garnet