High-Resolution Nuclear Magnetic Resonance of Inorganic Solids

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During the past 3 years there has been increased interest in applying high-resolution solid-state nuclear magnetic resonance (NMR) spectroscopy to the study of inorganic solids such as minerals and heterogeneous catalysts (1, 2). This increased activity has been primarily brought about by the commercial availability of sensitive Fourier-transform NMR spectrometers with superconducting magnets. In addition, NMR techniques for observing, in solids, nuclei with both spin \( I = 1/2 \) and spin \( I = 3/2 \), 5/2, 7/2, and 9/2 (quadrupolar nuclei) have been developed (3–8). In the next few years, such techniques will have a major impact on geochemistry, materials research, and heterogeneous catalysis; and solid-state NMR spectroscopy will become as routine a tool in these inorganic areas as liquid-state NMR has been in other areas of chemistry over the past 20 years.

In geochemistry, the nucleus that is the most desirable candidate for NMR studies is oxygen, since it constitutes 62.5 percent of the earth’s crust. Unfortunately, its only NMR-active nuclide is \(^{17}\text{O}\). Oxygen-17 has a 0.037 percent natural abundance and a quadrupole moment of \( 2.6 \times 10^{-30} \text{ m}^2 \), which together give rise to broad and weak spectral lines. Silicon, 21.2 percent of the earth’s crust, and aluminum, 6.5 percent, are the next most abundant elements. Aluminum-27 has a 100 percent natural abundance, resulting in a strong resonance, although its low quadrupole moment, \( 0.149 \times 10^{-28} \text{ m}^2 \), makes the resonance broad.

Silicon-29 has only a 4.7 percent natural abundance; but it has a nuclear spin, \( I \), of 1/2, so it gives sharp spectral lines. Thus, early research on the NMR spectra of geochemically and catalytically interesting solids has been confined to \(^{27}\text{Al}\) and \(^{29}\text{Si} \) (1–4).

**Theory and Experiment**

Figure 1a shows a nuclear energy level diagram for \(^{29}\text{Si}\), \( I = 1/2 \), in a strong magnetic field; Fig. 1b, a typical spectral line shape for a stationary \(^{29}\text{Si}\) NMR sample; and Fig. 1c, a \(^{29}\text{Si}\) NMR spectrum obtained from a rapidly rotated crystalline silicate [obtained at 71.5 MHz, corresponding to a magnetic field strength of 8.45 Tesla (T) or a \(^1\text{H}\)-resonance frequency of 360 MHz].

When \(^{29}\text{Si}\) is placed in a strong magnetic field, the energy levels with \( I = 1/2 \) and \(-1/2\) have their degeneracy lifted, and transitions between the levels may be detected in the NMR experiment. In the absence of any other interaction, this gives rise to a sharp resonance at some frequency, \( \omega_0 \). However, a number of orientation-dependent interactions perturb these energy levels and result in line broadening. For example, in the sheet silicate \( \text{Na}_2\text{Si}_2\text{O}_5 \), the NMR resonance frequency of \(^{29}\text{Si}\) (its chemical shift) is strongly dependent on the spatial orientation of the silicate group because of the nonspherical electron distribution around the silicon nucleus. This leads to a broad spectral line (Fig. 1b) whose breadth and shape are determined by a chemical-shielding tensor. Dipolar interactions between the nuclear spins and, for nuclei having \( I \geq 1 \), quadrupolar interactions between the nuclear quadrupole moment \( (eQ) \) and the electric field gradient \( (eq) \) at the nucleus may cause further spectral broadening.

All of these interactions lead to decreased spectral resolution and low ratios of signal to noise. For years they impeded the use of NMR for studying the structures of most inorganic solids. Fortunately, it was shown that each of these second-rank tensor interactions may be eliminated by rapid mechanical rotation of the sample at a unique angle to the main magnetic field, the “magic angle,” \( \theta = 54.7^\circ \). If the sample rotation rate, when expressed in frequency units, is much greater than the spectral broadening, the mathematical term \( 3 \cos^2 \theta - 1 \) that appears in the time-average values of these interactions vanishes (9–12). Under these conditions, scalar couplings (13), isotropic chemical shifts, and Knight shifts (14, 15) may be observed. This technique is called magic-angle sample-spinning (MASS) NMR.

With less rapid rotation, well-resolved spinning sidebands form about the isotropic centerband at multiples of the spinning frequency \( \omega_0 \). For the anisotropic chemical-shift interactions or Knight-shift interactions, these sidebands may be considered a mechanical echo in the time domain after one rotor revolution (16). Figure 1c shows a typical result for the chemical shift anisotropy of \(^{29}\text{Si}\) in \( \text{Na}_2\text{Si}_2\text{O}_5 \).

In the experiment, samples of a few hundred milligrams are rotated on air bearings at frequencies of up to 5 kHz (~300,000 rpm). A typical rotor design and the orientation of the axis of rotation in the magnetic field is shown in Fig. 1d (11). The materials used for such rotor assemblies are chosen to provide low background signals from an empty probe. They typically include plastics.

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such as Delrin or Kel-F and inorganics and ceramics such as sapphire, BN, and Macor. With appropriate design, both solid-packed and vacuum-sealed samples can be studied, and sample temperatures from ~5 K to ~500 K are accessible.

**Silicon-29 NMR**

Silicon was the first inorganic element to be studied in a variety of catalyst and mineral samples (1–3). Silicon-29 resonates at 39.7 MHz in a 4.7 T magnetic field (corresponding to a \(^1\)H-resonance frequency of 200 MHz). Because there is no associated quadrupole moment, the absorption lines are quite narrow and the sensitivity is high. Indeed, very early investigation by Holzman et al. (17) indicated considerable promise for high-resolution, solid-state NMR of silicon. However, it was only after the advent of commercial, high-field Fourier-transform NMR spectrometers some 20 years later that the promise was realized.

The results obtained to date show that NMR has great potential for investigating the structures of amorphous phases—glasses and various fine-grained materials such as clays and zeolites—that cannot be readily investigated by means of single-crystal diffraction techniques. Quantitative information on the type of sites present and the order or disorder at a given site may usually be obtained in short time periods (minutes to a few hours). The data obtained—chemical shifts, chemical-shielding tensors, and, for quadrupolar nuclei, electric-field-gradient tensors—can be interpreted in terms of types of chemical bonding—covalency, bond angles, and bond distances. Moreover, in many cases, NMR may be used to determine the rates of motion of the various species present.

In Fig. 2 we show \(^{29}\)Si spectra that illustrate the points discussed above. For example, in Fig. 2a we show \(^{29}\)Si NMR spectra of diopside (CaMgSiO\(_4\)), clinoenstatite (MgSiO\(_3\)), and α-silicon carbide (SiC). From x-ray crystallography, we know diopside has only one silicon site, whereas clinoenstatite has two (18, 19). The \(^{29}\)Si NMR spectra indeed show one center band resonance for diopside (at ~84 ppm from an external sample of tetramethylsilane), but two peaks for enstatite, at ~81 and ~83 ppm (20). The spinning sidebands, which are marked with an asterisk for both samples, are due to the presence of a large chemical shift anisotropy. For α-SiC there are three peaks—a rather unexpected result due, perhaps, to the polytypic nature of this sample.

For the silicate minerals, the ranges of isotropic chemical shifts are a function of the different states of polymerization of the SiO\(_4\) tetrahedra (\(Q_0, Q_1, Q_2, Q_3\), and \(Q_4\)). This makes \(^{29}\)Si NMR a most useful structure-sensitive tool.

Aluminum in framework \((Q_4)\) silicates, such as feldspar minerals and synthetic zeolites, causes a systematic deshielding at \(^{29}\)Si (corresponding to so-called low-field, high-frequency, or paramagnetic shifts). For example, in the zeolite Linde A, there is only one silicon resonance (at about ~88.5 ppm, depending on the countermions present), corresponding to Si(4AI), in accord with a framework Si:Al ratio of 1.0 and obeyance of Loewenstein’s rule (21, 22). For Linde Y, there are a series of peaks, corresponding to Si(1AI) through Si(4AI) (23), as shown in Fig. 2b. Analysis of the relative integrated peak intensities for Linde Y yields the ratio of silicon to aluminum in the framework. That value is difficult to obtain by other analytical methods owing to the frequent occurrence of extra-framework aluminum, which may be directly detected by \(^{27}\)Al NMR.

The silicon spectra shown in Fig. 2, a and b, are from materials that are fairly well-defined crystallographically. In contrast, Fig. 2c shows the \(^{29}\)Si MASS NMR spectrum of a sample of shocked sandstone from Meteor Crater, Arizona, together with spectra of quartz (SiO\(_2\)) crystal and quartz glass. Our results (24) indicate that while much of the SiO\(_2\) in the meteor-crater sample is present as crystalline quartz, as demonstrated by the sharp resonance at ~108 ppm, approximately 5 percent is also present as the high-pressure polymorphs stishovite and coesite, as demonstrated by the peaks at ~191.1 ppm for stishovite, which contains six-coordinate silicon at-

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**Fig. 1 (left).** (a) Energy level diagram for \(^{29}\)Si nucleus (\(I = 1/2\)) in a strong magnetic field. The effect of perturbation of the nuclear Zeeman levels due to chemical shielding is illustrated. (b) Powder-pattern line shape due to anisotropic chemical shielding in an NMR spectrum for \(^{29}\)Si in a silicate. (c) High-field (8.45 T) \(^{29}\)Si NMR spectrum of Na\(_2\)Si\(_2\)O\(_5\) obtained by means of magic-angle sample spinning (MASS). Abbreviation: CB, center band; SSB, spinning side bands. (d) Rotation axis of NMR sample with respect to the direct-current and radio-frequency field directions. **Fig. 2 (right).** Silicon-29 MASS NMR spectra of minerals, zeolites, and a glass. Peaks marked with asterisks are spinning sidebands. (a) Spectra of diopside (CaMgSiO\(_4\)), clinoenstatite (MgSiO\(_3\)), and silicon carbide (SiC), showing the presence of one silicon site and two and three nonequivalent silicon sites, respectively. (b) Spectrum of Linde A and Linde Y, showing the deshielding effects of aluminum. (c) Spectra of SiO\(_2\) phases: quartz; sandstone from Meteor Crater, Arizona, showing quartz (Q), coesite (C), and stishovite (S) peaks; and glass.
for coesite, which contains four-coordinate silicon atoms. When long recycle times are used in the experiment (to avoid saturation of the quartz resonance), observation of the stishovite peak is most difficult (24). With short recycle times, quantitative analysis of the high-pressure polymorphs in whole-rock samples is quite feasible (24). Thus, 29Si MASS NMR should be capable of detecting such species in other mineral saftihile that have been subjected to intense pressure.

Finally, we also show in Fig. 2c the 29Si spectrum of vitreous SiO2, prepared by rapidly quenching a SiO2 melt from about 1850°C. The resonance here is quite broad, and it extends from about -95 to -125 ppm. To date, there have been four main approaches to the analysis of such chemical shift information. First of all, the early studies of Lippmaa et al. (1, 3) and Frye and Thomas and their co-workers (2), suggested the presence of nonoverlapping chemical shift ranges, that is, the chemical shift for 29Si nuclei in Q0 compounds did not overlap with those for 29Si in Q1 compounds. Such optimistic relations soon broke down as more samples were examined. There is great overlap in the range of isotropic 29Si chemical shifts for silicon sites with different states of polymerization (Q0 to Q6) and for framework silicates with one to four aluminum atoms as next-nearest neighbors.

One successful method for interpreting these chemical shifts has been the Brown and Shannon (26) bond-strength method (29, 27). These bond strengths are similar to the electrostatic bond strengths of Pauling but have been modified to include the effects of interatomic distance. To do this, the cation-oxygen bond strengths for all cations bonded to the four oxygens of a silica tetrahedron are totaled. These "cations" include the silicon atom itself and all cations outside the tetrahedron that are coordinated to these oxygens.

Pauling's original postulate was that the sum of the electrostatic bond strengths of the cations surrounding an oxygen atom should equal the absolute value of the valence of oxygen, where the bond strength for a cation is its valence divided by its coordination number. This rule has been used in evaluating crystal structures determined by x-ray and neutron diffraction. However, the rule does not hold exactly for many structures, and bond lengths increase or decrease to compensate for too much or too little charge (28).

The relation between bond strength and chemical shift shown in Fig. 3a offers an explanation for the ranges of chemical shifts for the different structural types observed by Lippmaa et al. (1, 3), for the overlap of these ranges, and for the deshielding caused by the substitution of aluminum into the silicon sites (27).

The sums of the bond strengths for a particular structural type tend to fall into one range, because the average number of silicon atoms bonded to a silicate tetrahedron decreases with decreasing polymerization. Silicon atoms have the largest effect on the 29Si chemical shift, which is understandable since the Si-O bond is the strongest one involved [443 kJ/gram-atom (29)]. Variation in the kind and arrangement of other cations within a given structural type, however, causes the ranges in chemical shift to be large enough to overlap. This is especially true if the aluminum is six coordinate, as in the Al2SiO5 polymorphs. Substitution of aluminum for silicon in the tetracoordinated sites results in a lower bond-strength sum because the Al-O bond is weaker (330 to 422 kJ/gram-atom) than the Si-O bond, which corresponds with the less negative chemical shift. Bonds to monovalent or divalent cations are even weaker and result in further deshielding. Overall, the observed correlation between chemical shift and the sum of bond strengths is very good (correlation coefficient of 0.88), as shown in Fig. 3a.

However, when only framework (Q4) silicates are examined (30, 31) an even better chemical-shift correlation may be made with the secant of the Si-O-T (T = Si, Al) bond angle, θ, a relation suggested by the molecular orbital calculations of Gibbs (32). We have extended these results to framework silicates containing zero, one, two, and four aluminum atoms per SiO4 tetrahedron (Fig. 3b), and Ramdas and Klinowski have recently obtained similar excellent correlations based on total Si···T nonbonded distances for silicon in the five kinds of Si (or Al) environments (33). Figure 3 thus indicates that, for silicates of unknown structure, proposed structural models must be consistent with the observed 29Si chemical shifts; it also shows that, for framework silicates, Si-O-T bond angles may be determined with some accuracy from the NMR observations. Such observations hold considerable promise for the structural analysis of amorphous materials. For example, the broad line shape of the SiO2 glass in Fig. 2c may be analyzed in terms of various distribution functions of the Si-O-Si bond angles (34).

NMR of Quadrupolar Nuclei: Theory and Background

Most of the nuclei in the Periodic Table have a nuclear spin I ≥ 1 and thus possess a quadrupole moment, which in most chemical environments leads to extensive line broadening. Fortunately, however, most of these quadrupolar nuclei also have a nonintegral spin (I = 3/2, 5/2, 7/2, or 9/2). As shown in the energy-level diagram for 23Na (I = 3/2) in Fig. 4a, the central transition (1/2 ↔ -1/2) of each such nucleus is unaffected, to first order, by this quadrupole interaction. For 23Na, the first-order quadrupole interaction leads to a static NMR spectrum composed of two broad absorptions due to the satellite transitions (3/2 ↔ 1/2, -1/2 ↔ -3/2) and a sharp central absorption (1/2 ↔ -1/2) broadened only by dipole, chemical-shift, and scalar-coupled interactions (Fig. 4b). In general, with MASS NMR, these interactions are again averaged, and the sharp central absorption is observed together with a number of sidebands due to the satellite transitions (Fig. 4c).

When the quadrupole coupling constant is about 1 MHz, only the central (1/2 ↔ -1/2) resonance is readily detected experimentally, because there is usually significant broadening of the satellite lines due to either small fluctuations around the magic angle caused by rotor
wobble or a slight missetting of the magic angle. In fact, it is sometimes desirable to deliberately misset the magic angle in order to better define the line shape from the central transition. Missetting the magic angle introduces a residual broadening equal to about 2.5 percent of the line width from the solid sample if it were static, per degree of misset. In the case of the $^{51}$V NMR spectrum of NaVO$_3$, for example, residual broadening of the first-order satellite lines is nearly two orders of magnitude larger than that of the central (1/2 $\leftrightarrow$ -1/2) line, which is broadened by chemical shift anisotropy. This difference in broadening allows an accurate determination of the $^{51}$V chemical shift tensor (35), yielding $\sigma_{11} = -213$ ppm, $\sigma_{22} = -56$ ppm, and $\sigma_{33} = 269$ ppm, from an analysis of the sideband intensities (36).

When the quadrupole coupling constant is even larger, about 3 to 10 MHz, fine structure appears on the central line, a result of the higher order effects that arise when the quadrupole interaction is a significant fraction of the actual resonance frequency. For example, in Na$_2$MoO$_4$ the quadrupole coupling constant for $^{23}$Na is approximately 2.6 MHz, and at all fields in the range 3.52 to 11.7 T there is pronounced second-order broadening of the central transition (Fig. 5a). Spinning the sample at the magic angle is only partially effective in removing this broadening (Fig. 5b), because it is described by a more complex angle dependence than the first-order interaction and does not vanish for any rotational angle. There are, however, optimal angles, which depend on the value of the asymmetry parameter of the electric-field-gradient tensor (6, 37-41). Figure 5c shows that spinning a sample of $^{23}$Na$_2$MoO$_4$ at 75° from the magnetic field gives a resonance line twice as narrow as that obtained at 54.7°. However, dipolar interactions and chemical-shift anisotropy interactions do not vanish under these conditions and can thus cause additional unwanted line broadening.

For most materials, the best initial strategy for studying a quadrupolar nucleus is to perform the experiment at as high a magnetic field strength as possible while spinning the sample at the magic angle (54.7°). This generally provides the best sensitivity and resolution and minimizes the need to correct the chemical shift for the second-order shift (42, 43). However, the case where two nuclei, A and B, have the same isotropic chemical shift but different quadrupole coupling constant ($e^2qQ/Ih$) is an exception. In a high field, A and B will be unresolvable, whereas in a low field, the second-order quadrupole interaction shifts the resonance with the larger value of $e^2qQ/Ih$, permitting its resolution. An example, the case of $^{11}$BO$_4$ and $^{13}$BO$_3$ units in a borosilicate glass, is shown in Fig. 5, d and e (44). With this information we can now discuss the high-field NMR spectra of a number of quadrupolar nuclei of interest to chemists and earth and materials scientists.

**Oxygen-17 NMR Spectra**

Oxygen-17 has a nuclear spin $I = 5/2$ and a quadrupole moment of $-2.6 \times 10^{-30}$ m$^2$, is only 0.037 percent abundant in nature, and resonates at 67.8 MHz in a magnetic field of 11.7 T (500 MHz 1H resonance frequency). When it is in sites of less than cubic symmetry, there is thus considerable line broadening in its spectrum due to the quadrupole interaction. This line broadening and the low abundance have, until recently, precluded observation with NMR spectroscopy of this most important element—the most abundant element in the earth's crust.

However, in sites with cubic or close-to-cubic symmetry, $^{17}$O MASS NMR lines are very narrow, $\sim 1$ ppm (7, 8), and spectra may be obtained even at natural abundance (45-47). The range of chemical shifts for group IIA oxides spans 618 ppm (47), from 22 ppm for BeO to 640 ppm for BaO; and the shifts are a function of the cation electronegativities, as observed in the $^{19}$F NMR spectra of the group IA fluorides (48). There is also an excellent relation between the $^{17}$O chemical shifts and the cation radius (47). Furthermore, in some cases, complete powder patterns may be obtained for static samples, yielding accurate values for $e^2qQ/Ih$. For example, with ZnO, $e^2qQ/Ih = 120$ kHz (47).

While such results with the group II elements might have been expected, more startling was the observation of
high resolution spectra of complex oxo-
ions [tungstates, molybdates, and van-
adates (8)], as well as of $^{17}$O in the CO
ligands of a number of metal carbonyls
(49). Such spectra are visible, because the $e^2q/\hbar$ values are small, and, thus
MASS line widths of only 1 or 2 ppm are
obtained at high magnetic field strengths;
in many such systems the corresponding
chemical shielding tensors are large,
even though the quadrupole interactions
are small. Figure 6, a and b, shows
typical $^{17}$O MASS NMR spectra of solid
Mo(bipy)(CO)$_4$ (bipy = bipyridine) and
K$_2$WO$_4$, both enriched to about 20
percent with $^{17}$O, which exhibit sharp,
multiline spectra. For Mo(bipy)(CO)$_4$,
both cis and trans CO ligands may be
detected, and their shift tensors deter-
mined (49). For the WO$_4^{2-}$ ion there are
center band peaks together with nine
sets of spinning side bands. The
isotropic peaks have a 2:1:1 intensity
ratio and correspond to the three non-
equivalent oxygens observed by means
of x-ray crystallography (50). Analysis of
the side band intensities as a function of
spinning rate once again yields the com-
plete chemical-shielding tensors for each
nonequivalent oxygen (8). However, not
all species isoelectronic with WO$_4^{2-}$
have such large shift tensors—indeed,
for KMnO$_4$, $\Delta \sigma$ is approximately
zero (8). Such information will permit more
detailed analyses of chemical bonding in
polyoxoanions, polyoxocations, and
metal carbonyls than before. Already we
have shown that the $^{17}$O chemical shift is a
function of the metal-ion radius for
nine MO$_4$ species isoelectronic with
WO$_4^{2-}$ (8). These results suggest that
observation of $^{17}$O shifts in less well
defined oxide phases of catalytic interest
could give useful information on struc-
ture and bonding.

Of more general interest in $^{17}$O NMR
are the magnitudes of the quadrupole
coupling constants and the values of the
asymmetry parameters of the electric-
field-gradient tensors. For Mo(CO)$_6$ and
K$_2$WO$_4$, $e^2q/\hbar$ values are small, $\approx 1$
MHz; in the case of the carbonyl, this is
in part due to x-backbonding, and in the
case of the WO$_4^{2-}$ ion, to a fairly weak
W-O bond. Indeed, the early x-ray stud-
ies were prompted by the idea that the
oxygen in such systems might best be
regarded as the spherically symmetric
O$^2-$ species (50); that is, the phase was
considered a candidate for a mixed-oxide
formulation. These systems are clearly
not ideal for determining $e^2q/\hbar$ values
because of the lack of observable quad-
rupole structure, although such informa-
tion may often be deduced with a fair
degree of certainty from the field-depen-
dence of the isotropic chemical shift (42).

By contrast, the silicate minerals offer
a wealth of information, not only about
chemical shifts but also about $e^2q/\hbar$ and \( \eta \) values. We show in Fig. 6, c and d,
the $^{17}$O MASS NMR spectra of the oliv-
ine mineral forsterite (Mg$_2$SiO$_4$) and the
pyroxene mineral diopside (CaMg$_2$Si$_2$O$_6$),
both enriched to about 20 percent with
$^{17}$O. Both spectra appear quite complex,
but they can be refined into three sets of
resonances by means of computer simu-
lations, as shown. For forsterite, there
are once again three nonequivalent oxy-
gen sites, as determined by x-ray diffra-
c tion (51), which give rise to three oxygen
resonances with the following $e^2q/\hbar$, $\eta$, and $\sigma_1$ values: $O_a$ (2 oxygens), 2.35 MHz,
0.2, 61.0 ppm; $O_b$ (1 oxygen), 2.35 MHz,
1.0, 62.0 ppm; and $O_c$ (1 oxygen), 2.70
MHz, 0.3, 47.0 ppm (8). For diopside,
there are also three nonequivalent oxy-
gen sites, two nonbridging and one bridg-
ing. We assign the $e^2q/\hbar$, $\eta$, and $\sigma_1$ as
values follows: $O_{ab}$, 2.7 MHz, 0.0, 84
ppm; $O_{ac}$, 2.8 MHz, 0.2, 63 ppm; and $O_c$,
4.3 MHz, 0.2, 67 ppm. These latter
assignments are based on the observa-
tion of an intense $O_{ab}$ resonance in the
range of 40 to 160 ppm in a variety of
pyroxenes, which becomes more de-
shielded with increasing cation radius,
and a weaker $O_c$ resonance in the range
of 60 to 70 ppm, which does not shift
(52). Thus, even in quite complex silicate
phases, considerable information may be
obtained by means of high-field MASS
NMR spectroscopy (8).

For more covalent species, such as
SiO$_2$, we expect an increase in $e^2q/\hbar$, and
indeed, for SiO$_2$ in the form of low cristobalite we obtain $e^2q/\hbar = 5.8$
MHz, $\eta = 0.1$, and $\sigma_1 = 36.1$ ppm. Even
at 11.7 T, the overall breadth of the
second-order powder pattern is about 20
kHz, much larger than our highest attain-
able sample-rotation frequencies (27
kHz); so it is clearly preferable to utilize
variable-angle sample spinning (at 75°)
for high-resolution studies of SiO$_2$ (8).

To a first approximation, all of the
results we have obtained from $^{17}$O NMR
may be interpreted in terms of the ionic
nature of the bonds between oxygen and
its counterions. In Fig. 7a we show
$e^2q/\hbar$ values plotted as a function of the
average ionic nature of the bonds to
oxygen, $I$. As an example, for a silicate
containing solely Si-O-Mg bonds, we use
Pauling electronegativities to calcu-
late a 51 percent ionic character for the
Si-O bond and a 74 percent ionic charac-
ter for the O-Mg bond, yielding an aver-
age of 62.5 percent. Since the data in Fig.
7a may be well fit by a line of the form

\[
e^2q/\hbar = -0.198 I + 14.66
\]

equation predicts an $e^2q/\hbar$ value for the
Si-O-Mg fragment of 2.29 MHz, in
good agreement with the 2.47 MHz
observed experimentally in forsterite (8).

This is not unexpected, since similar
ideas are employed in Townes-Dailey
calculations of $e^2q/\hbar$ values, and simi-
lar relations have been observed by oth-
ers in the $^{35}$Cl nuclear quadrupole reso-
nance of 170 shifts in less well
defined oxide phases of catalytic interest
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ture and bonding.

Of more general interest in $^{17}$O NMR
are the magnitudes of the quadrupole
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Fig. 6. Oxygen-17
NMR spectra from in-
organic solids. (a) MASS NMR spec-
trum of Mo(bipy)
(CO)$_4$ at 11.7 T show-
ing resolution of cis
and trans carbonyls,
large (700 ppm)
chemical shift anisot-
ropy, and small ($\approx 1$
MHz) quadrupole
coupling constant. (b)
MASS NMR spec-
trum of K$_2$WO$_4$
at 11.7 T, showing reso-

nance of all three non-
equivalent oxygen
sites and a large
chemical shift anisot-
ropy. (c) MASS NMR
spectra of enriched
forsterite (Mg$_2$SiO$_4$)
and diopside (CaMg$_2$Si$_2$O$_6$) at 11.7 T, to-
gether with (above)
their computer simu-
lations, showing ob-
serveration of non-
equivalent, chemically
shifted $^{17}$O reson-
ances.
We are now in a position to obtain a wide body of information about the $e^2\sigma Q/h$ and $\eta$ values for oxygen in geologically and chemically interesting species. It may soon be possible to resolve long-standing questions, such as the degree of $\pi$-bonding in silicates (54-56).

For example, in Fig. 7b we show the relation between $e^2\sigma Q/h$ and hybridization state (plotted as Si-O-Si bond angle, $\theta$, in SiO$_2$, for bonding schemes involving sigma bonds only (A) and sigma and $\pi$-bonds (B)).

Fig. 7. (a) Oxygen-17 quadrupole coupling constant ($e^2\sigma Q/h$) plotted as a function of the percent ionic character, $I$, of the A-O-B bond in a series of oxides and oxyanions. (b) Oxygen-17 $e^2\sigma Q/h$ values plotted as a function of Si-O-Si bond angle, $\theta$, in SiO$_2$, for bonding schemes involving sigma bonds only (A) and sigma and $\pi$-bonds (B).

Aluminum-27 NMR Spectra

Aluminum-27 has a nuclear spin $I = \frac{1}{2}$ and a quadrupole moment of $0.149 \times 10^{-26}$ m$^2$, is 100 percent abundant, and resonates at 130.3 MHz in a magnetic field of 11.7 T. It is thus a most sensitive nucleus and has been investigated extensively in mineral and catalyst systems (1-5). Because of this sensitivity, $^{27}$Al NMR enables us to carry out a number of studies that would be most difficult with $^{17}$O or $^{29}$Si, and by way of example we shall discuss three types of experiments.

First, the high sensitivity of $^{27}$Al permits the observation of both MASS and static NMR spectra of $^{27}$Al nuclei having large $e^2\sigma Q/h$ values. For example, we recently obtained $^{27}$Al NMR spectra, both MASS and static, of the basic aluminum-sulfate cluster Na[AlO$_4$Al$_{11}$ (OH)$_{16}$(H$_2$O)$_{12}$][SO$_4$] - $\sim$13H$_2$O at 11.7 T and a static spectrum at 8.45 T (360 MHz $^1$H-resonance frequency). The aluminum sulfate contains an Al$_{13}$-polyoxo-hydroxo cluster with a central AlO$_4$ unit and 12 octahedral AlO$_6$ groups (58). In the MASS experiment at 11.7 T (59), only the central AlO$_4$ resonance is well resolved, because the absorption from the 12 octahedral alumins covers about 35 kHz, and a very complex pattern is obtained. At high field, the static spectrum may be recorded with minimal distortion and good sensitivity, but unfortunately, at 11.7 T, the resonance from the single tetrahedral site overlaps one of the singularities of the powder pattern from the 12 octahedral aluminums, and is thus not resolved. By contrast, at 8.45 T there is a substantial second-order shift and an increase in the width of the octahedral aluminum resonance, so both tetrahedral and octahedral sites are clearly seen. Computer simulation of this latter spectrum yields $e^2\sigma Q/h = 10.2$ MHz, in good agreement with the NMR experiment, but the relation appears to break down for small values of $e^2\sigma Q/h$ (59). Interestingly, in the Al$_{13}$ cluster found in the mineral zunyite, very sharp MASS NMR resonances for both tetrahedral and octahedral Al have been reported (63), corresponding to $e^2\sigma Q/h$ values of about 0.6 MHz and 2.5 MHz, respectively. Because the structure of the Al$_{13}$ cluster is essentially the same in the basic sulfate and zunyite, and bond lengths are similar, this suggests that the apparent facial ligand arrangement in zunyite could be the primary cause of the small electric field gradient (64). Thus, both the nature and symmetry of the ligand field must always be considered when interpreting $e^2\sigma Q/h$ data. In any case, it is clear that there are considerable opportunities for theoretical developments in interpretation of the $e^2\sigma Q/h$, $\eta$, and $\sigma$ values for $^{27}$Al in inorganic solids now that experimental data may be obtained for numerous materials.

Finally, there has been little rigorous study of the quantitation of quadrupolar signal intensities, especially for aluminum. In some materials—for example, in high-surface-area $\gamma$-Al$_2$O$_3$ (65) and many glasses (66)—only a small fraction of the total aluminum present is detected in the MASS NMR experiment. While some...
sites may be so distorted as to yield spectral lines that are simply too broad to be observed, especially at low magnetic field strength, other complications can arise because the energy levels with \( I = \frac{1}{2} \) and \(- \frac{1}{2}\) are not isolated from the other levels. There may be large spectral intensity changes as a function of the extent to which the various states are excited by the radio-frequency pulse. These effects have been studied (67), and they have led to a number of interesting two-dimensional experiments by Samson and Lippmaa (67) that may result in information about quadrupole coupling in the presence of other interactions, such as dipolar broadening. In order to observe sites that are so distorted they are not seen in a conventional pulsed NMR experiment, continuous-wave spectrometers that provide very high fields may be needed. In addition, nuclear quadrupole resonance and "zero-field" NMR (68) will likely have great utility.

**Spectra from Hydrogen and Other Nuclei**

Hydrogen (\(^1\)H) has a nuclear spin \( I = \frac{1}{2} \), is 99.985 percent abundant, and resonates at 500 MHz in a magnetic field of 11.7 T. It is thus an extremely sensitive nucleus for NMR. However, because of its abundance and large gyromagnetic ratio, the proton-proton dipolar interaction is extremely strong and cannot be removed solely by MASS in, for example, ice, where line widths on the order of 80 kHz are found.

Fortunately, in many technologically interesting materials such as zeolites and some ceramics, the hydrogen content is low, and if the hydrogen is not clustered, relatively narrow lines are expected because the dipole-dipole interaction is inversely proportional to \( r_{HH}^6 \), where \( r_{HH} \) is the interproton distance. Furthermore, if there is molecular motion present, even further narrowing can occur. This has permitted, for example, the detection of \( ^2\)H on Rh-TiO\(_2\) under conditions that give high-resolution spectra (69).

Application of MASS NMR to zeolite systems has resulted in high-resolution \(^1\)H spectra of solids (70), and resonances at 2 and 7 ppm from TMS have been observed for amorphous silica-aluminas. Only the 7 ppm resonance is attributed to catalytically active acidic hydroxyl groups, because the cracking rate of cations as a function of \( Al_2O_3 \) content closely parallels the presence of this spectral feature. In other studies, the dehydroxylation of an HY zeolite has been investigated; as expected, the combination of MASS with a multipulse \(^1\)H line-narrowing sequence (71) permits the recording of highly resolved \(^1\)H spectra, even in the presence of moderate dipolar broadening.

The presence of hydrogen in a sample can also cause line broadening of resonances from other nuclei, and this broadening often cannot be removed by MASS alone. For example, in KH\(_2\)PO\(_4\) and the borate mineral inyoite, high-field MASS NMR spectra that are \(^1\)H-coupled are available through advances in NMR spectroscopy. Given the impact that high-resolution NMR of solutions has had in many areas of chemistry over the past 20 years, we believe that a similar impact can be predicted for the NMR of inorganic solids.

**References and Notes**

Promoting Functional Plasticity in the Damaged Nervous System

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Not long ago it was commonly believed that the adult mammalian central nervous system (CNS) was structurally static—that severed neurites did not regrow and functionally significant structural adjustments did not occur. When recovery of function following brain lesions was observed it was attributed to the brain's capacity to circumvent the lesion by mechanisms such as derervation, regeneration, and collateral sprouting (1). In contrast, peripheral nerves were known to regenerate after being injured, sometimes with recovery of function (2, 3). The consequence of this pessimistic view was that scientific interest in neuronal plasticity was mainly directed at lower animals, immature systems, and peripheral nerves.

Terminal fields vacated as a consequence of CNS injury are commonly filled by the growth of axon collaterals, or collateral sprouting (4). Neuronal plasticity, and collateral sprouting in particular, appears to be a ubiquitous phenomenon in the mature CNS that can have functional consequences (5, 6). A considerable body of information pertaining to the cellular biology of collateral sprouting and synaptic plasticity now exists (7). Here we discuss neuronal plasticity from the perspective of functional restitution; that is: Can neuronal plasticity be manipulated or exploited to obtain functional benefits?

Axonal Plasticity in the Normal Nervous System

In the peripheral nervous system, severed neurites invariably regenerate. So vigorous is this regeneration that it persists in the stump even after removal of a limb, resulting in the formation of a neuroma (2, 3). As peripheral neurites grow, contact with Schwann cells stimulates myelination and some formation of new or additional basal lamina (8-10).

In the mature mammalian CNS, myelinated tracts, including those of the spinal cord, are unable to regenerate through the site of a lesion (11, 12). Certain categories of unmyelinated or thinly myelinated CNS neurites show substantial regeneration provided no physical barrier is produced when they are damaged (13).

Scarring at the site of a CNS lesion is greatly reduced in the immature animal; nonetheless, most studies agree that immature neurites cannot penetrate a CNS lesion to any greater degree than those of a mature animal (14). In most cases where regeneration is observed in either immature or adult animals, it occurs around, rather than through, the lesion site (11, 15-17). For example, function is spared after pyramidal and corticospinal tract lesions in infant animals (15, 16). The anatomical basis of this sparing is probably either a regrowth of late-devel-
High-Resolution Nuclear Magnetic Resonance of Inorganic Solids

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