Nuclear Magnetic Resonance Spectroscopy in the Earth Sciences: Structure and Dynamics

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Detailed knowledge of the structure and dynamics of the materials that make up the earth is necessary for fundamental understanding of most geological processes. Nuclear magnetic resonance spectroscopy is beginning to play an important role in investigations of inorganic solid materials, as well as of liquids and organic compounds; it has already contributed substantially to our knowledge of minerals and rocks, compositionally simplified analogs of magmas, and the surfaces of silicate crystals. The technique is particularly useful for determining local structure and ordering state in crystals, glasses, and liquids, and is sensitive to atomic motion at the time scales of diffusion and viscosity in silicates. New techniques offer promise for increased resolution for quadrupolar nuclei and for extension of experiments to high temperature and pressure.

BENEATH THE SURFACE OF THE EARTH, MOST GEOLOGICAL processes cannot be observed directly. There are two types of approaches that the experimental geochemist can take toward studying the geologic problems that include such processes. One is to try to stimulate nature and contend with complex material compositions and the intertwined effects of many variables. This remains the most common approach and is the basis of much of our present understanding. Such studies can be complemented and greatly extended by measurements that reveal more about the atomic scale details of the chemistry and physics of minerals and magmas. Because of the constraints of size and time scales, we will always ultimately be unable to duplicate nature in the laboratory, even if the technical problems of generating high temperature and pressure in experiments are overcome. Extrapolations to natural conditions will thus always be necessary and can be accurate only if processes are understood at a fundamental level.

The most basic information that needs to be known about a material in order to understand and eventually to predict its properties is its structure. The structures of highly ordered crystalline oxides and silicates are for the most part well known. In crystals that are disordered because of the effects of temperature, rapid growth, defects, or high surface area, however, structural information is generally incomplete because traditional techniques of x-ray diffraction may detect only long-distance averages, which can conceal energetically important details. In noncrystalline solids, structure is much more poorly known. In liquids the problem is even more complex, as the structure is highly mobile. The structures of both liquids and noncrystalline solids are related, however, in that some important aspect of the structure is not characterized by long-range crystallographic symmetry; instead, short- to intermediate-range order dominates. Local variations occur in the type and number of atoms in the first few coordination shells and the type and geometry of bonds. This commonality means that techniques that are useful for studying disorder in one class of materials may be useful for others. More important, it suggests the underlying mechanisms that control short- and intermediate-range order may be applicable to a wide range of materials and may be best elucidated by study of this full range.

The way that a structure changes with time is described by its dynamics. In the earth sciences, dynamics over an enormous range of time scales must be considered, from the vibrational (10^{-15} s) to the geological (10^{17} s). Dynamics are again best known for well-crystalline solids, where the vibrational, ultrasonic ($\sim 10^{-6}$ s), and laboratory (10^0 to 10^6 s) time scales are in some cases well explored. In the transformation of glassy solids to viscous liquids (for example, magmas), an intermediate range of dynamics [10^0 (?) to 10^{-8} (?) s] affects both transport and thermodynamic properties. Again, common mechanisms and concepts may be found: some types of dynamics, such as some solid-solid and solid-liquid phase transitions, might be controlled by rates of defect formation and bond breaking that are similar to those that govern the viscosity of liquids.

Nuclear magnetic resonance (NMR) spectroscopy has proven to be particularly useful in addressing questions of local structure and disorder and diffusive time-scale dynamics. Most elements have one or more stable isotopes with a nonzero nuclear spin. In a magnetic field, these nuclei can absorb and re-emit energy, typically in the radio-frequency (~ 10 to ~ 600 MHz) range in modern spectrometers with high-field superconducting magnets. The frequency of this absorption (the Larmor frequency) is characteristic of the isotope, and the intensity of the signal is, in principle, strictly proportional to the abundance of the number of spins of interest in a given sample. Nuclear spin energy levels and thus the absorption frequency are slightly perturbed by interactions with electrons; available technology allows routine detection of relative changes in frequency (usually measured in parts per million relative to a standard) as small as 4×10^{-10}. Thus NMR is a technique that is element specific and sensitive to local bonding environment. For spin-1/2 nuclei, such as ^{1}H, ^{13}C, and ^{29}Si, changes in the local magnetic field due to shielding by electrons produce "chemical" shifts in frequency. Absorption frequencies of quadrupolar nuclei, such as ^{2}H, ^{17}O, ^{23}Na, and ^{27}Al, are also sensitive to local gradients in the electric field. As in other spectroscopies, the absorption and re-emission of energy in NMR, and resulting line shapes, are sensitive to atomic motion at frequency scales ranging from those of line widths (0.1 Hz to >100 kHz) to those of the resonant frequency.

As in chemistry in general, the earliest and widest application of NMR spectroscopy in geochemistry has been to organic systems: soil, oil shale, coal, and petroleum have been routinely analyzed (*1*). Widespread application to inorganic earth materials and geochemical problems has only recently begun. Because of both common

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underlying processes and common materials, much of this work has been related to or a part of studies of materials for technological application, such as catalysts, glasses, and ceramics. Several recent reviews and books include descriptions of basic NMR physics and summarize the wide range of data that are now available for silicate and oxide solids (*2–5*). In this article, we discuss some examples of how NMR results can be tied directly to studies of geochemical and geological processes and emphasize several new types of applications.

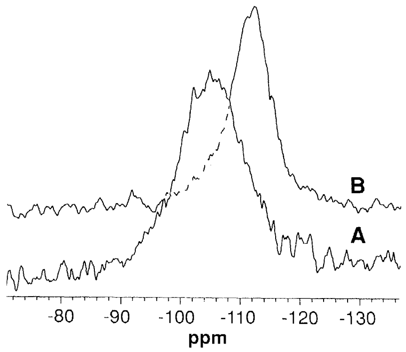

Fig. 1. Static (non-MAS) ^{29}Si NMR spectra of a highly strained quartzite (*12, 13*). Scale is in parts per million relative to tetramethylsilane (TMS). (**A**) Quartz grain crystallographic *c*-axes are distributed at all angles to the external magnetic field $\mathbf{B}_0$ ($\mathbf{B}_0$ is perpendicular to the foliation plane). A relatively broad spectrum is produced. (**B**) With the foliation plane rotated 90° so that it and the lineation direction are parallel to $\mathbf{B}_0$, a high proportion of the quartz grains have *c*-axes perpendicular to $\mathbf{B}_0$, producing a shifted and narrower line. Data collected at 79.5 MHz in a Varian VXR 400 spectrometer. One single $\pi/2$ pulse was given for each spectrum, preceded by a 4- to 12-hour equilibration period in the magnet.

Crystal Structure and Mineralogy

Work began on minerals with NMR soon after the technique was developed. Studies of nuclei that could be observed with early instruments, such as ^{1}H, ^{19}F, and ^{27}Al, gave results that supported the fundamental theory of nuclear spin interactions in solids (*6*). Subsequent systematic studies provided information on structure and phase transitions in a variety of geologically important oxides and silicates (*7–9*).

Most early work was done on single crystals of minerals because both chemical and quadrupolar frequency shifts are usually strongly dependent on the orientation of a crystal in the external magnetic field: both are described by second-rank tensors. NMR spectral lines of randomly oriented powders are thus usually too broadened to be very informative. For quadrupolar nuclei in minerals, particularly ^{27}Al, single-crystal studies have in many cases provided complete descriptions of the relation between structure and the electric field gradient. These results have been useful in understanding more recent magic-angle spinning (MAS) NMR data (described below), in which the quadrupolar effects are averaged by spinning about a single axis oriented at 54.7° to the magnetic field.

Analogous studies of the chemical shift anisotropy (CSA) tensor for low-abundance spin-1/2 nuclei in minerals are, however, much less common. The most or second most abundant cation in the earth, Si, has a spin-1/2 isotope, ^{29}Si (4.7% abundance). Although for cation sites with high symmetry much can be learned from powder spectra (*10*), complete characterization of the NMR properties must again come from single-crystal work. Only two such studies have been made, on forsterite (Mg_2SiO_4) (*11*) and quartz (SiO_2) (*12, 13*). This type of data has begun to be important in characterizing bonding in minerals (*10*), as it has been for ^{13}C in organic solids (*14*). Future work of this type should improve our understanding of the relations between structure and NMR spectra.

Information on the orientation dependence of chemical shifts in minerals can also be used for detection of nonrandom orientations of minerals in deformed rocks, which have often been studied by optical microscopy and used to infer past strain and stress histories. A test case is illustrated in Fig. 1. It is unlikely that NMR will replace traditional methods of fabric analysis of coarsely crystalline rocks, but the technique has potential for analysis of poorly crystalline, very fine-grained, and even amorphous materials. For example, orientation studies have been used recently to search for structural orientation in highly sheared silicate glass fibers (*15*).

Complete single-crystal studies are time-consuming and, at least for work with ^{29}Si at its natural abundance, require relatively large crystals (usually about 5 by 5 by 5 mm). For abundant nuclei such as ^{27}Al, dipole-dipole couplings can broaden lines and reduce chemical shift information. However, many of the line broadening effects seen in both single-crystal and powder spectra of silicates are eliminated with MAS NMR (*16*); as a result, many applications to silicate mineral structure have developed. Because calculation of an NMR spectrum for a complex structure from first principles is not yet possible, the first step in applying MAS NMR is empirical calibration of the effects of known structure on the isotropic average chemical and quadrupolar shifts that are observed by the technique.

The most progress in the study of inorganic solids has been made for ^{29}Si in silicates. The largest influence of structure on ^{29}Si spectra of silicates is the number of first neighbor oxygens. The high-pressure (>8.5 GPa), octahedrally coordinated polymorph of SiO_2 (stishovite), for example, has a chemical shift 80 or more parts per million away from silicates with four-coordinated Si, and can therefore be detected by NMR with relatively high sensitivity. Stishovite has been found only at known sites of meteor impacts and not in igneous rocks even of the deepest origin. Recently NMR has demonstrated that stishovite is present in a clay deposit at the Cretaceous-Teritary boundary (*17*), where it had not been previously detected with other techniques such as x-ray diffraction. This discovery further strengthens the case for a catastrophic impact at this time of widespread mass biological extinction.

For ^{27}Al, the difference in isotropic chemical shift between four and six coordinated sites is also relatively large (50 to 70 ppm). Although problems of quadrupolar broadening can complicate interpretations, this effect has allowed determination of site occupancies in minerals containing both tetrahedral and octahedral Al. The case of spinel ($MgAl_2O_4$) is a good example. This mineral is one end-member of a series of oxides that are commonly used in calculation of pressures and temperatures from coexisting mineral assemblages. Its overall average structure has long been known from x-ray diffraction, but site occupancies (crucial for calculating entropies) could not be precisely determined because of the similar x-ray scattering factors of Mg and Al. Both single-crystal (*9*) and MAS NMR (*18*) have now quantified the transition from a fully ordered, low-temperature cation distribution to a high-temperature, disordered phase. However, this mineral group also exemplifies one of the greatest limitations for the application of NMR to minerals: many natural spinels contain substantial amounts of paramagnetic Fe and Cr, which can broaden NMR lines to the point of being unobservable.

In most minerals of the earth's crust, Si and Al are in tetrahedral sites. Here, framework silicates are by far the most abundant (for example, quartz and feldspars), as well as being the major constituent of most common ceramics and of catalysts such as zeolites. For a given Si site in a mineral of this group, the isotropic chemical shift systematically changes with the relative number of Si and Al second neighbors (*2*). This relation often allows ^{29}Si MAS NMR peaks to be uniquely assigned in terms of numbers of Al and Si neighbors and the real, short-range distribution of these tetrahedrally coordinated cations to be determined. In many cases, this determination cannot

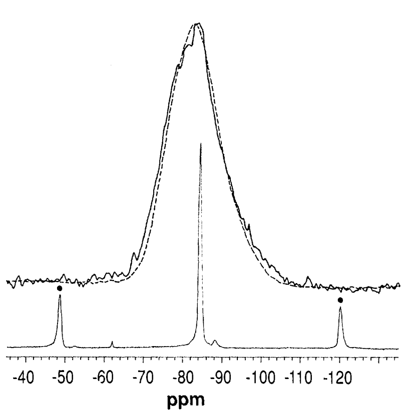

Fig. 2. ^{29}Si MAS NMR spectra of crystalline (below) and glassy (above, dashed line) diopside ($CaMgSi_2O_6$). Scale as in Fig. 1. Also shown is the cross-polarization (CPMAS) spectrum for a finely ground crystalline sample, in which Si sites near to surface protons are accentuated (above, solid line) (*29*). In the spectrum for the crystal, note the presence of small amounts of forsterite (Mg_2SiO_4, chemical shift, $\delta = -62$ ppm), enstatite ($MgSiO_3$, ≈ -82 ppm), and wollastonite ($CaSiO_3$, $\delta = -89$ ppm), which were by-products of the synthesis. The first two were of too-low abundance to be detected by routine powder x-ray diffraction. Dots mark spinning side bands.

be made by any other method: even single crystal x-ray diffraction analyses generally provide information on only the long-range average structure.

In several cases, ^{29}Si MAS NMR spectra have revealed that short-range order prevails even when x-ray data suggests that there is substantial long-range disorder. In the nepheline group [ideally $(Na,K)AlSiO_4$], for example, samples formed at high temperature in volcanic systems appeared from diffraction studies to have partial Al-Si disorder (*19*), but NMR work showed that they had nearly complete short-range order (*20*). This kind of result can have real thermodynamic significance. The calculated ideal configurational entropy of disordered nepheline (9.9 J mol^{-1} K^{-1}) (*21*) is about 4% of its total entropy at 1000 K and is nearly equal to the total entropy change for the reaction with quartz to form albite ($NaAlSi_3O_8$). This equilibrium is important in igneous processes and has been used to define the thermodynamic activity of silica in magmas (*22*). The finding of an ordered structure in nepheline resolved a major inconsistency in the systematic effects of composition on entropies of fusion of silicates, which are essential in predicting high-temperature phase equilibria (*23*). It also further supported the principle of aluminum avoidance, which states that AlO_4 tetrahedra do not share corners with each other if stoichiometry allows. This effect may be the prime cause of ordering in minerals with a 1 : 1 Al/Si ratio such as nepheline and has largely been confirmed for alkali aluminosilicates with both ^{29}Si and ^{27}Al MAS NMR [with a few exceptions (*24*)]. In addition, a recent ^{23}Na MAS NMR study of nepheline at temperatures as high as 500°C (*25*) has shown that there is a dynamic exchange of Na between alkali sites: such exchange influences both thermodynamic and transport properties.

Similar relations between ^{29}Si isotropic chemical shifts and second neighbor distributions occur in other mineral groups as well (*2, 16*). In framework silicates, all of these neighbors are tetrahedral Si or Al cations, and the four linking oxygens are described as "bridging." The tetrahedral site is described as Q^4, or quaternary, with four bridging oxygens. Successively replacing each of the surrounding tetrahedral cations with a larger, lower charged species such as Na^+ or Ca^{2+} causes a reasonably systematic change of about 10 ppm toward less negative (less shielded) chemical shifts as each bridging oxygen becomes a "nonbridging" anion. Thus, sites labeled Q^3, Q^2, Q^1, and Q^0 are produced. Generally, the abundance of such sites in minerals is well known from x-ray work; this correlation can be particularly useful for characterizing unknown structures of glasses and liquids (discussed below).

Chemical shifts in ^{29}Si are also systematically related to local structural variables such as bond lengths and angles (*1–5*). Consideration of these effects together in a single geometric term produces a good linear relation for most silicates (*26*). Recently, better understanding of quadrupolar effects has allowed the calculation of ^{27}Al isotropic chemical shifts for tetrahedral sites from MAS data (*27*), and relations between structure and shift similar to those for ^{29}Si have been demonstrated.

The interaction of all of the effects of structure on chemical shift can, of course, lead to ambiguities in assignment of peaks in spectra of unknown structures. In many cases, useful information can still be obtained by detailed comparison of line shapes between two materials, however. Good examples are recent studies of the disordering processes that occur at mineral and glass surfaces (*28, 29*). This type of work has wide applicability: most geochemical processes involve multiphase systems, and surface reactions often govern kinetics and even equilibrium. The effect of water on surfaces is particularly important in problems ranging from the formation of hydrothermal ore deposits to the diagenesis of sediments to the effect of radioactive waste on storage media. The technique of cross-polarization MAS (CPMAS) NMR, in which nuclear spin energy is usually transferred from ^1H to other nuclei such as ^{29}Si, can greatly enhance the strength of the signal from sites within a few angstroms of a proton (*2, 5*) and can therefore accentuate the sites in a mineral that have interacted with water. Even water adsorbed from the air onto a silicate surface can provide enough proton coupling to observe near-surface sites. For example, in Fig. 2, the ^{29}Si CPMAS spectrum of the surface of diopside ($CaMgSi_2O_6$) can be seen to be nearly identical to that of the glass produced directly from the molten phase (*29*). This suggests that the disordering that takes place on melting is closely related to that which results from grinding. The overall extent of this disorder can be appreciated by comparison with the spectrum for crystalline diopside, even though specific structural differences cannot be uniquely determined (*30*).

Several recent technical innovations are widening the applicability of MAS NMR techniques even further. For spin-3/2 and spin-5/2 nuclei such as ^{23}Na, ^{27}Al, and ^{17}O, second-order quadrupolar effects are not completely averaged by the usual MAS technique and often cause broadening that is severe enough to limit resolution substantially. This broadening can be reduced, however, at higher magnetic fields, and some relatively high-resolution quantitative work has been done, particularly for ^{27}Al (*2, 3*). Second-order quadrupolar broadening can be a particular problem in work on amorphous materials, where local structural variations lead to distributions in quadrupolar coupling constants and asymmetry parameters, as well

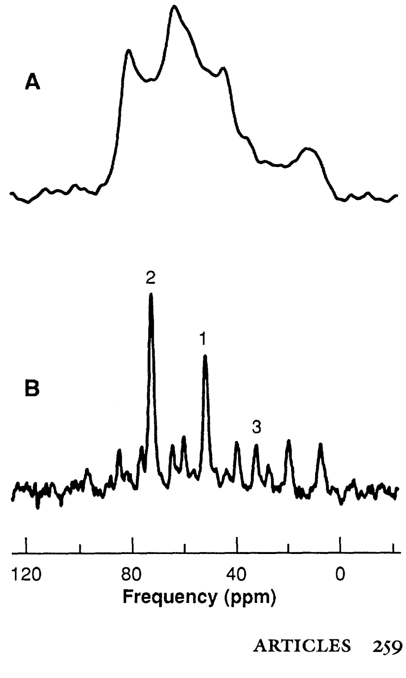

Fig. 3. ^{17}O spectra of crystalline diopside, $CaMgSi_2O_6$ (*32*). Scale in parts per million, relative to H_2O. (**A**) Standard MAS spectrum showing severe broadening by second-order quadrupolar coupling. (**B**) Double rotation or DOR spectrum. Three numbered, narrow lines are present, corresponding to the three nonequivalent oxygens in the structure. All other peaks are spinning side bands.

as in chemical shifts. These complications have made it difficult to determine the real extent of disorder. Second-order quadrupolar broadening can be eliminated with two new techniques (*31, 32*), which can greatly simplify spectra. Both methods work by averaging out not only the second rank spherical harmonics that appear in expressions for the orientation dependence of frequency (as in MAS) but also the fourth-order terms. In the first technique, double rotation or DOR, a powdered sample is spun about an axis that itself is spinning about a second axis. In what is a real advance in mechanical engineering as well as in NMR physics, double rotor spin rates of up to 1 and 3 kHz have been simultaneously achieved. In the second method (dynamic angle spinning, or DAS), a single rotor is flipped back and forth between two orientations, and a two-dimensional spectrum is recorded and analyzed. Wide ^{17}O MAS NMR lines in the mineral diopside ($CaMgSi_2O_6$) have been reduced in width by a factor of about 20 by the DOR method (Fig. 3) (*32*). This great increase in resolution should allow much more accurate determination of isotropic chemical and quadrupolar shifts and permit the distinction among oxygen sites with subtle differences in local structure.

Silicate Liquids

Much or most of the crust, and perhaps most of the mantle of the earth, originally crystallized from silicate liquids at high temperature. Natural magmas are chemically complex and contain nine or ten major oxide components as well as a number of volatile constituents. They are highly viscous, structured materials, whose behavior falls somewhere between the relatively well-understood realms of molten salt and organic polymer chemistry. The role of silicate liquids in the glass and ceramics industries has led again to a long history of fertile interactions between materials and earth scientists.

Basic ideas about silicate liquids combine concepts of structure and dynamics. Small, highly charged cations (such as Si^{4+} and Al^{3+}) that are four-coordinated and form strong, partially covalent bonds to oxygen are considered to be "network formers." Larger, lower charge cations that have six or more oxygen neighbors (such as Na^+ and Ca^{2+}) are termed "network modifiers," because addition of their oxides to SiO_2 liquid dramatically lowers viscosity. Silicate liquids are volumetrically dominated by oxygen anions, which may be bridging if bonded to two network-forming cations, or nonbridging if bonded to a network former and one or more network-modifying cations. These distinctions are not always clear: cations such as Fe^{2+} and Li^+ are at least sometimes four-coordinated in silicate liquids but are bonded weakly enough to still depolymerize the silica network structure. Models of viscosity often are based on abundances of bridging and nonbridging oxygens, and models of thermodynamics are often formulated on assumptions of the distribution of cations and of anionic species that may contain many linked polyhedral units. Identifying the roles played by different ions and the short- and intermediate-range order that they create in a liquid are thus needed for structural understanding. Specifically, the size and distribution of anionic species enters into calculations both of total configurational entropy and of activity coefficients for thermodynamic components, whose formulae are often chosen to match ideas of what structural units are present. In addition, characterization of the energetics and lifetimes of links between structural units is required for understanding transport properties such as viscosity and diffusivity.

The first approach to determining the structure of magmatic liquids has been spectroscopy on glasses, as most if not all of geological compositions and their representative simplified systems form glasses on quenching. Significant contributions have been made with both static and MAS NMR. As for crystals, these techniques have served at least qualitatively to constrain models of thermodynamics used in calculating phase equilibria and of properties, such as viscosity, that are needed for prediction of mass transport. In amorphous materials, NMR is particularly useful because it samples local structure. Intepretation of spectra are based on relations derived from known mineral structures. Again, the largest and clearest changes in chemical shifts are those attributed to coordination changes.

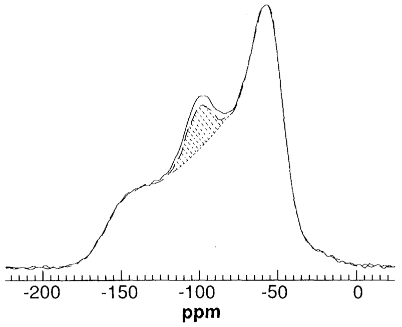

Fig. 4. Static ^{29}Si NMR spectra of $Na_2Si_2O_5$ glass (*45*). Scale as in Fig. 1. The large, asymmetric, broad peak is due primarily to Q^3 sites; the small central peak (cross-hatched) is due to Q^4 sites. The signal from the latter is greatly accentuated because of the high local symmetry. Solid curve is for a rapidly quenched sample. Dashed curve is for a slowly cooled sample, which has a slightly smaller proportion of Q^4 sites.

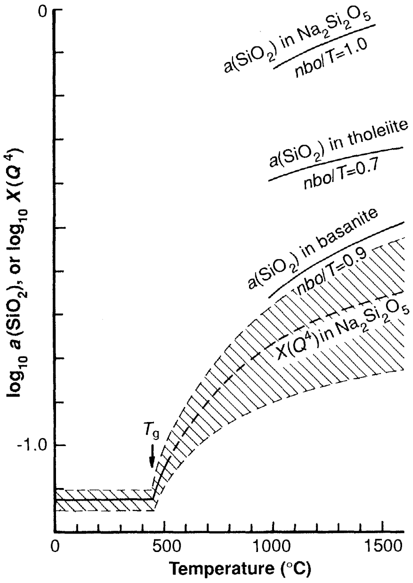

Fig. 5. Comparison of thermodynamic activity of silica, $a(SiO_2)$, estimated from solid-liquid phase diagrams (solid curves at high temperatures) with the estimated abundance of Q^4 species in $Na_2Si_2O_5$ liquid (dashed curve with wide error band); T_g is the glass transition temperature for a slowly cooled sample. The change with temperature in Q^4 abundance is quite similar to that for $a(SiO_2)$, although absolute abundances do not match activities: these solutions are known to be highly nonideal; *nbo/T* is the estimated mean number of nonbridging oxygens per tetrahedral cation. Speciation data are from (*45*); silica activities for various magma compositions (tholeiite and basanite) are from (*47*).

Shifts from fourfold to sixfold coordination of Al as a function of composition or increased pressure have frequently been used to rationalize bulk property data for aluminosilicate melts. Adding Al_2O_3 in excess of charge-balancing network modifiers, for example, reduces viscosity, suggesting that some Al^{3+} shifts out of network-forming sites. One major finding of MAS NMR has been a largely negative result: in most systems for which the higher coordinates have been suggested, well-defined sixfold Al seems to be absent. Exceptions are seen for some compositions in the Al_2O_3-SiO_2 binary (*33*). In some glasses, however, some of the Al may be in sites that are distorted enough to be difficult to detect with NMR, and thus their coordination cannot be resolved (*2*). In low-pressure glasses, six-coordinated Si in glasses has been detected by NMR only in samples rich in P_2O_5 (*34*).

Measured density increases of silicate liquids at high pressure are consistent with increases in both Al and Si coordination (*35*). Increasing pressure also reduces the viscosity of many silica-rich liquids (*36*), again perhaps indicating a shift of structural roles. Studies by vibrational spectroscopy and x-ray scattering of samples quenched from pressures as high as 4 GPa have not shown clear evidence for these changes (*37*), but ^{27}Al MAS NMR on a sample of $NaAlSi_3O_8$ glass quenched from 8 GPa has, however, suggested the presence of six-coordinated Al (*38*). Study of isotopically enriched samples with ^{29}Si MAS NMR has recently documented that small amounts of both six- and five-coordinated Si are present in alkali silicate liquids even at pressures as low as 1.9 GPa (*39*).

More subtle features of glass structure are often masked by the broadening of NMR lines caused by positional disorder. However, this disorder is the primary distinction between a glass and a crystal, and needs to be quantified to estimate entropies (*40*). The overall extent of disorder is in good qualitative agreement with what is expected from other properties. For example, ^{29}Si MAS NMR line widths systematically increase as the field strength of the network-modifying cation increases (*41*). This trend correlates with trends in liquid heat capacities, entropies of fusion, and thermodynamic activities that also suggest increasing disorder as interstitial cations interact more strongly with oxygens (*23*).

In many cases, Raman, infrared absorption, and other types of spectroscopy may provide more details of glass structure than NMR; however, NMR provides the potential for highly quantitative data. Some MAS spectra for simple compositions can be curve-fit to yield quantitative estimates of *Q*-species abundances, although this practice has generated considerable controversy (*2, 4, 30, 42*). For a relatively small range of compositions, static spectra on glasses can be more definitive because the small chemical shift anisotropy (*42*) of the Q^4 species compared with those of the Q^2 and Q^3 species allows even small Q^4 peaks to be distinguished (Fig. 4). Identification of peaks has allowed accurate quantitation of one of a series of disproportionation reactions that describe the relation between a system with a highly ordered distribution of Q species and one with greater disorder: $2Q^3 = Q^2 + Q^4$. Again, trends of speciation with composition agree with those inferred from other methods (*42, 43*). Simple entropy calculations suggest that as much as half of the total difference in disorder between glass and crystal could be attributed to the mixing of these species in the glass. The distribution of Q species can also be related directly to the extent of disorder among the bridging and nonbridging oxygens, which enters into models of viscosity.

In many systems, the change in heat capacity from glass to liquid is as large or larger than the gas constant *R* per gram atom (*23, 44*). This relation suggests that there is a major configurational component to the entropy caused by a continuous change in structure with temperature above the glass transition temperature T_g. The structure of a given glass thus reflects that of the liquid only at T_g, which at normal cooling rates in many systems is many hundreds of degrees below the melting points of interest to geologists. We thus must seek to explain both the structural cause of the increase in heat capacity (as well as in expansivity and compressibility), as well as to determine how glass structures change at higher temperatures.

One aspect of this problem has been examined by taking advantage of the kinetic nature of the glass transition: liquids quenched more rapidly transform to glassy solids at higher T_g's. The abundance of Q^4 species in alkali silicate glasses tends to increase as values of T_g increase (Fig. 4), indicating corresponding increases in Q^2 abundances and greater disproportionation from the ordered Q^3 distribution (*45*). The contribution to the overall configurational entropy change from this effect is minor. However, it may have real significance in controlling the thermodynamic activity of silica, $a(SiO_2)$, which is the most abundant component of most magmas. The $a(SiO_2)$ has major influence on solid-liquid phase equilibrium, which in turn controls the chemical evolution of magma systems. Relations between $a(SiO_2)$ and the abundance of the locally silica-like Q^4 species have been suggested from the systematic effect of cation field strength on the position of the silica liquidus in binary phase diagrams (*43, 46*). The spectroscopic observation of a change in the Q^4 abundance with temperature implies that there is a comparable change in $a(SiO_2)$. For example (Fig. 5), the slopes $[d\log a(SiO_2)/dT]$ calculated both from the Na_2O-SiO_2 phase diagram and from a solution model of complex natural magmas (*47*) agree surprisingly well with that estimated by long extrapolation of NMR data on $Na_2Si_2O_5$ liquid. This result provides hope that models of magma solution chemistry, firmly grounded in quantitative spectroscopic data, may eventually be feasible.

One recent success in relating structure to thermodynamics was initially based on infrared absorption spectroscopy of water dissolved in glasses. This work has shown that both OH and H_2O groups can be abundant in such glasses (*48*) and that such systems can be accurately treated with spectroscopically based models. The solution of water in magmas is of crucial importance in explosive volcanism, the formation of granitic intrusions, and in the genesis of many kinds of ore deposits; ^{1}H, ^{2}H, and ^{29}Si NMR have all been applied to confirm and extend these findings (*49*). For example, NMR data have begun to show which cations are attached to the OH groups and the extent of hydrogen bonding.

The relative abundances of different types of species and bonds, as frozen in at T_g, place some constraints on dynamics at higher temperatures. Spectroscopy on glasses can only reveal part of the information needed to understand equilibrium liquids, however. Liquids are fundamentally different, in that their structure is mobile enough to adapt to rising temperature through continuously increasing configurational disorder. The dynamics of this change can reveal something about the nature of the structural change and thus plays a central role in thermodynamic properties. Theoretical work recently applied to silicates has successfully linked configurational entropy to viscosity (*44*), suggesting the possibility that the same local-scale dynamics may be fundamental to both. Viscosity is one of the major variables controlling the style of magma emplacement, dictating whether a volcanic eruption will produce a catastrophic explosion or a quiescent lava flow. Models of dynamics in silicate liquids range from the simple pair interactions of molecular dynamics simulations (*50*) to systems involving chains and sheets of many atoms. In the former, flow is assumed to be dominated by short-range processes of transition state formation, bond breaking, and bond formation. In the latter, viscosity is related to entanglement models from polymer science. At present, there is little direct information on atomic-scale dynamics in silicate liquids. NMR spectroscopy is particularly useful here, because line shapes and relaxation times are sensitive to changes in local bonding arrangements at a frequency scale appropriate to viscous liquids. The NMR dynamics of an ionic liquid are thus expected to be significantly different from those of a polymeric system.

Use of NMR spectroscopy to study nonspinning samples of molten silicates at temperatures as high as 1300°C has recently begun to quantify such dynamics (*51–53*). As is true in general for NMR studies of dynamics, two types of measurements are made (*54*). The first is the determination of spin-lattice relaxation times (t_1), which are inherently sensitive to local atomic or molecular motion on diffusional time scales. This sensitivity is present because energy transfer out of a nuclear spin system in general must be stimulated by local fluctuations in magnetic field (or electric field gradient for quadrupolar nuclei) at the Larmor resonant frequency. This frequency is on the order of tens to hundreds of megahertz in modern spectrometers, many orders of magnitude below typical vibrational frequencies. In detail, data on relaxation times for complex systems such as silicates can be difficult to interpret.

However, the qualitative meaning is clear: close to or at the bulk T_g in all silicate liquids studied, a radical change in the mechanism of relaxation occurs. Thus, the style of atomic motion of the anionic network structure changes fundamentally just at the point where thermodynamic properties change abruptly (*52, 53*). The traditional view of T_g as the point where the silicate network can begin to rearrange on heating is well supported by these results.

In contrast, ^{23}Na t_1 data on these same systems show only minor inflections at T_g, indicating a subsidiary role in bulk thermodynamic properties for network-modifying cations (*52*). However, high-temperature activation energies are the same as those determined for tracer diffusion, indicating that NMR may prove useful for studying this geochemically important aspect of mass transport as well.

More direct information of rates of structural change can be obtained by analysis of line shapes. Shown in Fig. 6 are the static ^{29}Si spectra of a silica-rich liquid as a function of temperature (*53*). Just above the annealed T_g, the spectrum is identical to that at room temperature (*43*), which is dominated by the signals from Q^3 and Q^4 species. As temperature rises, these two signals begin to narrow and eventually collapse to form a single narrow line. Line narrowing in liquids is a common phenomena in NMR, as orientation-dependent shifts are averaged by local rotation or other kinds of rearrangement. Here, however, the presence of only a single line requires that the multiple species not only reorient rapidly, but also exchange with one another at a rate much higher than the separation in frequency between the two lines. This exchange can only take place by breaking and reforming Si-O bonds, which are the strongest in the system. Thus, molecules made up of interlinked tetrahedral units, if they are present at all in silicate liquids, can be estimated to have lifetimes of only microseconds to nanoseconds at melting temperatures. Simplified models of this exchange process can be generated that allow NMR spectra to be simulated. In the interpretation of the spectra in Fig. 6, a Si cation is assumed to jump rapidly among bonding states whose range of chemical shifts maps out the low-temperature static line shape. This process approximates the random motion of second-neighbor Si and alkali cations into and out of the second coordination sphere. Calculated line shapes can be matched to experimental data to estimate the exchange rate as a function of temperature. A linear correlation of the logarithms of these rates with inverse temperature gives an estimate of the activation energy of the process, which is within 10% of that determined from bulk viscosity measurements (*53*). Furthermore, simple approximations of shear moduli permit the viscosity to be predicted to within about 0.5 orders of magnitude of the measured value. In that viscosity can vary by 13 or more orders of magnitude as a function of composition and temperatures of interest in petrology, this agreement cannot be fortuitous. These findings strongly suggest that this species exchange is closely related to the fundamental mechanism of viscous flow in these systems: it is probably tied directly to the local diffusive motion of O and Si atoms, which may dominate bulk dynamics (*55*). Future work on ^{17}O NMR of such liquids should refine this picture.

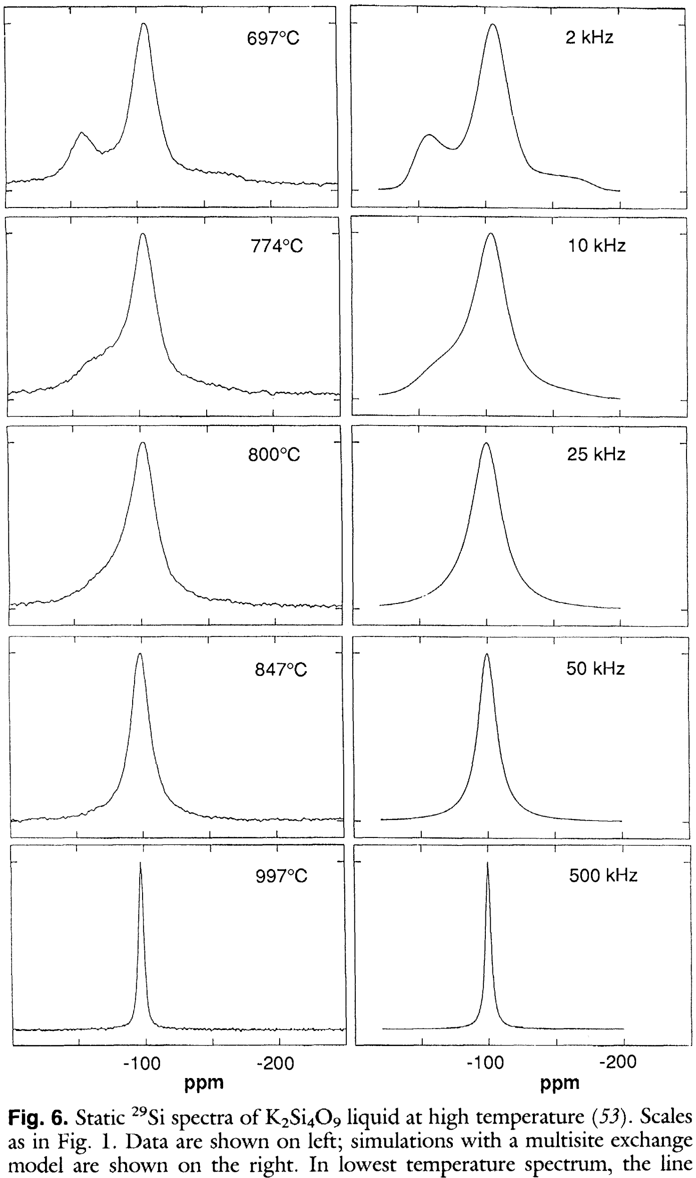

Fig. 6. Static ^{29}Si spectra of $K_2Si_4O_9$ liquid at high temperature (*53*). Scales as in Fig. 1. Data are shown on left; simulations with a multisite exchange model are shown on the right. In lowest temperature spectrum, the line shape is the same as that in the glass at room temperature. As in Fig. 4, the narrow central peak is due to Q^4 groups, and the broad asymmetric peak is primarily due to Q^3 sites. With increasing temperature, the two features narrow and merge. Simulations give exchange frequencies noted.

In conclusion, NMR spectroscopy has begun to play an important role in the earth sciences. It is becoming the method of choice for quantifying thermodynamically significant variations in short-range disorder in aluminosilicate minerals, glasses, and liquids. Applications of NMR to dynamics in geochemical processes are even newer, but should be increasingly important as studies of surface reactions, transport in liquids, and phase transitions progress.

REFERENCES AND NOTES

1. M. A. Wilson, *NMR Techniques and Applications in Geochemistry and Soil Chemistry* (Pergamon, Oxford, 1987).
2. G. Englehardt and D. Michel, *High-Resolution Solid-State NMR of Silicates and Zeolites* (Wiley, New York, 1987); R. J. Kirkpatrick *et al.*, *Annu. Rev. Earth Planet. Sci.* **13**, 29 (1985); E. Oldfield and R. J. Kirpatrick, *Science* **227**, 1537 (1985).
3. R. J. Kirkpatrick, in *Spectroscopic Methods in Mineralogy and Geology*, F. C. Hawthorne, Ed. (Mineralogical Society of America, Washington, DC, 1988), pp. 341–404; D. E. Woessner, *Am. Mineral.* **74**, 203 (1989); R. A. Kinsey, R. J. Kirkpatrick, J. Hower, K. A. Smith, E. Oldfield, *ibid.* **70**, 537 (1985).
4. R. J. Kirkpatrick *et al.*, in *Structure and Bonding in Noncrystalline Solids*, G. E. Wolrafen and A. G. Revesz, Eds. (Plenum, New York, 1986), pp. 303–328; P. J. Bray and M. L. Lui, *ibid.*, pp. 285–302.
5. C. A. Fyfe, *Solid State NMR for Chemists* (CFC Press, Guelph, Ontario, 1983).
6. G. E. Pake and E. M. Purcell, *Phys. Rev.* **74**, 1168 (1948); G. E. Pake, *J. Chem. Phys.* **16**, 327 (1948); R. V. Pound, *Phys. Rev.* **79**, 685 (1950).
7. S. Ghose and T. Tsang, *Am. Mineral.* **58**, 748 (1973).
8. J. L. Staehli and D. Brinkmann, *Z. Kristallog.* **140**, 360 (1974).
9. E. Brun and S. S. Hafner, *ibid.* **117**, 37 (1962).
10. A.-R. Grimmer, *Chem. Phys. Lett.* **119**, 416 (1985).
11. N. Weiden and H. Räger, *Z. Naturforsch. Teil A* **40**, 126 (1985).
12. D. R. Spearing and J. F. Stebbins, *Eos* **69**, 1518 (1988).
13. ———, *Am. Mineral.*, in press.
14. S. Pausak, A. Pines, J. S. Waugh, *J. Chem. Phys.* **59**, 591 (1973); P. M. Henrichs, *Macromolecules* **20**, 2099 (1987).
15. J. F. Stebbins, D. R. Spearing, I. Farnan, *J. Non-Cryst. Solids*, in press.
16. E. Lippmaa *et al.*, *J. Am. Chem. Soc.* **102**, 4889 (1980).
17. J. F. McHone, R. A. Nieman, C. F. Lewis, A. M. Yates, *Science* **243**, 1182 (1989).
18. G. C. Gobbi *et al.*, *Chem. Lett.* **1985**, 771 (1985); B. J. Wood *et al.*, *Am. Mineral.* **71**, 999 (1985); R. Dupree *et al.*, *Philos. Mag. A* **53**, L17 (1986).
19. W. B. Simmons and D. R. Peacor, *Am. Mineral.* **57**, 1711 (1972).

20. J. F. Stebbins, J. B. Murdoch, I. S. E. Carmichael, A. Pines, *Phys. Chem. Mineral.* **13**, 371 (1986); G. L. Hovis *et al.*, *Eos* **70**, 353 (1989).
21. H. H. Ulbrich and D. R. Waldbaum, *Geochim. Cosmochim. Acta* **40**, 1 (1976).
22. M. S. Ghiorso and I. S. E. Carmichael, *Contrib. Mineral. Petrol.* **90**, 121 (1985).
23. J. F. Stebbins, I. S. E. Carmichael, L. K. Moret, *ibid.* **86**, 131 (1984).
24. J. Klinowski *et al.*, *Nature* **330**, 56 (1987); J. F. Stebbins, *ibid.*, p. 13. Violations of strict aluminum avoidance are more common in aluminosilicates containing higher field-strength interstitial cation such as Ca^{2+} and Mg^{2+}; A. Putnis, in *Physical Properties and Thermodynamic Behavior of Minerals*, E. K. H. Salje, Ed. (Reidel, Dordrecht, 1988); B. L. Phillips *et al.*, *Eos* **70**, 351 (1989).
25. J. F. Stebbins, paper presented at the 30th Experimental NMR Conference, Asilomar, CA, April 1989; ———, I. Farnan, E. Williams, in preparation.
26. B. L. Sheriff and H. D. Grundy, *Nature* **332**, 819 (1988).
27. B. L. Phillips, R. J. Kirkpatrick, G. L. Hous, *Phys. Chem. Mineral.* **16**, 262 (1988).
28. B. C. Bunker *et al.*, *Phys. Chem. Glasses* **29**, 106 (1988).
29. J. A. Peck, I. Farnan, J. F. Stebbins, *Geochim. Cosmochim. Acta* **52**, 3017 (1988).
30. E. Schneider, J. F. Stebbins, A. Pines, *J. Non-Cryst. Solids,* **89**, 371 (1986).
31. A. Samosen, E. Lippmaa, A. Pines, *Mol. Phys.* **65**, 1013 (1988).
32. B. F. Chmelka *et al.*, *Nature* **339**, 42 (1989).
33. S. H. Risbud *et al.*, *J. Am. Ceram. Soc.* **70**, C10-C12 (1987).
34. R. Dupree, D. Holland, M. G. Mortuza, *Nature* **328**, 416 (1987).
35. S. M. Rigden, T. J. Ahrens, E. M. Stolper, *J. Geophys. Res.* **93**, 367 (1988).
36. C. M. Scarfe *et al.*, in *Magmatic Processes: Physicochemical Principles*, B. O. Mysen, Ed. (Geochemical Society, University Park, PA, 1987), pp. 59–68.
37. M. E. Fleet *et al.*, *Geochim. Cosmochim. Acta* **48**, 1455 (1984); M. F. Hochella, Jr., and G. E. Brown, Jr., *ibid.* **49**, 1137 (1985); P. F. McMillan and C. M. Graham, in *Progress in Experimental Petrology*, C. E. Ford, Ed. (National Environmental Research Council, London, 1981), pp. 112–115; B. O. Mysen *et al.*, *Neues. Jahrb. Mineral. Abh.* **147**, 281 (1983). Vibrational spectra of glasses at high pressure and room temperature have indicated increases in Si coordination with pressure [Q. Williams and R. Jeanloz, *Science* **239**, 902 (1988)].
38. E. Ohtani, F. Taulelle, C. A. Angell, *Nature* **314**, 78 (1985).
39. X. Xue, J. F. Stebbins, M. Kanzaki, R. C. Tronnes, *Science*, in press; J. F. Stebbins, P. McMillan, *Am. Mineral.*, in press.
40. R. F. Pettifer *et al.*, *J. Non-Cryst. Solids* **106**, 408 (1988).
41. J. B. Murdoch, J. F. Stebbins, I. S. E. Carmichael, *Am. Mineral.* **70**, 332 (1985).
42. J. F. Stebbins, *Nature* **330**, 465 (1987).
43. ———, *J. Non-Cryst. Solids* **106**, 359 (1988).
44. P. Richet, *Geochim. Cosmochim. Acta* **48**, 471 (1984); C. A. Angell, in *Relaxation in Complex Systems*, K. L. Ngai and G. B. Wright, Eds. (Office of Naval Research, Washington, DC, 1985), pp. 3–12.
45. M. E. Brandriss and J. F. Stebbins, *Geochim. Cosmochim. Acta* **52**, 2659 (1988).
46. For example, B. H. W. S. De Jong, K. D. Keefer, G. E. Brown, Jr., C. M. Taylor, *Geochim. Cosmochim. Acta* **45**, 1291 (1981).
47. M. S. Ghiorso *et al.*, *Contrib. Mineral. Petrol.* **84**, 107 (1983).
48. E. M. Stolper, *Geochim. Cosmochim. Acta* **46**, 209 (1982).
49. H. Eckert, J. P. Yesinowski, L. A. Silver, E. M. Stolper, *J. Phys. Chem.* **92**, 2055 (1988); H. Eckert, J. P. Yesinowski, E. M. Stolper, T. R. Stanton, J. Holloway, *J. Non-Cryst. Solids* **93**, (1987); I. Farnan, S. C. Kohn, R. Dupree, *Geochim. Cosmochim. Acta* **51**, 2869 (1987).
50. S. Brawer, *Relaxation in Viscous Liquids and Glasses* (American Ceramic Society, Columbus, OH, 1985); M. F. Hochella, Jr., and G. E. Brown, Jr., *Geochim. Cosmochim. Acta* **48**, 2631 (1984).
51. J. F. Stebbins *et al.*, *Nature* **314**, 250 (1985).
52. S.-B. Liu *et al.*, *Phys. Chem. Minerals* **15**, 155 (1987); S.-B. Liu, J. F. Stebbins, E. Schneider, A. Pines, *Geochim. Cosmochim. Acta* **52**, 527 (1988).
53. I. Farnan and J. F. Stebbins, *Eos* **69**, 1482 (1988); in preparation.
54. J. F. Stebbins, in *Spectroscopic Methods in Mineralogy and Geology*, F. C. Hawthorne, Ed. (Mineralogical Society of America, Washington, DC, 1988), pp. 405–430.
55. D. B. Dingwell and S. L. Webb, *Phys. Chem. Mineral.* **16**, 508 (1989).
56. We acknowledge the support of National Science Foundation grants EAR 8707175 and EAR 85-53024 and the continued assistance of D. R. Spearing. The spectrometer used for much of the work described here was funded by the NSF, the Pew Foundation, and a gift from Varian Associates.

The Applications of Closure Phase to Astronomical Imaging

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Closure phase is a number measured by triplets of Michelson interferometers that is completely independent of certain types of otherwise severe instrumental errors. In the 30 years since closure phase was invented, it has been applied to a diverse number of different problems in astronomical imaging. Methods based on the closure phase now allow imaging of complex objects in the presence of severe aberrations and are vital to the success of modern, high-resolution astronomical imaging both at radio and at optical wavelengths. Over the past 10 to 15 years, the concept of closure phase has been extended and generalized. One of the most important advances has been the development of automatic or self-calibration techniques. This article reviews closure phase methods and some of the many spin-offs and related ideas.

A MICHELSON INTERFEROMETER CAUSES THE LIGHT COLLECTED at two mirrors to undergo wave interference at a common focus (see Fig. 1). Interference fringes will be seen with a contrast that depends on the structure of the light source. A change in the optical path length in one arm (such as occurs if mirror A is moved to position A′) will shift the fringe position. This fringe position is known as the fringe phase, and one can measure it by rapidly modulating a mirror between two different positions corresponding to a change in the delay of the signal by $\lambda/4$, where λ is wavelength. The fringe phase contains useful information about the structure of the source, but it is nearly always corrupted by either mechanical instabilities or path length changes above the mirrors due to atmospheric turbulence. Furthermore, rapid changes in the fringe phase lead to washing out of the fringes, an effect that ultimately limited Michelson's original observations.

Although Michelson first demonstrated interferometry at optical wavelengths, the sustained development of his technique was substantially easier at radio wavelengths and was pursued vigorously in the late 1940s and early 1950s by a number of groups. The principal reason for preferring radio wavelengths was that the radiation could be amplified and detected easily with the electronics technology developed in World War II. Ryle's phase-switching interferometer (*1*) was used for cosmological studies and for studies of the structure of radio sources. Modern radio telescopes consist of arrays of phase-switching interferometers connected to sample the coherence function of the electromagnetic field. From such samples, it is possible to image complex objects. However, even in radio interferometry, the difficult problem of measuring the phase of the interference fringes often remains. Fortunately, as I will show in this article, in many

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