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PROPOSED APPLICATIONS OF NQR TECHNIQUES TO THE GEOSCIENCES*

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ABSTRACT

Many energy-related areas such as nuclear waste isolation, continental drilling, fossil fuel recovery, and geothermal energy are directly associated with an in-depth understanding of the earth sciences. Of particular interest is the development of analytical techniques which can augment existing ones in developing a better understanding of mineralogy.

Presently, available instrumental techniques for studying mineralogical problems such as x-ray, electron and neutron diffraction, nuclear magnetic resonance (NMR), electron microscopy and transmission electron microscopy have inherent limitations. These manifest themselves in being unable to characterize mineral samples fully, especially if they are polycrystalline.

Nuclear Quadrupole Resonance (NQR) spectroscopy offers the potential for being able to obtain accurate high resolution spectra. These can then be interpreted to give structural information which can be related to local electronic structure, atomic arrangement, order/disorder phenomena, and crystal phase transformation. In addition, molecular dynamics in the solid state can be studied. Furthermore, since NQR data are sensitive to changes in temperature and pressure, there is the possibility of obtaining stress/strain information.

Given the role of aluminum in the architecture of the rock-forming minerals in the earth's crust, aluminum-27 (100% abundance, $I = 5/2$) is easily shown to be the most generally useful NQR probe nucleus. Initial studies will be performed on the plagioclase mineral suite, already well characterized by x-ray and by single crystal NMR studies. The anticipated instrumental difficulties and likely solutions to the problem of efficient detection of aluminum-27 NQR will be discussed.

INTRODUCTION

This paper addresses the long-term potential of Nuclear Quadrupole Resonance Spectroscopy (NQR) to the geosciences with emphasis on energy-related problems. The subject matter discussed herein represents the current combined thoughts of staff and faculty respectively of the Geosciences Group, Lawrence Berkeley Laboratory; the Physics Department, Hunter College of CUNY; and the Department of Geology and Geophysics, University of California, Berkeley. The authors fully recognize that, based on the present state-of-the art, many of the suggestions made are speculative. It is felt, however, that NQR theory does not preclude any of the proposed work and that the development of NQR methodology, instrumentation and data handling techniques will permit the designated research to be accomplished.

Many of the United States Department of Energy's technology missions are intimately concerned with the physical and chemical properties of rocks and sediments composing the upper few kilometers of the earth's crust. These rocks and sediments are made up principally of aluminosilicate minerals containing oxygen, silicon, and aluminum. Other elements are present in varying amounts, depending on their crustal abundance, and occur either in solid solution in major rock-forming minerals or in discrete accessory minerals. For many reasons, the rock-forming minerals must be characterized as to their chemical composition, crystal structure, and other chemical and physical properties, in order to provide informative support and to solve technical problems associated with energy related activities.

Instrumental techniques to characterize mineral properties have become extremely important during the last twenty years, and promise to be even more so in the years ahead. Several mineral properties have not received sufficient attention, however, for want of practical instrumental methods. These properties, which permit the measurement and interpretation of phase transitions, atomic arrangements, and structural defects in minerals, have potentially important applications in several technological areas. Existing methods to measure those properties, such as x-ray, electron, and neutron diffraction, and several spectroscopic techniques have disadvantages not possessed by nuclear quadrupole resonance (NQR) spectroscopy, a technique that has found limited practical application in the past due, primarily, to the lack of sufficiently sophisticated measurement equipment. NQR spectroscopy permits the study of some aspects of crystal structures which are difficult, inconvenient, or impossible to determine by other techniques. Furthermore, the technique has high precision, specificity, and speed of measurement. Because of these features, NQR spectroscopy can become a powerful tool with many diverse applications and this more than justifies the uncertainties of the NQR research.

A selection of potential applications to various energy technologies is listed in Table 1. It should be emphasized that implementation of the applications

described in this table may take many years of effort in the theoretical, experimental, and instrumental development fields. It is an initial research goal to establish what this potential is and how much development is required before NQR spectroscopy becomes a fully viable technique for the geosciences (and related disciplines).

TABLE 1

Potential Applications of NQR to Energy Related Problems

Mission	Potential Application
Nuclear Waste	<ol style="list-style-type: none"> 1. Identification of lattice sites of radionuclides in glasses and synthetic and natural minerals. 2. In situ measurement of stress in salt. 3. In situ measurement of stress in rock formations.
Continental Drilling Program	<ol style="list-style-type: none"> 1. Down-hole sensing of elemental compositions and the crystal structures that contain them. 2. In situ measurement of stress at depth.
Fossil Fuels	<ol style="list-style-type: none"> 1. Continuous measurement of the distribution of sulfur between organic and inorganic phases in coal. 2. Measurement of organic complexes of V, Cu, Ni, and S in crude oil. 3. Stability of mining excavations, i.e., by wall, room, and pillar mining methods in coal mines, block caving, and in situ retorting of oil shales.
Geothermal Energy	<ol style="list-style-type: none"> 1. The use of compounds containing stable isotopes as tracer materials.
Uranium Resource	<ol style="list-style-type: none"> 1. Down-hole measurement of uranium ore grade and type both in and adjacent to the bore-hole wall. 2. Continuous monitoring of uranium in cores and mill feed, and identification of the mineral phases containing uranium. 3. Monitoring of uranium by-product elements such as Cu, V.
Fundamental Research in Support of Energy Development	<ol style="list-style-type: none"> 1. Characterization of phase transitions in common rock-forming minerals, i.e., feldspars, pyroxenes, amphiboles, phyllosilicates, and zeolites. 2. Interpretation of ordering in minerals with respect to thermodynamic properties. 3. Evaluation of localized stress in non-isotropic materials.

Two major areas of research are being undertaken. The first involves the evaluation of NQR spectroscopy as an effective tool in studying the ordering of ions in crystals, phase transitions, and the response of a given element in different minerals. This capability has already been demonstrated for nitrogen-14 compounds (ref. 1). Initial investigations are planned that will center on the response of aluminum-27 because this isotope is particularly abundant in rock-

forming minerals, has important scientific value, and should be detectable by NQR spectroscopy with modifications to existing instrumentation (ref. 2). During subsequent investigations, other important probe nuclei will be considered, including the actinides.

The second area of study covers the development of new NQR instrumentation techniques which includes such areas as the detection of NQR lines of various intensities, widths and shapes; improved sensitivity; remote analysis (ref. 3) and measurement of small samples (ref. 4). Anticipated improvements will increase the range of applications and should lead to the design of practical field instruments.

BACKGROUND

The structural properties of minerals are traditionally investigated by x-ray diffraction. Refinements give accurate information on atomic positions, temperature factors, and site occupancies in most cases where large (0.1 mm) homogeneous crystals are available. In special cases, techniques such as Mossbauer spectroscopy have applied to such problems as determining the Fe-Mg order in pyroxenes and olivines (ref. 5). Infrared and Raman spectroscopy also aid in determining the position and bonding state of hydrogen in silicate structures. Most recently the exploitation of synchrotron radiation makes it possible to use x-ray absorption methods to obtain structural information on the environment of acentric cation sites (ref. 6).

The measurement of Nuclear Quadrupole Coupling Constants (NQCC's) has long been used as a tool for sensitive structure-and-bonding studies in solids (refs. 7-9). This is one of the more desirable approaches because the nuclear quadrupole coupling interaction is very sensitive to the local electrical environment of the probe nucleus. Thus NQCC's reflect, in a unique way, both the chemical (valence electron) and physical (crystal phase) state of the resonant site. Ghose and Tsang (ref. 50) have compiled the work of a number of investigators (refs. 10-49) who show that aluminum-27 NQCC in mineral samples can provide significant structural information that complements x-ray data. This compilation, updated with more recent studies (refs. 49, 51, 52), is summarized in Table 2. These measurements are made indirectly using the technique of nuclear magnetic resonance (NMR). The best data are obtained by observing changes in the NMR spectra as a function of the orientation of a single crystal while the sample material is in an applied external magnetic field. The same NQCC data, at higher spectral resolution, should be directly obtainable from NQR spectral measurements. In the NQR approach however, neither single crystals nor an external magnetic field are required; this is a very important advantage for geoscientific applications.

TABLE 2

Summary of Aluminum-27 Mineral Data Obtained by Single Crystal Nuclear Magnetic Resonance (NMR) Techniques (the quadrupole coupling constant e^2qQ/h , in MHz, and the dimensionless asymmetry parameter η are shown for each resolved site of coordination number N)

Mineral:formula	N	e^2qQ/h (MHz)	η	Reference and Comments
Albite:NaAlSi ₃ O ₈	4	3.37		15,23
	4	3.29	0.62	26
Andalusite:Al ₂ SiO ₅	8	15.6	0.08	37
	5	5.9	0.7	37
Anorthite:CaAl ₃ Si ₂ O ₈	4	8.42	0.66	32, eight magnetically inequivalent sites are resolved. Al/Si order is found in samples studies.
	4	2.66	0.66	
	4	7.25	0.76	
	4	6.81	0.65	
	4	6.30	0.88	
	4	5.44	0.42	
	4	4.90	0.75	
	4	4.32	0.53	
Berlinite:AlPO ₄	4	4.09	0.37	18
Beryl:Be ₂ Al ₂ (SiO ₃) ₆	8	3.09	0	12, quadrupole data also obtained for ⁹ Be
Chrysoberyl:BeAl ₂ O ₄	8	2.85	0.94	13, site Al ₁ (i)
	8	2.85	0.76	13, site Al ₂ (m)
Cordierite:Mg ₂ Al ₄ Si ₅ O ₁₈ · H ₂ O	4	10.6	0.38	46, T ₁ -site
	4	5.6	0.34	46, T ₁ -site
Corundum: α -Al ₂ O ₃	8	2.39	0	20
Epidote:Ca ₂ Al ₂ (Fe,Al)Si ₃ O ₁₃ H	8	9.8	0.2	50, site Al ₁
	8	4.6	0.34	50, site Al ₂
	8	11.9	0.3	51, site Al ₁
	8	4.6	0.34	51, site Al ₂
Euclase:HBeAlSiO ₅	8	5.17	0.70	11
Gahnite:ZnAl ₂ O ₄	8	3.68	0	20
Almandine garnet: (Fe,Mg) ₃ Al ₂ (SiO ₄) ₃	8	1.51	0	27
Gd,Al-garnet:Gd ₃ Al ₅ O ₁₂	4	5.47	0	43
	8	<0.1	0	43
Thulium Aluminum garnet	4	0.892	0	41, a-site
	4	6.155	0	41, d-site

(continued)

TABLE 2
(continued)

Mineral:formula	N	e^2qQ/h (MHz)	η	Reference and Comments
Y,Al-garnet:Y ₃ Al ₅ O ₁₂	4	6.02	0	29
	8	0.63	0	29
Grossular:Ca ₃ Al ₂ (SiO ₄) ₃	8	3.61	0	34
Kyanite:Al ₂ SiO ₅	8	10.04	0.27	30, site Al ₁
	8	3.70	0.89	30, site Al ₂
	8	6.53	0.59	30, site Al ₃
	8	9.37	0.38	30, site Al ₄
Lithium Aluminate:LiAl ₅ O ₈	8	0.683	0.347	25
	4	0.284	0	
Microcline:KAlSi ₃ O ₈	4	3.22	0.21	14,23,26
Natrolite:Na ₂ Al ₂ Si ₃ O ₁₀ · 2H ₂ O	4	1.66	0.50	21, also ²³ Na NMR in this fibrous zeolite
Orthoclase:KAlSi ₃ O ₈				24, at least partial Al/Si order is found in four studied orthoclases
Sillimanite:Al ₂ SiO ₅	4	6.77	0.53	40
	8	8.93	0.46	40
Spinel:MgAl ₂ O ₄	8	3.72		16,17
	8	3.68	0	20
Spodumene:LiAl(SiO ₃) ₂	8	2.95	0.94	10,14 44,52, temperature and pressure dependence studied
Topaz:Al ₂ SiO ₄ F ₂	8	1.67	0.38	45, AlO ₄ F ₂ octahedra
	8	1.5918	0.704	34 Two magnetically-
	8	1.6506	0.501	34 distinct sites were found
Zoisite:Ca ₂ AlSi ₃ O ₁₂ OH	8	8.05	0.46	35, sites Al ₁ , Al ₂
	8	18.50	0.16	35, sites Al ₃

CHOICE OF PROBE NUCLEUS

Given the areas of interest, it still remains to be shown why aluminum-27 should be singled out as the probe nucleus for the initial studies. First, it must be stated that from the point of view of its natural abundance as a quadrupolar isotope, aluminum-27 is the natural first choice. This follows from considering all the elements, in order of their atomic abundance in the earth's crust. Among constituents of the lithosphere (ref. 53) it ranks third, with 8 weight percent. Oxygen (47 weight

percent) and silicon (28 weight percent) are the only two elements with greater abundance. Both of these more abundant elements are ruled out because they have no abundant isotopes which have spin $I \geq 1$, and therefore, are not subject to the NQR interaction. Aluminum-27, on the other hand, has a sufficiently high nuclear spin ($I = 5/2$), and natural isotopic abundance (~ 100 wt. percent) to satisfy the basic experimental requirements. In addition, its relative abundance in the lithosphere, mentioned earlier, us to the expectation that it is sufficiently abundant to be a generally useful probe nucleus, but still dilute enough so that signals from more than one crystal site can be unraveled.

MINERALOGICAL CONSIDERATIONS

There are several mineralogical problems that are of interest when considering energy related problems and these can be researched once the response of the NQR spectrometer to aluminum-containing compounds is fully understood.

Over 70 percent of the continental crust consists of feldspars, alumino-silicates occurring as solid discontinuous or continuous solutions of the three end-member components, microcline (KAlSi_3O_8), albite ($\text{NaAlSi}_3\text{O}_8$), and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). Thus, any model of chemical, structural, and deformation processes occurring in the earth must almost always has to include the properties of feldspars. They are present in almost every type of rock, including those which may be suitable hosts for radioactive waste repositories, those forming reservoirs associated with the production of geothermal energy, and in many sedimentary rocks containing or associated with fossil fuels.

Aluminum in feldspars is tetrahedrally coordinated. AlO_4 and SiO_4 tetrahedra form a continuous three-dimensional framework. In feldspars formed at low temperature, Al and Si are usually fully ordered. The feldspars, plagioclase, form a solid solution series, albite ($\text{NaAlSi}_3\text{O}_8$)--anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), at elevated temperatures. This has been found to contain different ordering schemes at lower temperatures which more or less satisfy Loewenstein's Al-O-Al avoidance principle (ref. 54), Figure 1. In albite there are 4 nonequivalent tetrahedral positions, Figure 1a, while in anorthite there are 8 Figure 1c. In intermediate compositions, such as labradorite, partial disorder occurs Figure 1b. At high temperatures (close to the melting point), Al and Si are disordered. Ordered and disordered phases have significantly different free energies. Such differences are important in calculations of stability relations in multicomponent geochemical systems and it is essential to determine their Al-Si distribution in order to correlate disorder with this and other important thermodynamic parameters.

Unfortunately, Al and Si have very similar atomic numbers and direct determination of site occupancies by x-ray diffraction measurements is, therefore, not possible. Neutron diffraction studies have met with more success since scattering amplitudes for Al and Si show a greater difference (refs. 55, 56), but this technique

is very costly to implement and suitable equipment is available only in a few places with high flux neutron reactors such as the Oak Ridge National Laboratory.

It is common to assume a linear occupancy bond length relationship, and one might expect a linear change in bond length with the chemical composition of plagioclase. Recent structure refinements of several plagioclases have shown that this is not the case. Particularly, small substitutions of Si on the Al-site have a very strong effect on bond lengths, while substitutions of Al on Si sites follow closely a linear relationship. This could be due to the existence of superstructures with more complex ordering patterns, but it is suspected that it may be caused by a nonlinear bond length occupancy relationship. A linear relation corresponds to an ideal solution model with ideal mixing and no interaction between substituting atoms. The authors suspect that mixing may follow regular solution behavior, particularly for the Al site, with Al being close to the transition from tetrahedral to octahedral coordination. There is no way to confirm this hypothesis with x-ray techniques. It is fortunate that NQR is very sensitive to the local Al environment and may permit the determination of the site occupancies directly and, thereby, help evaluate the possibility of nonlinear forces during atom substitutions.

Figure 1. Si/Al arrangements in plagioclases.

Another area where information is needed is the phase transformation from an ordered to a disordered Al-Si distribution. The state of ordering at specific

temperatures will be determined both with indirect x-ray and direct NQR measurements. This will allow quantitative investigation of the thermodynamics of these phase transformations. Whether this process is first or second order is still unclear. The result of such an investigation is crucial in establishing and understanding the behavior of igneous rocks (particularly volcanic rocks) during cooling.

Since NQR is most sensitive to the immediate environment of a nucleus, it should be applicable to study differences between truly disordered structures and those with short-range order. A distinction between these two is very difficult on the basis of x-ray data. It can be suggested that there is considerable order over a few unit cells based on diffuse background scattering, but this is unconfirmed. This problem is presently being investigated with transmission electron microscopy (TEM) which also supports a model with short-range order. Confirming this postulation using NQR could have great impact on understanding ordering kinetics.

Feldspars seem to be an ideal system to test the applicability of NQR techniques on Al-Si order for two reasons. First, it is possible to define specific research as previously discussed, and second, samples of albite from the California Coast Ranges (Franciscan), labradorite from Plush, Oregon, and anorthite from Grass Valley, California, have already been analyzed in some detail by the existing techniques thus providing an initial data base.

At a later stage, as the NQR technique matures, it would be desirable to apply it to other minerals such as the phyllosilicate to determine distribution of Al on octahedral and tetrahedral sites, with particular emphasis on the degree of order on the tetrahedral sites. In this way it should be possible to resolve the question whether some micas possess higher ordering and lower symmetry than has previously been believed (ref. 57). Furthermore, since NQR does not require large single crystals, it seems ideally suited to study clays and finely crystalline zeolite minerals which are of great importance in the weathering or diagenesis of rocks, and potentially important ion exchangers when in contact with groundwater.

EXPERIMENTAL TECHNIQUES

The primary experimental technique proposed is multiple pulse nuclear quadrupole resonance spectroscopy. Sufficient information has been obtained from crystallographic and NMR studies so that the characteristics of Aluminum-27 NQR spectra in minerals are fairly well understood. The frequencies of the NQR signals in distorted tetrahedra and octahedra are expected to cluster in the 1 MHz frequency domain and have line widths of the order of 10 to 50 kHz. Also, generally low values of spin lattice relaxation time, T_1 (msec) and the spectral bandwidth function, T_2^* (10 to 100 μ sec) are expected. In order to achieve efficient detection of aluminum-27 NQR lines with these properties, the various line-narrowing techniques which have been developed for NMR (refs. 59-61) will be extended to NQR. Work has already begun on these procedures (ref. 61).

Secondary experimental techniques which may be useful in specific cases are:

a) NQR-NQR double resonance based on the work of Emswiler, Hahn, and Kapland (ref. 62) can be very useful in determining neighboring atoms, and b) low field double resonance which is the more standard type of nuclear double resonance (ref. 63).

NQR DATA AND ITS INTERPRETATION

The purpose of the NQR measurements is to obtain information about identification and detection, crystallographic information and order/disorder determination, structure and bonding, and lattice dynamics. To accomplish this it is necessary to determine the nuclear quadrupole coupling constant, (e^2qQ/h), and the asymmetry parameter, η , for every crystallographic site; the multiplicity (total number) of NQR lines for each sample; the line-shape function of each NQR transition; the relaxation times T_1 , T_2 , and relevant cross-relaxation times; and the temperature dependence of these parameters.

INSTRUMENTATION

At present, two state-of-the-art NQR spectrometers exist which can be adapted for use on this program. Both of these instruments were designed and constructed by two of the authors (R. A. Marino and S. M. Klainer) for studying nitrogen-14 as the probe nucleus. One of these instruments is fully described in a paper to appear in the near future (ref. 2).

Presently the authors are modifying one of the spectrometers from a nitrogen-14 system (Spin, $I = 1$) to aluminum-27 (Spin, $I = 5/2$). The initial modifications necessary to prove the suitability of NQR to mineral characterization are being done, to a great extent, with commercial components, thus permitting the preliminary measurements to be made within a reasonable time period. Simultaneously, as the program progresses, state-of-the-art systems are being designed to assure maximum sensitivity, optimum use of the spectral data output, the ability to do small samples, and the capacity for remote detection.

RESEARCH GOALS

The goal of the present research is to determine how NQR spectrometric techniques can be used effectively to solve energy-related problems such as outlined in Table 1. Long-term research objectives are, at this time, indeterminate. This is so because the present study of NQR techniques is intended to develop a general approach and associated instrumentation which will apply to the solution of yet unspecified energy-related problems. Initially the specific capabilities of NQR to provide the crystallographic information of the kind listed in Table 3 will be evaluated.

TABLE 3

Crystallographic Information Needed from NQR

-
1. Determine basic crystallographic properties.
 2. Study structure and bonding in molecular and ionic crystals.
 3. Detect and identify compounds.
 4. Study intermolecular interactions.
 5. Analyze samples quantitatively.
 6. Detect phase changes and order/disorder phenomena.
 7. Study lattice vibrations and molecular and ionic motions in the solid state.
 8. Determine temperature and pressure dependence of all the above.
-

TABLE 4

Aluminum-27 Research

-
1. Investigate simple Al-O and Al-O-Si compounds to locate aluminum-27 resonances and to calibrate the NQR spectrometer. This will include looking at such materials as spodumene, albite, microcline, corundum, etc., to determine the effects of chemical structure and aluminum coordination state on the NQR spectra.
 2. Determine Al-Si order/disorder in feldspars.
 3. Make high resolution determination of crystallographic inequivalence of aluminum sites in mineral samples.
 4. Detect and identify specific exsolved crystal phases in host crystals.
 5. Conduct structure and bonding studies of aluminum sites in substances unsuitable for x-ray work, e.g., clay minerals.
-

TABLE 5

Investigate Other Probe Nuclei

-
1. Determine the NQR resonances for minerals containing actinides such as uranium-235, neptunium-237, plutonium-241, etc.
 2. Determine the NQR resonances for stable isotopes such as oxygen-17, sulfur-33, etc., in relevant crystalline hosts.
 3. Apply information from (1) and (2) to energy-related problems as identified in Table 1.
-

TABLE 6

Upgrade NQR Spectrometer for Maximum Performance

-
1. Develop transmitter-with-signal cancellation in the receiver coils.
 2. Investigate various coil designs for use with standard-size laboratory samples.
 3. Continue study of the suitability of cooled ferrite coils for the analysis of small samples (from mg to μ g).
 4. Continue evaluation of coil designs for remote detection (up to 12 inches away from coil) where coil diameter is less than three inches.
 5. Optimize all electronics for lowest noise background.
 6. Develop software programs and associated hardware to resolve individual NQR peak shapes which may be present in a composite NQR line.
 7. Provide improved dedicated computers, computer peripherals and displays.
-

TABLE 7

Field System

-
1. Construct a self-contained field NQR instrument for direct NQR measurements and data interpretation to solve energy-related problems or to continuously monitor energy-generating systems.
-

The initial research, therefore, should focus on establishing proof of principle using minerals containing aluminum-27 as the probe nucleus while providing sufficient flexibility to investigate compounds having other nuclei should the need arise. The broad scope of research tasks can be divided into the four work areas delineated in Tables 4 through 7.

SUMMARY

The ultimate goal of this program is a broad understanding of NQR so that the data from many probe nuclei in natural materials can be properly handled, processed, and interpreted and applied to the maximum number of energy problems that can be addressed.

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