**27**Al and **23**Na NMR spectroscopy and structural modeling of aluminofluoride minerals

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**ABSTRACT**

Simulations of high-resolution **19**F-decoupled **27**Al and **23**Na magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra of the aluminofluoride minerals, cryolite, cryolithionite, thomsenolite, weberite, chiolite, prosopite, and ralstonite combined with theoretical modeling have given accurate values of chemical shift (δiso), and quadrupolar interaction parameters (C_q and η), thereby eliminating ambiguities incurred by the complex nuclear interactions. These NMR data have been correlated with local electronic environments in the minerals, which were calculated using Full Potential Linearized Augmented Plane Wave (FP LAPW) modeling based on the structures from X-ray diffraction (XRD) data. This combination of NMR, XRD, and modeling techniques allowed the analysis and optimization of the crystal structures.

The electronegativities and distances of neighboring ions, represented here by an environmental parameter χ, are shown to control δiso of both **23**Na and **27**Al. The calculations using χ also show that the ions beyond the nearest neighbor play an important role in determining δiso of **27**Al and **23**Na in these aluminofluoride minerals, and the substitution of OH for F significantly affects the shielding around **27**Al in prosopite and ralstonite. There is a positive correlation between the site distortion at the Na and Al sites and the values of C_q in these aluminofluoride minerals.

**Keywords:** Cryolite, cryolithionite, elpasolite, weberite, thomsenolite, prosopite, chiolite, ralstonite, aluminofluoride minerals, **23**Na, **27**Al MAS NMR, FP LAPW calculations

**INTRODUCTION**

For nuclei such as **27**Al and **23**Na, with spin quantum number I > ½, the non-spherical symmetry of the nuclear charge distribution produces a nuclear quadrupole moment (eQ) (Slichter 1992). Electrostatic interactions between the eQ and the electric field gradient (EFG) result in nuclear magnetic resonance (NMR) quadrupolar lineshapes, from which structural information can be obtained. In this study, the relationship between quadrupolar interactions (QI) and structure is investigated for the aluminofluoride mineral group.

QI can be described by the quadrupolar coupling constant (C_q) and asymmetry parameter (η), which are determined from the EFG at the site (Slichter 1992):

\[
C_q = eV_{zz}Q/h
\]

(1)

\[
η = (V_{xx} - V_{yy})/V_{zz}
\]

(2)

where V_{zz}, V_{xx}, V_{yy} are the EFG components in the Principal Axis System (PAS) and |V_{zz}| ≥ |V_{xx}| ≥ |V_{yy}|, e is the electron unit, h is Planck’s constant, and Q is the quadrupole moment with values of 14.6 and 10.2 fm² for **27**Al and **23**Na, respectively (Pyykkö 2001).

The relationship between **27**Al chemical shift, QI parameters, and aspects of mineral structures for aluminosilicate minerals such as bond angle, coordination number, polyhedral distortion, and degree of polymerization has been well established (Smith 1993; Kirkpatrick and Phillips 1993). **27**Al becomes more shielded with a higher degree of polymerization and larger coordination number. The distortion of the Al polyhedron plays a crucial role for **27**Al QI, i.e., the more regular the polyhedron, the smaller the QI parameters (Smith 1993; Kirkpatrick and Phillips 1993).

Compared with the research on aluminosilicate minerals, relatively little has been done on aluminofluoride minerals (Dirken et al. 1992; Spearing et al. 1994; Kotecha et al. 2005). High-resolution magic-angle spinning (MAS) NMR spectra of aluminofluoride minerals are difficult to obtain because of the strong residual dipole-dipole interactions (**27**Al-**19**F, **23**Na-**19**F) caused by the abundant **19**F isotope with its large magnetogyric ratio (γ). These interactions cause broad featureless peaks, which cannot be averaged out completely even in MAS NMR experiments with high spinning speeds (Lacassagne et al. 1998). Depending on the program and methodology used, simulations of these broad peaks with different combinations for C_q and η may give very similar results especially for multiple sites. For some aluminofluoride minerals, QI is so small that the weak second order QI lineshape cannot be distinguished from residual dipolar interactions. As a result, different sets of the values of C_q and η have been obtained from the spectra of even very ordered aluminofluoride minerals (Dirken et al. 1992; Spearing et al. 1994; Lacassagne et al. 1998).

In this paper, we report accurate quadrupolar and chemical shift parameters for several aluminofluoride minerals, with Al(F,OH)₆ octahedra in differing degree of polymerization. Cryolite, cryolithionite, pachnolite, thomsenolite, and weberite have