

CATION ORDERING IN SPINEL FROM A CALCIUM-ALUMINIUM-RICH INCLUSION IN CARBONACEOUS CHONDRITE NORTHWEST AFRICA 2364 TO QUANTIFY TEMPERATURE IN THE EARLY SOLAR NEBULA. V. L. Houde¹, R. L. Flemming¹, A. Bouvier¹ and V. Tersikh², ¹Department of Earth Sciences, Western University, London, ON, Canada (vhoude@uwo.ca), ²Department of Chemistry, University of Ottawa, Ottawa, ON, Canada.

Introduction: Calcium-Aluminium-Rich Inclusions (CAIs) are the first solids thought to have condensed in the early solar nebula [1, 2, 3]. They are common in carbonaceous chondrites (CCs) [3, 4]. Some CCs have been relatively unaltered by high-temperature processes in planetary bodies since their formation [5].

Spinel ($MgAl_2O_4$) is commonly found in CAIs [3]. Spinel has a cubic closest packed arrangement of oxygen anions, with cations occupying 1/2 of the octahedral and 1/8 of the tetrahedral voids. The distribution of cations between octahedral and tetrahedral sites is dependant on the temperature of formation or latest equilibration of the spinel. In a fully ordered normal spinel, the tetrahedral and octahedral sites are occupied by Mg^{2+} and Al^{3+} , resp. Cation disorder between the octahedral and tetrahedral sites is described by $^{[4]}(Mg_{1-x}Al_x)^{[6]}(Al_{2-x}Mg_x)O_4$, where x is called the inversion parameter and represents the amount of Al^{3+} in the tetrahedral site.

The inversion parameter (x) can be used to estimate the formation/equilibration temperature of spinel [6, 7, 8]. x can be measured directly using ^{27}Al MAS NMR spectroscopy [6, 7, 9]. By studying spinel from pristine CAIs, the cation ordering temperature should represent the temperature at which the spinel formed in the early solar nebula. For CCs which have undergone little high temperature alteration in parent bodies, spinels will yield a calculated temperature which represents the formation temperature in the solar nebula and not a result of parent body processing.

Methods: *Micro X-ray diffraction.* Micro X-ray diffraction (μ XRD) was done on a Bruker D8 Discover X-ray diffractometer with a 60 mm cobalt Gobel mirror and a 300 μ m nominal beam diameter. μ XRD was used to identify minerals in a spinel-bearing CAI in Northwest Africa 2364 (NWA 2364). It was also used to confirm the mineral composition of CAI separates after heavy liquid density separation.

Heavy liquids density separation. Methylene iodide (density = 3.32 g/cm^3) was used to separate light and heavy density fractions from a crushed and sieved 30-63 μ m fraction of the crucible CAI from NWA 2364 (following methods described in [10, 11]). The heavy fraction contains spinel, gehlenite, and fassaite by μ XRD.

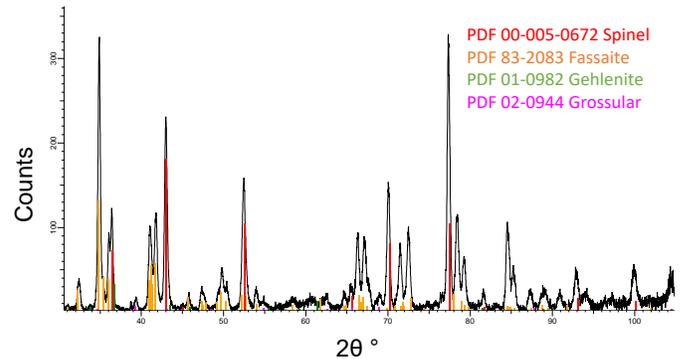


Fig. 1. μ XRD results for NWA 2364 showing presence of spinel, fassaite, and possible grossular and gehlenite.

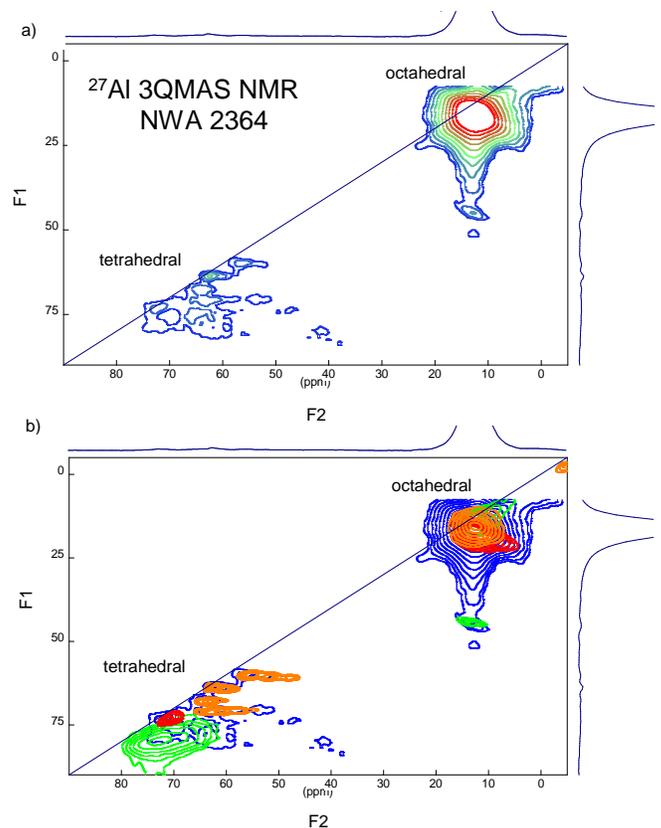


Fig. 2. a) ^{27}Al 3Q MAS NMR spectrum of NWA 2364 (multi-coloured) b) ^{27}Al 3Q MAS NMR spectrum of NWA 2364 (blue) overlain by spinel standard (red) [Syn, MEQ-003], gehlenite standard (green) [Crestmore, CA, Dana 3461], and fassaite standard (orange) [Allende CAI TS62B [12]], showing the overlap of the spinel standard with the spinel peak from NWA 2364.

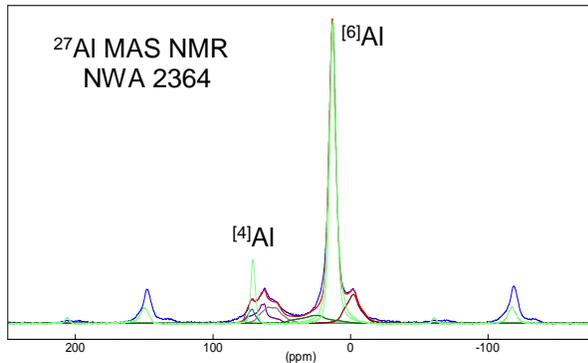


Fig. 3. NWA 2364 MAS NMR spectrum (blue) with fitted spectrum (red) overlain by spinel standard (green). Showing the three peaks under the tetrahedral (^{4}Al) site and the peak at 72 ppm lining up with the spinel standard. The peak at 62 ppm is interpreted as gehlenite (^{4}Al) and the peak at 54 ppm is interpreted as fassaite (^{4}Al). The octahedral (^{6}Al) spinel peak is at 13 ppm and a fassaite (^{6}Al) peak is at -2 ppm.

Nuclear Magnetic Resonance Spectroscopy. ^{27}Al Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectroscopy was done with a 21.1 T (^{27}Al at 243.6 MHz) Bruker Avance II NMR spectrometer at the National Ultra High-Field NMR Facility in Ottawa, Ontario (www.nmr900.ca). 3 to 5 mg of meteorite sample was packed in 2.5 mm zirconium rotors, using Kel-f inserts to ensure the small amount of powder was centered in the rotor, in a H/X MAS Bruker probe. The parameters were chosen to ensure quantitative data: pulse of 0.5 μs , at 30 degrees relative to the solid 90 degree tip angle, with a relaxation delay of 5 s. Two-dimensional 3Q MAS NMR and one-dimensional MAS NMR experiments were rotosynchronized, with samples spinning at 31.25 kHz.

Results: μXRD shows mineralogical composition of samples (Fig. 1) and NMR results show the aluminium environments within the minerals (Fig. 2 and Fig. 3). The MAS NMR spectrum was fit [13] using the center band only, assuming the ratio of octahedral to tetrahedral Al is the same in the spinning side bands.

The octahedral and tetrahedral spinel peaks occur at 13.5 ppm and 70.1 ppm respectively. $^{6}\text{Al}/^{4}\text{Al}$ ratio = $62.22/3.03 = (2-x)/x$, or $x = 2/[1+^{6}\text{Al}/^{4}\text{Al}] = 0.093$ [6].

Discussion: The calculated inversion parameter of $x = 0.093$ yields a temperature of 600 K using a calibration curve of x vs temperature from [6]. Using a similar calibration curve from [7], yields a temperature of 773 K. It yields a temperature of 581.5 K if using the B-value ($B = ^{4}\text{Al}/^{\text{tot}}\text{Al}$) as described in [8]. This would be a minimum temperature because the spinel may have undergone some reordering upon cooling [6]. This temperature may record only one of several heating events the CAI may have undergone, given the complex

history it shows [4, 11]. The temperature may also correspond to the temperature the meteorite experienced within the parent body and may reflect the temperature of a deformation event. This is consistent with the interpretation of this CAI, ‘the Crucible’ from NWA 2364, as having undergone a large deformation event in the nebula and another on its parent body [11].

Errors due to tetrahedral peak overlap were mitigated by running NMR standards of co-existing phases. μXRD results were used to identify coexisting minerals, for which NMR standards were run for comparison. The NMR signals of the CAI materials matched the standards identified by μXRD . Grossular needs to be run as a NMR standard.

Gehlenite and fassaite signals overlap with the signal for the tetrahedral site in spinel. There are three peaks apparently resolvable under this group of signals. The spinel peak was interpreted to occur at 72 ppm, based on its position in the spinel standard. Running an additional spinel standard will help confirm the chemical shift for the tetrahedral spinel peak. Errors due to peak overlap appear to be minimal, because NMR standards of co-existing phases yielded little overlap. Although the spinel peak appears to be distinguishable from the gehlenite and fassaite peaks, pure fractions of separated spinel from CAIs would provide better confirmation of peak position and $^{6}\text{Al}/^{4}\text{Al}$ ratio.

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