Crystal Structure and Cation Ordering in Fassaite from Type B CAI TS62B in Allende CV3. M. M. Haring[1], R. L. Flemming[1], V. Terskikh[2], L. Grossman[3,4] and S. B. Simon[3], [1] Dept. of Earth Sciences, University of Western Ontario, London, ON, N6A 5B7 mharing@uwo.ca; rflemmin@uwo.ca, [2]Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, ON, K1A 0R6, Victor.Terskikh@nrc-cnrc.gc.ca, [3]Dept. of Geophysical Sci., University of Chicago. Chicago, IL 60637, [4]Enrico Fermi Institute, University of Chicago.

Introduction: Extraterrestrial fassaite (Al-rich, Ti-bearing diopside), first reported in CAIs in the Allende and Vigarano CV3 chondrites in [1], was found to be structurally similar to terrestrial fassaite by crystal structure refinement [1]. Now known from all CV3s, fassaite is a major phase, primarily in Type B CAIs, where it is variable in composition and shows concentric and sector zoning [2]. Unlike terrestrial fassaite, it lacks Fe but contains significant Ti^{3+} and Ti^{4+}. Al enters both the octahedral and tetrahedral sites via Tschermak's substitution, along the diopside (Di: $CaMgSi_2O_6$) - Ca-Tchermak (CaTs: $CaAlAlSiO_6$) join. In this work, we report the crystal structure of fassaite from Allende Type B TS62B by single crystal X-ray diffraction (XRD), as well as cation ordering data by ^{29}Si and ^{27}Al Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) and triple quantum (3Q) MAS NMR spectroscopy. This is the first ^{29}Si and ^{27}Al NMR data reported for fassaite in a meteorite.

Methods: Images of the TS62B polished thin section were collected using a Hitachi SU6600 Field Emission Gun Scanning Electron Microscope (FEG SEM). Quantitative composition data for the fassaite were collected on the same section by Electron Probe Microanalysis (EPMA) using a JEOL JXA-733 Superprobe with an accelerating voltage of 15 KV and a beam current of 11 nA. Due to zonation of fassaite, 35 spots were analysed to obtain an average composition.

4.3 mg of a fassaite-rich concentrate were hand-picked from material scraped from the surface of a "potted butt" using stainless steel dental tools under a binocular microscope in a clean room. A 100 μm crystal showing no twinning was chosen for single crystal XRD. X-ray intensity data were collected using a Bruker Kappa Apex II diffractometer with MoKα radiation and a crystal-to-detector distance of 4.0 cm. The crystal structure of the fassaite was solved using the SHELX-97 data reduction software [3]. ^{29}Si and ^{27}Al MAS NMR spectra were collected on ~4 mg of fassaite packed in a 2.5 mm MAS rotor using a 21.1 T (^1H at 900 MHz) Bruker Avance II NMR Spectrometer at the Canadian National Ultrahigh-Field NMR Facility for Solids. (www.nmr900.ca) Other NMR experimental conditions (r.f. pulse widths, relaxation delays) were carefully chosen to ensure quantitative spectra.

Results & Discussion:

Single Crystal X-ray Diffraction (XRD). From single crystal X-ray analysis, the fassaite was determined to have unit cell parameters of *a* 9.770(2), *b* 8.840(2), *c* 5.340(1) and β 105.90(3) and space group *C*2/*c*, in good agreement with [1]. *C*2/*c* indicates that fassaite from TS62B has long-range cation disorder [4].

Scanning Electron Microscopy (SEM).

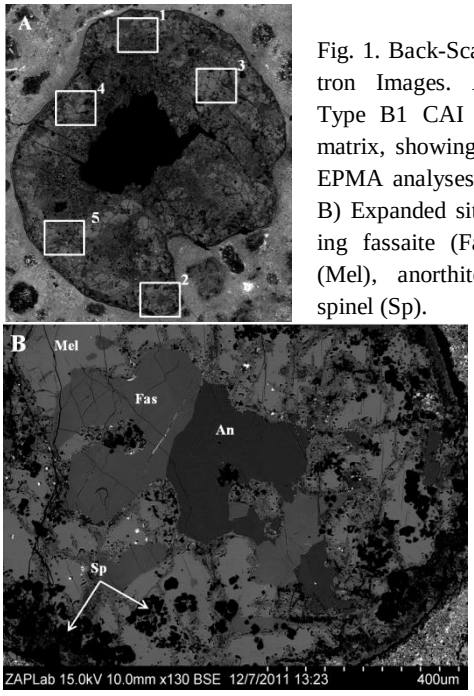

Fig. 1. Back-Scattered Electron Images. A) Allende Type B1 CAI TS62B in matrix, showing location of EPMA analyses in Table 1. B) Expanded site 2, showing fassaite (Fas), melilite (Mel), anorthite (An), & spinel (Sp).

Electron Probe Micro-Analysis (EPMA). EPMA data demonstrate composition variation in the fassaite consistent with past studies [2]. An average composition of all 35 points gives the chemical formula $Ca_{1.01}[Mg_{0.55}Al_{0.25}Ti^{3+}_{0.09}Ti^{4+}_{0.08}](Si_{1.43}Al_{0.57})O_6$.

Table 1. Representative EPMA analyses (wt% oxide) of Fassaite from the five locations in Fig. 1.

	1	2	3	4	5
SiO_2	37.49	38.06	40.85	37.44	42.42
TiO_2	3.29	2.81	2.39	3.31	1.90
Ti_2O_3	3.85	2.99	2.20	3.89	1.31
Al_2O_3	18.90	20.75	15.61	19.67	15.50
Cr_2O_3	0.08	0.11	0.03	0.08	0.05
FeO	0.06	0.07	0.08	0.05	0.01
MgO	9.84	8.88	12.27	8.73	12.81
MnO	0.10	0.09	0.02	0.05	0.00
CaO	26.10	25.84	26.10	26.13	25.64
Na_2O	0.01	0.00	0.03	0.04	0.00
Sum	100.25	100.01	99.85	99.95	99.83

^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) Spectroscopy. Three peaks were resolved in the ^{29}Si MAS NMR spectrum of fassaite, at -81.4, -84.4, and -90.1 ppm, consistent with spectra for synthetic Di-CaTs samples [5]. Relative peak intensities show that 54% of Si atoms in TS62B fassaite have one Al next nearest neighbor (NNN) on the tetrahedral single chain, 34% of Si alternate with Al in the chain (2 Al NNN), and 12% of Si have no Al NNN. This interpretation suggests the presence of local disorder on the Si chain, consistent with C2/c.

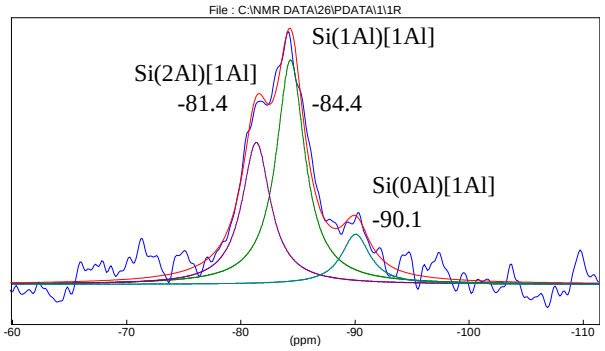

Fig. 2. ^{29}Si MAS NMR spectrum of TS62B at 21.1 T shown together with a deconvolution into three individual components labelled according to [5]. ( ) = tetrahedral, [ ] = octahedral NNN.

^{27}Al MAS NMR. The ^{27}Al MAS NMR spectrum of the fassaite from TS62B (Fig. 3a) shows two distinct sets of peaks, broadly similar to synthetic CaTs (Fig. 3b). The regions at ~ 40 to 80 ppm and ~ 20 to -20 ppm represent tetrahedral and octahedral sites, respectively, as is well documented [6]. The two narrow octahedral peaks demonstrate cation ordering in the six tetrahedral sites bonded to octahedral Al.

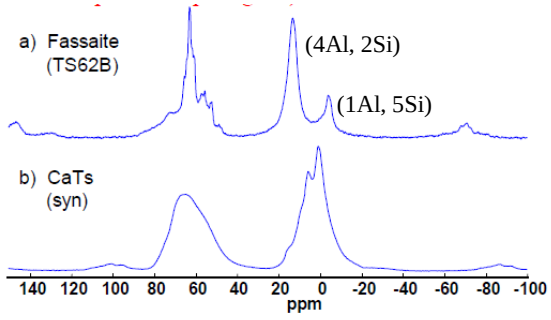

Fig. 3. ^{27}Al MAS NMR spectra at 21.1 T of (a) TS62B and (b) synthetic CaTs.

^{27}Al 3QMAS NMR. The ^{27}Al 3QMAS NMR spectrum of the TS62B fassaite provides additional resolution of the tetrahedral sites showing at least five peaks in 2D (Fig. 4). The five peaks represent five different tetrahedral aluminum sites and narrow peak widths also indicate ordering on the tetrahedral site.

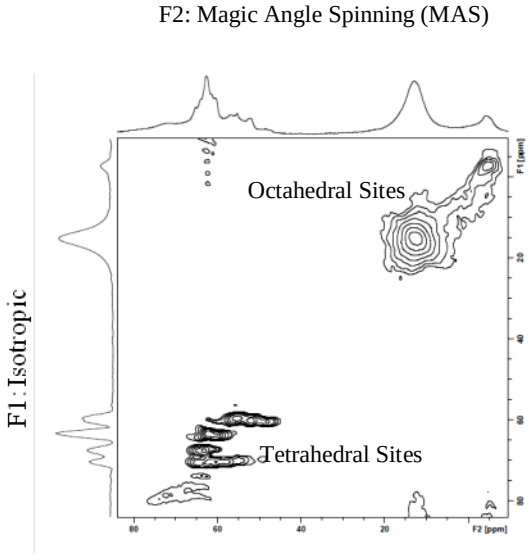

Fig. 4. ^{27}Al 3QMAS NMR spectrum showing five tetrahedral (distorted) and two octahedral (undistorted) sites.

Conclusions: Fassaite from the TS62B CAI has a disordered structure as suggested by the C2/c symmetry and ^{29}Si MAS NMR. The narrow peaks in the ^{27}Al MAS and ^{27}Al 3QMAS NMR spectra, however, show considerable Al ordering in the structure. Most likely this indicates the occurrence of short-range ordering above the transition temperature to a long-range ordered structure, as the calculated short-range ordering energy for fassaite [7] predicts the disorder-order transition to take place at low temperatures and thus be kinetically inhibited [7]. The temperature of transformation to ordered fassaite is not yet known as ordered fassaite has not yet been found on Earth [7]. Cation ordering could provide an independent estimate of temperature and cooling rate on the Allende parent body, once the transformation temperature is known.

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