

[4]

CRYSTAL STRUCTURE AND COMPOSITIONAL VARIATION OF ANGRA DOS REIS FASSAITE

ROBERT M. HAZEN and LARRY W. FINGER

Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C. 20008 (USA)

Received February 4, 1977

Revised version received March 21, 1977

The crystal structure of fassaite from the Angra dos Reis meteorite has been determined by least-squares refinement of three-dimensional X-ray data to an R value of 3.3%. The pyroxene is monoclinic, space group $C2/c$, with unit-cell dimensions $a = 9.738(1)$, $b = 8.874(2)$, $c = 5.2827(5)$ Å, $\beta = 105.89(1)^\circ$, and $V = 439.1(1)$ Å³. Average bond lengths are (Si,Al)-O = 1.651, M1-O = 2.061, and M2-O = 2.489 Å. The distribution of iron and magnesium between M1 and M2 suggests a temperature of equilibration greater than 1000°C.

Electron microprobe analysis of several fassaite grains reveals small but statistically significant variations of (Mg + Si) versus (Al – Ti). The range of fassaite composition may be represented by $En_3Hd_{2.2}TiCpx_6(Di_{5.3\pm 2}CaTs_{1.6\mp 2})$, where $En = Mg_2Si_2O_6$, $Hd = CaFeSi_2O_6$, $TiCpx = CaTiAl_2O_6$, $Di = CaMgSi_2O_6$, $CaTs = CaAl_2SiO_6$. Most fassaite analyses calculated on the basis of four cations yielded greater than six anions, suggesting that part of the titanium or chromium might be reduced to Ti^{3+} or Cr^{2+} .

1. Introduction

An aluminous clinopyroxene (fassaite) of composition $(Ca_{0.97}Mg_{0.58}Fe^{2+}_{0.22}Al_{0.16}Ti_{0.06})(Si_{1.73}Al_{0.27})O_6$ is the principal modal component (over 90%) of the Angra dos Reis (ADOR) achondrite. The present study was designed to determine details of the crystal structure of this mineral and to analyze the cation distribution among the three structural positions (M1 octahedron, M2 8-coordinated polyhedron, and T tetrahedron) to learn whether it would be possible to place a limit on the temperature of equilibration from analysis of cation disorder in M1 and M2. Previous analyses of the crystal structure of fassaites include a study of a terrestrial sample from Oka, Quebec, by Peacor [1] and a titaniferous variety from the Allende meteorite by Dowty and Clark [2].

2. Experimental

A single crystal of fassaite with excellent (110) cleavage, approximately $250 \mu m \times 150 \mu m \times 60 \mu m$,

was selected for data collection. Intensity measurements were made on an automated four-circle Picker diffractometer with Nb-filtered, Mo- K_α radiation, using the constant precision intensity technique described by Finger et al. [3]. All reflections in one hemisphere of reciprocal space from 0.1 to 0.7 $\sin \theta/\lambda$ were collected, including 655 symmetrically non-equivalent reflections. Of these reflections 590 were observed ($I > 2\sigma$). Table 1 lists the pertinent crystal data.

The observed intensities were corrected for absorption ($\mu_l = 27.2 \text{ cm}^{-1}$), and refinement was accomplished using program RFINE [4]. Neutral scattering factors of Cromer and Mann [5] and the anomalous scattering coefficients of Cromer and Liberman [6] were used for all atoms.

The pyroxene has a relatively complicated composition, and it was necessary to simplify the site assignments before beginning the refinement. As a first step, all Fe, Cr, and Mn were combined as Fe' . It was further assumed that the tetrahedral site contained only Si and Al; the remaining Al and the Ti were located in the M1 site, and the Ca was placed in M2.

TABLE 1

Crystal data for fassaite from the Angra dos Reis achondrite

Space group	<i>C2/c</i>	
Unit cell	<i>a</i>	9.738(1)
	<i>b</i>	8.874(2)
	<i>c</i>	5.2827(5)
	β	105.89(1)
	<i>V</i>	439.1(1)
Crystal size (mm)	0.25 × 0.15 × 0.06	
Number of reflections measured		1383
Number of independent reflections		655
Number of independent observed reflections (<i>I</i> > 2 σ)		590
Weighted <i>R</i> *, all data		6.2%
<i>R</i> **, all data		4.2%
Weighted <i>R</i> , observed data		5.6%
<i>R</i> , observed data		3.3%
Extinction coefficient		0.000047(3)

* Weighted $R = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$.

** $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

The Mg and Fe' were refined subject to the constraint of determined bulk composition. An isotropic extinction coefficient was also refined [7].

2.1. Compositional variations

Keil et al. [8] presented compositional data on the ADOR fassaite and stated that "there are no grain to grain compositional variations exceeding the precision of the analyses". Because a precise composition is important in evaluating details of the crystal structure, a suite of fassaites was analyzed using the automated electron microprobe at the Geophysical Laboratory. Thirty-eight analyses of nine different fassaite grains were performed; the average composition for all 38 analyses is presented in Table 2. Boyd and Finger [9] have demonstrated that the homogeneity of a set of analyses may be determined by comparison of the calculated standard deviation with a theoretical standard deviation for an ideally homogeneous set of analyses. This calculation has been used to test the variability of Si, Ti, Al, Fe, Mg, and Ca (Table 2). Within the precision of the analyses, Fe and Ca are homogeneous; the other elements, however, have

TABLE 2

Electron microprobe analyses of Angra dos Reis fassaite

Oxide	Average composition *	σ_o / σ_e **	Element	Number of cations per 4 cations
SiO ₂	46.2(7)	3.8	Si	1.728(16)
TiO ₂	2.11(11)	3.7	Ti ⁴⁺	0.059(3)
Al ₂ O ₃	9.86(49)	9.8	Al	0.433(22)
Cr ₂ O ₃	0.21(5)	—	Cr	0.005(2)
FeO	7.16(19)	1.5	Fe ²⁺	0.223(6)
MnO	0.09(3)	—	Mn	0.002(1)
MgO	10.4(2)	3.2	Mg	0.578(9)
CaO	24.2(2)	1.3	Ca	0.968(7)
Na ₂ O	0.04(2)	—	Na	0.002(1)
			O	6.006(8)
Total	100.3			

* The numbers in parentheses correspond to the standard deviation of 38 point analyses.

** σ_o is observed standard deviation, σ_e is expected standard deviation based on counting statistics (see Boyd and Finger [9] for description of this calculation).

statistically significant variations within and between grains. The samples analyzed in this study were crushed fragments from a mineral separate; therefore, no attempt was made to correlate compositional variations with crystallization history.

The ADOR fassaite may be modeled as a combination of several ordered end-member clinopyroxenes, and chemical variations may be represented as solid solutions between pairs of these idealized components. No significant correlation was found between Mg and Fe²⁺ ($r = 0.29$), indicating that there are no systematic variations in the solid solution between enstatite and ferrosilite. Moderate correlations were observed between Al and Ti ($r = 0.74$) and Mg and Si ($r = 0.80$). Significant correlations exist between Al and Si ($r = -0.90$) and Al and Mg ($r = -0.90$). The most significant correlation, however, was between Al and (Mg + Si) ($r = -0.95$), which represents the solid solution between CaMgSi₂O₆ and CaAl₂SiO₆. This relationship is illustrated in Fig. 1, and the equation for the regression line is:

$$N(\text{Al}) = 2.44 - 0.87 N(\text{Mg} + \text{Si}),$$

where $N(R)$ represents the number of R per four cations. The slope of the regression line is close to that of the diopside-CaAl₂SiO₆ substitution (ideal slope =

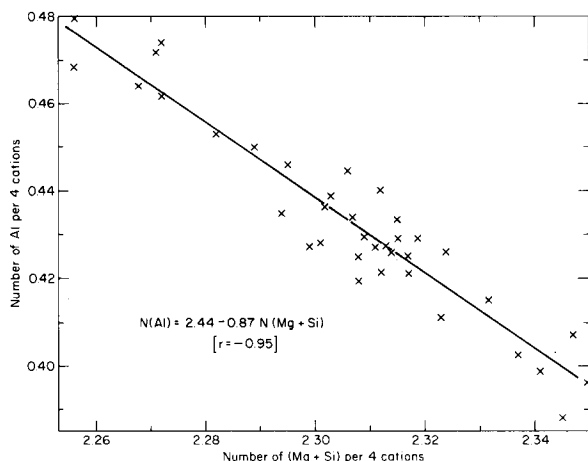


Fig. 1. Number of Al versus number of (Mg + Si) per four cations. X's represent point analyses from nine grains of Angra dos Reis fassaite.

–1.00). Taking this solid solution model into account, the ADOR clinopyroxene may be represented as $\text{En}_3\text{Hd}_{22}\text{TiCpx}_6(\text{Di}_{53\pm 2}\text{CaTs}_{16\mp 2})$, where $\text{En} = \text{Mg}_2\text{Si}_2\text{O}_6$, $\text{Hd} = \text{CaFeSi}_2\text{O}_6$, $\text{TiCpx} = \text{CaTiAl}_2\text{O}_6$, $\text{Di} = \text{CaMgSi}_2\text{O}_6$, and $\text{CaTs} = \text{CaAl}_2\text{SiO}_6$. Note (Table 2) that this simplified formula neglects minor amounts of Na, Mn, and Cr.

For most of the point analyses of fassaite, as well

as the analysis presented by Keil et al. [8], mineral formulae calculated on the basis of four cations yielded more than six anions. This excess of oxygen indicates that the oxidation state of one or more elements was too high, assuming no cation vacancies. Because iron was assumed to be divalent, in agreement with Mössbauer data [10], this element may not be used to correct the charge imbalance; the elements that may be reduced are Cr^{3+} and Ti^{4+} . The average number of anions is 6.006, suggesting that 0.012 cation is reduced. This possibility is consistent with the observation of a strong charge-transfer band with maximum absorption parallel to the M(1) strip [10].

3. Results

Atomic coordinates and isotropic temperature factors are presented in Table 3. Magnitudes and orientations of thermal vibration ellipsoids are given in Table 4, and bond distances and bond angles, in Table 5.

Apparent thermal vibration ellipsoids are similar to those of other fassaite [1,2], but are significantly larger than in many clinopyroxenes of end-member composition [11]. These differences are presumably due to local positional variation of the several different cations in M1, M2, and T, rather than unusual vibration effects.

TABLE 3

Atomic coordinates, equivalent isotropic temperature factors, and site occupancies of Angra dos Reis fassaite

Atom	x	y	z	B_{eq}	Occupancy
M1	0.0000	0.9071(1)	0.2500	0.55(2)	
Mg					0.568(4)
Fe'					0.210(4)
Al					0.161
Ti					0.059
M2	0.0000	0.3030(1)	0.2500	0.72(2)	
Ca					0.968
Mg					0.010(4)
Fe'					0.020(4)
T	0.2871(1)	0.0933(1)	0.2277(2)	0.46(2)	
Si					0.864
Al					0.136
O1	0.1135(2)	0.0872(2)	0.1392(5)	0.71(4)	
O2	0.3629(3)	0.2529(3)	0.3204(5)	0.88(4)	
O3	0.3520(2)	0.0191(3)	0.9924(5)	0.75(4)	

TABLE 4

Magnitudes and orientations of principal axes of thermal vibration ellipsoids of Angra dos Reis fassaite

Atom	<i>i</i> of axis r_i	r.m.s. displacement (Å)	Angle (deg.) with respect to		
			<i>a</i>	<i>b</i>	<i>c</i>
M1	1	0.070(3)	131(7)	90	25(7)
	2	0.089(3)	90	180	90
	3	0.090(4)	41(7)	90	65(7)
M2	1	0.078(3)	93(3)	90	13(3)
	2	0.095(2)	90	180	90
	3	0.110(2)	3(3)	90	103(3)
T	1	0.059(4)	131(5)	81(5)	27(5)
	2	0.082(3)	108(18)	160(23)	91(12)
	3	0.086(3)	47(12)	107(24)	63(4)
O1	1	0.067(8)	23(8)	97(7)	127(7)
	2	0.101(5)	110(9)	137(22)	119(17)
	3	0.111(5)	79(10)	132(22)	50(15)
O2	1	0.088(6)	107(10)	62(17)	28(17)
	2	0.103(5)	112(11)	149(17)	64(17)
	3	0.124(5)	29(10)	103(10)	80(8)
O3	1	0.078(7)	124(24)	56(11)	42(9)
	2	0.090(6)	146(24)	110(16)	102(18)
	3	0.119(5)	93(8)	139(7)	50(6)

Distortions of the M1 octahedron are close to those of the Allende fassaite described by Dowty and Clark [2] and Burns and Huggins [12]. Implications of these distortions relative to crystal-field effects of Ti and Fe in ADOR fassaite will be discussed by P.M. Bell et al. (in preparation).

Although metal-oxygen bond distances in ADOR fassaite are similar to those of other calcic clinopyroxenes, detailed analysis of these distances provides important information about cation distribution among M1, M2, and T.

3.1. The T site

T-O distances are sensitive to Al/Si, and electron density of the T site is sensitive to the amounts of Fe and Ti. Because both T-O distances and electron density are evaluated in a crystal structure refinement, the site occupancy of the tetrahedral position can be determined. Several previous refinements of the crystal structure of high-Ca pyroxenes provide data on the variation of T-O distances with tetra-

hedral Al/Si. These studies include diopside by Clark et al. [13], Allende fassaite by Dowty and Clark [2], Quebec fassaite by Peacor [1], and synthetic $\text{CaAl}_2\text{-SiO}_6$ (CaTs) by Okamura et al. [14]. Variation of T-O (bridging, non-bridging, and mean) distances with aluminum content for these pyroxenes is illustrated in Fig. 2. It is obvious that a linear relationship holds for all samples except CaTs. Grove and Burnham [15] noted evidence for short-range Al-Si order in CaTs, a structural difference that might explain its deviation from the linear trend. Linear regression analysis yields:

$$\langle \text{T-O} \rangle_{\text{Br}} = 1.675 + 0.065 \cdot X_{\text{Al}}^{\text{IV}} \quad (r = 0.997)$$

$$\langle \text{T-O} \rangle_{\text{NBr}} = 1.594 + 0.163 \cdot X_{\text{Al}}^{\text{IV}} \quad (r = 0.999)$$

$$\langle \text{T-O} \rangle_{\text{Mean}} = 1.634 + 0.117 \cdot X_{\text{Al}}^{\text{IV}} \quad (r = 1.00)$$

The high correlation between T-O distances and $X_{\text{Al}}^{\text{IV}}$ suggests that the composition of the tetrahedral site of the ADOR fassaite is $(\text{Si}_{1.73}\text{Al}_{0.27})$ as initially modeled. As further evidence, the electron density difference (ΔF) map revealed no unaccounted for

TABLE 5

Metal-oxygen bond distances and selected bond angles for Angra dos Reis fassaite

Bond	Distance (Å)	Atoms	Angle (deg.)
M1-O1A1 } M1-O1B2 }	2.115(3)	O1A2-M1-O1B2 O1A1-M1-O2D1 [2]	177.2(1) 170.6(1)
M1-O1A2 } M1-O1B1 }	2.051(3)	O1A1-M1-O1B1 O2C1-M1-O2D1	81.8(1) 94.5(2)
M1-O2B [2]	2.016(3)	O1A1-M1-O2C1 [2]	92.3(1)
Mean M1-O	2.061	O1A1-M1-O1A2 [2] O1A1-M1-O1B2 [2] O1A2-M1-O2C1 [2] O1A2-M1-O2D1 [2]	94.6(1) 83.3(1) 90.0(1) 92.0(1)
M2-O1A } M2-O1B }	2.363(3)		
M2-O2A } M2-O2B }	2.349(3)	O1-Si-O2	118.0(1)
M2-O3A1 } M2-O3B2 }	2.687(3)	O1-Si-O3C1 O1-Si-O3C2	110.3(1) 110.0(1)
M2-O3A2 } M2-O3B1 }	2.556(3)	O2-Si-O3C1 O2-Si-O3C2	109.7(1) 103.3(1)
Mean M2-O	2.489	O3C1-Si-O3C2	104.5(1)
T-O1	1.627(3)		
T-O2	1.610(3)	O3C2-O3C1-O3C2	165.4(2)
T-O3	1.676(3)		
T-O3	1.693(3)	Si-O3-Si	135.5(2)
Mean T-O	1.651		

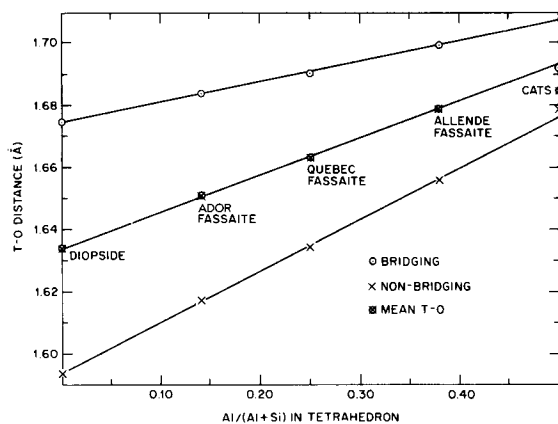


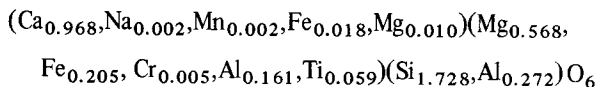
Fig. 2. Tetrahedral-oxygen bond distances (bridging, non-bridging, and mean) versus tetrahedral Al/(Al + Si) for clinopyroxenes on the join diopside-CaTs.

electron density in the vicinity of the tetrahedral site, indicating the absence of Ti or Fe at the T position. It must be noted that Fig. 2. does not apply to clinopyroxenes with significantly less than one calcium per formula unit [16].

3.2. The M1 and M2 sites

It was assumed that all Ca was in the M2 site and that all Ti and nontetrahedral aluminum were in M1. The distribution of Fe' and Mg between M1 and M2 was refined with a constrained chemical composition. The resulting occupancy of Fe' in M2 is 0.020 ± 0.004 , consistent with the Mössbauer results [10]. Assuming all Mn in M2 and all Cr in M1, the refined occu-

pancies suggest a structural formula of:



4. Discussion

The distribution coefficient for Fe-Mg partitioning between M1 and M2 is:

$$K_D = \frac{\text{Fe(M1)}/\text{Mg(M1)}}{\text{Fe(M2)}/\text{Mg(M2)}} = 0.20 \pm 0.09$$

This value of K_D is consistent with a high temperature of equilibration. Extrapolation of the equilibration curves for augites of McCallister et al. [17] to the calcium content of the ADOR fassaite yields a temperature of equilibration of 1100°C. This temperature estimate must be considered tentative as little is known of the effects of Al in M1 on Fe-Mg ordering.

References

- 1 D. Peacor, Refinement of the crystal structure of a pyroxene of formula $\text{M}_1\text{M}_{II}(\text{Si}_{1.5}\text{Al}_{0.5})\text{O}_6$, *Am. Mineral.* 52 (1967) 31–41.
- 2 E. Dowty and J.R. Clark, Crystal structure refinement and optical properties of a Ti^{3+} fassaite from the Allende meteorite, *Am. Mineral.* 58 (1973) 230–242.
- 3 L.W. Finger, C.G. Hadjidakos and Y. Ohashi, A computer-automated, single-crystal X-ray diffractometer, *Carnegie Inst. Washington Yearb.* 72 (1973) 694–699.
- 4 L.W. Finger and E. Prince, A system of Fortran IV computer programs for crystal structure computations, *Natl. Bur. Stand. (U.S.) Tech. Note* 854 (1975) 128 pp.
- 5 D.T. Cromer and J.B. Mann, X-ray scattering factors computed from numerical Hartree-Fock wave functions, *Acta Crystallogr.* A24 (1968) 321–324.
- 6 D.T. Cromer and D. Liberman, Relativistic calculations of anomalous scattering factors for X-rays, *J. Chem. Phys.* 53 (1970) 1891–1898.
- 7 W.H. Zachariasen, Experimental tests of the general formula for the integrated intensity of a real crystal, *Acta Crystallogr.* A24 (1968) 212–216.
- 8 K. Keil, M. Prinz, P.F. Hlava, C.B. Gomes, W.S. Curvello, G.J. Wasserburg, F. Tera, D.A. Papanastassiou, J.C. Huneke, A.V. Murali, M.-S. Ma, R.A. Schmitt, G.W. Lugmair, K. Marti, N.B. Scheinin and R.N. Clayton, Progress by the consorts of Angra dos Reis, in: *Lunar Science VII* (Lunar Science Institute, Houston, Texas, 1976) 443–445.
- 9 F.R. Boyd and L.W. Finger, Homogeneity of minerals in mantle rocks from Lesotho, *Carnegie Inst. Washington Yearb.* 74 (1975) 519–525.
- 10 H.K. Mao, P.M. Bell and D. Virgo, Crystal-field spectra of fassaite from the Angra dos Reis meteorite, *Earth Planet. Sci. Lett.* 35 (1977) 352–356.
- 11 M. Cameron, S. Sueno, C.T. Prewitt and J.J. Papike, High-temperature crystal chemistry of acmite, diopside, hedenbergite, jadeite, spodumene, and ureyite, *Am. Mineral.* 58 (1973) 594–618.
- 12 R.G.J. Burns and F.E. Huggins, Visible-region absorption spectra of a Ti^{3+} fassaite from the Allende meteorite: a discussion, *Am. Mineral.* 58 (1973) 955–961.
- 13 J.R. Clark, D.E. Appleman and J.J. Papike, Crystal-chemical characterization of clinopyroxenes based on eight new structure refinements, *Mineral. Soc. Am. Spec. Paper* 2 (1973) 31–50.
- 14 F.P. Okamura, S. Ghose and H. Ohashi, Structure and crystal chemistry of calcium Tschermak's pyroxene, CaAlAlSiO_6 , *Am. Mineral.* 59 (1974) 549–557.
- 15 T.L. Grove and C.W. Burnham, Al-Si disorder in calcium Tschermak's pyroxene, $\text{CaAl}_2\text{SiO}_6$, *EOS, Trans. Am. Geophys. Union* 56 (1974) 1202 (abstract).
- 16 H. Takeda, Crystallographic studies of coexisting aluminan orthopyroxene and augite of high-pressure origin, *J. Geophys. Res.* 77 (1972) 5798–5811.
- 17 R.H. McCallister, L.W. Finger and Y. Ohashi, Intracrystalline Fe^{2+} -Mg equilibria in three natural Ca-rich clinopyroxenes, *Am. Mineral.* 61 (1976) 671–676.