

CRYSTAL STRUCTURE OF A NATURAL TITANOMAGNETITE

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INTRODUCTION

Several models have been proposed for the cation distribution between tetrahedral and octahedral sites in the magnetite-ulvöspinel solid solution series: Fe_8O_4 - Fe_2TiO_4 . Barth & Posnjak (1932) indicate that the end members are inverse spinels (with both Fe^{2+} and Ti^{4+} in octahedral sites), although the distribution of Fe^{2+} , Fe^{3+} and Ti^{4+} within the series has not been strictly defined. Akimoto (1954) suggests that Fe^{3+} occupies equally both tetrahedral and octahedral sites with Ti^{4+} in octahedral sites, whereas Néel (1955) suggests that more Fe^{3+} occupies tetrahedral than octahedral sites, with Ti^{4+} in octahedral sites. Forster & Hall (1965) found that although Ti^{4+} has a preference for octahedral sites, ordering is not complete and some Ti^{4+} is present in tetrahedral sites in the two ulvöspinel specimens they examined.

Stephenson (1969) suggests that the distribution of iron is dependent upon the temperature of formation. If quenched at a high temperature a random distribution would occur over both sites. If equilibrium is attained at a low temperature, cation ordering would be expected due to the preference of Fe^{3+} for tetrahedral sites. Bleil (1971) found that only temperature-dependent distributions gave good agreement with measured magnetization data.

Jensen & Shive (1973) found an average cation distribution similar to that of Akimoto (1954), but consider that most of the titanium occurs in small titanium-rich clusters surrounded by a magnetite matrix. This clustering may be affected by sample preparation, which could explain the variation in magnetization measurements reported in the literature. Jensen & Shive (1973) also state that retention of a high-temperature Fe^{2+} - Fe^{3+} distribution by quenching is improbable, because of rapid electron transfer.

Since the cation distribution is not fully understood and most of the previous work has been done on synthetic specimens, it was considered worthwhile to determine the cation distribution in a natural titanomagnetite.

SAMPLE

The McKinney lava flow in the Snake River Plain, Idaho, U.S.A., is iron-rich, alkali olivine basalt of Pleistocene age. Olivine and plagioclase occur as phenocrysts. In the groundmass, the basalt contains olivine, plagioclase, augite and two Fe-Ti oxide solid solutions: magnetite-ulvöspinel and ilmenite-hematite. A titanomagnetite was extracted from the groundmass for a single crystal *x*-ray diffraction study.

The titanomagnetite was analyzed with an ARL electron microprobe using procedures described in detail by Ghent (1970), MacQueen & Ghent (1970) and Jones & Ghent (1971). Correction procedures outlined by Bence & Albee (1968) and Albee & Ray (1970) were used to reduce the raw data. CaO most closely approaches its limit of detection of 0.05%. All other oxides are further above their respective limits of detection. The precision of the results for minor oxides (SiO_2 , Al_2O_3 , V_2O_5 , Cr_2O_3 , MnO , MgO and CaO) is approximately $\pm 30\%$ of the amount present and for the major oxides (FeO and TiO_2) is approximately $\pm 0.2\%$ of the amount present. The analytical results and calculated atomic proportions, which are based upon a 24-cation unit cell, are presented in Table 1. FeO and Fe_2O_3 atomic proportions are calculated assuming stoichiometric $R_3\text{O}_4$ spinel. Homogeneity across the grains shows that no exsolution or zoning is present.

A formation-temperature of $980 \pm 50^\circ\text{C}$ is obtained with the Fe-Ti oxide geothermometer of Buddington & Lindsley (1964).

METHOD

The single crystal selected for *x*-ray diffraction study was an octahedron with the dimensions $58.5 \times 67.3 \times 95.2 \mu\text{m}$. Systematic absences indicate the space group is *Fd3m*. This crystal was mounted along an *a** axis and integrated intensities were collected on a Picker four-circle diffractometer. A graphite monochromator and $\text{MoK}\alpha$ radiation were used. Intensities were measured at a scanning speed of $1^\circ 2\theta$ per minute within the range of $\sin \theta/\lambda$ from 0.1 to 0.9. Twenty-second background counts

TABLE 1. ELECTRON MICROPROBE ANALYSIS AND ATOMIC PROPORTIONS.

WEIGHT %		ATOMIC PROPORTIONS			
SiO ₂	0.2	Fe ²⁺	7.820	} 8.001	
TiO ₂	21.1	Mn ²⁺	0.114		
Al ₂ O ₃	2.1	Si ⁴⁺	0.067		TETRAHEDRAL
V ₂ O ₃	0.7				
Cr ₂ O ₃	1.3	Fe ²⁺	4.420	} 16.002	
Fe ₂ O ₃	23.4	Fe ³⁺	5.245		OCTAHEDRAL
FeO	49.1	Ti ⁴⁺	4.726		
MnO	0.5	Al ³⁺	0.706		
MgO	0.9	Mg ²⁺	0.400		
CaO	0.1	Cr ³⁺	0.310		
TOTAL	99.4	V ³⁺	0.155		
		Ca ²⁺	0.040		
		O ²⁻	32.000		

(FeO and Fe₂O₃ are calculated by assuming stoichiometric R₃O₄ spinel.)

were made on both sides of each reflection, and a standard reflection was measured for every 50 reflections.

Lorentz polarization and absorption corrections were applied with the method of Wuensch & Prewitt (1965). The linear absorption coefficient is 125 cm⁻¹ and results in transmission factors within the range of 0.60 to 0.72. From one quadrant, 473 reflections were measured to give 114 symmetry-independent reflections. All reflections were included in the refinement.

Initial positional parameters for the oxygen anions are taken from Azároff (1968). All cations are in special positions fixed by symmetry. The positional parameters for these tetrahedral and octahedral cations are taken from the *International Tables* (1962). The atomic scattering factors of Doyle & Turner (1968) are corrected for anomalous dispersion with the values of Cromer (1965). The least-squares program (ORFLS) of Busing *et al.* (1962) was used to refine the structure. No secondary extinction corrections were applied.

RESULTS AND DISCUSSION

Cell dimensions calculated from 2θ values measured on the diffractometer, and positional and thermal parameters obtained from the least-

squares refinement are given in Table 2. Observed and calculated structure factors are listed in Table 3.

A final unweighted R factor of 0.037 was obtained for all 114 reflections. The cation distribution is refined upon scattering factors. In gen-

TABLE 2. POSITIONAL AND THERMAL PARAMETERS (STANDARD DEVIATIONS IN PARENTHESES).

POSITIONAL PARAMETERS

X OXYGEN 0.26277(8)

ISOTROPIC TEMPERATURE FACTORS

B OXYGEN ANIONS 0.723(15)

B TETRAHEDRAL CATIONS 0.701(5)

B OCTAHEDRAL CATIONS 0.616(5)

CELL PARAMETERS: $a = 8.3976(4)\text{\AA}$

TABLE 3. STRUCTURE FACTORS.

<i>h</i>	<i>K</i>	<i>L</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>K</i>	<i>L</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>K</i>	<i>L</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>K</i>	<i>L</i>	<i>F</i> _o	<i>F</i> _c
1	1	1	9	9	8	4	0	16	15	11	3	3	8	9	8	8	8	18	18
2	0	2	25	24	9	1	1	5	5	9	7	3	12	12	13	5	1	4	4
3	1	1	34	34	7	5	3	1	1	10	6	2	10	10	11	7	5	1	0
2	2	2	12	15	8	4	2	1	1	12	0	0	9	9	12	6	4	1	1
4	0	0	37	37	6	6	4	8	8	8	8	4	10	9	14	2	0	5	5
3	3	1	1	0	9	3	1	17	17	11	5	1	1	1	10	10	0	6	7
4	2	2	18	18	8	4	4	31	31	7	7	7	1	2	10	8	6	4	4
5	1	1	32	32	9	3	3	3	3	12	2	2	6	6	13	5	3	10	10
3	3	3	23	22	7	7	1	2	1	10	6	4	8	8	11	9	1	8	8
4	4	0	59	59	7	5	5	4	2	11	5	3	9	9	14	2	2	8	8
5	3	1	4	5	10	2	0	9	9	9	7	5	12	11	10	10	2	8	8
4	4	2	1	1	8	6	2	8	8	12	4	0	21	21	12	8	0	7	7
6	2	0	15	14	9	5	1	17	17	9	9	1	4	4	11	9	3	1	1
5	3	3	23	23	7	7	3	10	10	12	4	2	2	1	9	9	7	3	2
6	2	2	14	15	10	2	2	11	11	8	8	6	2	2	12	8	2	2	2
4	4	4	22	21	6	6	6	11	11	10	8	2	6	6	14	4	2	5	5
7	1	1	1	1	9	5	3	4	4	13	1	1	12	12	12	6	6	4	4
5	5	1	7	7	8	6	4	1	1	11	7	1	8	8	10	10	4	4	3
6	4	2	13	13	10	4	2	7	7	11	5	5	9	9	13	7	1	9	9
7	3	1	17	17	11	1	1	11	11	9	3	9	11	12	13	5	5	10	10
5	5	3	22	22	7	7	5	11	11	10	6	6	9	9	11	7	5	5	5
8	0	0	40	40	8	8	0	25	25	12	4	4	8	8	12	8	4	15	15
7	3	3	2	2	11	3	1	1	1	13	3	1	3	3	15	1	1	1	0
6	4	4	1	1	9	7	1	3	2	11	7	3	2	1	13	7	3	3	2
8	2	2	11	11	9	5	5	5	5	9	7	7	2	2	11	9	5	2	1
6	6	0	12	13	10	4	4	1	0	10	8	4	0	1	14	4	4	0	0
7	5	1	17	17	8	8	2	2	2	12	6	2	5	6	10	8	8	1	1
5	5	5	22	22	10	6	0	6	5	13	3	3	10	11					
6	6	2	12	13	8	6	6	8	8	9	9	5	12	12					

eral the distribution of ten similar cations (Fe^{2+} , Fe^{3+} , Mn^{2+} , Cr^{3+} , V^{3+} , Ti^{4+} , Ca^{2+} , Si^{4+} , Al^{3+} and Mg^{2+}) between two sites would result in many solutions. However the lowest unweighted R factor is obtained when the heaviest cation (Fe^{2+}) only occupies the tetrahedral sites and all the other lighter cations (Fe^{3+} , Mn^{2+} , Cr^{3+} , V^{3+} , Ti^{4+} , Ca^{2+} , Si^{4+} , Al^{3+} and Mg^{2+}) occupy the octahedral sites. In addition, the temperature factor of the tetrahedral and octahedral cations become closer when only the heaviest cation (Fe^{2+}) occupies the tetrahedral sites. No attempt was made to use interatomic distances for site selection, since the oxygen-to-tetrahedral site of 2.004 (1) Å is similar to the oxygen-to-octahedral site of 1.998(1) Å.

The cation distribution is a normal spinel with respect to the distribution of Fe^{2+} and Fe^{3+} between tetrahedral and octahedral sites. Fe^{2+} occupies both tetrahedral and octahedral sites in the ratio of 2:1, and Fe^{3+} occupies only octahedral sites. The Ti^{4+} distribution is consistent with that of an inverse spinel, that is, the Ti^{4+} occupies only octahedral sites. Most minor elements (Al^{3+} , Cr^{3+} , Mg^{2+} , V^{3+} and Ca^{2+}) occupy only octahedral sites. Si^{4+} , based upon ionic size, and Mn^{2+} , based upon crystal field stabilization energy, are assigned to tetrahedral sites. Only a negligible reduction in the unweighted R factor results when these two cations, which are present in very minor amounts, are placed in octahedral sites.

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