

CRYSTAL STRUCTURE OF TWO FERRIAN ULVÖSPINELS FROM BRITISH COLUMBIA

MAVIS Z. STOUT AND PETER BAYLISS

Department of Geology and Geophysics, University of Calgary, Calgary, Alberta T2N 1N4

ABSTRACT

The crystal structures of two ferrian ulvöspinels (\equiv titanomagnetite) from British Columbia have been refined (R values of 0.022 and 0.036). The Ti^{4+} and most minor cations occupy octahedral sites only. There is no crystal structure variation within the ranges of formation temperature (970–1015°C) and composition (59–74 mole % ulvöspinel) of these specimens.

Keywords: crystal structure, ulvöspinel, titanomagnetite, spinel group, order-disorder, British Columbia.

SOMMAIRE

La structure de deux cristaux d'ulvöspinelle ferrique (\equiv titanomagnétite) de Colombie britannique a été affinée (résidus R de 0.022 et 0.036). Le Ti^{4+} et la plupart des cations en traces occupent uniquement les sites octaédriques. On ne détecte aucune différence structurale à l'intérieur du domaine de température de formation (970 vs. 1015°C), ou de composition (59 vs. 74% d'ulvöspinelle) de ces deux spécimens.

(Traduit par la Rédaction)

Mots-clés: structure cristalline, ulvöspinelle, titanomagnétite, groupe des spinelles, ordre-désordre, Colombie britannique.

INTRODUCTION

Several models have been proposed for the cation distribution over the tetrahedral and octahedral sites in the magnetite-ulvöspinel series (Lindsley 1976). The study of Stout & Bayliss (1975) has been continued to characterize the cation distribution in natural ferrian ulvöspinels.

SPECIMENS

The crystals used in this study were taken from the Aiyansh basalt lava flow, Nass River valley, British Columbia (NR5) and the Itcha Mountain hawaiite lava flow, central British Columbia (IM7). The flows are Pleistocene to Recent in age. The groundmass Fe-Ti oxide crystals show no evidence of secondary oxida-

tion; they range in size from 0.01 to 0.1 mm and coexist with both ilmenite and hematite; this coexistence enables the formation temperature to be determined (Buddington & Lindsley 1964).

The specimens were analyzed by an electron microprobe with the operating procedures described by Stout & Bayliss (1975); the data, which were refined with the computer program SLAVE of Nicholls *et al.* (1977), are presented in Table 1. Atomic proportions have been calculated assuming a stoichiometric R_3O_4 spinel, with the Fe^{2+} and Fe^{3+} contents calculated as outlined by Carmichael (1967). The mole % ulvöspinel and the formation temperature are given in Table 2.

METHOD AND RESULTS

The single crystals selected for X-ray diffraction study were an octahedron with dimensions 44 x 49 x 69 μm (NR5) and half an octahedron with dimensions 24 x 31 x 22 μm (IM7). Experimental and data-reduction

TABLE 1. ELECTRON MICROPROBE ANALYSIS OF FERRIAN ULVÖSPINEL

Oxide	Weight %		Atom	Atomic Proportions	
	IM7	NR5		IM7	NR5
CoO	0.1		Co ²⁺		
FeO	53.0	51.7	Fe ²⁺	1.66	1.60
Fe ₂ O ₃	15.4	16.5	Fe ³⁺	0.44	0.46
MnO	0.6	0.7	Mn ²⁺	0.02	0.02
V ₂ O ₃	0.4	0.2	V ³⁺	0.01	0.01
TiO ₂	26.4	26.3	Ti ⁴⁺	0.74	0.73
CaO	0.2	0.3	Ca ²⁺	0.01	0.01
SiO ₂	0.2	0.2	Si ⁴⁺	0.01	0.01
Al ₂ O ₃	1.2	1.4	Al ³⁺	0.05	0.06
MgO	1.1	1.8	Mg ²⁺	0.06	0.10
TOTAL	98.6	99.1		3.00	3.00

TABLE 2. ULVÖSPINEL PERCENTAGES, FORMATION TEMPERATURES, UNIT CELL PARAMETERS(α), POSITIONAL PARAMETERS(x), ISOTROPIC TEMPERATURE FACTORS(B), TETRAHEDRAL(T) AND OCTAHEDRAL(Oc) SITE OCCUPANCIES, EXTINCTION PARAMETERS, R VALUES, AND INTERATOMIC DISTANCES AND ANGLES

Specimen number	SR7	IM7	NR5
Ulvöspinel percentage	59	74	73
Formation temperature °C	980	970	1015
Unit cell parameter α	8.398(3)	8.504(3)	8.481(3)
x Oxygen	0.2620(2)	0.2595(2)	0.2599(2)
B Oxygen	0.71(4)	1.18(4)	1.04(3)
B Tetrahedral cations	0.81(3)	0.92(2)	0.84(2)
B Octahedral cations	0.63(2)	0.80(2)	0.64(1)
Tetrahedral sites(T)			
Fe ²⁺	0.35(55)	0.56(43)	0.47(2)
Fe ³⁺	0.65	0.44	0.46
Ti ⁴⁺			0.07
Octahedral sites(Oc)			
Fe ²⁺	1.18	1.10	1.13
Mn ³⁺	0.01	0.02	0.02
Cr ³⁺	0.04		
V ³⁺	0.02	0.01	0.01
Ti ⁴⁺	0.59	0.74	0.66
Ca ²⁺	0.01	0.01	0.01
Si ⁴⁺	0.01	0.01	0.01
Al ³⁺	0.09	0.05	0.06
Mg ²⁺	0.05	0.06	0.10
Extinction parameter $\times 10^{-6}$	-0.1(1)	-1.8(2)	-1.9(2)
R value unweighted	0.035	0.036	0.022
Interatomic Distances			
T - Oxygen Å	2.004	1.982	1.982
Oc - Oxygen Å	1.998	2.048	2.040
Interatomic Angles			
Oc-Oxygen-T		122°	122°
Oc-Oxygen-Oc		94°	95°
Oxygen-T-Oxygen		109°	109°
Oxygen-Oc-Oxygen		85°	85°
Oxygen-Oc-Oxygen		95°	95°

methods were those of Stout & Bayliss (1975). All reflections were included in the refinement of the crystal structures with RFIN4 (Finger & Prince 1975). All observations were weighted according to $\omega = 1/\sigma_f^2$, where σ_f is the standard deviation based on counting statistics. Approximate position parameters were taken from Azaroff (1968). Ionized atomic scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* (1974).

Initially the cation distribution between the tetrahedral and octahedral sites was set as an inverse spinel with Fe³⁺ at the tetrahedral sites and Ti⁴⁺ at the octahedral sites. Least-squares refinement of the Fe³⁺-Ti⁴⁺ occupancy of the tetrahedral sites was undertaken with the octahedral sites automatically reset to maintain the overall chemical composition, while the Fe²⁺ remained fixed. If no Ti⁴⁺ was found in the tetrahedral sites, then least-squares refinement of the Fe³⁺-Fe²⁺ occupancy of the tetrahedral sites was also undertaken with the octahedral sites automatically reset to maintain the overall chemical composition. The results for both crystals are listed in Table 2, together with the refinement by the above-mentioned least-squares method on an ulvöspinel from Idaho (sample SR7) previously called titanomagnetite (Stout & Bayliss 1975).

DISCUSSION

A comparison of the data (Table 2) for these structures shows that they are similar. Therefore, there is no crystal-structure variation within the range of formation temperature (970-1015°C) and composition (59-74 mole % ulvöspinel) of these specimens. The lowest unweighted R value is obtained when the heaviest cations (Fe²⁺, Fe³⁺) are completely ordered at the tetrahedral sites; in addition, the isotropic temperature-factors of the tetrahedral and octahedral sites (Table 2) become closer when only the heaviest cations (Fe²⁺, Fe³⁺) occupy the tetrahedral sites.

Because the atomic scattering factors of Fe²⁺ and Fe³⁺ are similar, least-squares refinements gave large standard deviations (0.5) in the tetrahedral-octahedral site-occupancy refinements. Therefore, no firm conclusion is reached with respect to the distribution of Fe²⁺ and Fe³⁺. As the ferrian ulvöspinel crystals (59-74 mole % ulvöspinel) were quenched from high temperatures, disorder is to be expected. In addition, electron transfer is possible between Fe in the tetrahedral and octahedral sites. The presence of both Fe²⁺ and Fe³⁺ in the tetrahedral sites is consistent with the model of O'Reilly & Banerjee (1965) and Banerjee & O'Reilly (1966). Their predicted site occupancies vary with the mole % of ulvöspinel in the solid-solution series $(1-x)\text{Fe}_3\text{O}_4-x\text{Fe}_2\text{TiO}_4$. In the replacement of Fe²⁺Ti⁴⁺ in ulvöspinel by 2Fe³⁺, Fe³⁺ enters tetrahedral sites down to $x = 0.8$, and then Fe³⁺ also enters octahedral sites

down to $x = 0.2$; finally, Fe^{3+} enters only octahedral sites down to $x = 0$. Abundant permissive evidence supports this theory (Lindsley 1976), as graphs of many physical properties plotted against composition show changes in slope near $x = 0.2$ and 0.8 .

The Ti^{4+} distribution is generally consistent with that of an inverse spinel with Ti^{4+} at the octahedral sites only. The exception is crystal NR5, which shows a minor amount (0.07) of Ti^{4+} at the tetrahedral sites; this is supported by significance tests (Hamilton 1965). Forster & Hall (1965) found that although Ti^{4+} has a preference for octahedral sites, cation-ordering is not complete, and some Ti^{4+} occupies tetrahedral sites in the two ulvöspinel specimens they examined.

There are eight minor cations (Co^{2+} , Mn^{2+} , Cr^{3+} , V^{3+} , Ca^{2+} , Si^{4+} , Al^{3+} and Mg^{2+}) present in these ferrian ulvöspinels. The refinements show that most of these cations must occupy octahedral sites, because they are lighter cations than Fe^{2+} and Fe^{3+} . However, one or two of these minor cations may occupy the tetrahedral sites.

ACKNOWLEDGEMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada. Associate Editor F.C. Hawthorne provided useful critical reviews of the manuscript.

REFERENCES

- AZÁROFF, L.V. (1968): *Elements of X-ray Crystallography*. McGraw-Hill, New York.
- BANERJEE, S.K. & O'REILLY, W. (1966): Coercivity of Fe^{++} in octahedral sites of Fe Ti spinels. *Inst. Elec. Electron Engrs., Trans. Magnetics Mag.* 2, 463-467.
- BUDDINGTON, A.F. & LINDSLEY, D.H. (1964): Iron-titanium oxide minerals and synthetic equivalents. *J. Petrology* 5, 310-357.
- CARMICHAEL, I.S.E. (1967): The iron-titanium oxides of salic volcanic rocks and their associated ferromagnesian silicates. *Contr. Mineral. Petrology* 14, 36-64.
- FINGER, L.W. & PRINCE, E. (1975): A system of Fortran IV computer programs for crystal structure computations. *Nat. Bur. Stand. Tech. Note* 854.
- FORSTER, R.H. & HALL, F.O. (1965): A neutron and X-ray diffraction study of ulvöspinel, Fe_2TiO_4 . *Acta Cryst.* 18, 857-862.
- HAMILTON, W.C. (1965): Significance tests on the crystallographic R factor. *Acta Cryst.* 18, 502-510.
- IBERS, J.A. & HAMILTON, W.C. (1974): *International Tables for X-ray Crystallography. IV. Revised and Supplementary Tables*. Kynoch Press, Birmingham, England.
- LINDSLEY, D.H. (1976): The crystal chemistry and structure of oxide minerals as exemplified by the Fe-Ti oxides. *Mineral. Soc. Amer. Short Course Notes* 3, L1-60.
- NICHOLLS, J., FIESINGER, D.W. & ETHIER, V.G. (1977): Fortran IV programs for processing routine electron microprobe data. *Comp. Geosci.* 3, 49-83.
- O'REILLY, W. & BANERJEE, S.K. (1965): Cation distribution in titanomagnetites $(1-x)\text{Fe}_3\text{O}_4 - x\text{Fe}_2\text{TiO}_4$. *Phys. Lett.* 17, 237-238.
- STOUT, M.Z. & BAYLISS, P. (1975): Crystal structure of a natural titanomagnetite. *Can. Mineral.* 13, 86-88.

Received March 1980, revised manuscript accepted June 1980.