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HIGH TEMPERATURE STUDY OF THE SYSTEM
Fe_2SiO_4-Mn_2SiO_4 - Mg_2SiO_4

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ABSTRACT

(Fe,Mn,Mg)-olivines were produced out of stoichiometric oxide mixtures in an arc furnace. The melted samples were homogenized at 1000°C in evacuated quartz tubes and quenched to room temperature. The experimental products, the purity, crystallinity and homogeneity of the synthetic olivines were examined by petrographic microscope, X-ray diffraction, microprobe and scanning electron microscope(SEM).
The produced olivines are poorer in Fe and Mn, and richer in Mg compared to the theoretical composition derived from the starting oxide mixtures. This depletion of Fe and Mn is due to the formation of small amounts of oxides(magnetite and/or jacobsite).
At temperature 1000°C and pressure 0 bar a complete solid solution exists on the Mg-rich side of the fayalite-tephroite-forsterite system. The cell parameters (a,b,c and V) of different (Fe,Mn,Mg)-olivines have been correlated with their chemical composition. The general trend is that the cell dimensions are increasing with increasing Fe -and Mn-content, and decreasing Mg-content. The unit cell volumes increase when Mn^{2+} is replacing the smaller Fe^{2+} and Mg^{2+} ions in the (Fe,Mn,Mg)-olivines.

ΣΥΝΟΨΗ

Με την τήξη μειγμάτων οξειδίων σε φούρνο βολταϊκού τόξου, παρασκευάστηκαν ολιβίνες στο πλούσιο σε Mg πεδίο του συστήματος φαϋαλίτη - τεφροΐτη - φορστερίτη. Τα τήγματα ομογενοποιήθηκαν σε κενό αέρος και θερμοκρασία 1000°C. Η ψύξη έγινε με εμβάπτιση της κάψουλας σε νερό.
Τα προϊόντα των πειραμάτων και ιδιαίτερα οι ολιβίνες εξετάζονται μικροσκοπικά, ακτινογραφικά και χημικά. Οι σταθερές του πλέγματος (a,b,c) των ολιβινών αυξάνονται με την αύξηση του Fe και Mn, και την ελάττωση του Mg. Ο όγκος της κυψελίδας του ολιβίνη αυξάνεται όταν το Mn^{2+} αντικαθιστά τα μικρότερα ιόντα, όπως Fe^{2+} και Mg^{2+}.

Α. ΦΙΛΙΠΠΙΔΗΣ - Μελέτη του συστήματος Fe_2SiO_4 - Mn_2SiO_4 - Mg_2SiO_4 σε υψηλές θερμοκρασίες.

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1. ΕΙΣΑΓΩΓΗ - INTRODUCTION

The presence of divalent ions such as Zn(e.g., Brown, 1980; Filippidis, 1987), Ni(e.g., Nord et. al., 1982; Filippidis, 1982, 1985), Co(e.g., Waal and Calk, 1973), Mn(e.g., Smyth and Hazen, 1973; Brown, 1980) and Ca(e.g., Birle et. al., 1968; Lager and Meagher, 1978) in the (Mg,Fe)-olivine structure is of great importance. These divalent ions, even in low concentrations, may be partly responsible for the Mg-Fe distribution in natural olivines.

The intracrystalline Mg-Fe distribution in olivines is dependent on temperature(Finger and Virgo, 1971; Virgo and Hafner, 1972) and on oxygen fugacity(Will and Nover, 1979). Another possibility may be the influence of a third element, for example Mn.

In natural (Mg,Fe)-olivines, Mn is an important constituent. This paper reports on an experimental investigation on the Mg-rich side of the fayalite - tephroite - forsterite system.

2. ΠΕΙΡΑΜΑΤΙΚΕΣ ΜΕΘΟΔΟΙ - EXPERIMENTAL METHODS

Two synthetic (Fe,Mn,Mg)-olivines were produced out of stoichiometric oxide mixtures in an arc furnace. The mixtures were melted twice, using Ar as protecting gas and afterward homogenized at 1000°C in evacuated quartz tubes for two weeks. The tubes were quenched in water.

The oxide mixtures were prepared by drying, weighing and mixing appropriate proportions of Fe_2O_3, MnO, MgO and SiO_2. The SiO_2 was obtained as pure quartz, crushed to 325 mesh, fired at 1000°C for twelve hours to drive of adsorbed water and stored in a vacuum desiccator.

3. ΜΕΘΟΔΟΙ ΑΝΑΛΥΣΗΣ - ANALYTICAL METHODS

The experimental products were examined with a petrographic microscope. One polished section and one thin section of each product were examined in reflected and transmitted light. The synthetic olivines were examined for purity, crystallinity and homogeneity by X-ray diffraction, microprobe and scanning electron microscope(SEM).

X-ray powder diffraction traces were taken with a Philips diffractometer, Ni-filtered Cu_{ka} radiation, using silicon as internal standard. The scanning speed was 1/1° and 1/4° per minute over the interval 5-105° of 2θ. Cell parameters of the olivines were calculated from 13 to 15 different reflections using a computer program CELNE(Tegenfeldt and Ersson, 1976).

Au-plated pieces of the experimental products were observed using a JEOL JSM-U3 scanning electron microscope. Al-coated samples were examined in scanning mode over several grains for homogeneity of Fe and Mn.

Chemical analyses of the synthetic olivines were performed by standard techniques using a Cambridge Geoscan microprobe. Pure metals(Fe and Mn) and natural olivine(SiO_2 and MgO) were used as standards. Four different olivine grains were analyzed and the obtained values were corrected for back - ground, dead time, absorption, fluorescence and atomic number effects using a computer program. Relative errors are ±1.0-1.2% for FeO, ±1.2-1.4% for MnO, ±4.0-4.2% for SiO_2 and ±6.8-8.0% for MgO.

4. ΑΠΟΤΕΛΕΣΜΑΤΑ ΚΑΙ ΣΥΖΗΤΗΣΗ - RESULTS AND DISCUSSION

The optical investigation of the homogenized samples revealed the presence of small amounts of oxides(magnetite and/or jacobsite), along the olivine grain boundaries. The formation of these oxides resulted to the production of olivines which were poorer in Fe(27%) and Mn(24%), and richer in Mg(17%) compared to the theoretical composition derived from the starting oxide mixtures. Similar depletion of metals such as Zn, Ni, Fe and Mn were observed in previous experimental studies of different olivines by Annersten et. al. (1982, 1984), Ericsson and Filippidis (1986), Filippidis (1982,1985,1987) and Nord et. al. (1982). The oxide phases were carefully removed under acetone, using a hand magnet. The examination of the remaining materials revealed the absence of oxide phases, the presence of pyroxene (< 1%) and olivine (>99%).

Euhedral crystals of the synthetic olivines(Fig. 1) were large enough to allow microprobe analysis. Both olivines are Mg-rich(Fig. 2), their composition and unit cell parameters are presented in Table 1. Within the limit of the analyzing techniques, no significant zoning or inhomogeneity of the olivine grains was observed(Fig. 3).

A continuous solid solution exists along the Fe_2SiO_4-Mg_2SiO_4(e.g., Smyth and Hazen, 1973; Brown, 1980), Fe_2SiO_4-Mn_2SiO_4(e.g., Annersten et. al., 1984) and Mg_2SiO_4-Mn_2SiO_4(e.g., Glasser and Osborn, 1960; Francis and Ribbe, 1980) joins. However, Maresch et. al. (1978) demonstrated experimentally that a limited solid solution(two phase interval 40-73 mol% Mn_2SiO_4) exists along the Mg_2SiO_4-Mn_2SiO_4 join. The present experiments indicate that a complete solid solution exists on the Mg-rich side of the Fe_2SiO_4-Mn_2SiO_4-Mg_2SiO_4 system(Fig. 2) at temperature 1000°C and pressure 0 bar.

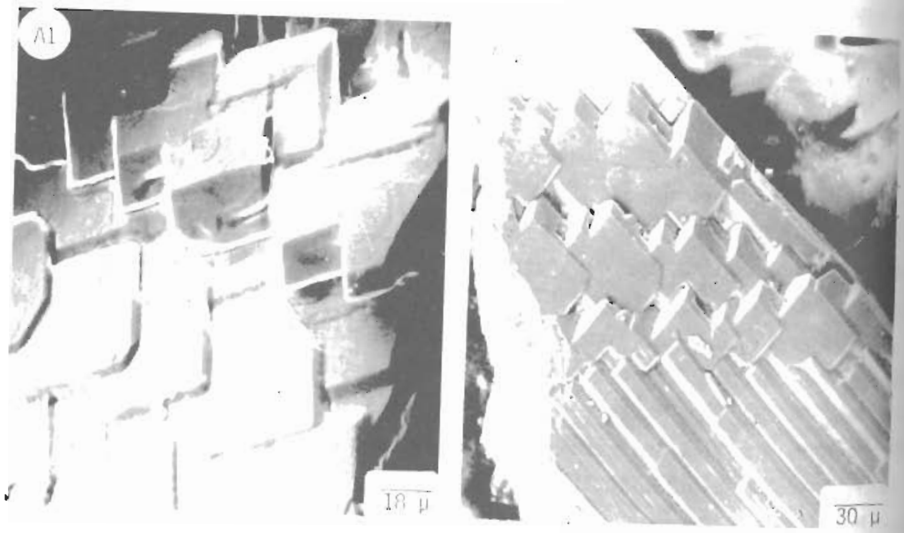
In this study the cell parameters(a,b,c and V) of different (Fe,Mn,-Mg)-olivines have been correlated with their chemical composition(Figs 4, 5 and 6). The correlation diagrams have been made using data of twelve different olivines(see footnotes to figs 4, 5 and 6) and the synthetic olivines of this study. The general trend is that the cell parameters(a, b, c and V)

Table 1. Composition and unit cell parameters of the synthetic olivines.

Sample	A1*	A2*
SiO_2	37.91	38.00
MgO	36.32	37.58
FeO	13.07	17.80
MnO	13.24	6.89
Total	100.54	100.27
--Numbers of ions on 4(0)--		
Si	1.00	1.00
Mg	1.42	1.47
Fe	0.29	0.39
Mn	0.29	0.15

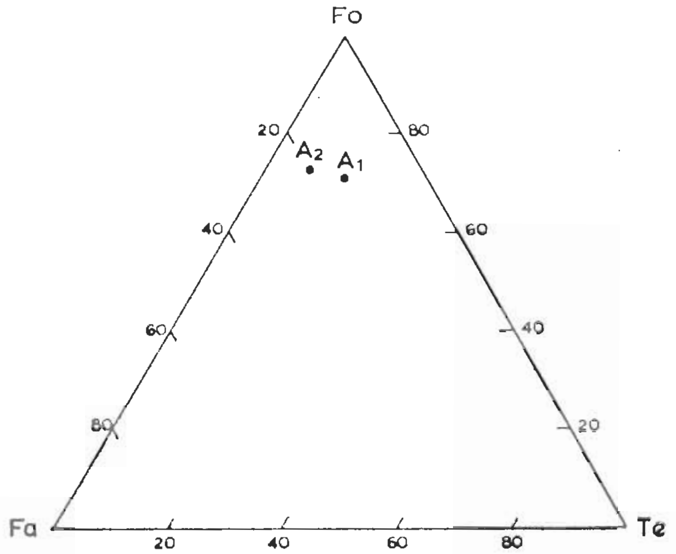
	A1	A2
X^{Mg}	0.710	0.731
X^{Fe}	0.145	0.194
X^{Mn}	0.145	0.075
---------- cell parameters ---------		
a(Å)	4.788(1)	4.773(1)
b(Å)	10.356(1)	10.319(1)
c(Å)	6.056(1)	6.033(1)
V(Å^3)	300.3	297.1

*) Average of 4 analyses in four different olivine grains. Figures in parentheses represent the estimated standard deviation, thus 4.788 (1) indicates estimated standard deviation of 0.001.



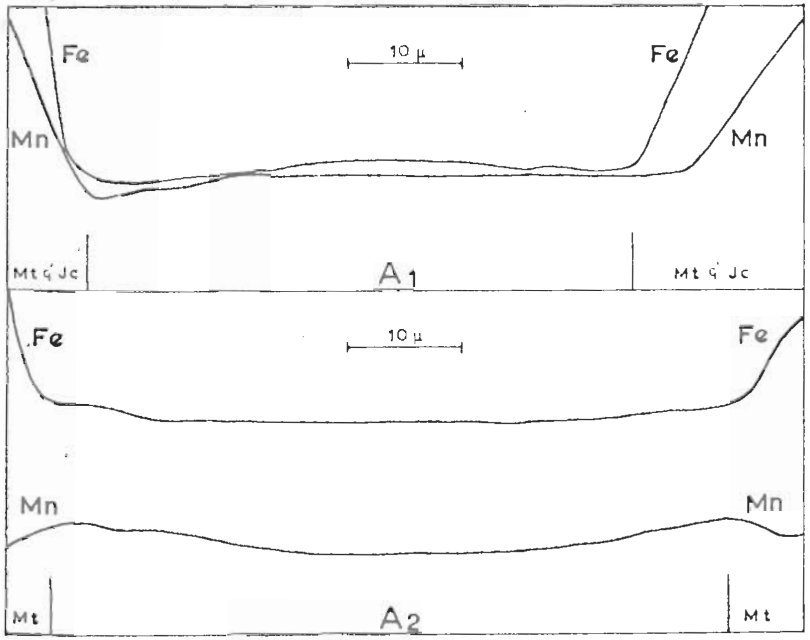
Σχ. 1.: Μικροφωτογραφίες (SEM) των συνθετικών (Fe,Mn,Mg)-ολιβινών από τα δείγματα A1 και A2.

Fig.1.: Scanning electron microphotograph of synthetic (Fe,Mn,Mg)-olivines from samples A1 and A2.



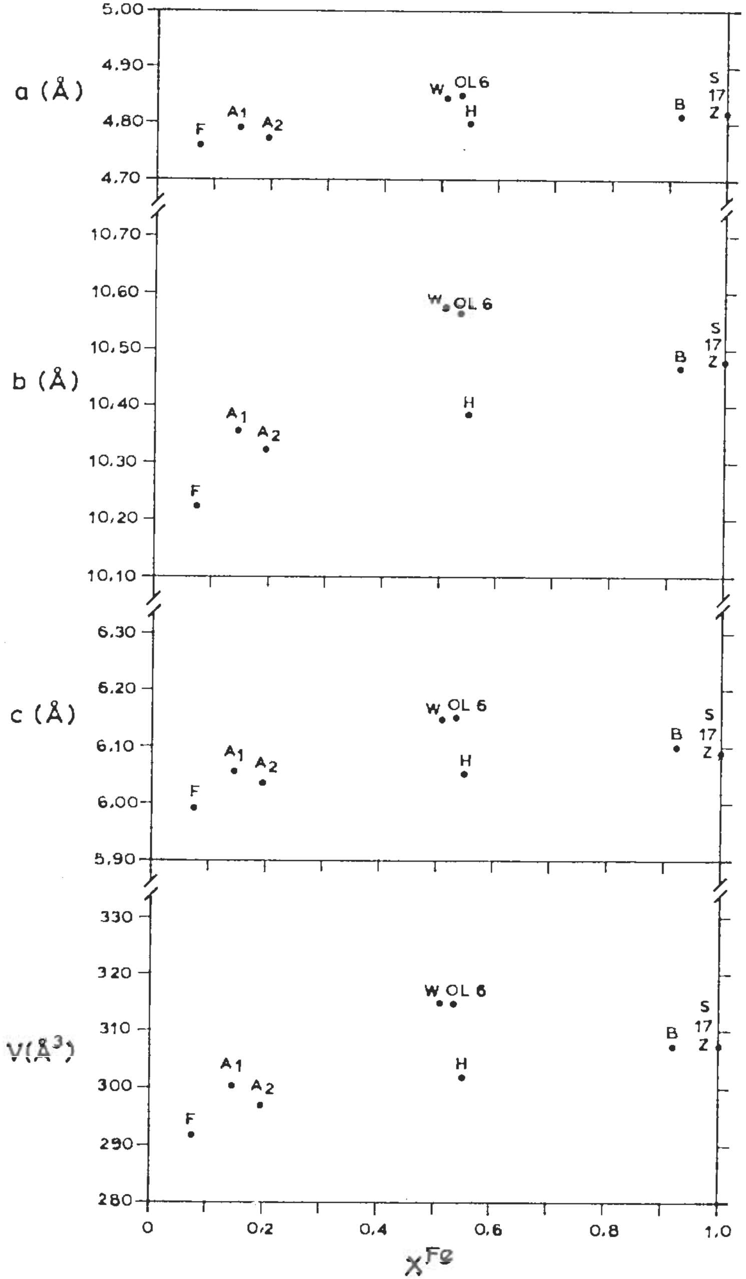
Σχ. 2.: Χημική σύσταση των συνθετικών ολιβινών στο σύστημα φαϋαλίτη(Fa)-τεφροΐτη(Te)-φορστερίτη(Fo).

Fig.2.: Chemical composition of synthetic olivines in the system fayalite(Fa)-tephroite(Te)-forsterite(Fo).



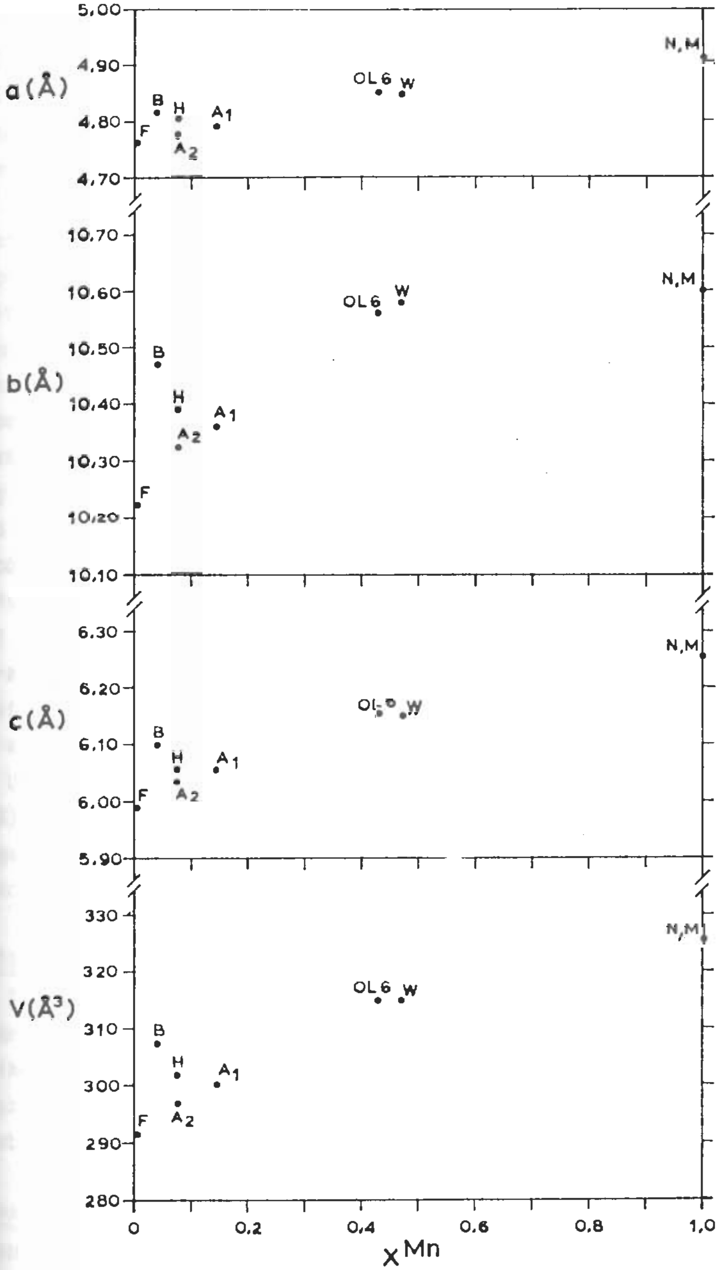
Σχ. 3.: Σαρωτικές τομές(Fe και Mn) σε συνθετικούς (Fe,Mn,Mg)-ολιβίνες.

Fig.3.: Scanning profiles(Fe and Mn) of synthetic (Fe,Mn,Mg)-olivines. A1 and A2= olivines(see table 1), Mt= magnetite, Jc= jacobsite.



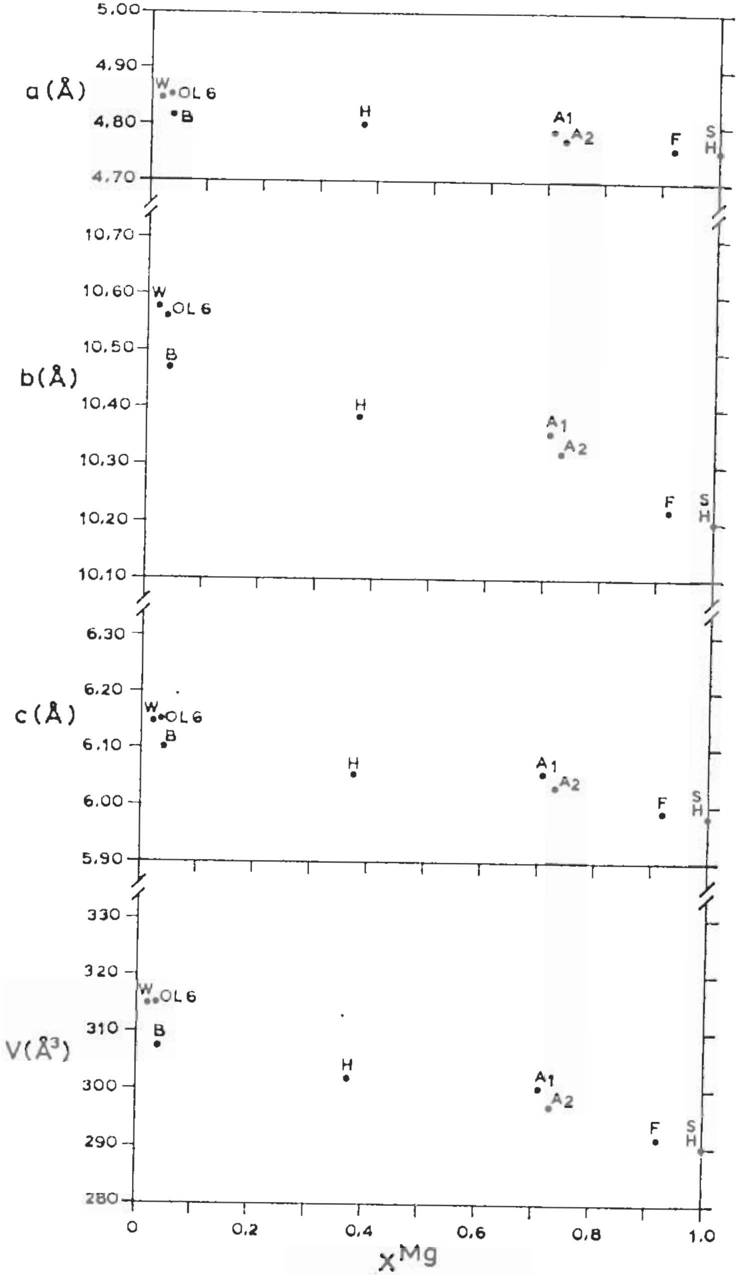
Σχ. 4.: Σχέση των σταθερών του πλέγματος(a,b,c,V) με την περιεκτικότητα Fe στους (Fe,Mn,Mg)-ολιβίνες.

Fig.4.: The variation of the cell parameters(a,b,c,V) with the Fe-content in (Fe,Mn,Mg)-olivines. A1&A2: this study, F: Fujino(1980), W:Brown(1980), OL6:Annersten et. al.(1984), H:Smyth&Hazen(1973), B:Birle et.al.(1968), S:Schwab&Kustner(1977), 17:Annersten et. al.(1982), Z:Hazen(1977).



Σχ. 5.: Σχέση των σταθερών του πλέγματος(a,b,c,V) με την περιεκτικότητα Mn στους (Fe,Mn,Mg)-ολιβίνες.

Fig.5.: The variation of the cell parameters(a,b,c,V) with the Mn-content in (Fe,Mn,Mg)-olivines. A1&A2:this study, F:Fujino(1980), H:Smyth&Hazen (1973), B:Birle et. al.(1968), OL6:Annersten et. al.(1984), W:Brown (1980), N:Nishizawa&Matsui(1972), M:Muller&Roy(1974).



Σχ. 6.: Σχέση των σταθερών του πλέγματος(a,b,c,V) με την περιεκτικότητα Mg στους (Fe,Mn,Mg)-ολιβίνες.

Fig.6.: The variation of the cell parameters(a,b,c,V) with the Mg-content in (Fe,Mn,Mg)-olivines. A1&A2:this study, B:Birle et. al.(1968), W:Brown (1980), OL6:Annersten et. al.(1984), H:Smyth&Hazen(1973), F:Fujino (1980), S:Schwab&Kustner(1977).

are increasing with increasing Fe -and Mn-content, and decreasing Mg-content in the (Fe,Mn,Mg)-olivines(Figs 4, 5 and 6). The cell parameter differences shown on figure 4, between olivines(W and OL6) and olivine(H) is due to their differences in composition. Olivine (H) is Mg-rich while olivines (W) and (OL6) are Mn-rich.

Some of the correlations between the cell parameters and the composition of the olivines(Figs 4, 5 and 6) show appreciable curvature. The most pronounced deviation from a linear relationship is shown by the cell parameter b(Fig. 5). A possible explanation to these deviations is the composition differences shown by the (Fe,Mn,Mg)-olivines used in these correlations. A second explanation is that the curvature partly reflects the cation distribution between the two octahedral sites(M1 and M2) in the olivine structure. Annersten et. al. (1984) observed a partially ordered distribution with Mn^{2+} entering the M2 site and Fe^{2+} entering the M1 site in (Fe,Mn)-olivines. Lumpkin and Ribbe (1983) concluded that in olivines, the cell parameter-a is positivly correlated to the mean ionic radius of the M1 cations, the cell parameter-b is positivly correlated to the mean redius of the M2 cations, while the cell volume - V and the cell parameter - c were found to be a function of the radius of both cations. The larger Mn^{2+} ion is firstly ordered into the M2 site, but at higher contents it has to enter the M1 site and its high positiv effect to the b-dimension is lost, especially above $X^{Mn} \simeq 0.5$(Fig. 5).

Using the effective ionic radius(IR) given by Shannon (1976) for Mn^{2+} (IR=0.83), Fe^{2+}(IR=0.78) and Mg^{2+}(IR=0.72), and the results of the present investigation it is quite clear that the unit cell volume increase when Mn^{2+} is replacing the smaller Fe^{2+} and Mg^{2+} ions in the (Fe,Mn,Mg)-olivines.

ΕΥΧΑΡΙΣΤΙΕΣ - ACKNOWLEDGEMENTS

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