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## EXPERIMENTAL INVESTIGATION ON THE Mg-RICH SIDE OF THE Mg<sub>2</sub>SiO<sub>4</sub> - Fe<sub>2</sub>SiO<sub>4</sub> - Zn<sub>2</sub>SiO<sub>4</sub> SYSTEM

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### A B S T R A C T

Synthetic olivines in the system Mg<sub>2</sub>SiO<sub>4</sub>-Fe<sub>2</sub>SiO<sub>4</sub>-Zn<sub>2</sub>SiO<sub>4</sub>, were produced from oxide mixtures (MgO, Fe<sub>2</sub>O<sub>3</sub>, ZnO and SiO<sub>2</sub>). The mixtures were melted in an arc furnace using argon as protecting gas. Afterwards the samples were homogenized at 1000°C in vacuum and quenched to room temperature. The experimental products, the purity, crystallinity and homogeneity of the synthetic olivines were examined by means of petrographic microscope, X-ray diffraction, scanning electron microscope (SEM) and microprobe techniques.

The experimental products consisted of olivine, magnetite and/or franklinite (around 5%) and enstatite (around 2%). At 1000°C and 0 bar, complete solid solution on the Mg-rich side of the Mg<sub>2</sub>SiO<sub>4</sub>-Fe<sub>2</sub>SiO<sub>4</sub>-Zn<sub>2</sub>SiO<sub>4</sub> system, was observed. The cell parameters (a, b, c and V) decrease when Fe<sup>2+</sup> is replaced by the smaller Mg<sup>2+</sup> ion in the (Mg, Fe, Zn)-olivines. Probably the same happens when Fe<sup>2+</sup> is replaced by the Zn<sup>2+</sup> ion.

### Σ Υ Ν Ο Ψ Η

Στη παρούσα μελέτη παρασκευάστηκαν συνθετικοί ολιβίνες στο πλούσιο σε Mg πεδίο του συστήματος Mg<sub>2</sub>SiO<sub>4</sub>-Fe<sub>2</sub>SiO<sub>4</sub>-Zn<sub>2</sub>SiO<sub>4</sub>. Αυτό έγινε με την τήξη μειγμάτων οξειδίων (MgO, Fe<sub>2</sub>O<sub>3</sub>, ZnO και SiO<sub>2</sub>) σε φούρνο βολταϊκού τόξου και σε ατμόσφαιρα αργού. Κατόπιν, το τήγμα ομογενοποιήθηκε σε κενό αέρος και θερμοκρασία 1000°C. Η ψύξη έγινε με εμβάπτιση της κάψουλας σε νερό. Τα προϊόντα των πειραμάτων καθώς επίσης η καθαρότητα, η ομοιογένεια και η κρυσταλλικότητα του ολιβίνη, εξετάστηκαν με πολωτικό και μεταλλογραφικό μικροσκόπιο, με ακτίνες-Χ, με σαρωτικό ηλεκτρονικό μικροσκόπιο (SEM) και με μικροαναλύτη.

Στα προϊόντα των πειραμάτων παρατηρήθηκε ότι εκτός του ολιβίνη σχηματίστηκε μαγνητίτης και/ή φρανκλινίτης (περίπου 5%) καθώς και ενστατίτης (περίπου 2%). Στο πλούσιο σε Mg πεδίο του συστήματος Mg<sub>2</sub>SiO<sub>4</sub>-Fe<sub>2</sub>SiO<sub>4</sub>-Zn<sub>2</sub>SiO<sub>4</sub>, σε θερμοκρασία 1000°C και πίεση 0 bar παρατηρήθηκε πλήρης σειρά μεικτών κρυστάλλων των φάσεων φορστερίτη-φουαλίτη-βιλλεμίτη. Οι σταθερές του πλέγματος (a, b, c και V) στους (Mg, Fe, Zn)-ολιβίνες ελαττώνονται, όταν ο Fe<sup>2+</sup> αντικατασταθεί από το μικρότερο ιόν Mg<sup>2+</sup>. Πιθανώς το ίδιο συμβαίνει όταν ο Fe<sup>2+</sup> αντικατασταθεί από το ιόν Zn<sup>2+</sup>.

### INTRODUCTION

In olivines, apart from Mg and Fe, other divalent ions such as Ni (e.g.,

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Bish 1981, Nord et. al. 1982), Co (e.g., Ghose & Wan 1974, Walsh et. al. 1976) and Mn (e.g., Francis & Ribbe 1980, Lumpkin et. al. 1983, Annersten et. al. 1984) are ordered in the olivine structure. The presence of other divalent ions in the (Mg,Fe)-olivines is of great importance; even in low concentrations they may affect the Mg-Fe distribution. This distribution may be dependent on temperature or on oxygen fugacity as suggested by Will & Nover (1979).

Forsterite ( $Mg_2SiO_4$ ) is orthorhombic and at room temperature the cell axes are  $a=4.754$ ,  $b=10.197$  and  $c=5.981$  Å (Schwab & Küstner 1977). Fayalite ( $Fe_2SiO_4$ ) is also orthorhombic with  $a=4.816$ ,  $b=10.469$  and  $c=6.099$  Å (Birle et.al.1968), while Willemite ( $Zn_2SiO_4$ ) is trigonal with hexagonal axes  $a=13.948$  and  $c=9.315$  Å (Klaska et. al. 1978). Ericsson & Filippidis (1986) showed that the introduction of Zn in fayalite gives a partial solid solution and on the Zn-rich side the structure is changed to trigonal.

Willemite occurs as an ore mineral in different deposits in New Jersey (U.S.A.) associated with crystalline marbles (Metsger et. al. 1958, Cook 1972, Fronde! & Baum 1974). It also occurs in deposits associated with diapiric breccias and limestones (Muller 1972), in fine-grained quartzite (Wilson 1971), in alkaline intrusions (Metcalf-Johansen 1977) and in nepheline-syenite pegmatites (Shlyukova et. al. 1980).

Studies on synthetic olivines containing three or more metals, are of great importance for geological interpretations. In natural olivines, Zn is an important solid solution constituent. This paper reports on an experimental investigation of the  $Mg_2SiO_4$ - $Fe_2SiO_4$ - $Zn_2SiO_4$  solid solution.

#### SAMPLE PREPARATION AND EXPERIMENTAL METHODS

Three synthetic (Mg,Fe,Zn)-olivines were produced out of stoichiometric oxide mixtures in an arc furnace. The oxide mixtures were prepared by drying, weighing and mixing appropriate proportions of MgO (free from sulphate, pro analysi, 99.2385%),  $Fe_2O_3$  (pro analysi, 99.712%), ZnO (pro analysi, 99.9438%) and  $SiO_2$  (quartz washed and calcined, pro analysi, 99.89%). The  $SiO_2$  was obtained as pure quartz, crushed to 325 mesh, fired at  $1000^{\circ}C$  for twelve hours to drive off adsorbed water and stored in a vacuum desiccator.

The mixtures were melted twice in the arc furnace using an argon atmosphere and afterwards annealed at  $1000^{\circ}C$  in evacuated quartz tubes ( $10^{-3}$  torr) for two weeks and quenched to room temperature.

#### CHARACTERIZATION OF THE EXPERIMENTAL PRODUCTS

The experimental products as well as the purity, crystallinity and homogeneity of the synthetic olivines, were examined by petrographic microscope, X-ray diffraction, scanning electron microscope (SEM) and microprobe. Polished and thin

sections of each sample were examined in reflected and transmitted light.

Phase analyses were obtained from X-ray powder diffraction, using  $\text{Cu K}\alpha$  radiation and scanning interval  $5\text{-}105^\circ(2\theta)$ . Cell parameters were obtained by using Si as standard and a computer refinement of 20 different reflections. Au-plated pieces of the samples were observed using a JEOL JSM-U3 scanning electron microscope in reflection geometry.

Al-coated samples were examined in scanning mode over several grains for homogeneity of Fe and Zn. Chemical analyses of the three olivines (called F1, F2 and F3) were performed using microprobe techniques. Pure metals (Fe and Zn) and natural olivine ( $\text{SiO}_2$  and  $\text{MgO}$ ) were used as standards. Six typically different grains were analyzed for each sample and the obtained compositions were corrected for background, dead time, absorption, fluorescence and atomic-number effects by using a computer program. Relative errors are  $\pm 1.4$  to  $1.6\%$  for  $\text{FeO}$ ,  $\pm 1.7$  to  $2.1\%$  for  $\text{ZnO}$ ,  $\pm 4.1$  to  $4.5\%$  for  $\text{SiO}_2$  and  $\pm 7.5$  to  $8.6\%$  for  $\text{MgO}$ .

## RESULTS AND DISCUSSION

The investigation of the homogenized samples revealed the presence of oxide phases (magnetite and/or franklinite), along the olivine grain boundaries. The final composition of the olivines, deviated from the starting oxide mixtures was different due to the formation of the opaque phases (around 5% of the experimental products). The produced olivines are poorer in Zn and Fe, and richer in Mg compared to the theoretical composition derived from the starting oxide mixtures. Similar depletion of the different metals such as Fe, Mn and Ni were observed in previous experimental studies of different olivines by Annersten et. al. (1982, 1984), Filippidis (1982, 1985) and Nord et. al. (1982). The oxide phases were easily removed under acetone from the finely powdered samples by a hand magnet. After this separation the remaining materials consisted mainly of olivine and small amounts of enstatite (around 2%).

The crystals of the olivines (Fig. 1), obtained from the experiments, were large enough ( $>40\mu\text{m}$ ) to allow microprobe analysis. The chemical composition of the synthetic olivines together with the refined unit cell dimensions are given in Table 1. The Mg-contents are almost similar in the three olivines (Table 1, Fig. 2). The olivines are Mg-rich with  $x_{\text{O1}}^{\text{Fe}} = 0.120 - 0.295$  and  $x_{\text{O1}}^{\text{Zn}} = 0.020 - 0.145$ . Within the limit of the analyzing technique, no significant zoning or inhomogeneity of the olivine grains was observed (Fig. 3). Ericsson & Filippidis (1986) observed a partial solid solution in the  $\text{Zn}_2\text{SiO}_4$ - $\text{Fe}_2\text{SiO}_4$  system with a two phase region occurring in the interval 17-48 mol%  $\text{Zn}_2\text{SiO}_4$ , at the same temperature ( $1000^\circ\text{C}$ ) and pressure (0 bar) as the present experiments, in which a complete solid solution on the Mg-rich side of the  $\text{Mg}_2\text{SiO}_4$  -  $\text{Fe}_2\text{SiO}_4$  -  $\text{Zn}_2\text{SiO}_4$  system is observed (Fig. 2).

Table 1. Composition and Unit Cell Parameters of the Synthetic Olivines.  
 Πιν. 1. Σύσταση και σταθερές του πλέγματος στους συνθετικούς ολιβίνες.

Sample	F1*	F2*	F3*		F1	F2	F3
SiO <sub>2</sub>	37.55	37.91	37.65	$x^{\text{Mg}}$	0.685	0.715	0.735
MgO	34.27	36.31	37.09	$x^{\text{Fe}}$	0.295	0.235	0.120
FeO	26.34	21.54	10.93	$x^{\text{Zn}}$	0.020	0.050	0.145
ZnO	1.77	5.13	14.88	-----Cell Parameters-----			
Total	99.93	100.89	100.55	a (Å)	4.775(1)	4.780(1)	4.771(1)
----Numbers of ions on 4(0)---				b (Å)	10.277(1)	10.288(1)	10.246(1)
Si	1.00	1.00	1.00	c (Å)	6.012(1)	6.019(1)	6.000(1)
Mg	1.37	1.43	1.47	V (Å <sup>3</sup> )	295.0	296.0	293.3
Fe	0.59	0.47	0.24				
Zn	0.04	0.10	0.29				

\*) Average of 6 analyses in six different olivine grains. Figures in parentheses represent the estimated standard deviation, thus 4.775(1) indicates estimated standard deviation of 0.001.

The cell parameters (a, b, c and V) of different olivines have been correlated with their chemical composition (Figs 4 and 5). The correlation diagrams have been made using data of five different olivines (see footnote to Fig.4) and the synthetic olivines of this study. The cell parameters are increasing with increasing Fe-content and decreasing Mg-content in the olivines. The same trends were observed by Nord et. al. (1982) for (Mg,Fe,Ni)-olivines. There is not a good correlation between  $x_{\text{ol}}^{\text{Zn}}$  and the cell parameters due to the low Zn-content in the olivines and to the few data available. The sample F14 (Ericsson & Filippidis 1986) shows greater cell dimensions than the present synthetic olivines due to the absence of Mg and high Fe-content ( $x_{\text{ol}}^{\text{Fe}} = 0.935$ ). Possibly the cell parameters are decreasing with increasing Zn-content in the olivines, comparing the average values of olivines F1 and F2 with the values of olivine F3 (Table 1).

Using the effective ionic radius (IR) given by Shannon (1976) for  $\text{Fe}^{2+}$  (IR = 0.78),  $\text{Zn}^{2+}$  (IR = 0.74) and  $\text{Mg}^{2+}$  (IR = 0.72), and the results of the present investigation it is quite clear that the unit cell volume decrease when  $\text{Fe}^{2+}$  is replaced by the smaller  $\text{Mg}^{2+}$  ion. Probably the same happens when  $\text{Fe}^{2+}$  is replaced by the  $\text{Zn}^{2+}$  ion. Lumpkin & Ribbe (1983) concluded that in olivines, the cell parameter (a) is highly correlated to the mean ionic radius of the M1 cation, while (b) is dependent on the mean radius of the M2 cations. The cell volume (V) and the cell parameter (c) were found to be function of the radius of both cations.

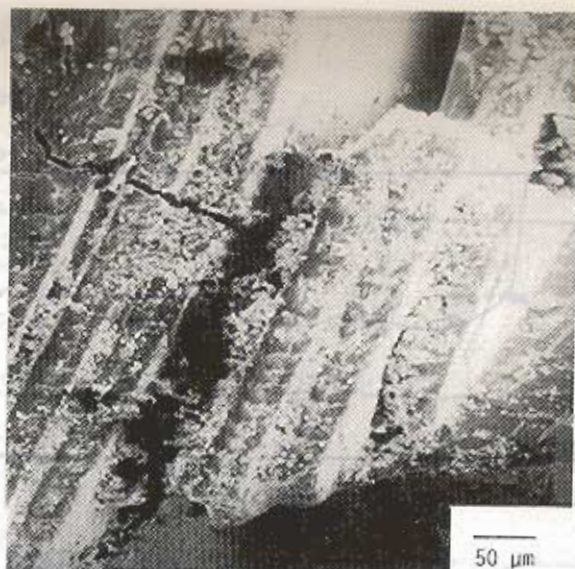


Fig. 1. Scanning electron microphotograph of synthetic (Mg,Fe,Zn)-olivine from sample F1.

Σχ. 1. Μικροφωτογραφία(SEM) συνθετικού (Mg,Fe,Zn)-ολιβίνης από το δείγμα F1.

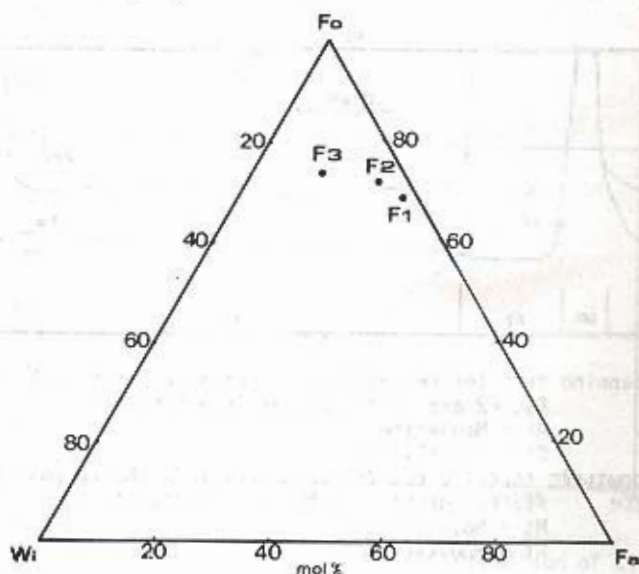


Fig. 2. Chemical composition of synthetic olivines in the quaternary system Forsterite(Fo)-Willemite(Wi)-Fayalite(Fa).

Σχ. 2. Χημική σύσταση των συνθετικών ολιβινών στο σύστημα φορστερίτη(Fo)-βιλλεμίτη(Wi)-φαισάλιτη(Fa).

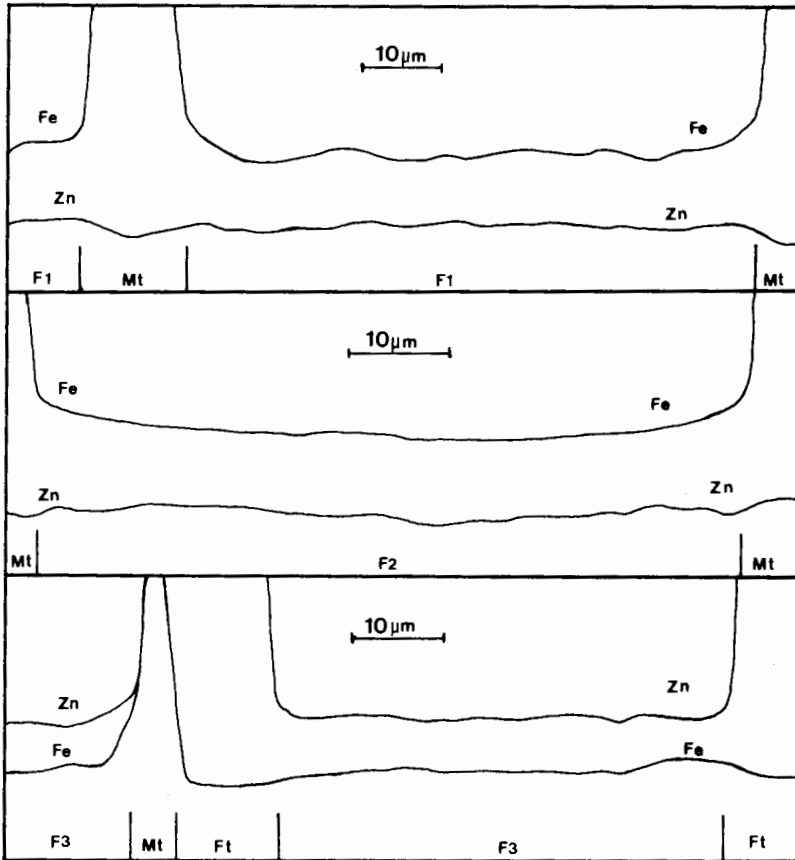


Fig. 3. Scanning profiles(Fe and Zn) of synthetic (Mg,Fe,Zn)-olivines. F1, F2 and F3 = Olivines (see Table 1).

Mt = Magnetite.

Ft = Franklinite.

Σχ. 3. Σαρωτικές τομές(Fe και Zn) σε συνθετικούς (Mg,Fe,Zn)-ολιβίνες. F1, F2 και F3 = Ολιβίνες (βλ. Πιν. 1).

Mt = Μαγνητίτης.

Ft = Φρανκλινίτης.

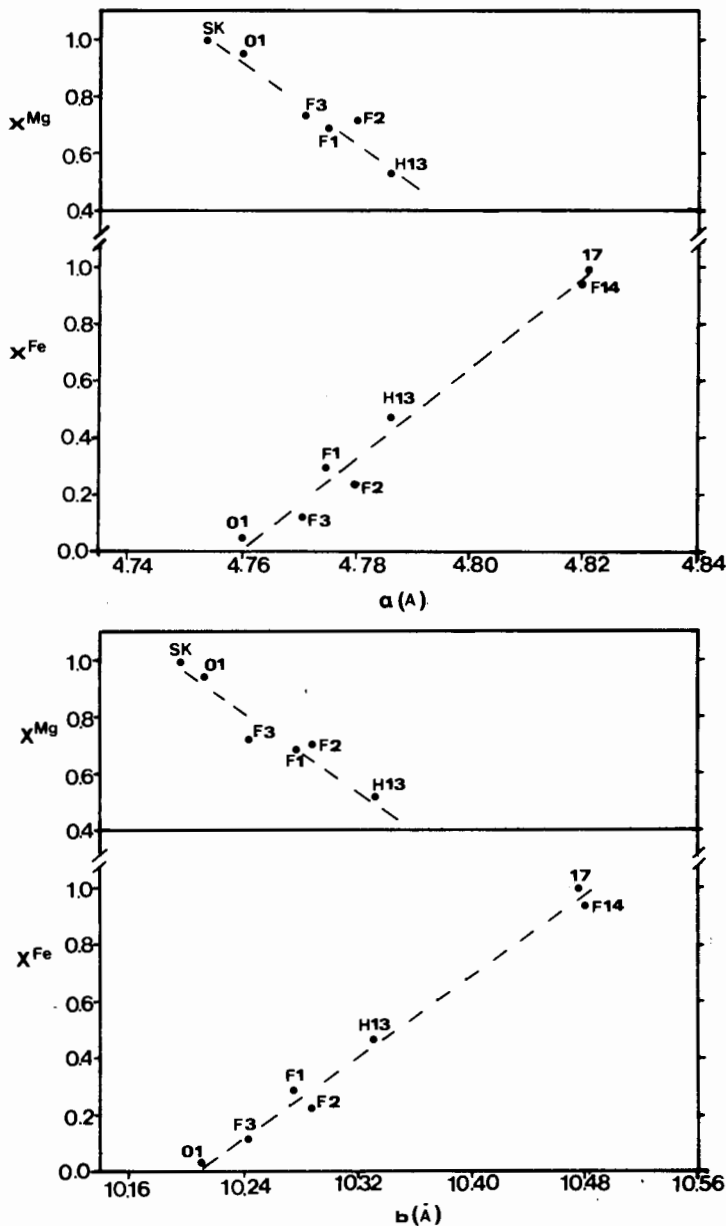


Fig. 4. Variation of the cell parameters (a&b) with composition of olivines. F1,F2 & F3=(Mg,Fe,Zn)-olivines from this study. 01=(Mg<sub>1.89</sub>Fe<sub>0.07</sub>Ni<sub>0.03</sub>)SiO<sub>4</sub> from Philippidis (1982). H13=(Mg<sub>1.05</sub>Fe<sub>0.95</sub>)SiO<sub>4</sub> from Nord et. al. (1982). F14=(Fe<sub>1.88</sub>Zn<sub>0.13</sub>)SiO<sub>4</sub> from Ericsson & Philippidis (1986). 17=Fe<sub>2</sub>SiO<sub>4</sub> from Annersten et. al. (1982). SK=Mg<sub>2</sub>SiO<sub>4</sub> from Schwab & Küstner (1977).

Σχ. 4. Σχέση των σταθερών του πλέγματος (a&b) με την χημική σύσταση των ολιβινών.

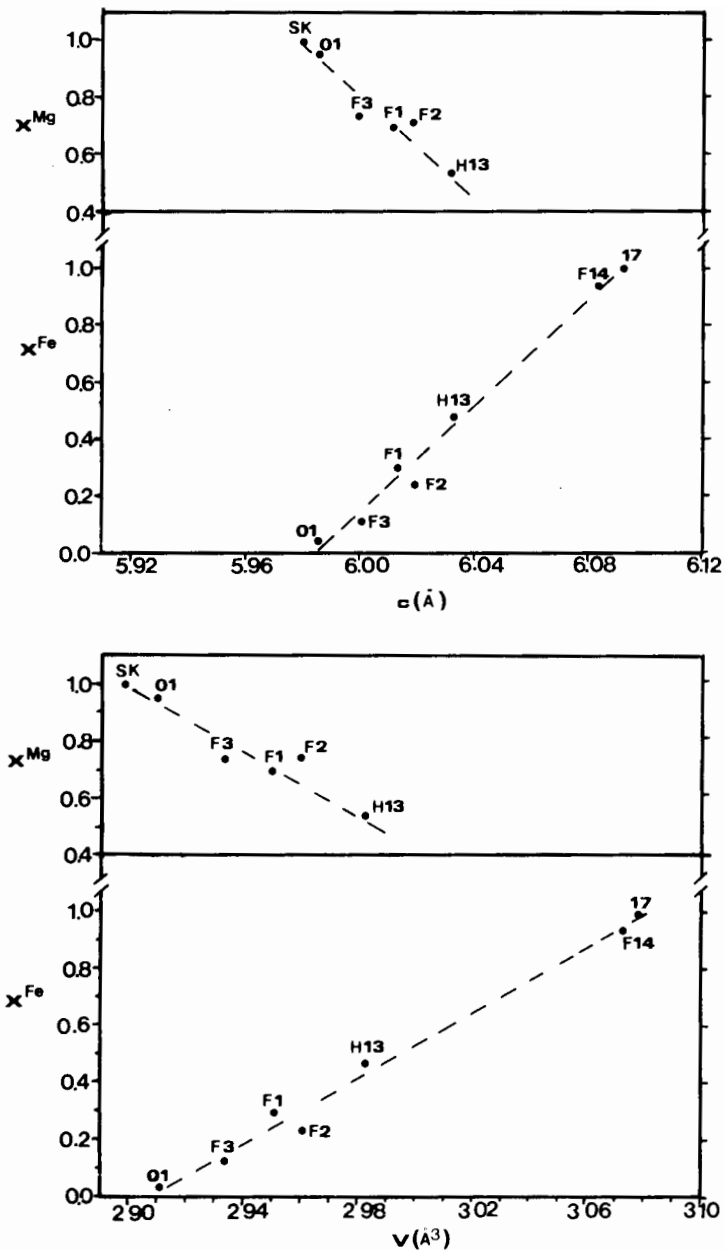


Fig. 5. Variation of the cell parameters (c&V) with composition of olivines. Olivines used: see footnotes to Fig. 4.

Σχ. 5. Σχέση των σταθερών του πλέγματος (c&V) με την χημική σύσταση των ολιβινών. Ολιβίνες που χρησιμοποιήθηκαν: βλ. επεξηγήσεις του σχ. 4.



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