SITE OCCUPANCIES OF MINOR ELEMENTS IN SYNTHETIC OLIVINES AS DETERMINED BY CHANNELING-ENHANCED X-RAY EMISSION

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Abstract

Major- and minor-element site occupancies have been determined for Ni- and Mn-rich synthetic forsteritic olivines that were equilibrated to 300, 600, 900, or 1050°C, by analyzing electron-channeling-enhanced x-ray emissions. Site preferences for minor elements (Ni>Cr for M1; Ca>Mn for M2) are consistent with those reported in previous studies. Degree of ordering at different elevated temperatures differ less than analytical errors, although there may be significant differences in ordering between olivines that have been rapidly quenched from 300°C of higher, and those that have undergone normal lava-flow cooling histories. An x-ray structure refinement of San Carlos olivine (R=0.031) gives major-element occupancies similar to those determined by electron-channeling on the same material. Thus, the channeling technique appears to give results that are consistent with other methods, and it may be used to identify olivines that have undergone rapid quenching.

Introduction

The process of channeling-enhanced x-ray emission has been used previously to determine site occupancies in various minerals (e.g. Tafto, 1982; Smyth and Tafto, 1982; Tafto and Spence, 1982; Tafto and Buseck, 1983; Self and Buseck, 1983). The terms ALCHEMI (Atom Location by CHanneling-Enhanced MIcroanalysis) and CHEXE (CHanneling Enhanced X-ray Emission spectroscopy) have been applied to this method. The technique is particularly useful for minor elements, for elements with similar x-ray or neutron scattering factors, or for crystals that are too small for x-ray or neutron refinements. A review of the approach used in these types of experiments has been presented by Self and Buseck (1983). The most important criterion for determination of element distribution in a mineral by this technique is that the sites of interest in the mineral lie on alternating crystallographic planes. In order to make quantitative estimates additional information is required, particularly, the occupancy of at least one element in one of the sites or in another site that lines up with one of the sites of interest.

In olivine (Pbnm setting), a suitable set of planes for electron channeling is (002). The structure of olivine projected down an axis normal to c reveals the M2 and Si sites lining upon (002) planes that alternate with planes containing only M1 sites (see Smyth and Tafto, 1982). Some confusion has arisen in the past concerning the space group setting in olivine, in which previous electron channeling experiments on olivine have referred to the (020) planes (based on Pnma space group) for the channeling.

Previous studies on minor element ordering in olivine (Smyth and Tafto, 1982; Tafto and Spence, 1982) have shown a tendency for disordering at temperatures

as low as 300°C and no significant increase in disorder above 300°C. However, analytical errors made interpretation of ordering profiles inconclusive. The present study has two objectives. The first is to reduce the analytical errors of previous studies on natural samples by synthesizing olivines with high concentrations of Ni and Mn. The second is to check the accuracy of the method by comparison of the results for major-element ordering in a heated natural sample with those from an x-ray structure refinement done on the same material.

Experimental Methods and Results

Sample Preparation.

The synthetic samples were prepared by melting powders in an Astrofurnace at 1580°C in an argon atmosphere. These were then cooled to 1400°C, quenched, and then attached to a Deltech thermocouple rod. The samples were then melted for 2 hours at 1540°C and subsequently cooled at 60°C/hr to 1300°C, at which temperature they remained for approximately 10 hours, before being quenched in air. The samples were then equilibrated at 1050, 900, 600, or 300°C and quenched. The time for cooling from the equilibration temperature to below 100°C was ~~approximately~~ in excess of 90 seconds. The 1050 and 900°C samples were equilibrated in the Deltech at an oxygen fugacity one log unit below QFM for 24 hours. The 600 and 300°C samples were equilibrated in a furnace under argon atmosphere for 48 hours and nine days, respectively. Two samples were prepared for each equilibration temperature except for 600°C for which there were three samples.

After the final quenching, the samples contained olivine and pyroxene and occasional skeletal plagioclase. Phases were analyzed by wavelength dispersive

I assume polished thin sections were made

analysis on the electron microprobe. Large olivine grains in the samples tend to be slightly zoned, with cores richer in Mg, Ni, and possibly Cr, and rims being richer in Fe, Mn, and Ca. Pyroxenes generally contain more Ca, about the same Mn, and less Ni than coexisting olivines. Average analyses for the synthetic olivines are given in Table 1. Analyses shown include those from the most homogeneous samples (nos. 7 and 10), and the sample showing the greatest zoning (no. 6) for which the average includes core and rim analyses for a number of grains.

Channeling.

Samples were crushed and dispersed on to carbon support films on copper mesh grids. A Philips 400 transmission electron microscope, fitted with a Kevex energy dispersive spectrometer and low-background sample holder, was used for the experiments. Crystal fragments were oriented to show the (00$\underline{1}$) systematic row of reflections, avoiding other low-index reflections. A spectrum was first collected near the symmetric position (i.e. with the electron beam nearly parallel to the (002) planes), and then the crystal was tilted to approximately the two-beam condition (with the central spot just outside the 002 Kikuchi line), and another spectrum obtained. A third spectrum was collected from the same area with the crystal randomly oriented. A 70 μm condenser aperture and a 2000 Å-diameter beam were used in most of the data collections. Spectra were generally collected for 250-500 seconds live time.

The spectrum from the random orientation is used to determine the Mg/Si ratio with no channeling-enhanced x-ray emission, and the two oriented spectra give the intensity ratio within modulated standing waves for inside the Bragg angle, and outside the Bragg angle, respectively. With the tilt less than the Bragg

correct?

angle for (002), the Bloch wave with maximum intensity along the M2 and Si direction is enhanced and with the tilt greater than θ_{002}, emission is enhanced from the M1 positions. A set of spectra for these two orientations is shown in Figure 1. Since the spectral acquisition conditions should be the same if the differences in tilt are small and if the same area of the crystal is used for all spectra, no further corrections should be required.

The synthetic olivines did not contain sufficient Ca to allow reasonable determination of occupancies. Olivines from the Pinacate volcanic field, northern Sonora, Mexico, are slightly enriched in Ca and Mn and these were used to determine relative occupancies of Ca.

A fragment of an olivine from San Carlos that had been equilibrated at 300°C and analyzed for an earlier study (Smyth and Tafto, 1982) was used for an x-ray structure refinement in order to compare results from channeling experiments with a known structure. A fragment of the same crystal was prepared as above for TEM work, except that a Be mesh grid was used instead of Cu to minimize background and reduce other analytical errors.

Occupancies for minor and major elements for synthetic olivines are shown in Table 2 and Figure 2. Details of the calculations to determine these values are outlined by Tafto and Spence (1983). Magnesium was assumed to be completely disordered for these calculations. The results achieved with this assumption are consistent with the mineral compositions. These results are similar to those presented by Smyth and Tafto (1982). Errors were not significantly reduced in this study, despite the much larger amounts of the minor elements present. No significant variation in ordering with quench temperature can be detected. Comparing the ordering of the synthetic olivines with that of Tafto

and Spence (1982), however, there appears to be a significant difference between olivines that have quenched rapidly from elevated temperatures and those that cooled under natural volcanic cooling conditions (Figure 2). Therefore, if the determinations by Tafto and Spence (1982) are accurate, the usefulness of this technique may be greatest in identifying those samples which have undergone extremely rapid quenching from high temperature.

Chromium levels are too low in the samples to determine a meaningful ordering trend with temperature. However an average of the proportions of Cr in M1 in 30 of the measurements listed is 0.64, with a standard deviation of 0.18. This result suggests a slight preference of Cr for M1 although complete disorder cannot be ruled out. Results for Ca - ordering in natural olivine was determined from olivines from the Pinacate volcanic field. The average of 7 measurements gave -0.07 (±0.10) and 0.13 (±0.13) for proportions of Ca and Mn on M1, respectively. Whereas many of the Ca occupancies in M1 are calculated to be negative, and the errors show no significant difference from Mn distributions, the Ca occupancy <u>relative</u> to Mn shows a significantly greater preference of Ca for M2 over Mn. The average of (C_{MnM1} - C_{CaM1}) for the 7 measurements is 0.20, with a standard deviation of 0.09. The absolute values calculated are very sensitive to measured intensities for Mg and Si, which are used as standards in the calculation, and thus relative concentrations of species in M1 may be more meaningful for minor elements than absolute concentrations. Nickel appears to be less susceptible to this problem than Ca, Cr, or Mn. In general, Ni is less affected by absorption, background subtraction, peak overlaps, sum peaks, and escape peaks than the lighter elements and so results appear to be more consistent.

The degree of ordering of the various elements is in general agreement with other published work. Brown (1980) has summarized results of olivine structure refinements and occupancies for a number of Ni, Ca, Fe, Mn, and Mg-bearing olivines. In Mg-rich olivines, Ni shows a strong preference for M1, Fe appears to be almost completely disordered, Mn shows a strong preference for M2 and Ca is completely ordered in M2. Distance-least-squares (DLS) modeling by Bish and Burnham (1984) predicts the site preferences that have been observed in olivine. Results of the channeling experiments are consistent with these observations and confirm that Ni, Mn, and Ca have the same site preferences when they occur as minor elements in natural magnesian olivines. In addition, Cr possibly shows slight preference for M1 in the channeling experiments although the errors are too large to be conclusive.

Rager (1977) found Cr^{3+} to be located in both M1 and M2, with slight preference of Cr for M1. The channeling results support these observations and lead to the conclusion that Cr in the synthetic olivines is most probably Cr^{3+}, occupying the smaller, more distorted M1 site (Lumpkin and Ribbe, 1983).

<u>X-Ray Structure Refinement</u>. natural or synthetic ?

A lens-shaped grain, approximately 100x300 μm in size, was used for the refinement. Data were collected on a Syntex diffractometer with Nicolet automation. Three standard reflections, collected every 100 reflections, showed no variation in intensity with time. A total of 3942 reflections were collected in a 2-theta range of 2° to 95°. The data were corrected for absorption using a semi-empirical correction based on 10 psi-scans collected on the diffractometer. This absorption correction reduced the standard deviation for averaging from .0326 to .0171 for the 36 measurements of each of the 10

reflections used in the psi-scans. Slight residual error due to the complex shape of the crystal was still evident, but systematic variation was greatly diminished. The intensities of symmetry-equivalent reflections were averaged yielding an R for the averaging of 0.0122. The refinements were performed on the averaged data set (1457 independent reflections) using RFINE (Finger and Prince, 1975). For the final refinement, three strong, low-angle reflections which appear to have been affected by extinction, were rejected. The R-value for this refinement was 0.031.

Final atom positions and thermal parameters from the structure refinement are given in Table 3. In order to determine occupancies of Fe and Mg, a comparison was made of refinements using both neutral and ionized scattering factors. The results from both sets of refinements are essentially identical, and both refinements show a slight preference of Fe for the M1 site. Site occupancies of the San Carlos olivine as determined by electron channeling, together with final occupancies from the structure refinement are shown in Table 4. The results from the two techniques are within errors. Channeling experiments on synthetic olivines appear to indicate a slight preference of Fe for M2. The synthetic samples were equilibrated under slightly reducing conditions. These results may reflect the preference of Fe for M2 noted by Will and Nover (1979) in reduced olivines.

Discussion

The measurements of site occupancies in synthetic olivines are consistent with those determined by Smyth and Tafto (1982) for heated, natural olivines from San Carlos. Despite the greater amounts of Ni in the synthetic samples, the errors are not significantly lower for this element. The reason for this

is not readily apparent. It appears that experimental errors, related to factors other than x-ray counting statistics, may be larger than any differences in ordering among the synthetic samples that have been quenched from different elevated temperatures.

Aikawa et al. (1985) noted extremely rapid exchange of Fe and Mg between M-sites in heated olivines (above 700°C), but suggest that at temperatures as low as 375°C the rate of cation exchange is slow. Our data suggest that such rapid exchange persists to as low as 300°C. Further, our data, plus that of previous studies using the channeling technique, would be consistent with a very small activation energy for the exchange of cations between M1 and M2, so that all heated samples show minor-element distributions characteristic of some temperature between 300 and 600°C. At temperatures above 600°C, then, our cooling may not have been sufficiently rapid to preserve the equilibrium distribution. The natural cooling in the lava flow at San Carlos was sufficiently slow to result in a distribution more ordered than our samples quenched from as low as 300°C. Thus, unheated natural volcanic olivines appear to be significantly more ordered with respect to Ni and Mn than synthetic and natural heated olivines (Tafto and Spence, 1982). Therefore, if analytical errors can be reduced to levels reported by Tafto and Spence (1982), it should be feasible to use the degree of ordering of Ni and Mn to identify samples which have undergone extremely rapid quenching from elevated temperatures and no reheating to temperatures above 300°C. In order to evaluate this possibility of constraining cooling rates in such samples, it will be necessary to measure distributions in natural or synthetic samples that have been equilibrated at 100, 200, and 300°C for several weeks to several months or samples that have

been quenched exceedingly rapidly from temperatures between 300 and 600°C. It may then be possible to use the technique to constrain thermal histories of samples such as olivine chondrules that appear to have been rapidly quenched.

Conclusions

In summary, the measured site preferences for olivine, as determined by electron channeling are as follows: Ni shows greater preference for M1 than Cr; Fe and Mg are essentially disordered; and Ca shows a greater preference for M2 than Mn. These results are consistent with findings reported previously. A crystal structure refinement of a heated natural olivine shows the same Fe and Mg occupancies as those determined from electron-channeling experiments. Thus, ALCHEMI provides results that are consistent with other methods.

For very minor elements, relative site preferences may be more meaningful than absolute values determined by electron-channeling. Minor element distributions appear to indicate a very small activation energy for exchange of cations between olivine M-sites. If this is true, it will not be possible to determine a meaningful equilibration temperature for most natural olivines. However, it may be possible to use the channeling technique to constrain thermal histories of samples that have undergone very rapid cooling.

Acknowledgments

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FIGURE CAPTIONS

Figure 1: Energy-dispersive x-ray spectra for olivine oriented slightly outside the Bragg angle for (002) (top) and for slightly inside the Bragg angle (bottom). Inset shows the region of the spectrum 2.5 to 10 KeV expanded to show the differences in Mn and Ni between the two orientations. Full scale is 0 to 10 KeV.

Figure 2: Proportions of Ni, Mn, and Fe on M1 in synthetic olivines as a function of equilibration temperature. Solid symbols are from Tafto and Spence (1982) for San Carlos olivine. Error bars are ± 1 std. dev.

Figure 1

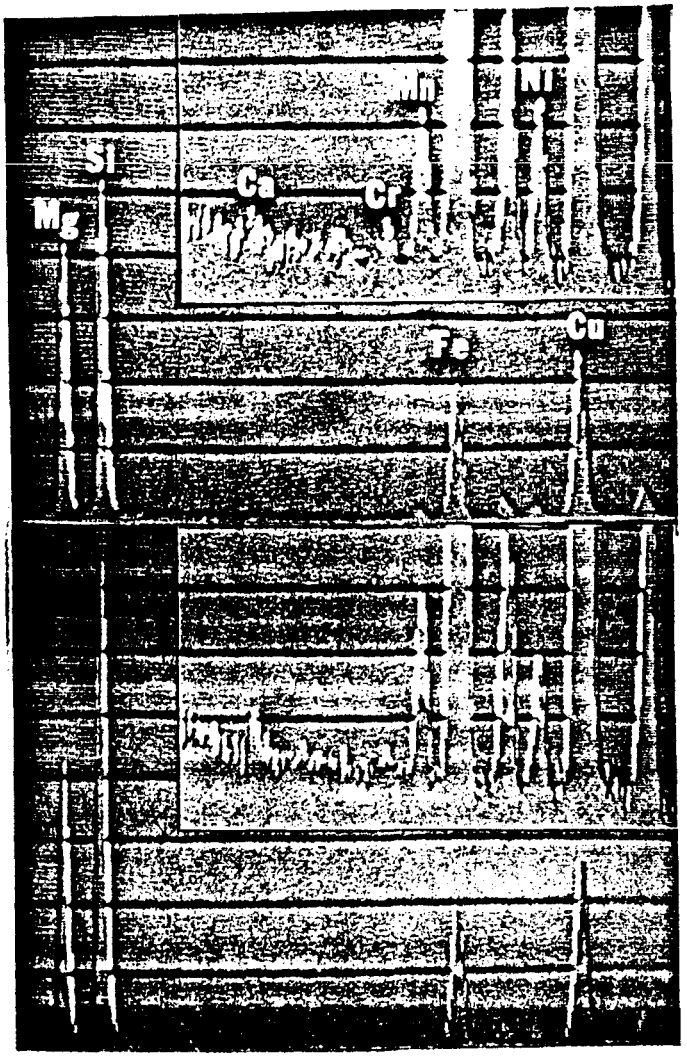

Figure 2

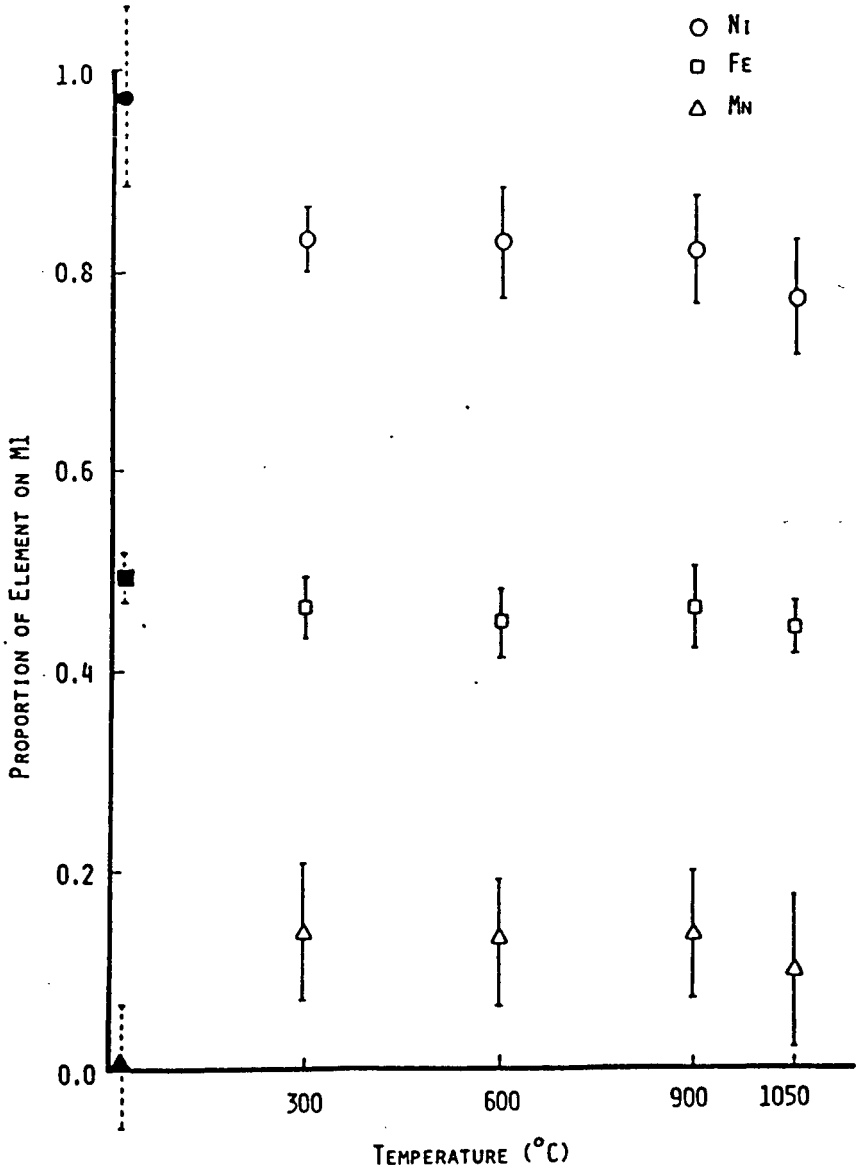
Ni
Fe
Mn
1.0
0.8
0.6
0.4
0.2
0.0
Proportion of Element on M1
300
600
900
1050
Temperature (°C)

Table 1: Microprobe analyses of synthetic olivines.

Equil. Temp.(°C)	300	600	900	1050
Sample No.	12	7	10	6
No. of Anal.	11	11	10	11
SiO_2	39.95(.34)*	40.35(.46)	40.56(.33)	39.65(.41)
Cr_2O_3	0.18(.03)	0.21(.03)	0.21(.04)	0.17(.06)
FeO	12.66(.56)	10.86(.28)	11.97(.24)	15.18(1.00)
MnO	0.90(.10)	0.86(.08)	0.94(.10)	1.03(.09)
NiO	1.46(.24)	1.12(.05)	1.01(.05)	1.40(.08)
MgO	44.82(.51)	46.86(.37)	46.42(.41)	43.18(1.03)
CaO	0.08(.02)	0.10(.02)	0.10(.03)	0.12(.02)
Total	100.05	100.36	101.21	100.73

*Standard deviations in parentheses.

Table 2: Proportion of minor elements in M1.

Temp. (°C)	No. of measurements	C_{Cr}	C_{Mn}	C_{Fe}	C_{Ni}
300	5	0.73(16)*	0.14(7)	0.46(3)	0.83(3)
600	9	0.49(22)	0.13(7)	0.45(3)	0.83(7)
900	7	0.72(15)	0.13(7)	0.46(4)	0.82(6)
1050	10	0.62(16)	0.10(8)	0.44(3)	0.77(6)

*Errors in last figure in parentheses.

Table 3: Atom coordinates and thermal parameters for San Carlos olivine. Errors in last figure are shown in parentheses.

Cell Parameters (in Angstroms):
$\underline{a}$ = 4.7641(7) $\underline{b}$ = 10.2269(17) $\underline{c}$ = 5.9952(8)

atom	x/$\underline{a}$	y/$\underline{b}$	z/$\underline{c}$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M1	0.00000	0.00000	0.00000	0.0035(1)	0.00122(3)	0.00232(8)	0.00001(4)	-0.00037(8)	-0.00040(4)
M2	0.99000(9)	0.27770(4)	0.25000	0.0049(1)	0.00082(2)	0.00278(8)	0.00011(4)	0.00000	0.00000
Si	0.42649(8)	0.09432(3)	0.25000	0.0020(1)	0.00069(2)	0.00193(6)	0.00004(4)	0.00000	0.00000
O 1	0.7661(2)	0.09172(8)	0.25000	0.00267(2)	0.00131(4)	0.0029(2)	0.00022(9)	0.00000	0.00000
O 2	0.2206(2)	0.44764(7)	0.25000	0.0044(2)	0.00074(4)	0.0034(2)	0.00004(9)	0.00000	0.00000
O 3	0.2783(1)	0.16309(5)	0.0337(1)	0.0040(2)	0.00120(3)	0.0030(1)	0.00000(7)	-0.0002(1)	0.00048(5)

R = 3.1 R_{wt} = 3.4

Table 4: Occupancies of Fe and Mg in San Carlos olivine: comparison of x-ray and electron-channeling results.

X-ray structure refinement:

Fe_{M1} = 0.097(1)* Fe_{M2} = 0.093(1)
Mg_{M1} = 0.903(1) Mg_{M2} = 0.907(1)
C_{FeM1} = 0.51(1)

Electron channeling:

No. of measurements = 7
C_{FeM1} = 0.49(4)

*Error in last figure shown in parentheses.