

Minor-element distributions in ilmenite and dolomite by electron channeling-enhanced X-ray emission

TAMSIN C. McCORMICK, JOSEPH R. SMYTH

Department of Geological Sciences, University of Colorado, Boulder, Colorado 80309-0250, U.S.A.

ABSTRACT

Electron-channeling experiments using planes normal to the hexagonal c axis and planes parallel to $\{10\bar{1}1\}$ have revealed site occupancies of minor elements in natural ilmenites and dolomites. In ilmenite, almost all of the Mg and Mn reside in the Fe site, whereas Cr shows a slight preference for the Ti site and most of the Al occupies the Ti site. In dolomite, Mn is strongly ordered into the Mg site, whereas Fe shows only a slight preference for the Mg site. Except for the Fe in dolomite, these results are consistent with simple cation-radius considerations.

INTRODUCTION

Using a technique commonly termed *ALCHEMI* (Atom Location by CHanneling-Enhanced MIcroanalysis), it is possible to directly measure site occupancies of major and minor elements in specific sites of certain minerals with the transmission electron microscope (TEM). The technique has been applied to olivine (Taftø and Spence, 1982a; Smyth and Taftø, 1982; Self and Buseck, 1983; McCormick et al., 1987), pyroxene (Self et al., 1983; McCormick, 1986), feldspar (Taftø and Buseck, 1983), spinels (Taftø, 1982; Taftø and Spence, 1982b; Christoffersen et al., 1984), and garnets (Ottensmeyer and Buseck, 1986) and relies on the enhanced transmission of charged particles along specific crystallographic directions. When a thin, perfect crystal is oriented in the TEM so that lattice planes lie nearly parallel to the electron beam, the channeling gives rise to enhanced X-ray emission from atoms lining up on these planes. Slight changes in tilt about the Bragg angle for these planes result in changes in the intensity distribution of the wave field near the surface of the crystal, so that enhanced X-ray emission may arise from adjacent sites. In order to determine site occupancies for two nonequivalent sites, a direction must be selected where the two sites line up on alternating crystallographic planes parallel to this direction. The technique has been described in detail by Spence and Taftø (1983).

The present study was initiated to investigate minor-element site preferences in rhombohedral ilmenite and the closely related rhombohedral structure of dolomite. Both structures have $R\bar{3}$ symmetry and contain two main cation sites. Ilmenite contains Fe sites lying on planes parallel to hexagonal $\{0001\}$ that alternate with planes of Ti sites, each surrounded by oxygens in octahedral coordination. In dolomite, planes of Mg sites alternate with planes of Ca sites, separated by planes of CO_3 groups in the hexagonal c direction. In both structures the two sites also line up on alternating planes parallel to $\{10\bar{1}1\}$. Therefore there are a number of orientations in which

channeling can be used to distinguish between these two sites. Calculations of X-ray emissions as a function of tilt were performed using a program written by Peter Self, formerly of Arizona State University, based on the formulation by Cherns et al. (1973). Results for a number of orientations are shown for ilmenite and dolomite in Figures 1 and 2, respectively. The channeling is much more efficient in dolomite than in ilmenite because in ilmenite there is not as large a difference in projected electron density between the two planes containing the different sites. The calculations demonstrate that for both structures, strong changes in calculated emission occur with slight tilting through the Bragg angle for planes normal to the hexagonal c axis, as well as for the $\{10\bar{1}1\}$ planes. These latter orientations are more accessible than the planes normal to the c axis, and many of the measurements reported here are based on the $\{10\bar{1}1\}$ channeling.

EXPERIMENTAL METHODS AND DATA REDUCTION

Fragments of each sample were finely crushed in acetone and dispersed on a copper grid with a holey carbon support film. A Philips 400 TEM, operating at 120 keV and fitted with a KEVEX energy-dispersive spectrometer, was used with a low-background holder for the experiments. Crystal fragments were oriented so that only the systematic row of reflections from the plane of interest was excited. Spectra were collected for 200 to 300 s live time, in three different directions: (A) with the angle between the incident beam and the crystallographic planes less than the Bragg angle for the planes; (B) with the crystal tilted slightly beyond the Bragg angle; and (C) with the crystal tilted to a random orientation off the systematic row. A spot size of 2000 Å and beam divergence of less than half the Bragg angle were used in the spectral acquisitions. Escape peaks and a modeled background were removed from the spectra, and integrated intensities were determined for each of the peaks. Typical measured emission ratios as a function of tilt about an axis in the (0003) plane are shown for ilmenite in Figure 1. Calculation of site occupancies followed the method outlined by Spence and Taftø (1983), using spectra of orientations A and B for occupancy de-

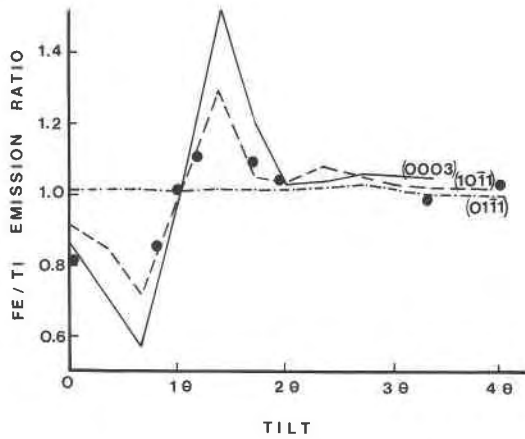


Fig. 1. Calculated and measured Fe/Ti X-ray emission ratios in ilmenite, as a function of tilt, for different channeling planes. Measured values (closed circles) are shown for progressive tilting of one crystal about an axis in the (0003) plane.

terminations. Thus, C_x , the proportion of element X in site 1 is given by $C_x = (R_x - 1) / [R_x - 1 + (I_1/I_2)_b - (I_1/I_2)_a R_x]$, where R_x is the ratio of counts for element X , relative to a reference element, for the two oriented spectra, and $(I_1/I_2)_a$ and $(I_1/I_2)_b$ are the intensity ratios of site 1 to site 2, for the two orientations. We assumed complete ordering of Ti in ilmenite, and so Ti was used as a reference element. Therefore, in this case, $R_x = (N_x/N_{Ti})_a / (N_x/N_{Ti})_b$.

A problem arises in determining values for the intensity ratios. If one assumes Fe and Ti to be fully ordered on the two sites, with no excess Fe in the Ti site, then the intensity ratios can be determined in each oriented spectrum by comparing the measured ratio for Fe/Ti to Fe/Ti in the random spectrum (for which the intensity is not modulated). If these assumptions are invalid, it is necessary to use bulk-chemical information to quantify the results.

RESULTS AND DISCUSSION

Ilmenite

Two samples of ilmenite were used in the channeling experiments. Both are fragments of nodules of ilmenite in kimberlite, collected from dumps at the Frank Smith diamond mine in South Africa. Both samples appear to be chemically homogeneous and show no evidence of oxidation-exsolution petrographically or in the TEM. The bulk compositions of the two samples are approximately $\text{Fe}_{0.85}\text{Ti}_{0.89}\text{Mg}_{0.20}\text{Cr}_{0.05}\text{Mn}_{0.01}\text{O}_3$ (TEM analyses) and $\text{Fe}_{0.76}\text{Ti}_{0.93}\text{Mg}_{0.30}\text{Al}_{0.01}\text{Mn}_{0.01}\text{O}_3$ (microprobe analyses).

Typical spectra from slight tilting about an axis in the (0003) plane are shown in Figure 3. Site occupancies were calculated using the bulk concentrations from chemical analyses given above, and the results are summarized in Table 1. Estimates of Cr distributions were determined from the Cr-rich sample. Because of overlap of the CrK_β with MnK_α peaks, Mn distributions were not measured in this sample. However, Mn distributions, together with Al distributions, were determined in an essentially Cr-free sample.

The results indicate the Mg and Mn show a strong pref-

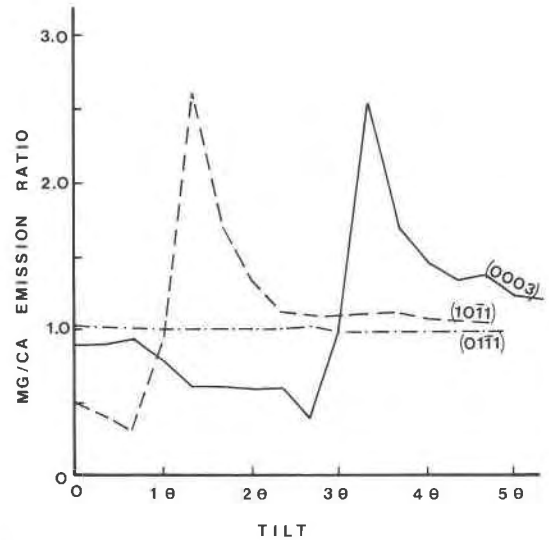


Fig. 2. Calculated Mg/Ca X-ray emission ratios in dolomite, as a function of tilt, for different channeling planes.

erence for the Fe site in ilmenite, consistent with the ordered end members giekelite (MgTiO_3) and pyrophanite (MnTiO_3). Fe distributions are consistent with stoichiometry if one calculates the amount of hematite in solution assuming Cr is in the Ti site and Mn and Mg are in the other site. Cr shows a significant preference for the Ti site, and Al appears to be even more strongly ordered into the Ti site. Many of the measured Ti-site occupancies for Mg are negative. This appears to be one of the limitations of quantitative ALCHEMI that has been noted in previous studies (e.g., Otten and Buseck, 1986; Self and Buseck, 1983) and may be related to delocalization of the excitation of lighter elements. However, comparison of results of occupancies determined by X-ray refinements with those determined by channeling in other Mg-Fe phases (e.g., olivine, McCormick et al., 1987) shows that the channeling results are consistent with these other methods, within errors. The occupancy of Mn in Table 1 is more strongly negative. This may in part be attributed to problems of peak deconvolution of the small Mn peak with the larger Fe peak.

The site preferences measured by channeling are con-

TABLE 1. Average proportions of various elements in the Ti site in ilmenite

Cr-bearing (11 measurements)	
Fe	0.06 (0.03)
Mg	-0.02 (0.13)
Cr	0.76 (0.14)
Mn-bearing (6 measurements)	
Fe	0.06 (0.02)
Mg	0.04 (0.06)
Al	0.90 (0.18)
Mn	-0.08 (0.06)

Note: Estimated standard deviations are given in parentheses.

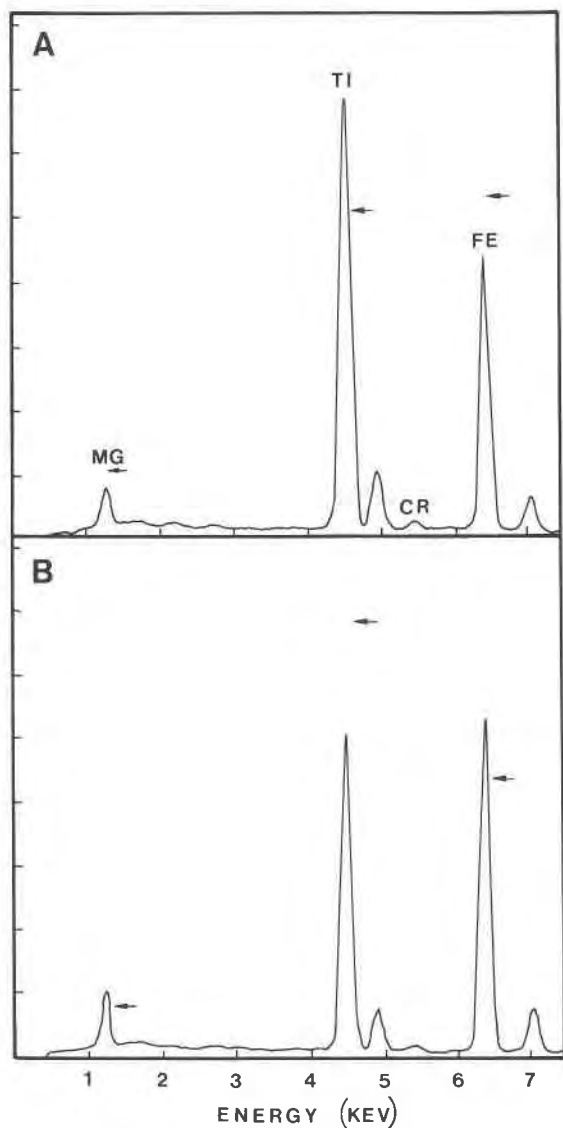


Fig. 3. Typical X-ray spectra for oriented crystals of ilmenite: (A) tilted slightly less than the Bragg angle for (0003); (B) tilted slightly greater than the Bragg angle for (0003). Arrows indicate peak heights for the spectrum in the opposite tilt direction.

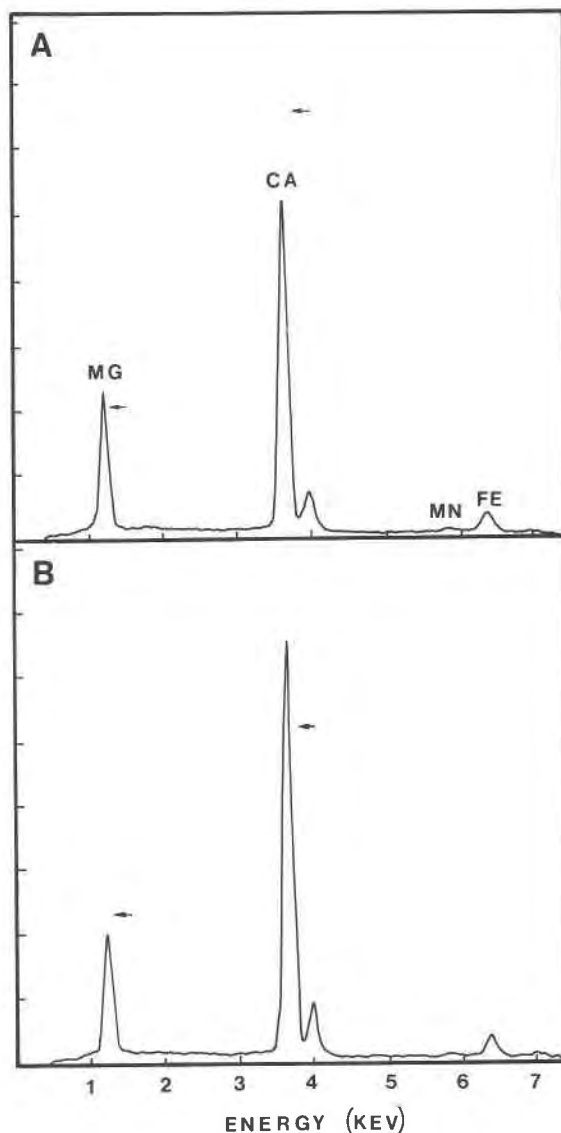


Fig. 4. Typical X-ray spectra for oriented crystals of dolomite: (A) tilted slightly less than the Bragg angle for $\{10\bar{1}1\}$; (B) tilted slightly greater than the Bragg angle for $\{10\bar{1}1\}$. Arrows indicate peak heights for the spectrum in the opposite tilt direction.

sistent with cation sizes. It would be of particular interest to determine whether these distributions change as a function of temperature, pressure, and f_{O_2} for possible application in geothermometry and geobarometry.

Dolomite

Most of the measurements on dolomite were done on a sample of baroque dolomite replacing siliciclastic rocks in the Fountain Formation, Colorado. The sample consists almost entirely of rhomb-shaped dolomite cores, surrounded by Fe-rich dolomite rims, with Mn-rich zones between the cores and rims. Microprobe analyses (Kindred, 1987) show the dolomites to be only slightly

enriched in Ca (up to 54 mol% $CaCO_3$), but strongly zoned, with MnO ranging from 0 to 2 wt%, and FeO, showing an inverse relationship to MnO, also ranging from 0 to 2 wt%. The crushed sample examined in the TEM therefore contained a variety of compositions from Fe-rich and Mn-poor, to Mn-rich and Fe-poor, to fairly pure Mg-Ca dolomite.

Typical spectra from the two channeling orientations are shown in Figure 4. In calculating site occupancies, it was assumed that all the Mg and 8% of the Ca are in one site and the remaining Ca is in the other site. The Mg-site occupancies for Fe in seven Fe-rich dolomites is 0.67 (± 0.17) and for Mn in seven Mn-rich dolomites is 0.95

(± 0.06). Whereas Mn appears to be almost completely ordered into the Mg site, Fe only shows slight preference for the Mg site. Since the conditions of formation of the core and rim dolomites may have been different, it would be of interest to compare the relative distributions of Fe and Mn in the same crystal fragment. Because of problems of MnK_{β} overlap with FeK_{α} and possible peak-deconvolution errors, the most useful dolomites for such an analysis would be those with Fe concentrations greater than, or equal to, those of Mn but with significant quantities of Mn. Several measured crystal fragments met these criteria, and additional measurements were made on a sample of dolomite from Tsumeb, Namibia, with Fe and Mn both up to about 0.5 at.%. In all measurements, Mn showed a significantly greater degree of ordering than Fe, and an average of seven measurements that had acceptable absolute occupancies showed, for the Mg site, $C_{Mn} - C_{Fe} = 0.24 (\pm 0.16)$.

The preference of Mn^{2+} for the Mg site has been shown by using electron paramagnetic resonance by Wildeman (1970). In this study he found a tendency for Mn to order with increasing hydrothermal alteration. A relatively high temperature of formation of the Fountain Formation dolomites was estimated by Kindred (1987) (120–140°C), and so the strong ordering of Mn in these dolomites is consistent with the earlier studies.

The degree of ordering of Fe has not been previously measured. Since Fe tends to oxidize more readily than Mn, one can rule out the possibility that the Mn is significantly smaller than the Fe cation. Therefore these distributions are controlled by factors other than simple cation sizes. It is possible that Fe may substitute readily in the Ca site owing to larger distortions in this site (Reeder, 1983). If Mn shows stronger ordering with increasing temperature, as suggested by Wildeman (1970), the ordering behavior for Fe may be quite different from that of Mn. It would be particularly interesting to determine site occupancies for Fe in dolomites from a number of different environments.

CONCLUSIONS

The technique of ALCHEMI has been used successfully to determine site preferences of minor elements in ilmenite and dolomite, using planes normal to the hexagonal c axis and the $\{10\bar{1}1\}$ set of planes for the channeling directions. Measurements of ilmenite nodules from a kimberlite pipe show strong preference of Mg and Mn for the Fe site, a slight preference of Cr for the Ti site and a strong preference of Al for the Ti site. These observations are consistent with cation-size considerations.

Channeling experiments on high-temperature dolomites, using similar channeling directions to those in ilmenite, revealed Mn to be almost completely ordered into the Mg site, consistent with earlier studies on dolo-

mite. In contrast, Fe shows significant disorder with only a slight preference for the Mg site, suggesting that factors other than cation size control Fe distribution.

ACKNOWLEDGMENTS

Financial support for this study was provided by National Science Foundation Grant EAR-8318674. Transmission-electron microscopy was done at the Center for Materials Science, Los Alamos National Laboratory. Valerie Kindred is gratefully acknowledged for providing samples of dolomite and allowing access to her unpublished data. The authors also thank Jim Smith (Center for Materials Science) for much of his valuable time during the study, and John Drexler (University of Colorado) for help with microprobe analyses. Gordon Nord and Peter Buseck provided many useful comments on an earlier version of the manuscript.

REFERENCES

- Cherns, D., Howie, A., and Jacobs, M.H. (1973) Characteristic X-ray production in thin crystals. *Zeitschrift für Naturforschung*, 28A, 565–571.
- Christoffersen, R., Buseck, P.R., and Dickenson, J. (1984) Determination of Mg-Al order-disorder in spinel by electron channelling (abs.) EOS, 65, 289.
- Kindred, V.P. (1987) The nature and origin of dolomite in the upper Fountain Formation (Pennsylvanian), east flank of Colorado Front Range, central Colorado. M.S. thesis, University of Colorado, Boulder.
- McCormick, T.C. (1986) Crystal-chemical aspects of non-stoichiometric pyroxenes. *American Mineralogist*, 71, 1434–1440.
- McCormick, T.C., Smyth, J.R., and Lofgren, G.E. (1987) Site occupancies of minor elements in synthetic olivines as determined by channeling-enhanced X-ray emission. *Physics and Chemistry of Minerals*, 14, 368–372.
- Otten, M.T., and Buseck, P.R. (1986) Zone-axis ALCHEMI for the rapid assessment of site occupancies in garnets. In G.W. Bailey, Ed., *Proceedings of the 44th Annual Meeting of the Electron Microscopy Society of America*, p. 706–707. San Francisco Press, San Francisco.
- Reeder, R.J. (1983) Crystal chemistry of the rhombohedral carbonates. *Mineralogical Society of America Reviews in Mineralogy*, 11, 1–47.
- Self, P.G., and Buseck, P.R. (1983) High-resolution structure determination by ALCHEMI. In G.W. Bailey, Ed., *Proceedings of the 41st Annual Meeting of the Electron Microscopy Society of America*, p. 178–181. San Francisco Press, San Francisco.
- Self, P.G., Spinnler, G.E., and Buseck, P.R. (1983) Pyroxenes—A novel case for atomic site occupancy determination by Alchemi. *Geological Society of America Abstracts with Programs*, 15, 683.
- Smyth, J.R., and Taftø, J. (1982) Major and minor element site occupancies in heated natural forsterite. *Geophysical Research Letters*, 9, 1113–1116.
- Spence, J.C.H., and Taftø, J. (1983) ALCHEMI: A new technique for locating atoms in small crystals. *Journal of Microscopy*, 130, 147–154.
- Taftø, J. (1982) The cation distribution in a (Cr,Fe,Al,Mg)₂O₄ spinel as revealed from the channelling effect in electron induced X-ray emission. *Journal of Applied Crystallography*, 15, 378–381.
- Taftø, J., and Buseck, P.R. (1983) Quantitative study of Al-Si ordering in an orthoclase feldspar using an analytical transmission electron microscope. *American Mineralogist*, 68, 944–950.
- Taftø, J., and Spence, J. (1982a) Crystal site location of iron and trace elements in an Mg-Fe-olivine using a new crystallographic technique. *Science*, 218, 49–51.
- (1982b) Atomic site determination using the channeling effect in electron induced X-ray emission. *Ultramicroscopy*, 9, 243–248.
- Wildeman, T.R. (1970) The distribution of Mn^{2+} in some carbonates by electron paramagnetic resonance. *Chemical Geology*, 5, 167–177.

MANUSCRIPT RECEIVED JANUARY 12, 1987

MANUSCRIPT ACCEPTED APRIL 6, 1987