

## Quantitative study of Al–Si ordering in an orthoclase feldspar using an analytical transmission electron microscope

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### Abstract

For certain crystal orientations and diffraction conditions, electron-induced characteristic X-ray emission produces anomalous intensities as a result of electron channeling. These intensities can be used to determine directly the chemical compositions of specific crystallographic sites within individual crystals. We have used this channeling method to determine the Al–Si ordering in gem orthoclase from Ampandrandava, Madagascar. We find that 71 atomic percent of the Al occupies the T1 site, in agreement with the values derived from standard X-ray powder diffraction data.

### Introduction

Over the years much attention has been given to the structural state of feldspars and thus to the determination of Al and Si ordering. Such ordering is kinetically controlled and so is a sensitive indicator of the thermal history of the feldspar. It is also the basis for understanding subsolidus phase relationships for plagioclase. However, the similar X-ray scattering amplitudes of Al and Si make it extremely difficult to determine the degree of ordering directly. The problem is especially severe if one of the species is present at low concentrations.

X-ray and neutron diffraction have been used to determine ordering (Fischer and Zehme, 1967; Brown, Hamilton, Prewitt and Sueno, 1971; Stewart and Wright, 1974; Ribbe, 1975; Stewart, 1975), but they have limitations. The X-ray determinations are based on bond lengths and are thus indirect, and the single crystal methods also require considerable time and effort. The data are averaged over relatively large volumes of crystal, of the order of  $10^{15}$  unit cells for single crystal X-ray results and many more unit cells for neutron data. Smith (1974) reviews some of the problems encountered when using such averaged data to quantify Al–Si ordering. Electron diffraction theoretically can also be used to determine ordering, but dynamical effects preclude reliable quantitative intensity measurements. However, there is another, more direct way that ordering can be determined.

In the transmission electron microscope (TEM) a focussed electron beam can be used to generate secondary X-ray emission from a sample; solid state detectors are

commonly utilized to monitor this radiation and thus perform chemical analyses of small volumes of crystal. TEMs with X-ray detectors are becoming increasingly widespread. In this paper we demonstrate how such instrumentation can be used to determine the concentrations of particular atoms on specific crystallographic sites in volumes of crystals containing between  $10^4$  and  $10^6$  unit cells. The emphasis is on the experimental procedures.

It is possible to use a crystal structure to modulate electron waves through the crystal in such a way that X-ray emission is enhanced from only certain crystallographic sites (Taftø, 1979). The result is that the electron wave field can be “tuned” so that the emitted X-ray intensities and, thus, atomic occupancies can be determined for specified elements residing on particular sites. Moreover, these intensities can be calibrated against the emitted intensities of other elements in the crystal, which thus can serve as an internal standard. The result is that by using *ALCHEMI* (atom location by channeling-enhanced microanalysis) it is possible to determine either major or minor element abundances on one or more crystallographic sites in a given mineral. Site occupancies in many types of crystal structures can thus be measured directly and, in many cases, rapidly for crystal volumes that are many orders of magnitude smaller than is possible by any other technique. The method has the advantages of being independent of existing means for determining Al–Si ordering and of being free of any adjustable parameters. It requires no external standards, and it can be used to determine concentrations down to 0.1 atomic percent and so can be used for both major and minor

elements. Furthermore, as in this paper, it can be used to distinguish between neighboring elements in the periodic table.

ALCHEMI has been used to locate V and Ti at concentrations as low as 0.1 atomic percent in spinels (Taftø, 1982) and Mn and Ni in olivine (Taftø and Spence, 1982). In the present paper we demonstrate the use of ALCHEMI for determining the Al-Si ordering in an orthoclase crystal. We have obtained direct measurements of site populations from areas of crystals that are several hundred angstroms in diameter and have shown that in our gem orthoclase 71 atomic percent of the Al atoms reside on the Tl site.

### The ALCHEMI technique

An electron beam (and associated plane wave) that is incident on a crystal that is oriented to produce Bragg diffraction builds up a modulated intensity over the crystal unit cell. This modulation results from the interference between the incident and the Bragg-reflected beam within the crystal and produces the enhanced characteristic X-ray emission on which the ALCHEMI method is based. Depending on the crystallographic direction of the incident beam, the resulting modulated intensity pattern may have an intensity maximum on a particular crystal site. This intensity maximum gives rise to an anomalously high production of X-rays. Such an enhanced emission and orientation dependence of secondary signals has been observed for a variety of primary radiations: neutrons (Knowles, 1956), electrons (Duncumb, 1962), X-rays (Batterman, 1964). By using slight changes in crystal orientations, the atom populations at different sites can be measured. The orientation dependence of the electron-induced characteristic X-ray emission, which we utilize in this study, has been treated in detail by Cherns, Howie and Jacobs (1973).

In ALCHEMI it is convenient to orient the crystal so that the first reflection along a systematic row in the diffraction pattern is strongly excited. This condition can be understood qualitatively from two-beam considerations, where only two Bloch waves are excited (Taftø, 1979). The intensity of the electron wave field can then be expressed as a sum of the intensities of these Bloch waves, and the period of these waves is equal to the repeat distance in the projected structure corresponding to the excited reflection. One of the Bloch waves has its intensity maxima in the region of largest projected charge density (in the direction parallel to the incident electron beam); the other Bloch wave has its maxima half a repeat distance from the first one. These are standing waves and, if the maxima correspond to the locations of atoms of special interest, then chemical analysis of specific sites is possible.

In order to develop the quantitative relationship between X-ray intensity and element concentration it is important to know the intensity of the electron wave field, averaged over thickness, at the sites of interest for a

given crystallographic direction of the incident electron beam. The phenomenon of enhancement of X-ray intensity is well understood, and so the intensity distribution within the crystal unit cell can, in principle, be calculated by many-beam dynamical calculations. For that purpose it is necessary to know accurately the thickness distribution of the specimen over the electron-illuminated area, the exact crystallographic direction of the incident beam, and the probability of diffuse scattering out of the Bragg beams. However, these parameters are not easily determined.

As an alternative to calculation from first principles, it is possible to use an empirical approach to determine the intensity of the wave field on the crystallographic sites of interest. This determination is done by comparing the X-ray signals generated by atoms with known crystallographic position in the structure (the reference atoms) to the signals from the atoms of interest. In the example of orthoclase, the Al and Si signals are calibrated with respect to the K signals. By use of this empirical approach, no adjustable parameters are involved in the interpretation. In order to use this procedure it is necessary to find a crystal orientation such that there is physical coincidence between the projected crystallographic sites of interest and those of the reference atoms. Grains of the mineral of interest must then be tilted so that the direction of the incident electron beam is perpendicular to the selected orientation. The tilting procedure is identical to that done for high-resolution imaging (*e.g.*, Buseck and Iijima, 1974).

### The sample

For study we selected a sample of gem quality orthoclase that is clear, colorless and shows no evidence of twinning in thin section and by electron diffraction. The specimen, from Ampandrandava, Madagascar, was originally supplied by Ward's Scientific Establishment, which indicated the locality and gave Lacroix (1922) as a reference. Lacroix describes gem orthoclase from Madagascar pegmatites in granitic rocks, but does not mention Ampandrandava. We presume that our crystal, like the ones described by Lacroix, comes from a pegmatite.

Electron microprobe analysis indicates the orthoclase composition (percent by weight) as: K<sub>2</sub>O 15.32, Na<sub>2</sub>O 0.87, Fe<sub>2</sub>O<sub>3</sub> 0.32, SiO<sub>2</sub> 65.00, and Al<sub>2</sub>O<sub>3</sub> 18.21. This corresponds to a formula of (K<sub>0.90</sub>Na<sub>0.08</sub>)(Al<sub>0.99</sub>Fe<sub>0.01</sub>Si<sub>3.01</sub>)O<sub>8</sub>. Its cell dimensions were measured by powder X-ray diffraction using CuK $\alpha$  radiation, a KCl internal standard, and a Guinier camera. The results, based on a least squares fit using 14 reflections and monoclinic constraints, are:  $a = 8.553(9)\text{\AA}$ ,  $b = 12.982(7)\text{\AA}$ ,  $c = 7.197(2)\text{\AA}$ ,  $\beta = 116.02^\circ$ , in substantial agreement with published cell parameters (*e.g.*, Stewart and Wright, 1974). The optical perfection and transparency, the electron microprobe analyses, and the sharpness of the X-ray reflections all indicate a lack of compositional zoning. Thus, on all counts it looks like a good orthoclase sample.

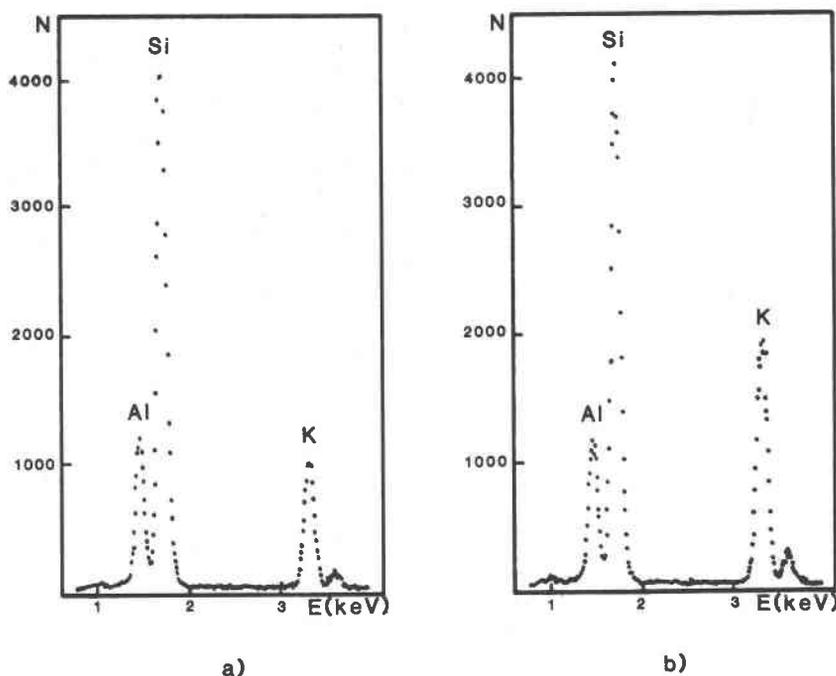


Fig. 1. X-ray emission spectra for two positions of the crystal around the  $(0k0)$  planar orientation. Number of counts ( $N$ ) is plotted vs. X-ray emission energy ( $E$ ). (a) The incident electron beam is parallel to the  $(020)$  planes. (b) The angle between the incident beam and the  $(020)$  planes is  $\sim 10$  mrad.

### Experimental

The specimen was prepared for electron microscopy by grinding in a mortar, and the resulting grains were dispersed on a copper grid covered with a holey carbon film. Thin, wedge-shaped crystals less than  $1000\text{\AA}$  thick were studied using a Philips 400T electron microscope equipped with a Tracor Northern energy dispersive X-ray analyzer. The primary energy of the electrons was 100 keV and the divergence of the incident beam about 1 mrad, resulting in a highly parallel incident electron beam. The beam diameter was roughly  $1000\text{\AA}$ . Planar cases (systematic rows) were studied, *i.e.*, the crystal was oriented so that, to the extent possible, only Bragg reflection from one set of planes occurred. Measurements lasting five minutes yielded between 13,000 and 30,000 counts on each of Al, Si, and K.

The electron-channeling effect is greatest for crystal orientations near those yielding strong Bragg reflections and at low scattering angles. For weak reflections, such as were used for the orthoclase measurements, it is particularly important to maximize the effect by using an orientation close to, but not exactly at the Bragg angle. For this study, angles of a few mrad from the critical Bragg angles were used.

Kikuchi lines were used for critical orientation of the crystal and for measuring tilt angles. The positions of the Kikuchi lines in diffraction patterns correspond to incident beam directions for which the Bragg reflection position is fulfilled. Thus, an  $hkl$  spot is at the exact Bragg reflecting position when it lies on the corresponding  $hkl$  Kikuchi line. By tilting the crystal so that the Kikuchi line moves to a position between the direct beam and the diffraction spot, the angle between the incident beam and the Bragg reflecting planes is smaller than the Bragg angle; when the

crystal is tilted in the opposite direction this angle becomes larger than the Bragg angle.

Figure 1a shows an X-ray emission spectrum obtained with the incident electron beam exactly parallel to the  $(0k0)$  orthoclase planes. Figure 1b shows a spectrum from the same area, but with the crystal tilted slightly so that the angle between the  $(020)$  planes and the incident beam is about 10 mrad; this angle is measured from the shift in position of the Kikuchi lines. The intensity of the  $K\alpha$  line of potassium is twice as large in Figure 1b as in Figure 1a, whereas the intensities of the  $K\alpha$  lines of Al and Si are essentially unchanged. Clearly, there is an orientation dependence for the K intensity, relative to that for Al and Si.

Figure 2 shows two spectra from one area, but with the incident beam nearly parallel to the  $(h00)$  planes. The corresponding diffraction patterns are also inserted. In Figure 2a the angle,  $\theta_1$ , between the  $(h00)$  planes and the incident beam is slightly smaller than the Bragg angle for the first reflection along  $a^*$ , the 200 reflection, *i.e.*,  $\theta_1 < \theta_{200}$ . In Figure 2b the orientation is changed a few mrad so that  $\theta_1 > \theta_{200}$ .

In order to evaluate the magnitude of the electron channeling effect, comparisons are made to reference spectra produced from the same areas of crystal as were used for the channeling measurements. The reference spectra are obtained by tilting the crystal so that no strong Bragg reflections are excited, *i.e.*, so that as close as possible to a uniform (non-modulated) intensity distribution of incident electrons results across the unit cell. Special care must be taken to orient the crystals so that no reflections close to 000 and none of the  $h00$  systematics out to about the tenth order are excited. Obtaining good reference spectra is especially important for the 200 planar case of orthoclase, where the channeling effect is relatively weak. In this case

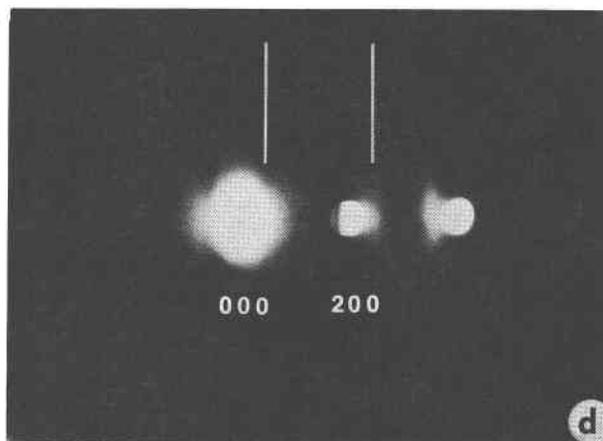
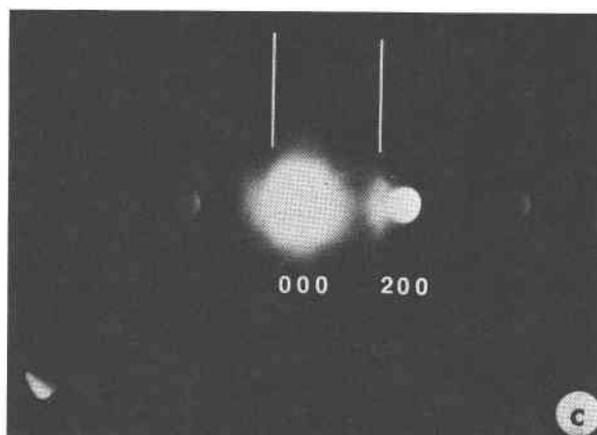
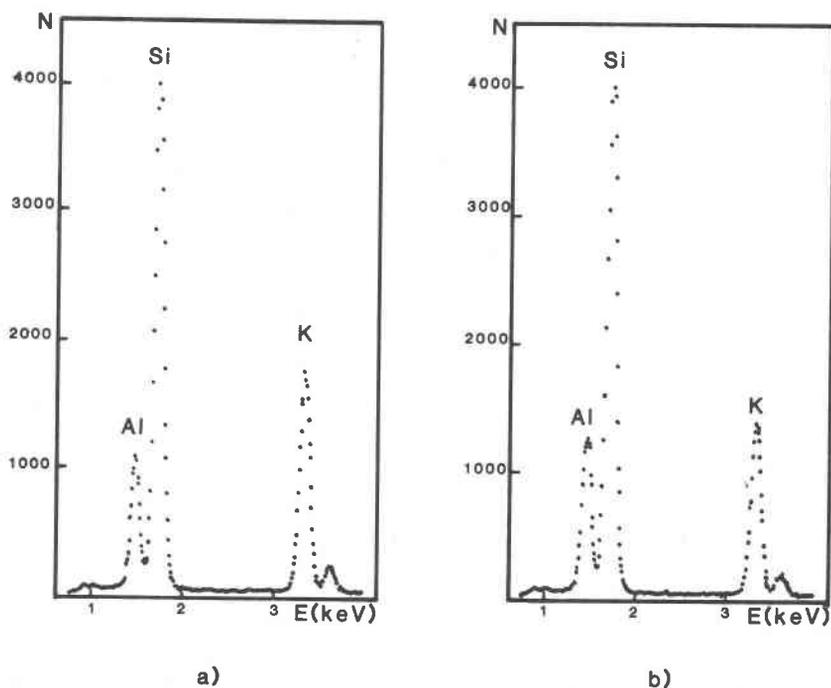


Fig. 2. X-ray emission spectra for two positions of the crystal around the (100) planar orientation. (a)  $\theta_i < \theta_{200}$ . (b)  $\theta_i > \theta_{200}$ . The diffraction conditions under which the spectra were taken are shown by portions of the respective electron diffraction patterns in (c) and (d), where the positions of the Kikuchi lines can be seen and those corresponding to the 200 Bragg reflections are indicated.

especially, it is also important to use tilting angles within a few degrees of the channeling orientation; otherwise the change in geometry, relative to the X-ray detector, produces different X-ray absorption effects that can perturb the results.

### Discussion

Figure 1 demonstrates a clear dependence on the incident beam direction for the yield of electron-induced X-ray emission. However, the crystal orientation used for Figure 1 is not suitable for determining the Si ordering; the wave-field intensities on T1 and T2, the two crystallographic sites where the Al and Si reside, cannot be

determined from the experiment. The two spectra in Figure 1 show no significant differences in the ratios between the  $K\alpha$  lines of the Al and Si, which indicates that either (a) there is complete disorder between Al and Si, or (b) the wave fields on the T1 and T2 sites have the same relative changes in going from the diffraction condition used in Figure 1a to the one used in Figure 1b.

The crystal orientations used to obtain Figure 2 result in decreased X-ray intensities of the potassium  $K\alpha$  line, as well as noticeable differences in the relative Al and Si intensities for the two tilting positions. It is the latter effect that indicates Al-Si ordering. The explanation can

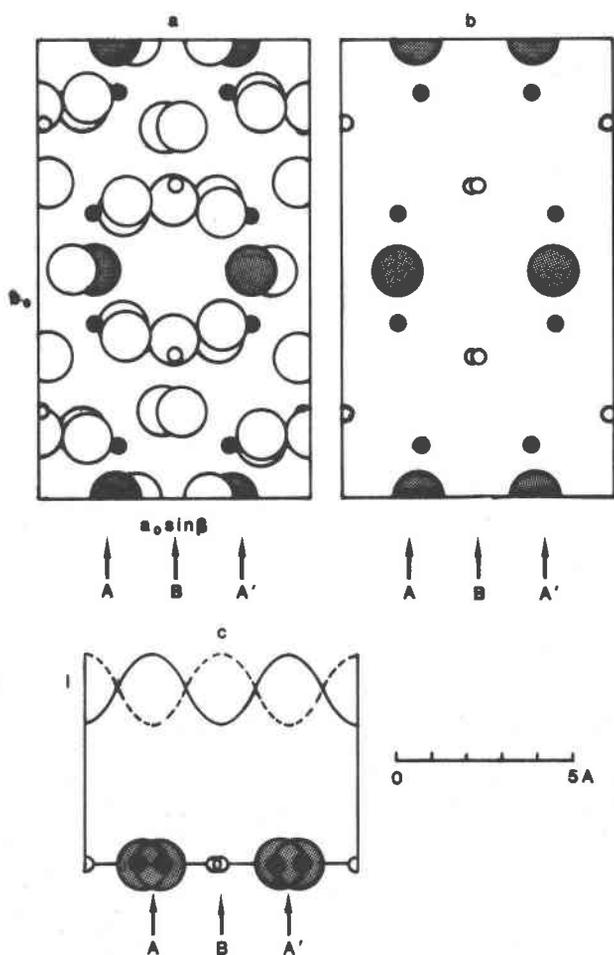


Fig. 3. Relation between the orthoclase crystal structure and the electron-channeling effect. (a) The orthoclase structure, projected along [001]. The atomic coordinates are from Wyckoff (1963). The large open and shaded circles represent the positions of the oxygen and K atoms, respectively, and the small open and filled circles represent T1 and T2, respectively. (b) The same projection as in (a), but showing only the positions of K and the T1 and T2 sites. Note that the K and the T2 sites, while slightly staggered, lie almost along (200) planes (marked by arrows A and A') and that these planes are midway between the (200) planes that contain the T1 sites (arrow B). (c) Plot of wave-field intensity vs. atomic position along  $a \sin \beta$ . The solid line represents the wave field modulation for  $\theta_i < \theta_{200}$  and the dotted line for  $\theta_i > \theta_{200}$ . The arrows mark the positions corresponding to those indicated in Fig. 3b. The nature of the sine modulation minimizes the effects of the slight displacement between the T2 sites and K atoms along given (200) planes.

be seen from Figure 3a, which is a projection along [001] and so illustrates the positions of both the (020) planes, used to obtain Figure 1, and the (200) planes, used for Figure 2. It is evident that the K and the T2 sites practically coincide along the (200) planes (Fig. 3b). Thus, for the orientation used in Figure 2, the wave field, which is modulated only along [100], is essentially the same on

the K atoms and the T2 sites. Figure 3c quantitatively indicates the way in which the wave field, averaged over thickness, is modulated for  $\theta_i < \theta_{200}$  and  $\theta_i > \theta_{200}$  (for an explanation see Taftø, 1979).

For a crystal orientation where the (200) planes are nearly parallel to the incident electron beam, the projected charge density is largest along the planes where the T2 sites and the K atoms are located. One of the Bloch waves (here called no. 1) has its intensity maxima located along the T2 and K sites, and this Bloch wave is strongly excited when  $\theta_i < \theta_{200}$ . The other Bloch wave (no. 2) has its intensity maxima located at the T1 sites and is excited when  $\theta_i > \theta_{200}$ . Thus, the observed decrease in intensity of the  $K\alpha$  line of potassium, relative to the  $K\alpha$  line of Si and Al, on changing from  $\theta_i < \theta_{200}$  to  $\theta_i > \theta_{200}$  in Figure 2 is consistent and as predicted. The  $K\alpha$  line of Al increases, relative to the  $K\alpha$  line of Si, on changing from  $\theta_i < \theta_{200}$  to  $\theta_i > \theta_{200}$ . It follows from the above argument that Al has a stronger preference than Si for the T1 sites. The relatively small changes of intensities in the two spectra of Figure 2 are a consequence of the fact that the 200 reflection is weak in orthoclase.

A quantitative site analysis with respect to Al-Si ordering can be performed for the crystal orientations used for Figure 2 without the need of calculating the intensity distribution in the crystal unit cell. Let  $I_{\text{ref}}$  be the intensity, integrated over time and thickness, for a uniform (nonmodulated) distribution of incident electrons over the unit cell. Then the number of X-ray counts from Al,  $N_{\text{Al,ref}}$ , from Si,  $N_{\text{Si,ref}}$ , and from K,  $N_{\text{K,ref}}$ , is:

$$N_{\text{Al,ref}} = k_{\text{Al}} I_{\text{ref}} \quad (1)$$

$$N_{\text{Si,ref}} = k_{\text{Si}} I_{\text{ref}} \quad (2)$$

$$N_{\text{K,ref}} = k_{\text{K}} I_{\text{ref}} \quad (3)$$

where  $k_{\text{Al}}$ ,  $k_{\text{Si}}$  and  $k_{\text{K}}$  are three constants that depend on the efficiency of the spectrometer and the concentrations of the different elements. In addition, for those orientations where there is a modulated intensity over the unit cell, let  $I_1$  be the intensity of the wave field of the incident electrons on the T1 site averaged over the thickness of the crystal in the direction of the electron beam, and let  $I_2$  be the intensity of the thickness-averaged wave field on the T2 site (and thus also on the K atoms). Then

$$N_{\text{Al}} = \alpha k_{\text{Al}} I_1 + (1 - \alpha) k_{\text{Al}} I_2 \quad (4)$$

where  $\alpha$  is the fraction of Al atoms on the T1 site and consequently  $1 - \alpha$  is the fraction of Al atoms on the T2 site. Orthoclase contains Al:Si in the ratio of 1:3. Therefore, the fraction of Si atoms on the T1 site has to be  $(2 - \alpha)/3$  and on the T2 site  $(1 + \alpha)/3$ . Thus

$$N_{\text{Si}} = \left( \frac{2 - \alpha}{3} \right) k_{\text{Si}} I_1 + \left( \frac{1 + \alpha}{3} \right) k_{\text{Si}} I_2 \quad (5)$$

The K atoms only experience the intensity  $I_2$  and so

$$N_{\text{K}} = k_{\text{K}} I_2 \quad (6)$$

From these six equations  $k_{Si}$ ,  $k_{Al}$ ,  $k_K$ ,  $I_1$ ,  $I_2$  and  $I_{ref}$  can be eliminated; solving for  $\alpha$ :

$$\alpha = \frac{2\left(\frac{N_K}{N_{K,ref}}\right) - 2\left(\frac{N_{Al}}{N_{Al,ref}}\right)}{4\left(\frac{N_K}{N_{K,ref}}\right) - \left(\frac{N_{Al}}{N_{Al,ref}}\right) - 3\left(\frac{N_{Si}}{N_{Si,ref}}\right)} \quad (7)$$

Equation 7 indicates that the ordering between Al and Si can be determined from two spectra, one taken under diffraction conditions that produce a modulated electron wave field over the projected unit cell and the other a reference spectrum with a uniform intensity over the unit cell.

Seven sets of measurements were made. The intensities of the  $K\alpha$  lines of Al, Si and K were integrated over 13 channels, each of width 10 eV, and the background was subtracted. The results are shown in Table 1. Based on the counting statistics, the inaccuracies in  $\alpha$  for each measurement are typically  $\pm 1.5\%$ . The actual spread in the results shows greater scatter, which may result from the excitation of accidental reflections when obtaining the spectra. Such accidental reflections may produce slightly different intensities on the T2 sites and the K atoms for the case where the wave field is modulated, and they may produce a slightly modulated (non-uniform) intensity for the reference case. Although minor, loss of K atoms as a result of electron irradiation may also occur. The above are not systematic errors; nonetheless, their efforts can be minimized by taking paired tilting measurements and by randomizing the point in the sequence where the reference spectra are obtained. In these ways the effects of accidental reflections tend to cancel, and the influence of possible K loss is minimized. For example, the effect of

progressive K loss will affect  $\frac{N_K}{N_{K,ref}}$  (Table 1) differently,

depending on whether  $N_K$  or  $N_{K,ref}$  are measured first; by changing the sequence the effects tend to cancel when dealing with the average value of  $\alpha$ .

The errors described above can be ignored for many minerals. However, the channeling effect is relatively weak for the ( $h00$ ) planar case in orthoclase, and special care had to be taken. A weak systematic error occurs because the T2 sites and the K atoms do not coincide exactly (Fig. 3). This lack of coincidence results in an underestimation of the ordering, but because the wave field varies slowly over the unit cell when low index reflections are excited, this error is estimated to influence  $\alpha$  by only about 1%.

There is an additional source of error that may arise whenever X-ray spectra are obtained using an electron microscope. Depending on their distribution, it is always possible that other dispersed feldspar grains on the TEM support grid may absorb X-rays from the sample that is being studied. It is therefore necessary to repeat the experiment several times for different geometrical config-

Table 1. The fraction,  $\alpha$ , of Al on the T1 sites as determined from replicate ALCHEMI measurements

Measurement no.	$\theta_1$	$\frac{N_{Al}}{N_{Al,ref}}$	$\frac{N_{Si}}{N_{Si,ref}}$	$\frac{N_K}{N_{K,ref}}$	$\alpha$
1	< $^{\theta}$ <sub>200</sub>	0.943	1.001	1.079	73
2	> $^{\theta}$ <sub>200</sub>	1.067	0.994	0.897	74
3	< $^{\theta}$ <sub>200</sub>	0.895	0.990	1.224	64
4	< $^{\theta}$ <sub>200</sub>	0.918	0.992	1.077	77
5	> $^{\theta}$ <sub>200</sub>	1.097	1.015	0.868	68
6	< $^{\theta}$ <sub>200</sub>	0.985	1.046	1.157	68
7	> $^{\theta}$ <sub>200</sub>	1.094	1.000	0.838	69

\*Paired measurements

urations in order to determine the value about which the parameter under study converges.

Apart from the two extreme measurements in Table 1, the values of  $\alpha$  are between 68% and 74%. Based on the average values and the spread in  $\alpha$ , we conclude that 71% with a probable range of  $\pm 3\%$  of the Al atoms occupy the T1 site. The sharpness of the X-ray diffractions also suggest a uniformity in ordering, consistent with the conclusion that the spread in the ALCHEMI results are experimental rather than the result of zoning.

We determined the unit cell parameters of the crystal after completing the quantitative analysis of ALCHEMI data. Using the relationship between the lattice parameters and the Al-Si ordering suggested by Phillips and Ribbe (1973), the fraction of Al occupying the T1 site is  $72 \pm 2\%$ , in excellent agreement with what we obtained by the more direct ALCHEMI technique. The  $b$ - $c$  plot of Stewart and Wright (1974) indicates that  $78 \pm 2\%$  of the Al atoms occupy the T1 site. The indicated errors of  $\pm 2\%$  are estimated solely from our X-ray data. The Stewart and Wright plot also yields an index of strain,  $\Delta a$ , of 0.03; this is less than their threshold for strained feldspars, suggesting that the Ampandrandava orthoclase is relatively unstrained.

In conclusion, the ALCHEMI method provides a result for Al-Si ordering in our orthoclase that is consistent with data derived from measurements made by X-ray and neutron diffraction. Moreover, the ALCHEMI method is based on X-ray emission and so provides an independent method of measuring Al-Si ordering. It can be performed directly and on volumes that are far smaller than are possible by the other methods. Future experiments of possible interest are the determination of ordering in zoned crystals, in samples that have been heated experimentally, and in critical samples (*e.g.*, low albite and "ideal" orthoclase) where diffraction data have yielded results whose interpretation is problematical. Also of potential interest is the site allocation of minor elements. For example, we observed an Fe signal from the orthoclase, but in order to obtain good statistics longer counting times will be required than we used.

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