A CENTURY OF MINERAL STRUCTURES: HOW WELL DO WE KNOW THEM?

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Abstract

This decade marks the centenary of the discovery of X-ray diffraction. The development of mineralogy as a scientific discipline in which the properties of minerals are understood in terms of their atomic-scale structures has paralleled the development of diffraction crystallography. As diffraction crystallography revealed more precise details of mineral structures, more subtle questions about mineral properties could be addressed and a deeper understanding of the relationship between the two could be attained. We review the developments in X-ray single-crystal diffraction crystallography over the last century and show how its power to provide fundamental information about the structures of minerals has evolved with the improvements in data quality and the increased technological capacity to handle the data. We show that modern laboratory X-ray diffraction data is of the quality such that mineralogical results are no longer limited by the data quality, but by the physical validity of the refinement models used to interpret the data.
Introduction

Minerals are, by definition, crystalline. Their structures are composed of atoms arranged in periodically repeating patterns. The same atoms in different minerals tend to occupy characteristic local environments with specific coordination geometries and bond lengths. The arrangements of atoms within minerals and the crystal-chemical concepts derived from them successfully explain many of the physical, chemical and thermodynamic properties of minerals. But how do we know that minerals are built of atoms? More than a century ago, there was no proof of the existence of atoms, although it was clear that gases behaved as if composed of particles that occupied some finite volume. It had been deduced from the regularity of their external form (but not proven) that crystalline materials and especially minerals were probably periodic arrays of ‘some things’; the common deduction was that crystals were composed of the same ‘molecular’ species that occur in gases, condensed into regular and periodic arrays (Kubbinga 2012). In the first half of 1912 three young men in the Institute for Theoretical Physics of the Ludwigs-Maximilians Universitaet Muenchen carried out an experiment that would confirm the atomistic view of the chemical and mineral world. Inspired by conversations with P.P. Ewald, Max von Laue had suggested the experiment to two other research assistants, Friedrich Knipping and Walter Friedrich. In May 1912 they submitted a manuscript to the Bavarian Academy for Science that reported the diffraction of X-rays by crystals (Friedrich et al. 1912). It was known from optics and physics that diffraction occurs due to constructive and destructive interference between waves scattered by a periodic array of objects; scattering by resonators was actually the subject of Ewald’s research at the time. Therefore, this single observation of the diffraction of X-rays by crystals proved two things; X-rays can behave as waves, and crystals are periodic arrays of X-ray scatterers. Within a year, the Braggs had used the intensities of the X-ray beams diffracted by crystals to determine the arrangements of the atoms in crystals of simple minerals such as the zinc blende used in the experiments in Muenchen, and NaCl, and showed that they were not molecular compounds (e.g. Gruner 1929). The subsequent development of mineralogy as a scientific discipline in which the properties of minerals are understood in terms of their atomic-scale structures (e.g. Gruner 1931; Kieffer and Navrotsky 1985) has paralleled the subsequent development of diffraction crystallography. As diffraction crystallography revealed more precise details of structures, more subtle questions about mineral properties could be addressed and a deeper understanding of the relationship between the two could be attained. By following the developments over the last century we can understand both the
power of diffraction crystallography to provide fundamental information about the structures of minerals, while at the same time appreciating its important intrinsic limitations and how these limitations have changed as the technology supporting X-ray diffraction has developed.

**The development of diffraction crystallography**

The very first diffraction measurements and structure solutions provided a way for diffraction crystallography to ‘boot-strap’ its own methodology. Bragg showed that the diffracted intensities from crystals of simple structures such as the alkali halides can be explained qualitatively in terms of scattering from point atoms that have a scattering power proportional to their atomic numbers. When the atoms scatter in phase, their scattering power adds together to give strong reflections, when they scatter in antiphase the reflection is weak. This approach is sufficient to establish the basic architecture of simple minerals such as halite, and to determine the number of atoms in the unit-cell of the structure (e.g. Bragg 1975). When combined with the measured density and an accurate value of Avogadro’s number (Millikan 1910), the unit-cell parameters of halides could be determined on an absolute basis. Subsequent application of what we now know as Bragg’s law allowed the determination of X-ray wavelengths, and then the determination of lattice parameters of new crystals without knowledge of their structures or densities.

The subsequent early development of diffraction crystallography was remarkably rapid, both in experimental techniques and in the theoretical developments necessary to determine structures from the measured diffracted intensities. It was quickly recognized that the idea of a simple reflection event by the lattice planes in the crystal was inadequate to explain the diffracted intensities in detail. Darwin (1914) solved the problem of dynamical diffraction of X-rays and thus identified the role of extinction, absorption and multiple diffraction in determining the intensities of diffracted beams and established the concept of the mosaic crystal. This concept, confirmed by experimental measurements of intensities, is that even gem quality crystals are actually comprised of small perfect crystal domains misaligned with respect to one another. We now understand that these domains are created by the defects in the crystal structure, such as dislocation walls. The key point for experimental measurements of X-ray intensities is that the individual domains do not diffract at exactly the same position because they are rotated with respect to one another, and this necessitates the measurement of diffracted beam intensities by rotating the crystal in the beam during diffraction.
measurements (Bragg and Bragg 1913). It is the resulting integrated intensities (not the peak
intensities), corrected for absorption and extinction and geometric factors that depend on the
graphology of the measurement, that are related to the scattering density in the crystal (e.g. as
summarized in Bragg and West 1928). Bragg (1915a) expressed the relationship between the
absolute intensities corrected for experimental effects and the scattering density in terms
equivalent to a Fourier series, later (Duane 1925; Bragg 1929) written as:
$$
\rho(xyz) = \sum |F(hkl)| (\cos 2\pi (hx + ky + lz) + \alpha(hkl))
$$
(1)

The quantity $|F(hkl)|$ is equal to the square-root of the absolute intensity of the reflection $hkl$.
It is the modulus (amplitude) of the structure factor. The $\alpha(hkl)$ is the phase of the reflection.
If the scattering density corresponds only to independent spherical atoms, each with a
scattering power $f_i$ which is isotropic but depends on $\sin(\theta)/\lambda$, the Fourier series can be
inverted to obtain the structure factor equation:
$$
F(hkl) = \sum_{i=1,n} f_i (\cos 2\pi (hx_i + ky_i + lz_i) + i \sin 2\pi (hx_i + ky_i + lz_i))B_i(hkl)
$$
(2)

This equation expresses the value of the structure factor of any reflection in terms of a
summation of the scattering power of the atoms within one unit cell, with phase factors that
depend on the atom positions expressed in fractional coordinates $x_i,y_i,z_i$ and the Miller indices
$hkl$ of the reflection. The effects of local atom displacements on the structure factors are
expressed by the factor $B_i$, which in general is an anisotropic function that is different for
different atoms. It causes a general decrease in the structure factors, and hence diffracted
intensities, with increasing diffraction angle (Debye 1914). Equation (2), which was later
justified in terms of the fundamental physics of X-ray scattering by atoms (e.g. Waller and
Hartree 1929), shows that the observed diffracted intensities represent a time-and-space
average over all of the atoms within the crystal. This average structure includes the static
displacements due to atoms occupying slightly different positions in different unit cells and
the dynamic displacements due to temperature-induced vibrations of all of the atoms. In the
1920’s the effects of atomic displacements on the diffracted intensities were subsumed into
the scattering factors of atoms derived from intensity measurements of known structures, but
nowadays the displacements are described by a model whose parameters are refined to the
intensity data along with the fractional coordinates of the atoms.

Thus, by 1920, all of the essential concepts of diffraction crystallography had been established
and could be used to determine the structures of crystals. They remain the basis of structure
determination and refinement from X-ray diffraction data to the present day. The key steps in
the determination of a crystal structure start with the collection of diffraction data, followed
by ‘indexing’ (the consistent assignment of Miller indices to each diffraction peak). This
allows the calculation of the unit-cell parameters from the diffraction angles of each
reflection, and the determination of the space group symmetry from the pattern of
systematically-absent reflections. The measured intensities are then corrected for
experimental factors and are reduced to the squares of structure factors $F^2(hkl)$. This is not
sufficient to determine the structure because while the intensities are known, the phase factors
$\alpha(hkl)$ required to calculate the scattering density through Eqn. 1 are not measured and are
therefore unknown. Structure solution, or the determination of at least some atom positions
within the unit cell, is thus the biggest challenge in diffraction crystallography. Once some
atoms are located, phases $\alpha(hkl)$ can be estimated from them using Eqn (2). A Fourier
synthesis (Eqn. 1) with these phases and the measured intensities is then used to determine the
positions of any missing atoms. The test of a model structure is made through Eqn. 2, by
comparing the values of the structure factors calculated from the structure model with those
derived from the measured intensities. The subsequent step of structure refinement is the
adjustment of the structure model by adjusting the values of the atom coordinates and
displacement parameters to improve the fit to the measured intensities.

The very first crystal structures to be determined had atoms in positions within the unit-cells
that are fixed by symmetry. The diffracted intensities could therefore be used to calculate the
actual scattering factors $f_i$ of the individual atoms, which could then be used in the analysis of
more complex structures. Later, scattering factors were determined by direct calculation from
a model of the electronic structure of isolated atoms or ions (e.g. Brown et al. 2006). By the
late 1920’s it is apparent from papers (e.g. Bragg and West 1928) that the methods of data
collection and reduction had become routine; Brown and West (1927) describe their
measurements as ‘The usual X-ray rotation photographs……’. Structure solution was the
challenge. It proceeded by a mixture of deduction from the chemical analysis combined with
determination of the space group symmetry of a crystal, and by use of the principles of crystal
chemistry as they emerged from previous structure solutions. Bragg (1937, page 27)
characterized early structure solution as ‘guessing the answer to a puzzle’. The idea that the
oxygens in structures often approximated close-packed layers quickly emerged from studies
of spinels (Bragg 1915b) and simple oxides, sulphides and halides (Bragg 1920) and it was
found to be true also for olivine type structures (Bragg and Brown 1926a). This allowed
structure solution to proceed by considering how to fit the close-packed arrays into the unit cell and then deciding which interstices in the oxygen array were occupied by cations (Bragg and Brown 1926b). The crystal structure of quartz and its high-temperature polymorphs showed that Si uniformly preferred tetrahedral coordination in common minerals. Other structure determinations showed that Al and Si could substitute for one another in tetrahedra, that Al could also be octahedrally coordinated, while cations such as Fe and Mg normally occupied octahedral sites. It should be emphasized that such crystal-chemical principles that were codified as ‘laws’ by Goldschmidt (1926) following Bragg’s (1920) ideas about ionic radii, translated for American Mineralogist by Wherry (1927) and expressed in terms of the ‘coordination method’ (Pauling 1929) or polyhedral model, were used as hypotheses to obtain initial structure solutions. The structure solutions, and hence the crystal-chemical ideas, were then tested by comparison to the measured intensities through the structure factor equation. There were still significant potential pitfalls in structure determination, as can be seen in the first paper to report a full structure determination in American Mineralogist (Buerger 1931). In determining the structure of marcasite Buerger (1931) showed that two previous determinations by diffraction were in error because of different errors in the author’s setting of the space group symmetry, while a third proposal although correct, was ‘of the nature of guesswork’.

By 1930 (e.g. Gruner 1929; Bragg 1930; Gruner 1931) the basic architecture of the crystal structures of most major rock-forming minerals and large numbers of sulphides, elements and oxides had been established by X-ray diffraction. The framework structures of zeolites and feldspars were the major exceptions because their low packing density meant that ideas of close-packed layers are not appropriate to describe these structures (Pauling 1929; Taylor et al. 1934). Thus initial models for structure solution were not available. Matchatschki (1928) argued from chemical considerations and knowledge of established alumino-silicate crystal chemistry that feldspars must be a fully-connected network of AlO₄ and SiO₄ tetrahedra. Taylor (1933) solved the structure of sanidine using this idea and knowing the cell dimensions, symmetry and, critically, the size of (Si,Al)O₄ tetrahedra from other structures. On Christmas Day 1932 (see Smith 1980) he solved the geometric problem of how to fit the necessary four tetrahedra as a ring into the asymmetric unit of the unit cell, without distorting them, by having the insight to place the external oxygen atoms of the ring on symmetry elements so that the connectivity of the framework was generated naturally by the space group symmetry. The K atoms were then located by comparing observed and calculated
intensities of a few reflections, and the final refinement of the atomic positions proceeded, as
for other structures determined in that era by ‘a laborious search for more accurate atomic
parameters which will give calculated $F$-values in agreement with the observed relative
intensities of a large number of reflections’ (Taylor 1933). Thus Bragg (1930) was wrong
when he had suggested that ‘The exactitude with which atomic coordinates can be determined
is only limited by the amount of labour expended in making measurements’; the experience of
his assistant Taylor (1933) shows that once the basic crystal structure was solved, structure
refinement was clearly limited not by quantity or quality of data, but by lack of computing
power. The final individual cation-oxygen (T-O) bond lengths in the tetrahedra of Taylor’s
initial sanidine structure ranged from 1.55 to 1.75Å, with the conclusion drawn that ‘both
tetrahedral groups are nearly regular’ (Taylor 1933). These statements indicate that
uncertainties in cation-oxygen distances were of the order of 0.1 Å at best, quite insufficient
to draw conclusions about the detailed crystal-chemistry, to follow structural changes due to
changes in $P$, $T$ or phase transitions, or even to determine basic patterns of Al, Si ordering. As
feldspars exhibit both displacive transitions and a variety of convergent and non-convergent
ordering processes that greatly influence their thermodynamic properties, the development of
methodologies in diffraction crystallography as they were enabled by increased computing
power can be followed by seeing how knowledge of the feldspar structures became more and
more precise. The basic theme here is that improved precision in structure refinements means
more precise determination of the atomic coordinates, which in turn requires more precise and
higher-resolution data. More precise data comes from both better measurement methods of the
raw diffraction data and more precise corrections for instrumental and experimental effects on
the measured diffracted intensities. Higher-resolution data also implies more data. Therefore,
crystallographers needed more computing power in order to obtain more precise crystal
structures.

Attempts in the 1930’s to provide aids for structure refinement were restricted to graphical
tools such as structure-factor graphs (Bragg and Lipson 1936) and mechanical tools such as
Beevers-Lipson strips (Beevers and Lipson 1934) both of which eased the calculation of the
terms in Fourier series such as Eqns. (1) and (2). They enabled Chao et al. (1940) and Cole et
al. (1949) to refine the crystal structure of an orthoclase, starting from the sanidine model of
Taylor (1933). Although the method of least-squares refinement was first applied to a crystal
structure refinement by Hughes (1941), and the first feldspar structure to be refined this way
was reported by Sörum (1953), the calculations were done by hand, severely limiting the
number of the data that could be handled. Nonetheless, Sörum (1953) was able to demonstrate
from differences in tetrahedral bond lengths that the ordering pattern in anorthite-rich
intermediate plagioclase is different from that in albite. The introduction of mechanical
calculators (‘Hollerith machines’) in the late 1940’s and 1950’s enabled larger datasets to be
handled, with attendant increase in precision. The architecture of mechanical calculators made
them more suitable for Fourier calculations (Cox and Jeffery 1949; Hodgson et al. 1949) than
for the implementation of least-squares refinements even though it was recognized this was
not the best way to determine accurate bond lengths and angles (Cochran 1948). So
refinement of structures continued to use the step-wise cycling of structure factor calculations
from trial coordinates (Eqn. 2) which were used in Fourier syntheses of the electron density
through Eqn. (1), from which better trial coordinates could be determined. Automation with
Hollerith machines, coupled with the assistance of several colleagues, wives and students to
feed them with punched cards did allow the number of data used in a refinement to be rapidly
increased. Bailey and Taylor (1955) used 2650 reflections (and four assistants including Mrs.
Bailey) to show from the T-O bond lengths that the structure of microcline was effectively
fully ordered with respect to Al and Si distribution.

The year 1962, a half-century from the discovery of X-ray diffraction, divides the era of
‘discovery’ of the basic architecture and principles of mineral structures from the modern era
of investigating the detailed crystal chemistry of minerals. By 1962 there had been 11 full
structure refinements of feldspars (Ribbe 1994), made over a period of 30 years since the
original structure determination of sanidine by Taylor (1933). With the larger datasets
collected in the 1950’s and processed with Hollerith machines and early mainframe
computers, the refined structures had a claimed precision in bond lengths of 0.002 Å (e.g.
Cole et al. 1949) although this uncertainty is clearly underestimated because it is derived
directly from the difference Fourier maps (Cochran 1948; Cruickshank 1949a; b). A more
realistic estimate from the least-squares refinement by Sörum (1953) would be of the order of
0.005-0.01 Å which is sufficient to determine the basic pattern of Al, Si ordering from the
difference between tetrahedra occupied only by Al (Al-O ~ 1.74 Å) and Si (Si-O ~ 1.62 Å)
but not really good enough to determine intermediate states of order, such as that found in
orthoclase (Cole et al. 1949; Jones and Taylor 1961). Fourier maps showed that the extra-
framework cations in albite, at least, exhibited anisotropic apparent motion (Ferguson et al.
1958), but anisotropic displacement parameters had not been refined for them or the
framework cations.
Although structures based on intensities collected by photographic methods continued to be reported well into the 1960’s, the first structure refinement of a feldspar of the modern era was published by Onorato et al. (1963). They collected the intensity data not by film, but with a commercial diffractometer, equipped with a point detector that recorded the intensity data digitally and a Mo X-ray tube that, because of the shorter wavelength, makes absorption less of a problem than with Cu radiation. Onorato et al. (1963) performed a structure refinement using the full-matrix least-squares method on a computer. The availability of University mainframe computers at the beginning of the 1960’s that could run programs written in high-level languages (mostly Fortran) that were compiled locally (making them portable) opened the modern era of diffraction crystallography. Programs were developed for data reduction including face-based absorption corrections (e.g. Busing and Levy 1957; Burnham 1966) to provide more accurate data, and programs to perform full-matrix least-squares refinement of the structure directly to the structure factors via Eqn. (2) became available (e.g. Busing et al. 1962; Stewart et al. 1972; Finger and Prince 1974; Sheldrick 2008). As computer storage and power increased, structures were refined to more and better data, which enabled a better description of the scattering density in terms of the anisotropic displacement parameters of the atoms. Thus while Onorato et al. (1963) reported a full-matrix least-squares refinement of sanidine with individual isotropic displacement parameters for each atom (a total of 28 parameters) to 960 reflections, within a few years it was practical to perform fully anisotropic refinements such as that of albite (Wainwright and Starkey 1967) with 117 parameters refined to 3530 data measured on a counter diffractometer. The increase in computing power, together with the widespread introduction of computer-controlled diffractometers to collect the data, resulted in the publication of about 150 feldspar structures over the two decades 1962-1982. The improvements in diffractometry and data processing led to T-O bond lengths being determined to a reproducibility of ~0.002 Å (e.g. Dal Negro et al. 1978), enabling the details of the crystal architecture to be determined and how the T-O bond lengths change with the Al, Si content of the tetrahedra (e.g. Brown et al. 1969; Kroll 1983; Kroll and Ribbe 1983; Ribbe 1994).

By the late 1980’s computing power was no longer a limitation to structure refinements of minerals; essentially arbitrarily large datasets could be used for full refinements of not only the positional parameters of the atoms, but also the anisotropic displacement parameters to describe the thermal vibrations of the atoms, without which the positions of the atoms can be...
biased to incorrect values (see Eqn. 2). The precision of refined structures was therefore
limited by the use of point detector diffractometers. To achieve higher resolution many more
reflections at higher diffraction angles have to be collected which, with a point detector
diffractometer, means a very large increase in data collection times to the order of weeks
because the data are collected one reflection at a time. For example, the extension of a data
collection on albite from 60° to 80°, which reduces the formal estimated standard deviations
(esd’s) on T-O bond lengths to 0.001 Å (e.g. Meneghinello et al. 1999) requires the
measurement of about twice the number of reflections, with the additional higher-angle
reflections being systematically much weaker and thus requiring much longer to collect to the
necessary precision.

In the anorthite-rich plagioclase feldspars where the ordering of Al and Si (and accompanying
structural changes) gives rise to systematically weak reflections the challenge is greater
because these weak reflections have to be collected in sufficient numbers with sufficient
precision (which means longer counting times) to determine precise bond lengths within the
structure. Even with rotating anode sources that became available for laboratories in the late
1980’s a data collection for such a plagioclase would still require several days in order to
collect ~3300 reflections to 2θmax = 60° (e.g. Angel et al. 1990). The introduction of CCD-
based area detectors for diffractometry speeded up data collections by allowing many
reflections to be collected simultaneously. Subsequent improvements in detector technology,
which have greatly reduced the intrinsic noise in X-ray detectors while increasing their
dynamic range, have allowed data collection times to be further greatly reduced.

As an example of modern laboratory capabilities, Figure 1 illustrates the uncertainties in T-O
bond lengths in end-member Val Pasmeda anorthite (Carpenter et al. 1985) determined from a
series of data collections. We measured a crystal of ~70μm diameter with a commercial
instrument, the Oxford Diffraction SuperNova diffractometer equipped with a Mo-target X-
ray micro-source and a Pilatus 200K area detector1. The detector has no intrinsic noise and
has no read-out delay, further speeding data collections compared to CCD detectors. The
ability to collect data faster also means that multiple measurements can be made of the same,
or symmetry-equivalent, reflections from the crystal at different positions of the
diffractometer. This redundancy in the data allows, with modern computing power, the

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1 Details of the data collections, data reduction and structure refinement procedures, and the final refined crystal
structures, are provided in the CIF deposited as supplementary material. All structure refinements were
performed with RFINE-2015, a development version of RFINE4 (Finger & Prince, 1974).
intensities to be corrected more accurately for experimental factors such as absorption by the crystal and its mount, the variations in incident beam intensity, and the detector response. As a consequence, as an extreme example, a partial data collection of just 90 seconds on anorthite is sufficient to determine the bond lengths to an accuracy of 0.02 Å (Figure 1) and thus the essential architecture of the structure! A full dataset to $2\theta_{\text{max}} = 60^\circ$ collected in 48 minutes yielded esd(T-O) = 0.004 Å, equivalent to the results from 6 days data collection 25 years ago from a significantly larger crystal (Angel et al. 1990) or several months in the 1950s (Kempster et al. 1962)! A data collection to $2\theta_{\text{max}} = 100^\circ$ yielded in excess of 95,000 individual reflections, took 81 hours and gives esd(T-O) = 0.0005 Å. The refined structures of anorthite show no significant differences in bond lengths when the data is restricted to lower resolution (down to $2\theta_{\text{max}} = 50^\circ$ for MoKα), or with decreasing exposure time at constant resolution in full datasets (Figure 1). The small offsets of bond lengths when the data is restricted to very low resolution ($2\theta_{\text{max}} < 50^\circ$) arises from correlations between the positional and displacement parameters in the refinement which are only suppressed with higher-resolution data. The esd’s in bond lengths for full datasets scale approximately with the inverse square root of the number of reflections used in the refinement, which means that modern diffraction data such as these are precise and accurate. Further, when the data are collected with sufficient resolution, conventional refinements also yield bond lengths that within the esd’s are mostly independent of experimental influences and detailed choices of refinement models and refinement parameters such as weighting schemes (Figure 2). In this sense, the determination by modern X-ray diffraction of the geometric details of the average crystal structure in terms of atom positions and inter-atomic distances and angles is reliable and robust.
Beyond geometry: chemistry and thermodynamics of minerals

Because accurate X-ray diffraction intensity data can be collected precisely and quickly with high redundancy, we now focus on the use and applicability of structure refinements to solving mineralogical problems beyond that of simply reporting the structural architecture, bond lengths and angles. Chemical and thermodynamic information about minerals can be obtained by determining the occupancies by different atomic species of individual crystallographic sites within the mineral. Cation partitioning between sites within a single mineral crystal has great potential to be used as a single-phase geo-thermometer or even a geo-speedometer, especially because the process of re-equilibration of the site occupancies after temperature change is rapid as the distances over which cations have to be exchanged is only of the order of the size of the unit cell. This contrasts with chemical re-equilibration between different mineral phases which requires diffusion over distances that are of the grain scale. Determination of the site occupancies also, obviously, allows the composition of the mineral to be obtained. Thus diffraction is an important tool for determining compositions of minerals that cannot be analyzed by microprobe, for example inclusions trapped within diamonds (e.g. Nestola et al. 2011) or other host minerals where extraction of the inclusion mineral is not permitted because it requires at least partial destruction of the host mineral. Chemical site occupancies can be obtained by direct structure refinement of the occupancies, or indirectly from the bond lengths, and we will discuss one example of each of these in turn. In doing so we will illustrate that the limitations of modern X-ray structure refinement are not in the diffraction data, but in the nature of the refinement models that are used to interpret the diffraction data and the crystal-chemical models used to interpret them.

When the contrast in X-ray scattering powers of the atoms of interest is small, for example as between Al and Si, the site occupancies cannot be determined by direct refinement. However, the example of the anorthite structure discussed above shows that the distances between the atom centres can be determined to high precision by conventional structure refinement to modern diffraction data (Figs. 1 and 2). If we suppose that T-O bond lengths in a feldspar vary linearly with Al content and that the difference between Al-O and Si-O is ~0.12 Å (e.g. Kroll and Ribbe 1983) then an uncertainty of the order of 0.0005 Å in a T-O bond length (Fig. 1) should allow Al contents to be determined with an uncertainty of less than 1%. However, while the primary factor controlling individual T-O bond lengths is the Al,Si content of the site, a number of secondary factors have also been shown to be significant. These include the
occupancy of the adjacent tetrahedra, the bonding of the extra-framework cation to the oxygen, and the T-O-T and O-T-O angles (e.g. Phillips and Ribbe 1973; Phillips et al. 1973). This explains why the individual bond lengths in any one of the nominally pure SiO₄ tetrahedra in anorthite range from <1.59 Å to ~1.65 Å (e.g. Fig. 2). This variation is more than half the expected difference between the bond lengths for pure AlO₄ and SiO₄ tetrahedra! Some of the geometric effects appear to be compensated internally within an individual tetrahedron, so it was recognized (e.g. Kroll 1983; Kroll and Ribbe 1983) that mean bond lengths of tetrahedra <T-O> were more reliable indicators of Al, Si content than individual bond lengths. As more precise structures became available it has become apparent that the mean values <T-O> in plagioclase feldspars are sensitive to Ca, Na content, and can be perturbed by different refinement models for the partially disordered structures (Angel et al. 1990; Ribbe 1994). There are further difficulties. It is not possible to determine by experiment whether anorthite and albite are fully ordered; techniques such as neutron diffraction and NMR have uncertainties of a few % in the determination of Al and Si site occupancies. Therefore we do not know the true value of <T-O> in pure AlO₄ or pure SiO₄ tetrahedra. Neither do we know whether the differences in <T-O> values for the individual Si-rich tetrahedra, for example as shown in Fig. 1, represent small differences in Si, Al contents or are simply the effects of other factors on bond lengths. The refined displacement parameters of the atoms also correspond to apparent displacements of T and O atoms along the bond of the order of 0.07-0.08 Å, but X-ray Bragg diffraction as expressed by Eqn. 2 does not tell us how these displacements are correlated. Different models for interpreting the refined displacement parameters in terms of correlated, uncorrelated or riding motions of one atom with respect to the other (e.g. Finger and Prince 1974) yield corrections to T-O bond lengths that are of the order of 0.02 Å. All of these factors mean that the absolute occupancy of tetrahedral sites in feldspars, or similar alumino-silicates such as zeolites, cannot be established to the precision that would be expected from the precision in bond lengths. However, all of these limitations arise strictly from the refinement models and crystal-chemical analysis. This means that if different crystal structures of the same type (e.g. albites) are refined with exactly the same model, then X-ray structure refinement can yield precise values for the differences between the structures, and thus changes in the state of Al, Si order, even if the absolute values of site occupancies are less well-defined (e.g. Angel et al. 1990; Meneghinello et al. 1999).

When the contrast in scattering power between the atoms is significantly greater than that between Al and Si, it is possible to determine the site occupancies by refining the scattering
power of each atomic site. This can be done in two ways. When just two atomic species are known to occupy a given site, and the site is assumed to be fully occupied, then the
occupancies can be refined directly. An alternative is to refine the occupancy of an atom chosen to represent the average scattering curve of the multiple occupants of the site, and then the actual site occupancies can be inferred from the total refined scattering power (measured in electrons) and the atomic numbers of potential occupants. Clearly, because structure refinement only yields the total scattering of the site through the scattering factor \( f \) (Eqn. 2), the interpretation of the result in terms of multiple occupancies requires further constraints or assumptions about the chemistry and the distribution of species between sites. One obvious additional constraint that can be used for structures at ambient pressure and temperature is the bond lengths of the site, if the atomic species of interest give rise to significantly different bond lengths. Such a combined approach has been successfully used in a number of mineral systems such as spinels (Della Giusta et al. 1996; Lavina et al. 2002).

In mantle olivines a simplified intermediate approach can be used because it is known from chemical analyses of olivine inclusions in diamonds that their compositional variation is dominated by variation in Mg,Fe content (Stachel and Harris 2008). These atoms have sufficiently different scattering powers that direct refinement of the atomic occupancies on the two M sites within the structure is possible, subject to the sites being assumed to be fully occupied. Mantle olivines also typically contain trace amounts of other elements, mostly Ca, Mn and Ni. The scattering powers of Ni and Mn for X-rays are very similar to that of Fe, so their contribution to the X-ray diffraction intensities is effectively included in the refined Fe content. As Ca has an atomic number approximately half-way between that of Mg and Fe, it can be considered as contributing equally to the refined Mg and Fe contents. We will denote the Mg occupancy obtained by structure refinement using only Mg and Fe as the site contents as \( \text{Mg}^* \). Its value should be equal to the fraction \( \frac{(\text{Mg} + 0.5\text{Ca})}{(\text{Mg}+\text{Fe}+\text{Mn}+\text{Ni}+\text{Ca})} \) determined by chemical analysis. Figure 3 shows the site occupancies refined to a single dataset collected from a mantle olivine crystal of approximate size 150 x 110 x 80 µm, out to a resolution limit of 100° 2θ with an average redundancy (number of symmetry-equivalent reflections measured) of 6, in 6 hours. The composition has been measured by chemical analysis as \( \text{Mg}^*=0.877(1) \). It is obvious that the refinement performed with scattering factors calculated for neutral atoms (the default for refinements of molecular structures in programs such as SHELX, Sheldrick 2008) yields an overall composition from the refined occupancies of the two M sites that is about 2-3% too high in Mg. The actual value also changes by >1%
in Mg* depending on the resolution of the data used. The agreement with the known
composition is better if scattering factor curves for charged atoms are used (Fig. 3a), but there
is still significant variation in the results with data resolution. Further, the values and the
variation with resolution of Mg* on individual sites and the overall composition is different if
different weighting schemes and/or the criteria for rejecting outlier data are changed (compare
Fig. 3b with 3a). If corrections for secondary extinction (the reduction in measured intensities
due to interactions between the incident and diffracted beams in the crystal, Becker and
Coppens 1974) are not made, then the value of Mg* can be shifted by 0.2%. Therefore,
because of the sensitivity of the results to refinement conditions, conventional refinements
using charged atom form factors cannot yield the composition of a mantle olivine more
reliably than +/-1%.

In the past some of this variation in refined site occupancies has been attributed to short-
comings in the experimental corrections to the data as well as to different choices of scattering
factors as we have discussed above (Kirfel 1996). However, refinements to structure factors
calculated by Fourier transformation of the electron density of end-member Mg2SiO4
determined by DFT computer simulation also show a strong variation in refined site
occupancies with resolution (Fig. 4a). This indicates that the experimental data is not at fault,
but that there are short-comings in the refinement model. The conventional refinement model
that we have discussed so far relies on scattering factors for atoms that are calculated for
spherical isolated atoms. For this reason it is sometimes called the ‘independent atom model’,
IAM. But the measured intensities from crystals are scattered by all of the electrons, including
those involved in bonding. Kroll et al. (1997) showed that the variation in refined site
occupancies of orthopyroxenes with 2θ range of the data arises from the change in the
contribution of the bonding electrons to the observed intensities as 2θ changes. In simple
terms, at low Bragg angles all electrons including the bonding electrons contribute to the
diffracted intensities. At high angles the broader spatial distribution of the bonding electrons
means that they contribute disproportionately less to the scattered intensities, and the
measured X-ray intensities are therefore dominated by scattering from the core electrons of
each atom. That is also why charged-atom form factors give the correct Mg* value for olivine
when we use high-angle data, while neutral-atom form factors yields Mg* values that are
~0.02 too high (Fig. 3). The variations in Mg* with data resolution arise from correlations
between the occupancies, the scale factors, the extinction parameters, and the parameters used
to describe the displacements of the atoms due to thermal and static positional disorder. As for
the bond lengths alone (Fig. 1) these correlations are only suppressed by the use of both high
and low- resolution intensity data, for which the displacement and occupancy factors have
significantly different contributions (Eqn. 2).

Kroll et al. (1997) suggested that the problem could be addressed by removing the correlation
between the site occupancies and the displacement parameters simply by fixing the latter at
values that ensure that the refined site occupancies became independent of data resolution.
This procedure was somewhat artificial and also very time consuming. Another approach was
to refine the effective charges on the atoms, by refining a mixture of fully-charged and neutral
atoms on each site in the structure, a careful study of several stoichiometric end-member
minerals (Sasaki et al. 1980) having indicated that the scattering density was best represented
by partially-charged atoms subject to the constraint that the resulting model is charged
neutral. This result was applied (e.g. Rossi et al. 1983; Hawthorne et al. 1995) to determine
site occupancies by site occupancy refinement using fixed partial charge scattering factors.
While releasing the constraint of charge balance can sometimes provide a better fit to the
diffraction data, it can result in a structure model that has a net charge and cannot be
considered physically realistic.

Fourier maps of the calculated electron density (Eqn. 1) from conventional refinements of
silicates indicate that the major misfit of the density is approximately midway along the Si-O
bond. This confirms that conventional refinements do not model the contribution of the
bonding electrons (e.g. Hawthorne et al. 1995). Heinemann et al. (1999) therefore
implemented the idea of Kirfel and Will (1980) to modify the crystal structure model in the
refinement in a manner that directly reflects this short-coming of a conventional independent
atom model. Heinemann et al. (1999) showed that by refining a structure model that has one
electron placed on the Si-O bonds (and then refining position along the bond and the
displacement parameters of the electron), the contribution of the bonding electrons to the
diffracted intensities can be successfully modelled. In a simplification of this model we find
that fixing the electron to a point 70% along the Si-O bond towards O, and restricting all such
electrons in the refinement model to have the same isotropic displacement parameters is
sufficient to eliminate nearly all of the variation in site occupancies with 2θ range (Fig. 4b)
for the DFT dataset of Mg2SiO4. Refinement of such a model with robust-resistant weights
and a realistic extinction model (Becker and Coppens 1974) to the data of the natural olivine
results in Mg,Fe site occupancies that are in agreement with the composition determined by
microprobe analysis. The accuracy of these X-ray structure refinements (Fig. 3c), is as good as that achieved by chemical analysis.

**Implications**

What we have shown in this paper is that the precision with which we can determine mineral structures has evolved over 100 years in parallel with the developments in X-ray diffraction crystallography that have improved the quality of the diffraction data, and with the increased technological capacity to handle the data. With modern instruments on laboratory sources Bragg diffraction data can be collected from small mineral crystals of 50-100 μm size at room conditions in a few hours that is of such quality that the accuracy and precision of the resulting structural parameters such as bond lengths and angles is beyond that required for crystal-chemical analysis. For synchrotron sources the time scales are shorter, or alternatively the crystal sizes can be smaller. At high pressures, high temperatures, or *in operando*, the data quality remains in the majority of cases the factor limiting the accuracy and precision of the resulting structures. Such data normally requires additional corrections for absorption by the environmental cell but, at the same time, the cell often restricts both the resolution and redundancy of the data, making such corrections more difficult to perform. The real challenge is therefore to make the data corrections accurately based on fewer data. For laboratory high-pressure studies the lack of redundant data means that the best approach is to base the corrections on appropriate physical models of both the crystal and the pressure cell. But the data quality never matches what can be achieved with the same instrument from the same crystal in air. An alternative is provided by recent developments in high-pressure single-crystal diffraction on synchrotron X-ray sources, where the use of much higher-energy, much more intense and much smaller X-ray beams reduces the magnitude of the experimental corrections required while at the same time providing raw intensity data of greater reciprocal space coverage, greater redundancy and much improved signal to noise (e.g. Hejny and Minkov 2015). As a consequence, the resulting quality of crystal structures at pressures of 10’s of GPa is starting to approach that which can determined at room pressure which opens a new frontier in ultra-high pressure crystal chemistry (e.g. Finkelstein et al. 2014; Glazyrina et al. 2014).

Laboratory X-ray diffraction data from crystals in air is now of the quality where the results are limited not by the data but by the physical validity of the refinement models used to interpret the measured data. Thus the standard structural models that are conventionally used
in refinements are based on independent atomic spherical scatterers and thus can be said to
‘neglect the chemistry’ – they do not model the modification of the electron density of the
atom due to bonding. For most minerals, this modification of the electron density is very
small, which is why the structural geometry from refinement of an IAM is accurate to a level
limited by the intrinsic noise of the data. We have seen that the site occupancies are more
affected and that the electron-in-bond model (Kirfel and Will 1980; Heinemann et al. 1999) is
a simple but under-utilized extension of the IAM which can be readily implemented at no
intellectual difficulty, tested, and used to provide site occupancies with a reproducibility that
is better than a routine microprobe analysis for simple chemical systems with high contrast in
atomic number such as Fe,Mg in olivine. However, the determination of site occupancies in
even simple systems to a precision better than 0.001 is unrealistic given the short-comings in
the IAM and the Bragg approach embedded in Eqn. 2 (see also Heinemann et al. 1999;
Stimpfl et al. 1999; Merli et al. 2000). In particular, in a crystal structure with mixed site
occupancies such as Al,Si in feldspars or Mg,Fe in olivines, the detailed local structural
geometry has been shown by a variety of local experimental probes such as NMR and IR
and DFT simulations to be dependent on the local arrangement and short-range ordering of
the cations. Therefore, the oxygen ‘positions’ obtained from structure refinement are some
kind of average position of their true local positions, and that is why the refined structure
exhibits bond lengths that reflect some kind of average of the bond lengths in the pure end-
member structures. At the same time, this average bond length is in some way also modified
by the correlation of positions with the refined displacement parameters, as is particularly
evident in plagioclase feldspars (Angel et al. 1990). With increased data quality, the IAM can
also be extended by refining parameters that correspond to the explicit population and
deformation of the electron density of each atom. Such ‘pseudo-atom’ (Stewart 1976) or
multipole models have been very successful in yielding the details of not only the bonding
density in pure materials such as pyrite (Overgaard et al. 2014), but even the core electron
deformations in diamond (Bindzus et al. 2014). However, multipole models require an
explicit atomic basis and are therefore not meaningfully defined for mixed-occupancy sites
typical of mineral solid solutions. The iterative Hirshfeld method is an intermediate approach
in which the structure is refined with multipole models, and then density-functional
simulations are used to re-calculate the scattering factors so as to include all of the electron
density in the effective scattering factors, which are then used in the next cycle of refinement
(Capelli et al. 2014; Farrugia 2014).
Data quantity and quality has enabled an alternative approach, known as the maximum entropy method (MEM), whose essence is to refine with the minimum constraints of ‘physical reasonableness’ the electron density of the crystal simply by adjusting the electron density in a pixelated array of boxes across the unit cell. While it still only provides an electron density averaged over all cells of the crystal, MEM results are model independent, which provides the possibility of visually and directly locating non-framework species, such as the cations in zeolites, based only on observed structure factors (Andersen et al. 2014). So MEM gives electron densities unbiased by a structural model but, like the IAM and its extensions, the interpretation of this scattering density requires assumptions about oxidation states, local ordering and distortions in structures with mixed site occupancies. We can get accurate electron densities but not occupancies from X-ray diffraction measurements, which only serves to illustrate the fundamental point that while an X-ray diffraction experiment, properly performed, provides an unbiased map of the average electron density of a crystal, the interpretation of the electron density is model dependent.

In the past, tour-de-force solution and refinement of crystal structures of common minerals such as sanidine (Taylor 1933) or anorthite (Kempster et al. 1962) represented a significant contribution to the science of mineralogy. Such breakthroughs continue for high-pressure phases; for example the recent demonstration of Al,Si disorder in the octahedral sites of high-pressure Al-rich phase D has major implications for water storage and recycling in the lower mantle of the Earth (Boffa-Ballaran et al. 2010; Pamato et al. 2015). In addition, the precision and accuracy of modern Bragg X-ray diffraction data can also be used to probe our understanding of bonding at the fundamental level in stoichiometric compounds, to provide the basic data for explaining the details of minerals at the crystal chemical level, and for providing the explanations in terms of structures of the physical and thermodynamic properties of minerals. If used with care, it can be used to provide site occupancies to a precision that starts to become useful for thermodynamic calculations. As a picture of the average structure it provides, in combination with local probes, information about local patterns of ordering. This basic idea that the Bragg X-ray intensities (Eqn. 2) represent the time-and-space average of the atomic structure of the mineral is also fundamental to studying all other variants on the crystalline state, such as surfaces and nanoparticles, all of whose intriguing properties can only be understood in the context of structural deviations from the ideal average structure of the bulk mineral.
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References


Figure Captions

Figure 1: The precision of X-ray structure refinements as illustrated by average bond lengths of the Si-rich and Al-rich tetrahedra in anorthite (open symbols) and one individual Al-rich and one Si-rich tetrahedron (closed symbols with error bars). Data from Kempster et al. (1962), Wainwright and Starkey (1971), Angel et al. (1990) and the current work. The deviations in earlier work are the consequence of limited data resolution.

Figure 2: There is no significant variation in individual T-O bond lengths in anorthite with different refinement models, as illustrated for the T1oo tetrahedron. Refinements are (1) using robust-resistant weights and refinement to structure factors $F$, (2) unit weights and refinement to $F$, and (3) normal weights and refinement to $F^2$. The intensity dataset had a resolution corresponding to $60^\circ 2\theta$ for MoK$\alpha$ radiation (labelled ‘60’ in Figure 1). Esd’s are approximately equal to the symbol size.

Figure 3: The results of site occupancy refinements of a natural olivine with composition $\text{Mg}^* = 0.877(1)$ as a function of data resolution. (a) Refinements of a conventional independent atom model (IAM) with neutral-atom scattering factors yield total $\text{Mg}^*$ values that are 2-3% too high. Charged atom refinements give results that are correct to within 0.01 in $\text{Mg}^*$. (b) The values and trends with resolution of $\text{Mg}^*$ from a conventional IAM refinement change are sensitive to the weighting scheme; the results from a robust-resistant refinement are shown. (c) Refinement of the electron-in-bond model of Heinemann et al. (1999) yields $\text{Mg}^*$ within 2 esd’s of the known composition, independent of resolution. The darker band is +/-1 esd, the lighter band +/- 2 esd’s.

Figure 4. The results of site occupancy refinements to a synthetic dataset calculated from a DFT simulation of end-member forsterite. (a) Refinements of a conventional independent atom model (IAM) with charged-atom scattering factors yield total $\text{Mg}^*$ values that are too low, and that vary significantly with data resolution. (b) Refinement of the electron-in-bond model of Heinemann et al. (1999) yields $\text{Mg}^*$ within 2 esd’s of the correct value (1.0), with less variation with data resolution.