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

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20 **Abstract**

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22 This decade marks the centenary of the discovery of X-ray diffraction. The development of

23 mineralogy as a scientific discipline in which the properties of minerals are understood in

24 terms of their atomic-scale structures has paralleled the development of diffraction

25 crystallography. As diffraction crystallography revealed more precise details of mineral

26 structures, more subtle questions about mineral properties could be addressed and a deeper

27 understanding of the relationship between the two could be attained. We review the

28 developments in X-ray single-crystal diffraction crystallography over the last century and

29 show how its power to provide fundamental information about the structures of minerals has

30 evolved with the improvements in data quality and the increased technological capacity to

31 handle the data. We show that modern laboratory X-ray diffraction data is of the quality such

32 that mineralogical results are no longer limited by the data quality, but by the physical validity

33 of the refinement models used to interpret the data.

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Introduction

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37 Minerals are, by definition, crystalline. Their structures are composed of atoms arranged in

38 periodically repeating patterns. The same atoms in different minerals tend to occupy

39 characteristic local environments with specific coordination geometries and bond lengths. The

40 arrangements of atoms within minerals and the crystal-chemical concepts derived from them

41 successfully explain many of the physical, chemical and thermodynamic properties of

42 minerals. But how do we know that minerals are built of atoms? More than a century ago,

43 there was no proof of the existence of atoms, although it was clear that gases behaved as if

44 composed of particles that occupied some finite volume. It had been deduced from the

45 regularity of their external form (but not proven) that crystalline materials and especially

46 minerals were probably periodic arrays of 'some things'; the common deduction was that

47 crystals were composed of the same 'molecular' species that occur in gases, condensed into

48 regular and periodic arrays (Kubbinga 2012). In the first half of 1912 three young men in the

49 Institute for Theoretical Physics of the Ludwigs-Maximillians Universitaet Muenchen carried

50 out an experiment that would confirm the atomistic view of the chemical and mineral world.

51 Inspired by conversations with P.P. Ewald, Max von Laue had suggested the experiment to

52 two other research assistants, Friedrich Knipping and Walter Friedrich. In May 1912 they

53 submitted a manuscript to the Bavarian Academy for Science that reported the diffraction of

54 X-rays by crystals (Friedrich et al. 1912). It was known from optics and physics that

55 diffraction occurs due to constructive and destructive interference between waves scattered by

56 a periodic array of objects; scattering by resonators was actually the subject of Ewald's

57 research at the time. Therefore, this single observation of the diffraction of X-rays by crystals

58 proved two things; X-rays can behave as waves, and crystals are periodic arrays of X-ray

59 scatterers. Within a year, the Braggs had used the intensities of the X-ray beams diffracted by

60 crystals to determine the arrangements of the atoms in crystals of simple minerals such as the

61 zinc blende used in the experiments in Muenchen, and NaCl, and showed that they were not

62 molecular compounds (e.g. Gruner 1929). The subsequent development of mineralogy as a

63 scientific discipline in which the properties of minerals are understood in terms of their

64 atomic-scale structures (e.g. Gruner 1931; Kieffer and Navrotsky 1985) has paralleled the

65 subsequent development of diffraction crystallography.   As diffraction crystallography

66 revealed more precise details of structures, more subtle questions about mineral properties

67 could be addressed and a deeper understanding of the relationship between the two could be

68 attained. By following the developments over the last century we can understand both the

69   power of diffraction crystallography to provide fundamental information about the structures

70   of minerals, while at the same time appreciating its important intrinsic limitations and how

71   these limitations have changed as the technology supporting X-ray diffraction has developed.

72

73   **The development of diffraction crystallography**

74

75   The very first diffraction measurements and structure solutions provided a way for diffraction

76   crystallography to 'boot-strap' its own methodology. Bragg showed that the diffracted

77   intensities from crystals of simple structures such as the alkali halides can be explained

78   qualitatively in terms of scattering from point atoms that have a scattering power proportional

79   to their atomic numbers. When the atoms scatter in phase, their scattering power adds together

80   to give strong reflections, when they scatter in antiphase the reflection is weak. This approach

81   is sufficient to establish the basic architecture of simple minerals such as halite, and to

82   determine the number of atoms in the unit-cell of the structure (e.g. Bragg 1975). When

83   combined with the measured density and an accurate value of Avogadro's number (Millikan

84   1910), the unit-cell parameters of halides could be determined on an absolute basis.

85   Subsequent application of what we now know as Bragg's law allowed the determination of X-

86   ray wavelengths, and then the determination of lattice parameters of new crystals without

87   knowledge of their structures or densities.

88

89   The subsequent early development of diffraction crystallography was remarkably rapid, both

90   in experimental techniques and in the theoretical developments necessary to determine

91   structures from the measured diffracted intensities. It was quickly recognized that the idea of

92   a simple reflection event by the lattice planes in the crystal was inadequate to explain the

93   diffracted intensities in detail. Darwin (1914) solved the problem of dynamical diffraction of

94   X-rays and thus identified the role of extinction, absorption and multiple diffraction in

95   determining the intensities of diffracted beams and established the concept of the mosaic

96   crystal. This concept, confirmed by experimental measurements of intensities, is that even

97   gem quality crystals are actually comprised of small perfect crystal domains misaligned with

98   respect to one another. We now understand that these domains are created by the defects in

99   the crystal structure, such as dislocation walls. The key point for experimental measurements

100   of X-ray intensities is that the individual domains do not diffract at exactly the same position

101   because they are rotated with respect to one another, and this necessitates the measurement of

102   diffracted beam intensities by rotating the crystal in the beam during diffraction

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103   measurements (Bragg and Bragg 1913). It is the resulting integrated intensities (not the peak

104   intensities), corrected for absorption and extinction and geometric factors that depend on the

105   geometry of the measurement, that are related to the scattering density in the crystal (e.g. as

106   summarized in Bragg and West 1928). Bragg (1915a) expressed the relationship between the

107   absolute intensities corrected for experimental effects and the scattering density in terms

108   equivalent to a Fourier series, later (Duane 1925; Bragg 1929) written as:

109
$$\rho(xyz) = \sum |F(hkl)| (\cos 2\pi(hx + ky + lz) + \alpha(hkl)) \qquad (1)$$

110   The quantity $|F(hkl)|$ is equal to the square-root of the absolute intensity of the reflection hkl.

111   It is the modulus (amplitude) of the structure factor. The $\alpha(hkl)$ is the phase of the reflection.

112   If the scattering density corresponds only to independent spherical atoms, each with a

113   scattering power f_i which is isotropic but depends on $\sin(\theta)/\lambda$, the Fourier series can be

114   inverted to obtain the structure factor equation:

115
$$F(hkl) = \sum_{i=1,n} f_i (\cos 2\pi(hx_i + ky_i + lz_i) + i \sin 2\pi(hx_i + ky_i + lz_i)) B_i(hkl) \qquad (2)$$

116   This equation expresses the value of the structure factor of any reflection in terms of a

117   summation of the scattering power of the atoms within one unit cell, with phase factors that

118   depend on the atom positions expressed in fractional coordinates $x_i y_i z_i$ and the Miller indices

119   hkl of the reflection. The effects of local atom displacements on the structure factors are

120   expressed by the factor B_i, which in general is an anisotropic function that is different for

121   different atoms. It causes a general decrease in the structure factors, and hence diffracted

122   intensities, with increasing diffraction angle (Debye 1914). Equation (2), which was later

123   justified in terms of the fundamental physics of X-ray scattering by atoms (e.g. Waller and

124   Hartree 1929), shows that the observed diffracted intensities represent a time-and-space

125   average over all of the atoms within the crystal. This average structure includes the static

126   displacements due to atoms occupying slightly different positions in different unit cells and

127   the dynamic displacements due to temperature-induced vibrations of all of the atoms. In the

128   1920's the effects of atomic displacements on the diffracted intensities were subsumed into

129   the scattering factors of atoms derived from intensity measurements of known structures, but

130   nowadays the displacements are described by a model whose parameters are refined to the

131   intensity data along with the fractional coordinates of the atoms.

132

133   Thus, by 1920, all of the essential concepts of diffraction crystallography had been established

134   and could be used to determine the structures of crystals. They remain the basis of structure

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135   determination and refinement from X-ray diffraction data to the present day. The key steps in

136   the determination of a crystal structure start with the collection of diffraction data, followed

137   by 'indexing' (the consistent assignment of Miller indices to each diffraction peak). This

138   allows the calculation of the unit-cell parameters from the diffraction angles of each

139   reflection, and the determination of the space group symmetry from the pattern of

140   systematically-absent reflections. The measured intensities are then corrected for

141   experimental factors and are reduced to the squares of structure factors $F^2(hkl)$. This is not

142   sufficient to determine the structure because while the intensities are known, the phase factors

143   $\alpha(hkl)$ required to calculate the scattering density through Eqn. 1 are not measured and are

144   therefore unknown. *Structure solution*, or the determination of at least some atom positions

145   within the unit cell, is thus the biggest challenge in diffraction crystallography. Once some

146   atoms are located, phases $\alpha(hkl)$ can be estimated from them using Eqn (2). A Fourier

147   synthesis (Eqn. 1) with these phases and the measured intensities is then used to determine the

148   positions of any missing atoms. The test of a model structure is made through Eqn. 2, by

149   comparing the values of the structure factors calculated from the structure model with those

150   derived from the measured intensities. The subsequent step of *structure refinement* is the

151   adjustment of the structure model by adjusting the values of the atom coordinates and

152   displacement parameters to improve the fit to the measured intensities.

153

154   The very first crystal structures to be determined had atoms in positions within the unit-cells

155   that are fixed by symmetry. The diffracted intensities could therefore be used to calculate the

156   actual scattering factors f_i of the individual atoms, which could then be used in the analysis of

157   more complex structures. Later, scattering factors were determined by direct calculation from

158   a model of the electronic structure of isolated atoms or ions (e.g. Brown et al. 2006). By the

159   late 1920's it is apparent from papers (e.g. Bragg and West 1928) that the methods of data

160   collection and reduction had become routine; Brown and West (1927) describe their

161   measurements as 'The usual X-ray rotation photographs……'. Structure solution was the

162   challenge. It proceeded by a mixture of deduction from the chemical analysis combined with

163   determination of the space group symmetry of a crystal, and by use of the principles of crystal

164   chemistry as they emerged from previous structure solutions. Bragg (1937, page 27)

165   characterized early structure solution as 'guessing the answer to a puzzle'. The idea that the

166   oxygens in structures often approximated close-packed layers quickly emerged from studies

167   of spinels (Bragg 1915b) and simple oxides, sulphides and halides (Bragg 1920) and it was

168   found to be true also for olivine type structures (Bragg and Brown 1926a). This allowed

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169   structure solution to proceed by considering how to fit the close-packed arrays into the unit

170   cell and then deciding which interstices in the oxygen array were occupied by cations (Bragg

171   and Brown 1926b). The crystal structure of quartz and its high-temperature polymorphs

172   showed that Si uniformly preferred tetrahedral coordination in common minerals. Other

173   structure determinations showed that Al and Si could substitute for one another in tetrahedra,

174   that Al could also be octahedrally coordinated, while cations such as Fe and Mg normally

175   occupied octahedral sites. It should be emphasized that such crystal-chemical principles that

176   were codified as 'laws' by Goldschmidt (1926) following Bragg's (1920) ideas about ionic

177   radii, translated for American Mineralogist by Wherry (1927) and expressed in terms of the

178   'coordination method' (Pauling 1929) or polyhedral model, were used as hypotheses to obtain

179   initial structure solutions. The structure solutions, and hence the crystal-chemical ideas, were

180   then tested by comparison to the measured intensities through the structure factor equation.

181   There were still significant potential pitfalls in structure determination, as can be seen in the

182   first paper to report a full structure determination in American Mineralogist (Buerger 1931).

183   In determining the structure of marcasite Buerger (1931) showed that two previous

184   determinations by diffraction were in error because of different errors in the author's setting

185   of the space group symmetry, while a third proposal although correct, was 'of the nature of

186   guesswork'.

187

188   By 1930 (e.g. Gruner 1929; Bragg 1930; Gruner 1931) the basic architecture of the crystal

189   structures of most major rock-forming minerals and large numbers of sulphides, elements and

190   oxides had been established by X-ray diffraction. The framework structures of zeolites and

191   feldspars were the major exceptions because their low packing density meant that ideas of

192   close-packed layers are not appropriate to describe these structures (Pauling 1929; Taylor et

193   al. 1934). Thus initial models for structure solution were not available. Matchatschki (1928)

194   argued from chemical considerations and knowledge of established alumino-silicate crystal

195   chemistry that feldspars must be a fully-connected network of AlO_4 and SiO_4 tetrahedra.

196   Taylor (1933) solved the structure of sanidine using this idea and knowing the cell

197   dimensions, symmetry and, critically, the size of $(Si,Al)O_4$ tetrahedra from other structures.

198   On Christmas Day 1932 (see Smith 1980) he solved the geometric problem of how to fit the

199   necessary four tetrahedra as a ring into the asymmetric unit of the unit cell, without distorting

200   them, by having the insight to place the external oxygen atoms of the ring on symmetry

201   elements so that the connectivity of the framework was generated naturally by the space

202   group symmetry. The K atoms were then located by comparing observed and calculated

203   intensities of a few reflections, and the final *refinement* of the atomic positions proceeded, as

204   for other structures determined in that era by 'a laborious search for more accurate atomic

205   parameters which will give calculated *F*-values in agreement with the observed relative

206   intensities of a large number of reflections' (Taylor 1933). Thus Bragg (1930) was wrong

207   when he had suggested that 'The exactitude with which atomic coordinates can be determined

208   is only limited by the amount of labour expended in making measurements'; the experience of

209   his assistant Taylor (1933) shows that once the basic crystal structure was solved, structure

210   refinement was clearly limited not by quantity or quality of data, but by lack of computing

211   power. The final individual cation-oxygen (T-O) bond lengths in the tetrahedra of Taylor's

212   initial sanidine structure ranged from 1.55 to 1.75A, with the conclusion drawn that 'both

213   tetrahedral groups are nearly regular' (Taylor 1933). These statements indicate that

214   uncertainties in cation-oxygen distances were of the order of 0.1 Å at best, quite insufficient

215   to draw conclusions about the detailed crystal-chemistry, to follow structural changes due to

216   changes in *P*, *T* or phase transitions, or even to determine basic patterns of Al,Si ordering. As

217   feldspars exhibit both displacive transitions and a variety of convergent and non-convergent

218   ordering processes that greatly influence their thermodynamic properties, the development of

219   methodologies in diffraction crystallography as they were enabled by increased computing

220   power can be followed by seeing how knowledge of the feldspar structures became more and

221   more precise. The basic theme here is that improved precision in structure refinements means

222   more precise determination of the atomic coordinates, which in turn requires more precise and

223   higher-resolution data. More precise data comes from both better measurement methods of the

224   raw diffraction data and more precise corrections for instrumental and experimental effects on

225   the measured diffracted intensities. Higher-resolution data also implies more data. Therefore,

226   crystallographers needed more computing power in order to obtain more precise crystal

227   structures.

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229   Attempts in the 1930's to provide aids for structure refinement were restricted to graphical

230   tools such as structure-factor graphs (Bragg and Lipson 1936) and mechanical tools such as

231   Beevers-Lipson strips (Beevers and Lipson 1934) both of which eased the calculation of the

232   terms in Fourier series such as Eqns. (1) and (2). They enabled Chao et al. (1940) and Cole et

233   al. (1949) to refine the crystal structure of an orthoclase, starting from the sanidine model of

234   Taylor (1933). Although the method of least-squares refinement was first applied to a crystal

235   structure refinement by Hughes (1941), and the first feldspar structure to be refined this way

236   was reported by Sörum (1953), the calculations were done by hand, severely limiting the

237   number of the data that could be handled. Nonetheless, Sörum (1953) was able to demonstrate

238   from differences in tetrahedral bond lengths that the ordering pattern in anorthite-rich

239   intermediate plagioclase is different from that in albite. The introduction of mechanical

240   calculators ('Hollerith machines') in the late 1940's and 1950's enabled larger datasets to be

241   handled, with attendant increase in precision. The architecture of mechanical calculators made

242   them more suitable for Fourier calculations (Cox and Jeffery 1949; Hodgson et al. 1949) than

243   for the implementation of least-squares refinements even though it was recognized this was

244   not the best way to determine accurate bond lengths and angles (Cochran 1948). So

245   refinement of structures continued to use the step-wise cycling of structure factor calculations

246   from trial coordinates (Eqn. 2) which were used in Fourier syntheses of the electron density

247   through Eqn. (1), from which better trial coordinates could be determined. Automation with

248   Hollerith machines, coupled with the assistance of several colleagues, wives and students to

249   feed them with punched cards did allow the number of data used in a refinement to be rapidly

250   increased. Bailey and Taylor (1955) used 2650 reflections (and four assistants including Mrs.

251   Bailey) to show from the T-O bond lengths that the structure of microcline was effectively

252   fully ordered with respect to Al and Si distribution.

253

254   The year 1962, a half-century from the discovery of X-ray diffraction, divides the era of

255   'discovery' of the basic architecture and principles of mineral structures from the modern era

256   of investigating the detailed crystal chemistry of minerals. By 1962 there had been 11 full

257   structure refinements of feldspars (Ribbe 1994), made over a period of 30 years since the

258   original structure determination of sanidine by Taylor (1933). With the larger datasets

259   collected in the 1950's and processed with Hollerith machines and early mainframe

260   computers, the refined structures had a claimed precision in bond lengths of 0.002 Å (e.g.

261   Cole et al. 1949) although this uncertainty is clearly underestimated because it is derived

262   directly from the difference Fourier maps (Cochran 1948; Cruickshank 1949a; b). A more

263   realistic estimate from the least-squares refinement by Sörum (1953) would be of the order of

264   0.005-0.01 Å which is sufficient to determine the basic pattern of Al,Si ordering from the

265   difference between tetrahedra occupied only by Al (Al-O ~ 1.74 Å) and Si (Si-O ~ 1.62 Å)

266   but not really good enough to determine intermediate states of order, such as that found in

267   orthoclase (Cole et al. 1949; Jones and Taylor 1961). Fourier maps showed that the extra-

268   framework cations in albite, at least, exhibited anisotropic apparent motion (Ferguson et al.

269   1958), but anisotropic displacement parameters had not been refined for them or the

270   framework cations.

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271

272   Although structures based on intensities collected by photographic methods continued to be

273   reported well into the 1960's, the first structure refinement of a feldspar of the modern era

274   was published by Onorato et al. (1963). They collected the intensity data not by film, but with

275   a commercial diffractometer, equipped with a point detector that recorded the intensity data

276   digitally and a Mo X-ray tube that, because of the shorter wavelength, makes absorption less

277   of a problem than with Cu radiation. Onorato et al. (1963) performed a structure refinement

278   using the full-matrix least-squares method on a computer. The availability of University

279   mainframe computers at the beginning of the 1960's that could run programs written in high-

280   level languages (mostly Fortran) that were compiled locally (making them portable) opened

281   the modern era of diffraction crystallography. Programs were developed for data reduction

282   including face-based absorption corrections (e.g. Busing and Levy 1957; Burnham 1966) to

283   provide more accurate data, and programs to perform full-matrix least-squares refinement of

284   the structure directly to the structure factors via Eqn. (2) became available (e.g. Busing et al.

285   1962; Stewart et al. 1972; Finger and Prince 1974; Sheldrick 2008). As computer storage and

286   power increased, structures were refined to more and better data, which enabled a better

287   description of the scattering density in terms of the anisotropic displacement parameters of the

288   atoms. Thus while Onorato et al. (1963) reported a full-matrix least-squares refinement of

289   sanidine with individual isotropic displacement parameters for each atom (a total of 28

290   parameters) to 960 reflections, within a few years it was practical to perform fully anisotropic

291   refinements such as that of albite (Wainwright and Starkey 1967) with 117 parameters refined

292   to 3530 data measured on a counter diffractometer. The increase in computing power,

293   together with the wide-spread introduction of computer-controlled diffractometers to collect

294   the data, resulted in the publication of about 150 feldspar structures over the two decades

295   1962-1982. The improvements in diffractometry and data processing led to T-O bond lengths

296   being determined to a reproducibility of ~0.002 Å (e.g. Dal Negro et al. 1978), enabling the

297   details of the crystal architecture to be determined and how the T-O bond lengths change with

298   the Al,Si content of the tetrahedra (e.g. Brown et al. 1969; Kroll 1983; Kroll and Ribbe 1983;

299   Ribbe 1994).

300

301   By the late 1980's computing power was no longer a limitation to structure refinements of

302   minerals; essentially arbitrarily large datasets could be used for full refinements of not only

303   the positional parameters of the atoms, but also the anisotropic displacement parameters to

304   describe the thermal vibrations of the atoms, without which the positions of the atoms can be

305   biased to incorrect values (see Eqn. 2). The precision of refined structures was therefore

306   limited by the use of point detector diffractometers. To achieve higher resolution many more

307   reflections at higher diffraction angles have to be collected which, with a point detector

308   diffractometer, means a very large increase in data collection times to the order of weeks

309   because the data are collected one reflection at a time. For example, the extension of a data

310   collection on albite from 60° to 80°, which reduces the formal estimated standard deviations

311   (*esd*'s) on T-O bond lengths to 0.001 Å (e.g. Meneghinello et al. 1999) requires the

312   measurement of about twice the number of reflections, with the additional higher-angle

313   reflections being systematically much weaker and thus requiring much longer to collect to the

314   necessary precision.

315

316   In the anorthite-rich plagioclase feldspars where the ordering of Al and Si (and accompanying

317   structural changes) gives rise to systematically weak reflections the challenge is greater

318   because these weak reflections have to be collected in sufficient numbers with sufficient

319   precision (which means longer counting times) to determine precise bond lengths within the

320   structure. Even with rotating anode sources that became available for laboratories in the late

321   1980's a data collection for such a plagioclase would still require several days in order to

322   collect ~3300 reflections to $2\theta_{max} = 60^o$ (e.g. Angel et al. 1990). The introduction of CCD-

323   based area detectors for diffractometry speeded up data collections by allowing many

324   reflections to be collected simultaneously. Subsequent improvements in detector technology,

325   which have greatly reduced the intrinsic noise in X-ray detectors while increasing their

326   dynamic range, have allowed data collection times to be further greatly reduced.

327

328   As an example of modern laboratory capabilities, Figure 1 illustrates the uncertainties in T-O

329   bond lengths in end-member Val Pasmeda anorthite (Carpenter et al. 1985) determined from a

330   series of data collections. We measured a crystal of ~70μm diameter with a commercial

331   instrument, the Oxford Diffraction SuperNova diffractometer equipped with a Mo-target X-

332   ray micro-source and a Pilatus 200K area detector[1]. The detector has no intrinsic noise and

333   has no read-out delay, further speeding data collections compared to CCD detectors. The

334   ability to collect data faster also means that multiple measurements can be made of the same,

335   or symmetry-equivalent, reflections from the crystal at different positions of the

336   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).

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337   intensities to be corrected more accurately for experimental factors such as absorption by the

338   crystal and its mount, the variations in incident beam intensity, and the detector response. As

339   a consequence, as an extreme example, a partial data collection of just 90 seconds on anorthite

340   is sufficient to determine the bond lengths to an accuracy of 0.02 Å (Figure 1) and thus the

341   essential architecture of the structure! A full dataset to $2\theta_{max} = 60^o$ collected in 48 minutes

342   yielded esd(T-O) = 0.004 Å, equivalent to the results from 6 days data collection 25 years ago

343   from a significantly larger crystal (Angel et al. 1990) or several months in the 1950s

344   (Kempster et al. 1962)! A data collection to $2\theta_{max} = 100^o$ yielded in excess of 95,000

345   individual reflections, took 81 hours and gives esd(T-O) = 0.0005 Å. The refined structures of

346   anorthite show no significant differences in bond lengths when the data is restricted to lower

347   resolution (down to $2\theta_{max} = 50^o$ for MoKα), or with decreasing exposure time at constant

348   resolution in full datasets (Figure 1). The small offsets of bond lengths when the data is

349   restricted to very low resolution ($2\theta_{max} < 50^o$) arises from correlations between the positional

350   and displacement parameters in the refinement which are only suppressed with higher-

351   resolution data. The esd's in bond lengths for full datasets scale approximately with the

352   inverse square root of the number of reflections used in the refinement, which means that

353   modern diffraction data such as these are precise and accurate. Further, when the data are

354   collected with sufficient resolution, conventional refinements also yield bond lengths that

355   within the esd's are mostly independent of experimental influences and detailed choices of

356   refinement models and refinement parameters such as weighting schemes (Figure 2). In this

357   sense, the determination by modern X-ray diffraction of the geometric details of the average

358   crystal structure in terms of atom positions and inter-atomic distances and angles is reliable

359   and robust.

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Beyond geometry: chemistry and thermodynamics of minerals

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364   Because accurate X-ray diffraction intensity data can be collected precisely and quickly with

365   high redundancy, we now focus on the use and applicability of structure refinements to

366   solving mineralogical problems beyond that of simply reporting the structural architecture,

367   bond lengths and angles. Chemical and thermodynamic information about minerals can be

368   obtained by determining the occupancies by different atomic species of individual

369   crystallographic sites within the mineral. Cation partitioning between sites within a single

370   mineral crystal has great potential to be used as a single-phase geo-thermometer or even a

371   geo-speedometer, especially because the process of re-equilibration of the site occupancies

372   after temperature change is rapid as the distances over which cations have to be exchanged is

373   only of the order of the size of the unit cell. This contrasts with chemical re-equilibration

374   between different mineral phases which requires diffusion over distances that are of the grain

375   scale. Determination of the site occupancies also, obviously, allows the composition of the

376   mineral to be obtained. Thus diffraction is an important tool for determining compositions of

377   minerals that cannot be analyzed by microprobe, for example inclusions trapped within

378   diamonds (e.g. Nestola et al. 2011) or other host minerals where extraction of the inclusion

379   mineral is not permitted because it requires at least partial destruction of the host mineral.

380   Chemical site occupancies can be obtained by direct structure refinement of the occupancies,

381   or indirectly from the bond lengths, and we will discuss one example of each of these in turn.

382   In doing so we will illustrate that the limitations of modern X-ray structure refinement are not

383   in the diffraction data, but in the nature of the refinement models that are used to interpret the

384   diffraction data and the crystal-chemical models used to interpret them.

385

386   When the contrast in X-ray scattering powers of the atoms of interest is small, for example as

387   between Al and Si, the site occupancies cannot be determined by direct refinement. However,

388   the example of the anorthite structure discussed above shows that the distances between the

389   atom centres can be determined to high precision by conventional structure refinement to

390   modern diffraction data (Figs. 1 and 2). If we suppose that T-O bond lengths in a feldspar

391   vary linearly with Al content and that the difference between Al-O and Si-O is ~0.12 Å (e.g.

392   Kroll and Ribbe 1983) then an uncertainty of the order of 0.0005 Å in a T-O bond length (Fig.

393   1) should allow Al contents to be determined with an uncertainty of less than 1%. However,

394   while the primary factor controlling individual T-O bond lengths is the Al,Si content of the

395   site, a number of secondary factors have also been shown to be significant. These include the

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396   occupancy of the adjacent tetrahedra, the bonding of the extra-framework cation to the

397   oxygen, and the T-O-T and O-T-O angles (e.g. Phillips and Ribbe 1973; Phillips et al. 1973).

398   This explains why the individual bond lengths in any one of the nominally pure SiO_4

399   tetrahedra in anorthite range from <1.59 Å to ~1.65 Å (e.g. Fig. 2). This variation is more than

400   half the expected difference between the bond lengths for pure AlO_4 and SiO_4 tetrahedra!

401   Some of the geometric effects appear to be compensated internally within an individual

402   tetrahedron, so it was recognized (e.g. Kroll 1983; Kroll and Ribbe 1983) that mean bond

403   lengths of tetrahedra <T-O> were more reliable indicators of Al,Si content than individual

404   bond lengths. As more precise structures became available it has become apparent that the

405   mean values <T-O> in plagioclase feldspars are sensitive to Ca,Na content, and can be

406   perturbed by different refinement models for the partially disordered structures (Angel et al.

407   1990; Ribbe 1994). There are further difficulties. It is not possible to determine by experiment

408   whether anorthite and albite are fully ordered; techniques such as neutron diffraction and

409   NMR have uncertainties of a few % in the determination of Al and Si site occupancies.

410   Therefore we do not know the true value of <T-O> in pure AlO_4 or pure SiO_4 tetrahedra.

411   Neither do we know whether the differences in <T-O> values for the individual Si-rich

412   tetrahedra, for example as shown in Fig. 1, represent small differences in Si,Al contents or are

413   simply the effects of other factors on bond lengths. The refined displacement parameters of

414   the atoms also correspond to apparent displacements of T and O atoms along the bond of the

415   order of 0.07-0.08 Å, but X-ray Bragg diffraction as expressed by Eqn. 2 does not tell us how

416   these displacements are correlated. Different models for interpreting the refined displacement

417   parameters in terms of correlated, uncorrelated or riding motions of one atom with respect to

418   the other (e.g. Finger and Prince 1974) yield corrections to T-O bond lengths that are of the

419   order of 0.02 Å. All of these factors mean that the absolute occupancy of tetrahedral sites in

420   feldspars, or similar alumino-silicates such as zeolites, cannot be established to the precision

421   that would be expected from the precision in bond lengths. However, all of these limitations

422   arise strictly from the refinement models and crystal-chemical analysis. This means that if

423   different crystal structures of the same type (e.g. albites) are refined with exactly the same

424   model, then X-ray structure refinement can yield precise values for the differences between

425   the structures, and thus changes in the state of Al,Si order, even if the absolute values of site

426   occupancies are less well-defined (e.g. Angel et al. 1990; Meneghinello et al. 1999).

427

428   When the contrast in scattering power between the atoms is significantly greater than that

429   between Al and Si, it is possible to determine the site occupancies by refining the scattering

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430   power of each atomic site. This can be done in two ways. When just two atomic species are

431   known to occupy a given site, and the site is assumed to be fully occupied, then the

432   occupancies can be refined directly. An alternative is to refine the occupancy of an atom

433   chosen to represent the average scattering curve of the multiple occupants of the site, and then

434   the actual site occupancies can be inferred from the total refined scattering power (measured

435   in electrons) and the atomic numbers of potential occupants. Clearly, because structure

436   refinement only yields the total scattering of the site through the scattering factor f (Eqn. 2),

437   the interpretation of the result in terms of multiple occupancies requires further constraints or

438   assumptions about the chemistry and the distribution of species between sites. One obvious

439   additional constraint that can be used for structures at ambient pressure and temperature is the

440   bond lengths of the site, if the atomic species of interest give rise to significantly different

441   bond lengths. Such a combined approach has been successfully used in a number of mineral

442   systems such as spinels (Della Giusta et al. 1996; Lavina et al. 2002).

443

444   In mantle olivines a simplified intermediate approach can be used because it is known from

445   chemical analyses of olivine inclusions in diamonds that their compositional variation is

446   dominated by variation in Mg,Fe content (Stachel and Harris 2008). These atoms have

447   sufficiently different scattering powers that direct refinement of the atomic occupancies on the

448   two M sites within the structure is possible, subject to the sites being assumed to be fully

449   occupied. Mantle olivines also typically contain trace amounts of other elements, mostly Ca,

450   Mn and Ni. The scattering powers of Ni and Mn for X-rays are very similar to that of Fe, so

451   their contribution to the X-ray diffraction intensities is effectively included in the refined Fe

452   content. As Ca has an atomic number approximately half-way between that of Mg and Fe, it

453   can be considered as contributing equally to the refined Mg and Fe contents. We will denote

454   the Mg occupancy obtained by structure refinement using only Mg and Fe as the site contents

455   as Mg*. Its value should be equal to the fraction (Mg + 0.5Ca)/(Mg+Fe+Mn+Ni+Ca)

456   determined by chemical analysis. Figure 3 shows the site occupancies refined to a single

457   dataset collected from a mantle olivine crystal of approximate size 150 x 110 x 80 µm, out to

458   a resolution limit of 100° 2θ with an average redundancy (number of symmetry-equivalent

459   reflections measured) of 6, in 6 hours. The composition has been measured by chemical

460   analysis as Mg*=0.877(1). It is obvious that the refinement performed with scattering factors

461   calculated for neutral atoms (the default for refinements of molecular structures in programs

462   such as SHELX, Sheldrick 2008) yields an overall composition from the refined occupancies

463   of the two M sites that is about 2-3% too high in Mg. The actual value also changes by >1%

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464   in Mg* depending on the resolution of the data used. The agreement with the known

465   composition is better if scattering factor curves for charged atoms are used (Fig. 3a), but there

466   is still significant variation in the results with data resolution. Further, the values and the

467   variation with resolution of Mg* on individual sites and the overall composition is different if

468   different weighting schemes and/or the criteria for rejecting outlier data are changed (compare

469   Fig. 3b with 3a). If corrections for secondary extinction (the reduction in measured intensities

470   due to interactions between the incident and diffracted beams in the crystal, Becker and

471   Coppens 1974) are not made, then the value of Mg* can be shifted by 0.2%. Therefore,

472   because of the sensitivity of the results to refinement conditions, conventional refinements

473   using charged atom form factors cannot yield the composition of a mantle olivine more

474   reliably than +/-1%.

475

476   In the past some of this variation in refined site occupancies has been attributed to short-

477   comings in the experimental corrections to the data as well as to different choices of scattering

478   factors as we have discussed above (Kirfel 1996). However, refinements to structure factors

479   calculated by Fourier transformation of the electron density of end-member Mg_2SiO_4

480   determined by DFT computer simulation also show a strong variation in refined site

481   occupancies with resolution (Fig. 4a). This indicates that the experimental data is not at fault,

482   but that there are short-comings in the refinement model. The conventional refinement model

483   that we have discussed so far relies on scattering factors for atoms that are calculated for

484   spherical isolated atoms. For this reason it is sometimes called the 'independent atom model',

485   *IAM*. But the measured intensities from crystals are scattered by all of the electrons, including

486   those involved in bonding. Kroll et al. (1997) showed that the variation in refined site

487   occupancies of orthopyroxenes with 2θ range of the data arises from the change in the

488   contribution of the bonding electrons to the observed intensities as 2θ changes. In simple

489   terms, at low Bragg angles all electrons including the bonding electrons contribute to the

490   diffracted intensities. At high angles the broader spatial distribution of the bonding electrons

491   means that they contribute disproportionately less to the scattered intensities, and the

492   measured X-ray intensities are therefore dominated by scattering from the core electrons of

493   each atom. That is also why charged-atom form factors give the correct Mg* value for olivine

494   when we use high-angle data, while neutral-atom form factors yields Mg* values that are

495   ~0.02 too high (Fig. 3). The variations in Mg* with data resolution arise from correlations

496   between the occupancies, the scale factors, the extinction parameters, and the parameters used

497   to describe the displacements of the atoms due to thermal and static positional disorder. As for

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498   the bond lengths alone (Fig. 1) these correlations are only suppressed by the use of both high

499   and low- resolution intensity data, for which the displacement and occupancy factors have

500   significantly different contributions (Eqn. 2).

501

502   Kroll et al. (1997) suggested that the problem could be addressed by removing the correlation

503   between the site occupancies and the displacement parameters simply by fixing the latter at

504   values that ensure that the refined site occupancies became independent of data resolution.

505   This procedure was somewhat artificial and also very time consuming. Another approach was

506   to refine the effective charges on the atoms, by refining a mixture of fully-charged and neutral

507   atoms on each site in the structure, a careful study of several stoichiometric end-member

508   minerals (Sasaki et al. 1980) having indicated that the scattering density was best represented

509   by partially-charged atoms subject to the constraint that the resulting model is charged

510   neutral. This result was applied (e.g. Rossi et al. 1983; Hawthorne et al. 1995) to determine

511   site occupancies by site occupancy refinement using fixed partial charge scattering factors.

512   While releasing the constraint of charge balance can sometimes provide a better fit to the

513   diffraction data, it can result in a structure model that has a net charge and cannot be

514   considered physically realistic.

515

516   Fourier maps of the calculated electron density (Eqn. 1) from conventional refinements of

517   silicates indicate that the major misfit of the density is approximately midway along the Si-O

518   bond. This confirms that conventional refinements do not model the contribution of the

519   bonding electrons (e.g. Hawthorne et al. 1995). Heinemann et al. (1999) therefore

520   implemented the idea of Kirfel and Will (1980) to modify the crystal structure model in the

521   refinement in a manner that directly reflects this short-coming of a conventional independent

522   atom model. Heinemann et al. (1999) showed that by refining a structure model that has one

523   electron placed on the Si-O bonds (and then refining position along the bond and the

524   displacement parameters of the electron), the contribution of the bonding electrons to the

525   diffracted intensities can be successfully modelled. In a simplification of this model we find

526   that fixing the electron to a point 70% along the Si-O bond towards O, and restricting all such

527   electrons in the refinement model to have the same isotropic displacement parameters is

528   sufficient to eliminate nearly all of the variation in site occupancies with 2θ range (Fig. 4b)

529   for the DFT dataset of Mg_2SiO_4. Refinement of such a model with robust-resistant weights

530   and a realistic extinction model (Becker and Coppens 1974) to the data of the natural olivine

531   results in Mg,Fe site occupancies that are in agreement with the composition determined by

532   microprobe analysis. The accuracy of these X-ray structure refinements (Fig. 3c), is as good

533   as that achieved by chemical analysis.

534

535   **Implications**

536   What we have shown in this paper is that the precision with which we can determine mineral

537   structures has evolved over 100 years in parallel with the developments in X-ray diffraction

538   crystallography that have improved the quality of the diffraction data, and with the increased

539   technological capacity to handle the data. With modern instruments on laboratory sources

540   Bragg diffraction data can be collected from small mineral crystals of 50-100 μm size at room

541   conditions in a few hours that is of such quality that the accuracy and precision of the

542   resulting structural parameters such as bond lengths and angles is beyond that required for

543   crystal-chemical analysis. For synchrotron sources the time scales are shorter, or alternatively

544   the crystal sizes can be smaller. At high pressures, high temperatures, or *in operando*, the data

545   quality remains in the majority of cases the factor limiting the accuracy and precision of the

546   resulting structures. Such data normally requires additional corrections for absorption by the

547   environmental cell but, at the same time, the cell often restricts both the resolution and

548   redundancy of the data, making such corrections more difficult to perform. The real challenge

549   is therefore to make the data corrections accurately based on fewer data. For laboratory high-

550   pressure studies the lack of redundant data means that the best approach is to base the

551   corrections on appropriate physical models of both the crystal and the pressure cell. But the

552   data quality never matches what can be achieved with the same instrument from the same

553   crystal in air. An alternative is provided by recent developments in high-pressure single-

554   crystal diffraction on synchrotron X-ray sources, where the use of much higher-energy, much

555   more intense and much smaller X-ray beams reduces the magnitude of the experimental

556   corrections required while at the same time providing raw intensity data of greater reciprocal

557   space coverage, greater redundancy and much improved signal to noise (e.g. Hejny and

558   Minkov 2015). As a consequence, the resulting quality of crystal structures at pressures of

559   10's of GPa is starting to approach that which can determined at room pressure which opens a

560   new frontier in ultra-high pressure crystal chemistry (e.g. Finkelstein et al. 2014; Glazyrina et

561   al. 2014).

562

563   Laboratory X-ray diffraction data from crystals in air is now of the quality where the results

564   are limited not by the data but by the physical validity of the refinement models used to

565   interpret the measured data. Thus the standard structural models that are conventionally used

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566   in refinements are based on independent atomic spherical scatterers and thus can be said to

567   'neglect the chemistry' – they do not model the modification of the electron density of the

568   atom due to bonding. For most minerals, this modification of the electron density is very

569   small, which is why the structural geometry from refinement of an IAM is accurate to a level

570   limited by the intrinsic noise of the data. We have seen that the site occupancies are more

571   affected and that the electron-in-bond model (Kirfel and Will 1980; Heinemann et al. 1999) is

572   a simple but under-utilized extension of the IAM which can be readily implemented at no

573   intellectual difficulty, tested, and used to provide site occupancies with a reproducibility that

574   is better than a routine microprobe analysis for simple chemical systems with high contrast in

575   atomic number such as Fe,Mg in olivine. However, the determination of site occupancies in

576   even simple systems to a precision better than 0.001 is unrealistic given the short-comings in

577   the IAM and the Bragg approach embedded in Eqn. 2 (see also Heinemann et al. 1999;

578   Stimpfl et al. 1999; Merli et al. 2000). In particular, in a crystal structure with mixed site

579   occupancies such as Al,Si in feldspars or Mg,Fe in olivines, the detailed local structural

580   geometry has been shown by a variety of local experimental probes such as NMR and IR

581   and DFT simulations to be dependent on the local arrangement and short-range ordering of

582   the cations. Therefore, the oxygen 'positions' obtained from structure refinement are some

583   kind of average position of their true local positions, and that is why the refined structure

584   exhibits bond lengths that reflect some kind of average of the bond lengths in the pure end-

585   member structures. At the same time, this average bond length is in some way also modified

586   by the correlation of positions with the refined displacement parameters, as is particularly

587   evident in plagioclase feldspars (Angel et al. 1990). With increased data quality, the IAM can

588   also be extended by refining parameters that correspond to the explicit population and

589   deformation of the electron density of each atom. Such 'pseudo-atom' (Stewart 1976) or

590   multipole models have been very successful in yielding the details of not only the bonding

591   density in pure materials such as pyrite (Overgaard et al. 2014), but even the core electron

592   deformations in diamond (Bindzus et al. 2014). However, multipole models require an

593   explicit atomic basis and are therefore not meaningfully defined for mixed-occupancy sites

594   typical of mineral solid solutions. The iterative Hirshfeld method is an intermediate approach

595   in which the structure is refined with multipole models, and then density-functional

596   simulations are used to re-calculate the scattering factors so as to include all of the electron

597   density in the effective scattering factors, which are then used in the next cycle of refinement

598   (Capelli et al. 2014; Farrugia 2014).

599

600   Data quantity and quality has enabled an alternative approach, known as the maximum
601   entropy method (MEM), whose essence is to refine with the minimum constraints of 'physical
602   reasonableness' the electron density of the crystal simply by adjusting the electron density in
603   a pixelated array of boxes across the unit cell. While it still only provides an electron density
604   averaged over all cells of the crystal, MEM results are model independent, which provides the
605   possibility of visually and directly locating non-framework species, such as the cations in
606   zeolites, based only on observed structure factors (Andersen et al. 2014). So MEM gives
607   electron densities unbiased by a structural model but, like the IAM and its extensions, the
608   interpretation of this scattering density requires assumptions about oxidation states, local
609   ordering and distortions in structures with mixed site occupancies. We can get accurate
610   electron densities but not occupancies from X-ray diffraction measurements, which only
611   serves to illustrate the fundamental point that while an X-ray diffraction experiment, properly
612   performed, provides an unbiased map of the average electron density of a crystal, the
613   interpretation of the electron density is model dependent.

614

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

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860   **Figure Captions**

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862   Figure 1: The precision of X-ray structure refinements as illustrated by average bond lengths
863   of the Si-rich and Al-rich tetrahedra in anorthite (open symbols) and one individual Al-rich
864   and one Si-rich tetrahedron (closed symbols with error bars). Data from Kempster et al.
865   (1962), Wainwright and Starkey (1971), Angel et al. (1990) and the current work. The
866   deviations in earlier work are the consequence of limited data resolution.

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869   Figure 2: There is no significant variation in individual T-O bond lengths in anorthite with
870   different refinement models, as illustrated for the T1oo tetrahedron. Refinements are (1) using
871   robust-resistant weights and refinement to structure factors F, (2) unit weights and refinement
872   to F, and (3) normal weights and refinement to F^2. The intensity dataset had a resolution
873   corresponding to 60° 2θ for MoKα radiation (labelled '60' in Figure 1). Esd's are
874   approximately equal to the symbol size.

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

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

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