

3.7. CRYSTALLOGRAPHIC DATABASES

structure described by the CIF can then be imported into the user's graphics or Rietveld package.

Free-text searches of the comments are also included on this screen. These are particularly useful, as ICSD collection codes and CSD refcodes are included in the comments. If the user has the CSD installed on the same machine as the PDF, the PDF entry links live to the coordinates in the CSD entry.

By using the Results menu option when a hit list is displayed, ranges of cells in the spreadsheet can be selected and simple descriptive statistics (mean, median and estimated standard deviation) can be generated. Also under Results is a Graph Fields option. The variables used for the x and y axes of the plot can be selected and both scatter plots and histograms can be generated. Each of the points in such a plot is 'live' and can be clicked to display the full PDF entry. Fig. 3.7.1 shows a plot of the cubic lattice parameter with respect to at.% Fe in FeO (Fe and O only, space group No. 225) under ambient conditions. From such data it is easy to generate a correlation between the Fe stoichiometry and the lattice parameter.

An optional add-on module to the PDF is *SIeve* (Search Index). This is a peak-based search/match program which enables the use of a manually entered (or imported) peak list or derives a

peak list from imported ASCII raw powder-diffraction data in several formats. It also has a flexible ASCII data-import module. Hanawalt, Fink, Long8 (the eight lowest-angle peaks in the pattern) or electron-diffraction searches can be carried out. Again, there is a Preferences option to customize the searches. A particularly useful (and easy-to-use) feature is the ability to apply a filter to the search/match. This filter can be selected from several pre-defined filters and/or any previous search in the session (stored in a history list). The combination of conventional search/match and Boolean searches can be very powerful, as illustrated in the next section.

3.7.2.4. Boolean logic in phase identification

Most phase identifications are carried out using the peak-based or full-pattern algorithms supplied by the instrument vendor. These often work well for major phases and can be customized to improve their success in identifying minor/trace phases. The native capabilities of the PDF (not all of which are accessible through some vendors' software) can be very powerful in identifying those extra peaks that result from a Rietveld difference plot (or any difference plot from pattern-fitting software) using the major phases. Below we use examples to illustrate several strategies.

3.7.2.4.1. Water-still deposit

A water still in my home eventually generates scale, much of which flakes off the walls, permitting easy analysis in the powder diffractometer. Any commercial search/match program will easily identify magnesian calcite (Fig. 3.7.2; files kadu1389.gsas, kadu1389.raw and iitd26_0510.prm, available in the supporting information). There are, however, three additional weak peaks at $d/I = 4.788/38$, $3.3089/51$ and $2.3697/56$. In Naperville, Illinois, the tap water comes from Lake Michigan. The bedrock underlying the Chicago region is the Racine Dolomite. Given the identity of the major phase in the scale and the source of the water, it seems likely that any minor phases will be mineral-related and contain some combination of the elements Ca, Mg, C, O and H (to include the possibility of hydrates and hydroxides). Accordingly, a search of mineral-related entries containing 'just' the elements Ca, Mg, C, O and H was performed and used as a filter in a Hanawalt search using these three peaks. This limits the search universe to 692 of the 328 660 entries in the PDF-4+ in 2012. The seven highest goodness-of-match entries in the hit list were brucite, $\text{Mg}(\text{OH})_2$. This phase was added to the Rietveld refinement. Analysis of the difference plot indicated an unaccounted-for peak at a d -spacing of 3.3089 \AA . A search for mineral-related entries with the same chemistry and having one of their three strongest peaks in the range $3.309 (30) \text{ \AA}$ yielded the vaterite polymorph of CaCO_3 as the hit with the highest goodness of match. This phase was added to the Rietveld refinement. The final quantitative phase analysis was: 94.7 (1) wt% $\text{Ca}_{0.84}\text{Mg}_{0.16}(\text{CO}_3)$, 5.2 (4) wt% $\text{Mg}(\text{OH})_2$ and 0.2 (1) wt% vaterite.

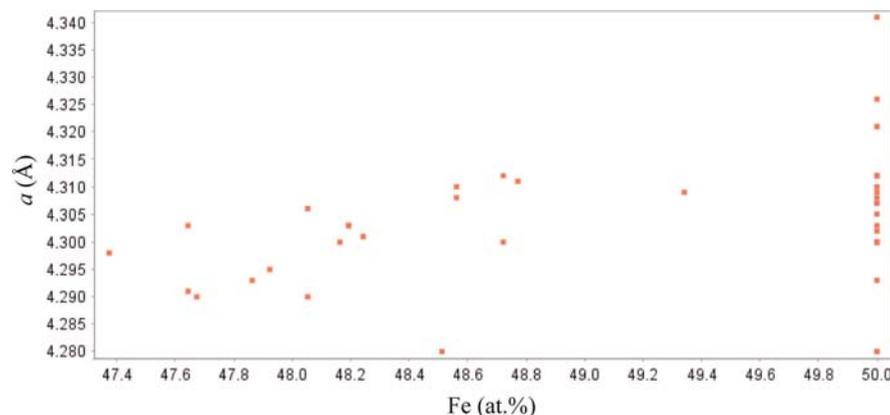


Figure 3.7.1

A plot generated by the Results/Graph Fields function in the Powder Diffraction File. The search was for entries containing only Fe and O and with space group No. 225 (resulting in FeO entries) measured under ambient conditions. One outlier was removed from the hit list manually. The trend in the cubic a lattice parameter with Fe content is apparent, as well as the large number of apparently stoichiometric FeO entries, some of which may not be correctly characterized.

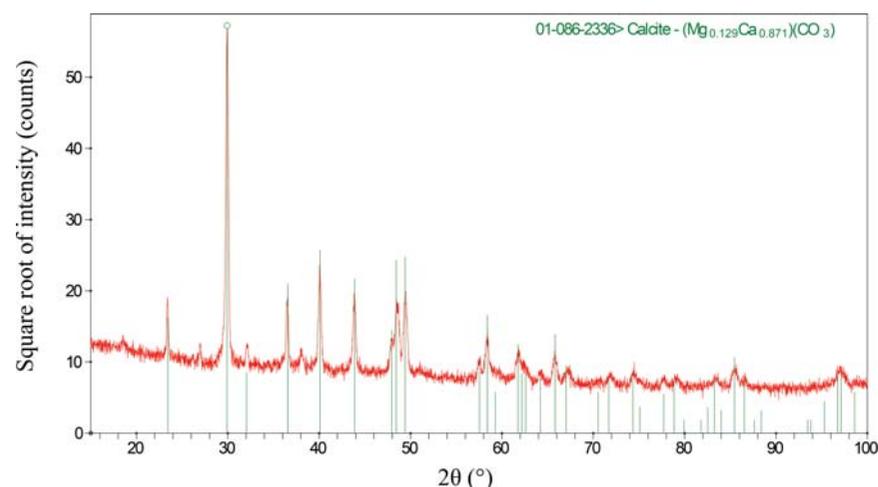


Figure 3.7.2

The result of applying a commercial search/match program (*Jade 9.5*; Materials Data, 2012) to the powder pattern of a water-still scale. Weak peaks not accounted for by the major magnesian calcite phase are apparent and additional tools in the Powder Diffraction File were needed to identify the additional phases.