Quantitative Phase Analysis of Tailings and Waste Rock using the Rietveld Method and X-ray Powder Diffraction Data

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TOPICS

- **Definition of quantitative phase analysis**

- **Introduction to X-ray diffraction**

- **Conventional uses of X-ray powder diffraction**

- **The Rietveld method**

- **Case study: determination of carbonates in waste rock**

- **Summary**

Definition of quantitative phase analysis

- **Quantitative phase analysis is the measurement of the relative abundances of the constituent minerals in a sample of rock – a very useful property to know**

- **Traditionally, geologists have referred to this procedure as modal analysis**

- **The units of the analysis may be in weight, mole or volume percent (calculated from area percent)**

- **In Rietveld analysis, the results are determined in weight percent, but these may be recalculated to any desired unit**

Introduction to X-ray Diffraction

- ■ **What is X-ray diffraction?**

- ■ **Conventional uses of X-ray powder diffraction**

What is X-ray diffraction?

- **The coherent scattering of radiation by periodic arrays of objects resulting in concerted constructive interference at specific angles is called diffraction.**

- **A familiar example is the optical grating. Lines ruled on the surface are spaced at a distance approximately the same as the wavelength of visible light.**

- **A beam of white light passing throught the grating will, depending on the angle, scatter the component wavelengths in white light.**

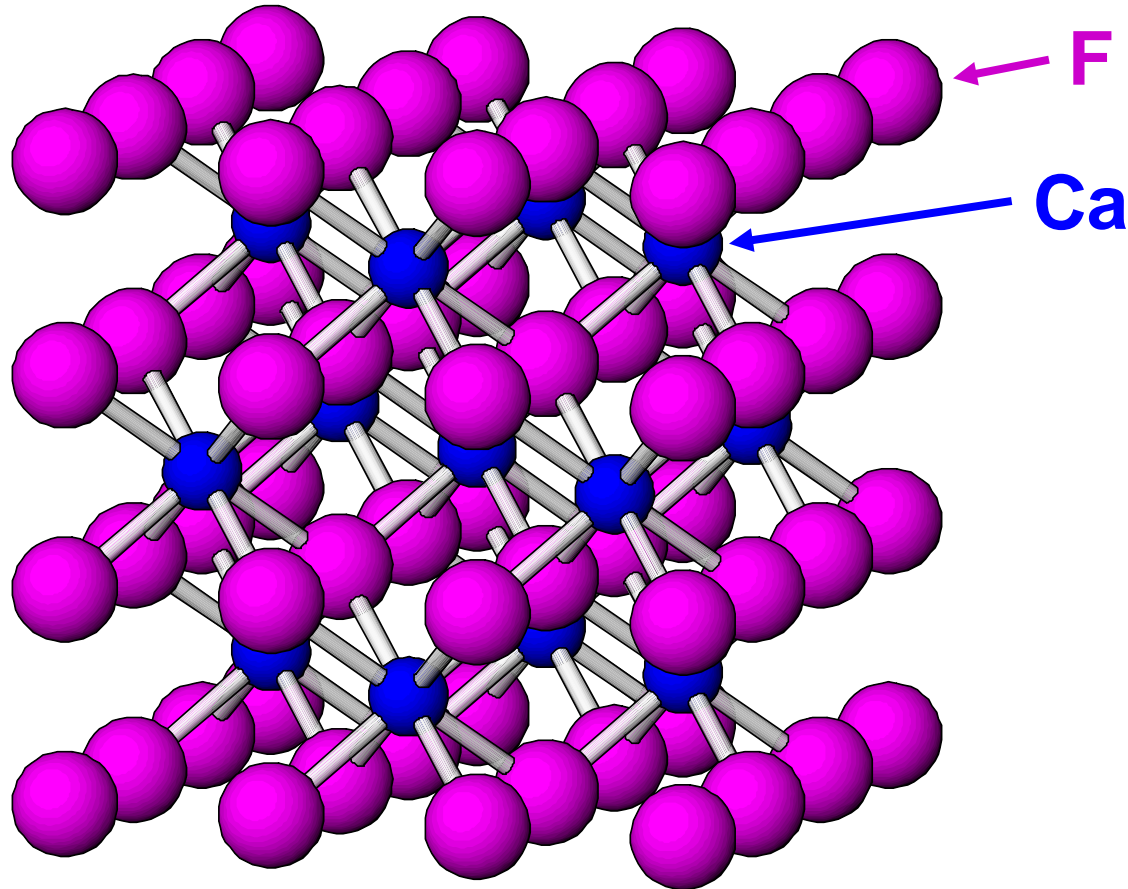# What is X-ray diffraction?
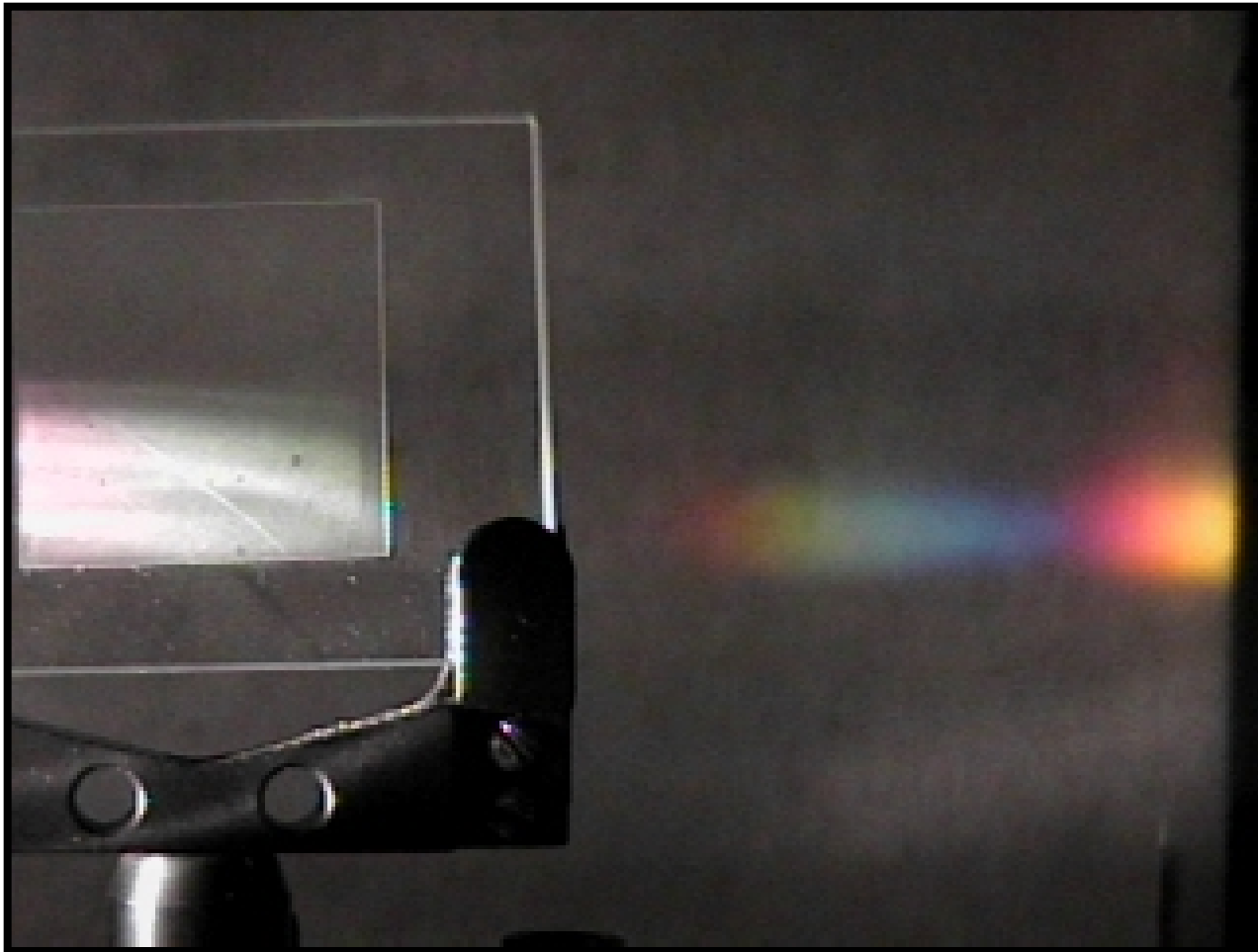
■ **Scattering of white light into its constituent wavelengths (colours) by an optical grating**

What is X-ray diffraction?

- **Of special interest to us is that crystalline matter consists of three dimensional arrays of atoms.**

- **Thus crystals may diffract monochromatic radiation in a number of different directions in three-dimensional space.**

- **X-rays are an ideal source of electromagnetic radiation for the study of crystals as the wavelength of X-rays is of the same order as the distances between the atoms in crystals.**

- **Using X-rays and single crystals, the crystal structure (atomic arrangement) can be determined.**

What is X-ray diffraction?

■ **Periodic array of Ca and F ions in fluorite – crystal structure.**

What is X-ray diffraction?

- **What is a "crystal structure" and why is this information important with regard to X-ray powder diffraction**

- **This information may be simply summarized thus:**
  - **atomic positions (x, y, z coordinates in 3-D space)**
  - **site occupancies (the kinds of atoms at each position)**
  - **unit cell parameters (size of the unit cell)**

- **Knowing this information, we can calculate the X-ray powder diffraction pattern of any crystal.**

What is X-ray diffraction?
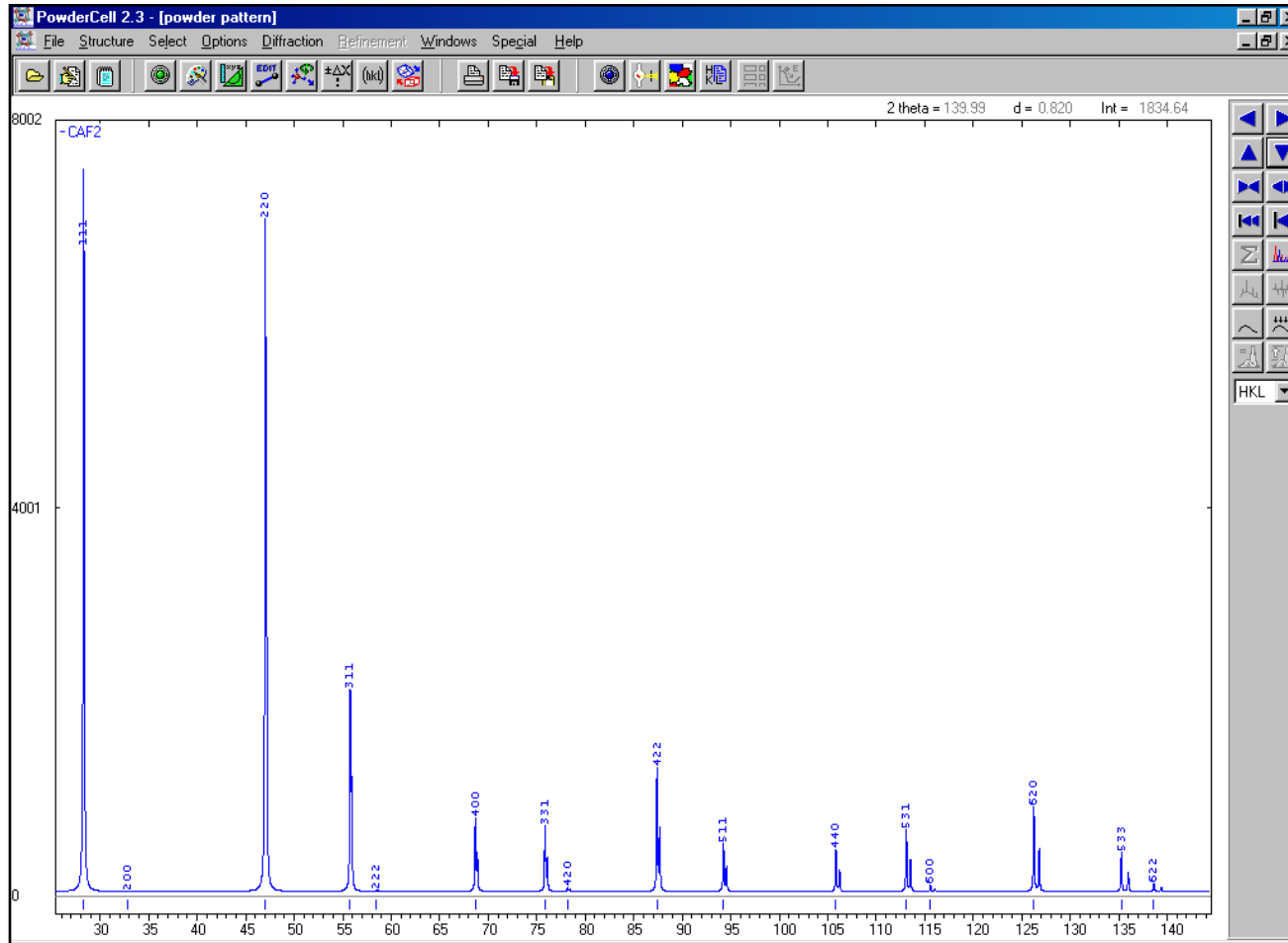
■ **Here is the calculated X-ray powder diffraction pattern of fluorite, using the information contained in the crystal structure. Each plane of atoms is represented by a peak of a particular intensity; the peak position is controlled by the spacing between the plane of atoms**
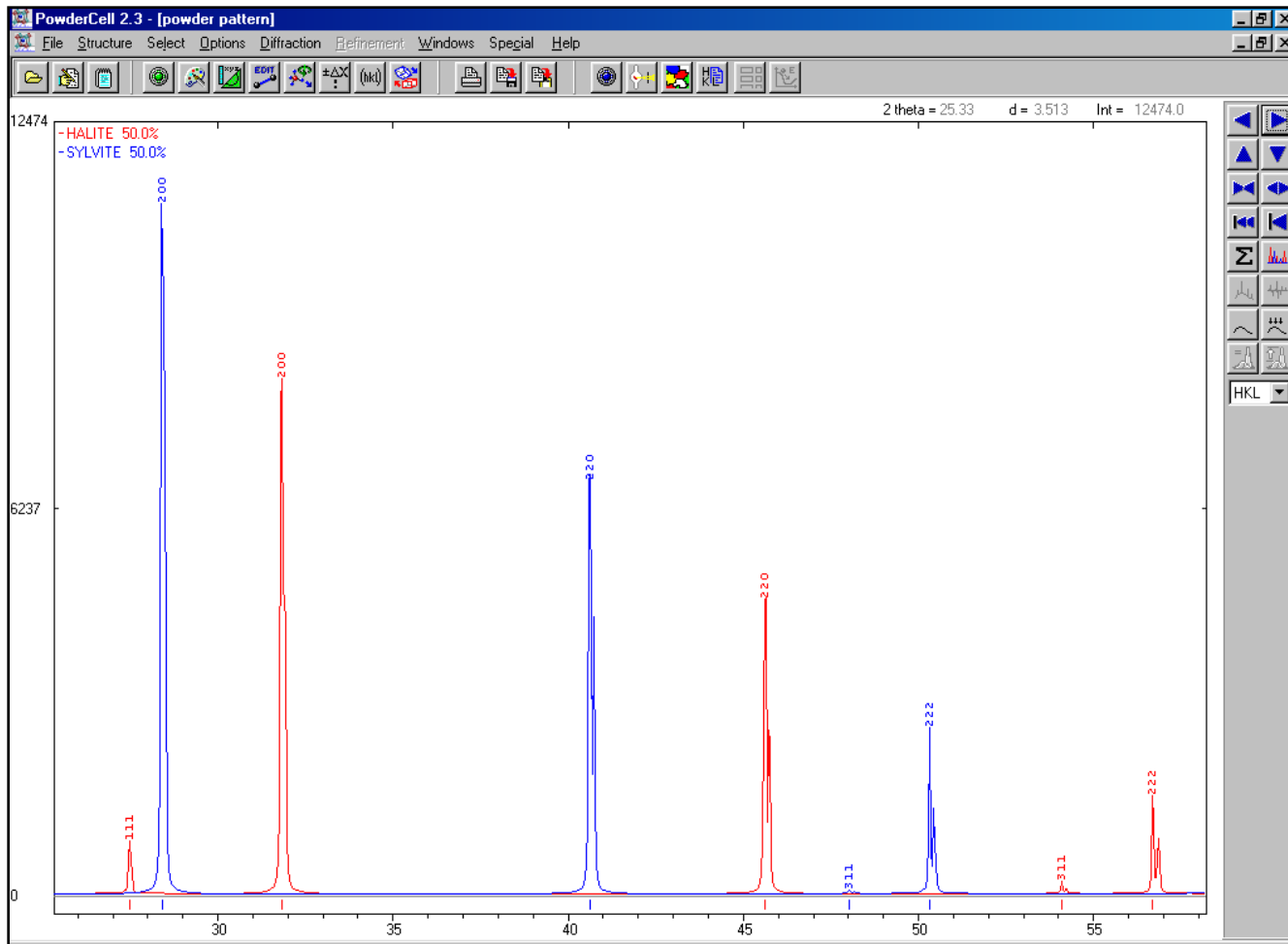
Conventional uses of X-ray powder diffraction

- From the atomic arrangement of a crystal (generally determined by single-crystal X-ray diffraction), we can calculate any powder diffraction pattern

- This ability is fundamental to doing quantitative phase analysis using the Rietveld method

- Before looking at the Rietveld method, let us review the most common use of X-ray powder diffraction – the identification of crystalline compounds

Conventional uses of X-ray powder diffraction

■ **In any X-ray powder diffraction pattern, the following is true:**

- ■ **the peak positions are a function of the radiation used, and the size and symmetry of the unit cell**

- ■ **The peak intensities are a function of the kinds of atoms and their arrangement in the unit cell, as modified by various instrumental and method-dependent parameters**

Conventional uses of X-ray powder diffraction

- **X-ray powder diffraction patterns of** **halite (NaCl)** **and** **sylvite (KCl)**. **Halite and sylvite have identical structures, but note the different peak intensities (K vs Na) and positions (K is larger than Na).**

Conventional uses of X-ray powder diffraction

- **The previous simple example demonstrated the following:**
  - **the intensities and positions of peaks in an X-ray powder diffraction pattern are characteristic of a crystalline compound with a particular composition and crystal structure**
  - **Therefore, the X-ray powder diffraction pattern of a phase may be used as a "fingerprint" to identify the phase**
  - **Traditionally, the simple identification of crystalline compounds has been the familiar goal of most X-ray powder diffraction studies**
  - **A database of reference standards such as that published by the International Centre for Diffraction Data is required**

The Rietveld Method

- **What is the Rietveld method?**

- **A simple 2-phase example of the Rietveld method**

What is the Rietveld Method?

- The **Rietveld method** is a **full-profile** approach to quantitative phase analysis using X-ray powder diffraction data

- The Rietveld method generates a **calculated diffraction pattern** that is compared with the **observed data**

- Using **least-squares** procedures to minimize the difference between the complete observed and calculated diffraction patterns the following parameters may be refined:

  - the **structural parameters** of each mineral (atomic coordinates, site occupancies, displacement parameters)

  - the various **experimental parameters** affecting the pattern (zero-point correction, peak shape, background, etc.)

- The Rietveld method is **standardless**

What is the Rietveld Method?

- **Of particular relevance to doing modal analysis of materials are the following:**
  - **the Rietveld refinement method can be used to characterize several phases simultaneously**
  - **the relative masses of all phases contributing to the diffraction pattern can be derived from the refinement using the simple relationship:**

$$W_r = S_r \, (ZMV)_r \, / \, \Sigma_t \, S_t \, (ZMV)_t$$

  - **where W_r is the *relative* weight fraction of phase r in a mixture of t phases, S is the scale factor derived from Rietveld refinement, Z is the number of formula units per unit cell, M is the mass of the formula unit (atomic mass units), and V is the volume of the unit cell ($\mathring{A}^3$).**

A simple 2-phase example of the Rietveld method
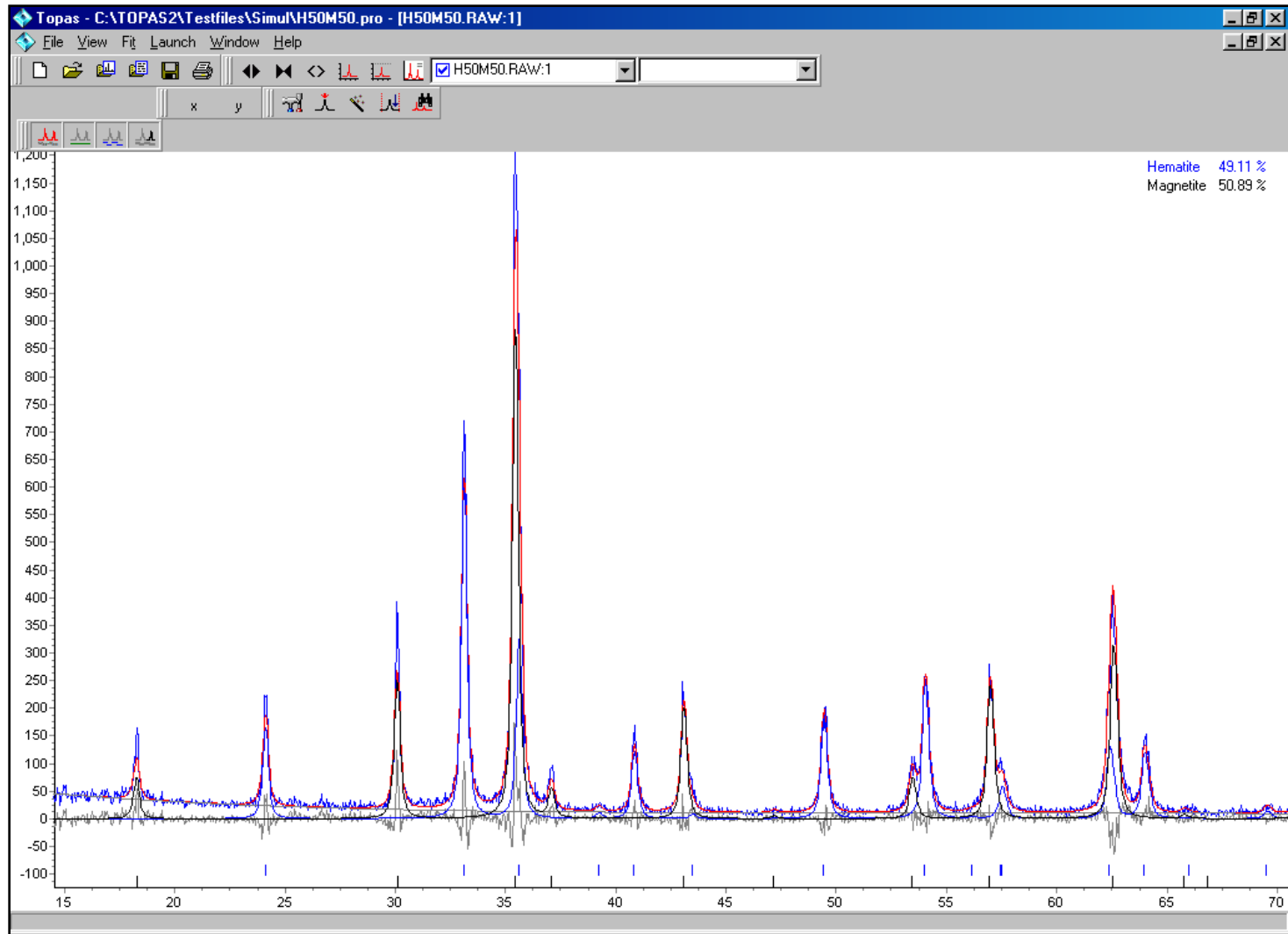
■ **Quantitative phase analysis of hematite (49.2 wt.%) – magnetite (50.8 wt.%) test mixture. Got hematite (49.1 wt.%) – magnetite (50.9 wt.%).**

Case Study:
Determination of carbonates in waste rock

- **Comparison of X-ray powder diffraction patterns of:**
    - **calcite and siderite**
    - **dolomite and ankerite**
- **Quantitative phase analysis of coexisting calcite, siderite and ankerite in waste rock from cherty sediments**

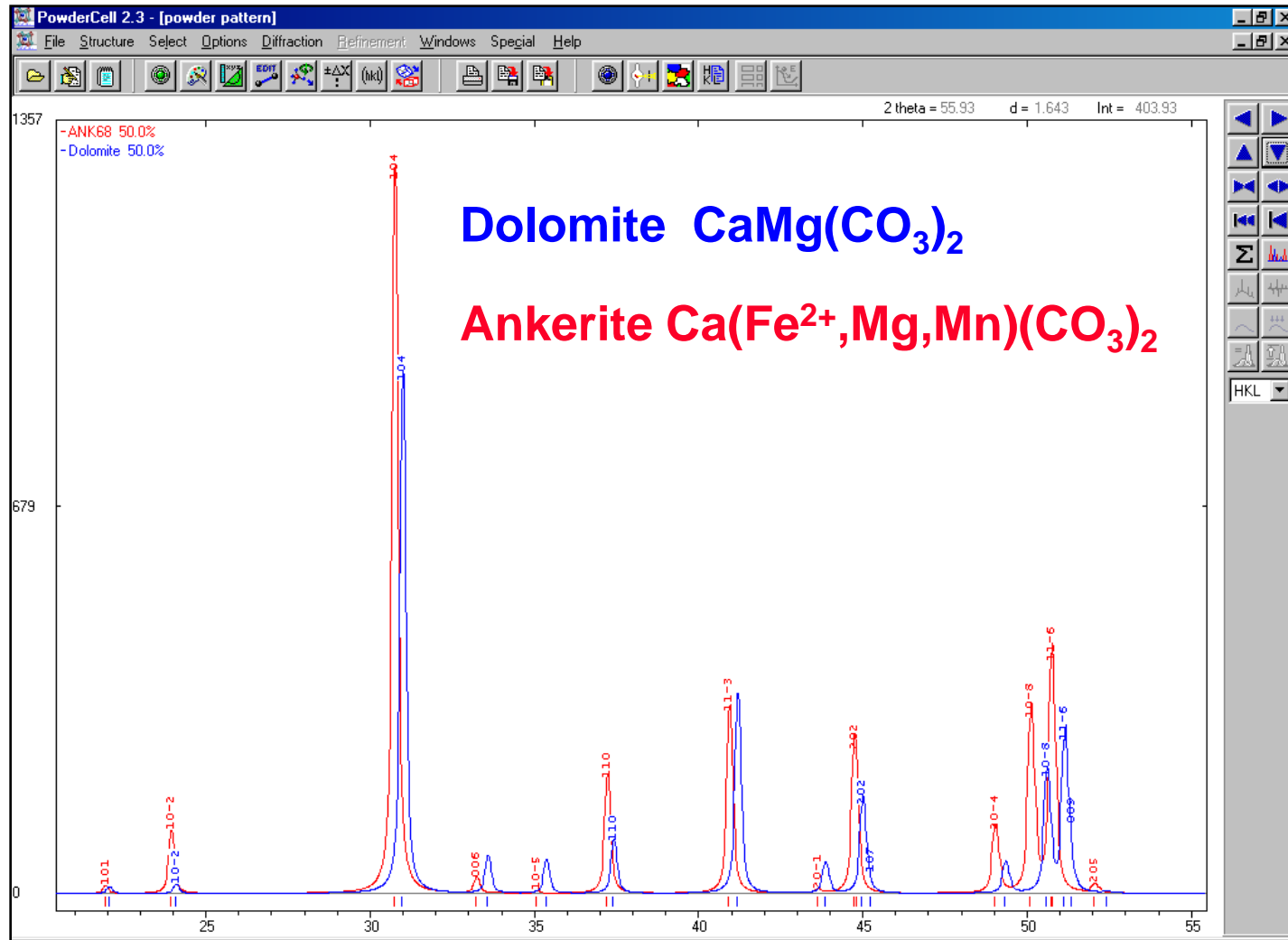# X-ray powder diffraction patterns: calcite and siderite
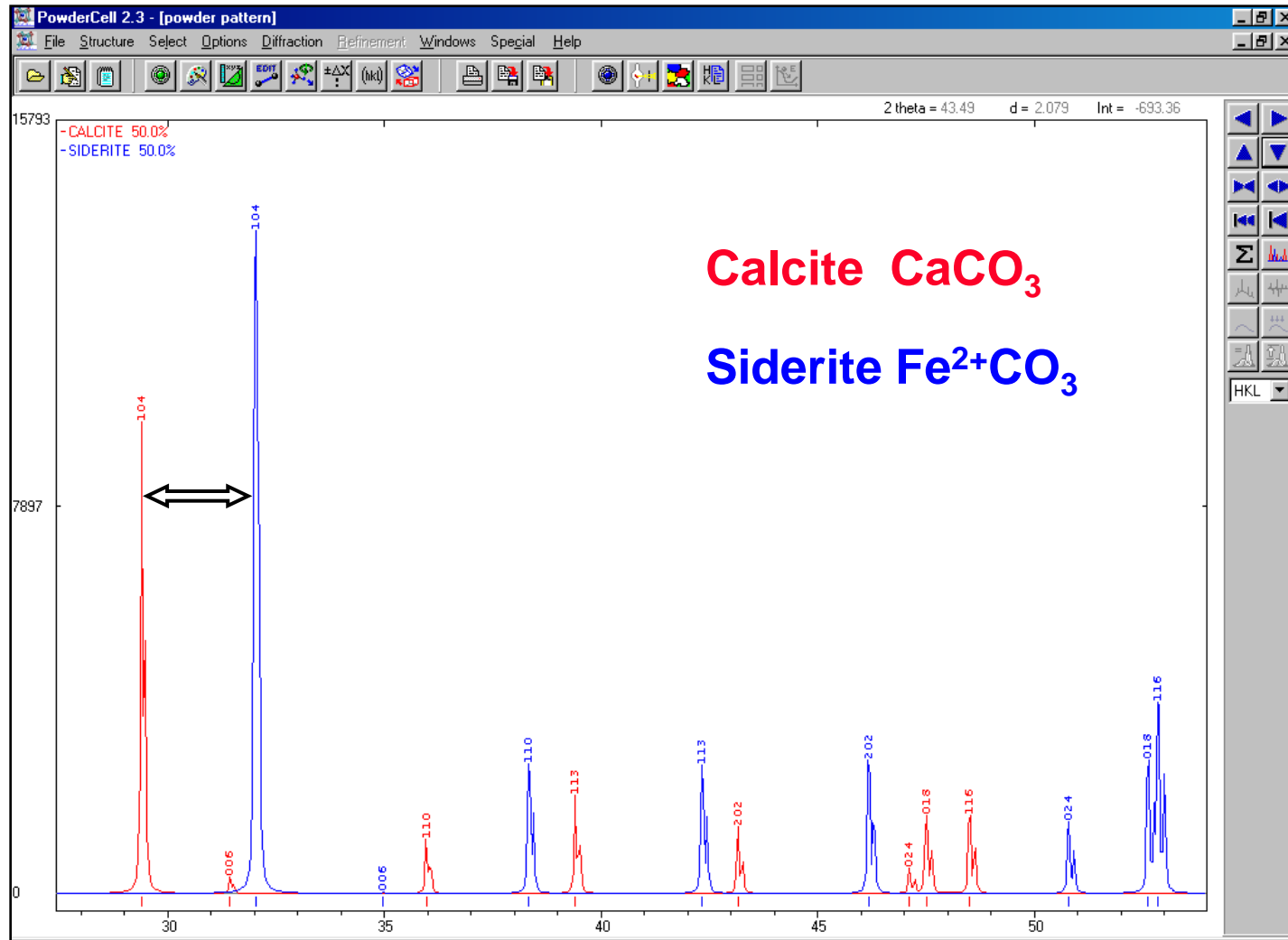
■ **Calculated X-ray powder diffraction patterns of calcite (red) and siderite (blue). Note, because of the large difference in the sizes of the unit cells, the patterns are easily distinguished.**

X-ray powder diffraction patterns: calcite and siderite

- **Calcite and siderite crystallize with the same crystal structure**

- **Because of the large difference in ionic radii of Ca and Fe, the sizes of the unit cells are quite different and the X-ray powder diffraction pattern of siderite is clearly displaced from that of calcite, and the two are easily distinguished**

- **Solid solution between Ca and Fe is quite limited**

- **The crystal structures of calcite and siderite are different from that of dolomite and ankerite**

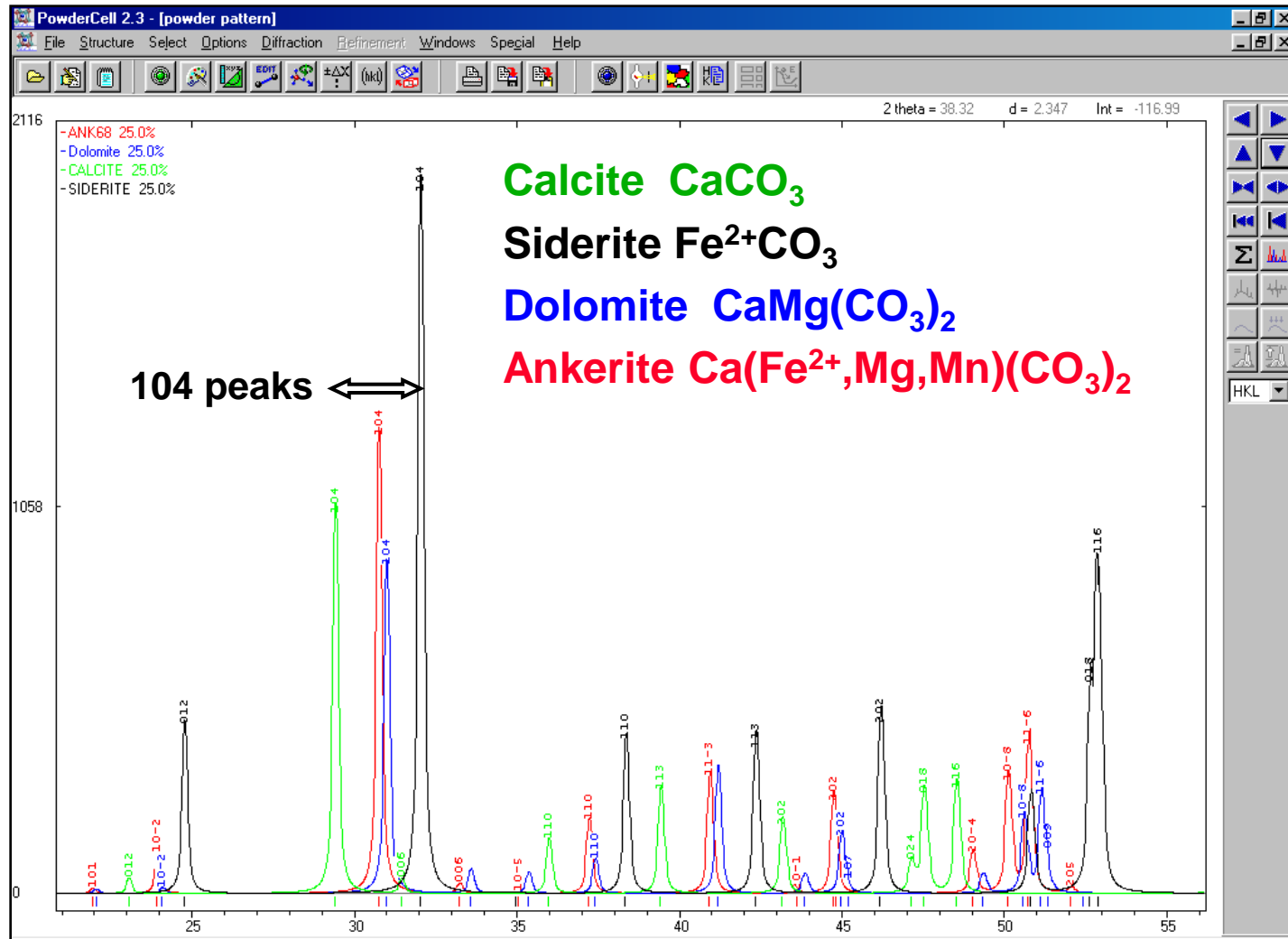# X-ray powder diffraction patterns: dolomite and ankerite

Dolomite CaMg(CO$_3$)$_2$

Ankerite Ca(Fe^{2+},Mg,Mn)(CO$_3$)$_2$

■ **Calculated X-ray powder diffraction patterns of ankerite (red) and dolomite (blue). Note, because of the similarity in the sizes of the unit cells, the patterns almost coincide, but relative intensities differ.**

X-ray powder diffraction patterns: dolomite and ankerite

- **Dolomite and ankerite crystallize with the same crystal structure**

- **There is a complete solid solution in Mg-Fe between dolomite and ankerite (and in Fe-Mn between ankerite and kutnahorite)**

- **Because the amount of Ca remains fairly constant across the solid solution, and there are not large differences in the ionic radii of Mg, Fe and Mn, the X-ray powder diffraction patterns of dolomite and ankerite are only slightly displaced.**

- **However, the relative intensities of the peaks are different**

XRPD patterns: calcite, siderite, dolomite and ankerite

Calcite CaCO$_3$

Siderite Fe^{2+}CO$_3$

Dolomite CaMg(CO$_3$)$_2$

Ankerite Ca(Fe^{2+},Mg,Mn)(CO$_3$)$_2$

104 peaks ⟺

■ **Calculated X-ray powder diffraction patterns of ankerite (red), dolomite (blue), calcite (green) and siderite (black).**

Quantitative phase analysis
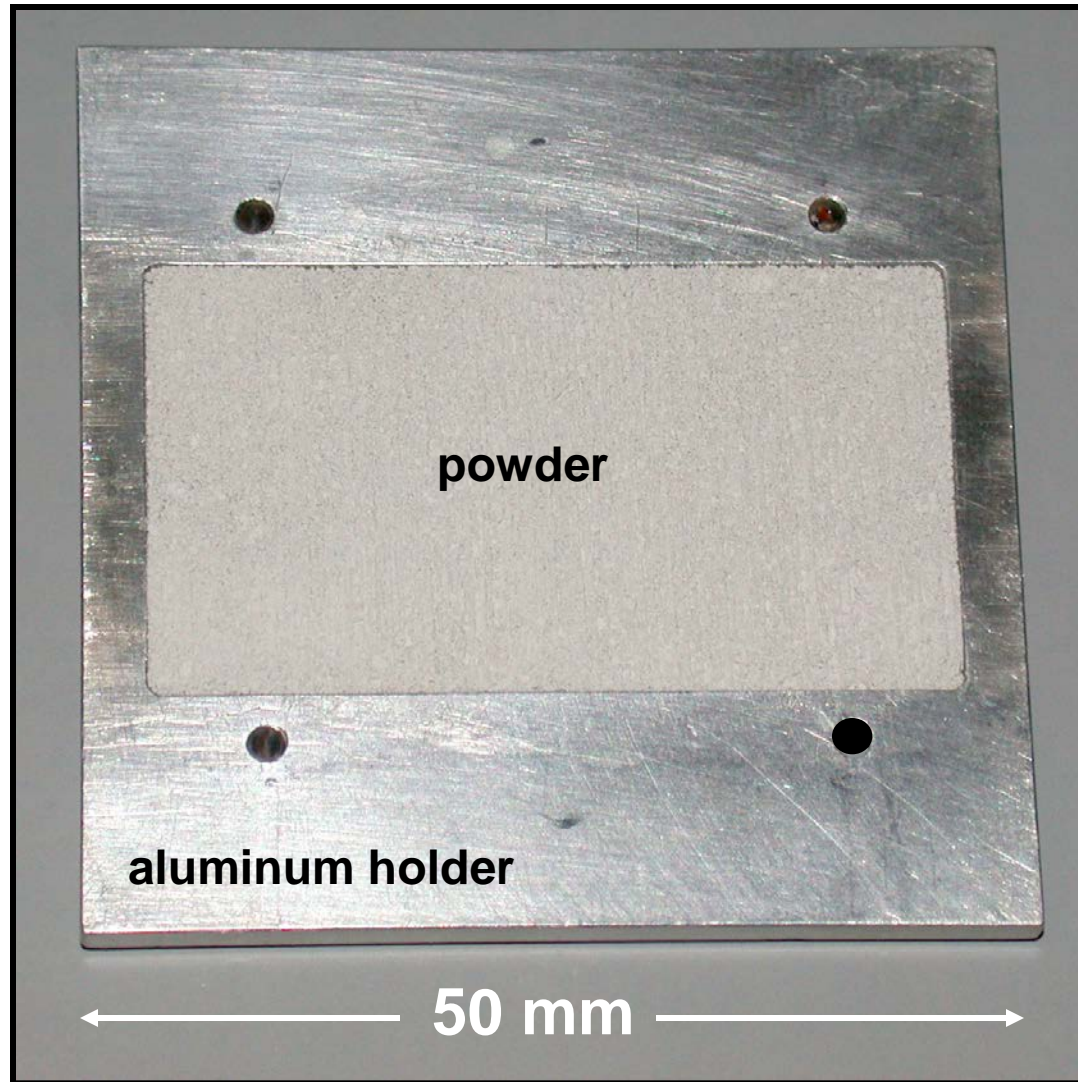## of coexisting calcite, siderite and ankerite in waste rock

- **Although the previous comparison of the X-ray powder diffraction patterns of carbonates show much overlapping of peaks, refining the structures of these minerals with the Rietveld method is relatively straightforward.**

- **A strength of the Rietveld method is that overlapping peaks are easily modelled and refined – this is not the case with traditional X-ray powder diffraction methods.**

- **In addition, we can use cell dimensions distinguish between dolomite and ankerite, and to estimate the (Fe + Mn) content.**

- **Even in the presence of many other phases, we can still successfully measure the amount of each carbonate which is present, even at low abundances.**

Quantitative phase analysis
of coexisting calcite, siderite and ankerite in waste rock

- **Sample for the case study:**
  - **waste rock from cherty sediments in contact with an intrusive orebody.**
  - **received as a pulp which is ideal to start with for Rietveld analysis.**
  - **further ground in a micronizing mill under alcohol to about 5 μm in grain size. Fine grain size essential to minimize microabsorption corrections, to give reproducible peak intensities and to minimize preferred orientation.**
  - **the powder was gently back-pressed into a standard aluminum holder against a ground glass slide to further minimize preferred orientation.**

Quantitative phase analysis
of coexisting calcite, siderite and ankerite in waste rock

powder

aluminum holder

50 mm

■ **Sample and holder for collection of X-ray powder diffraction data.**

Quantitative phase analysis
of coexisting calcite, siderite and ankerite in waste rock

X-rays

sample
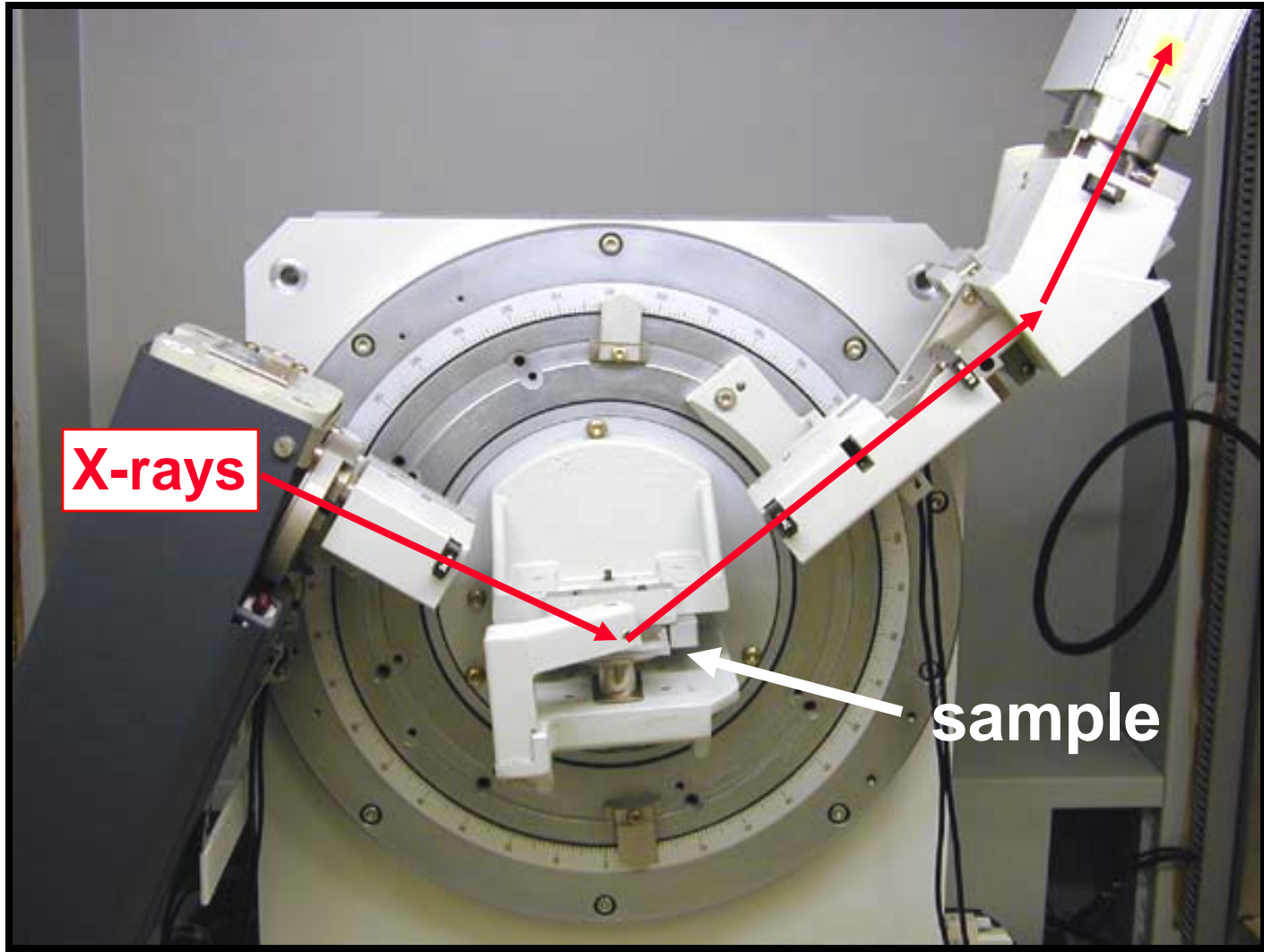
■ **Siemens (Bruker AXS) D5000 X-ray powder diffractometer.**

Quantitative phase analysis
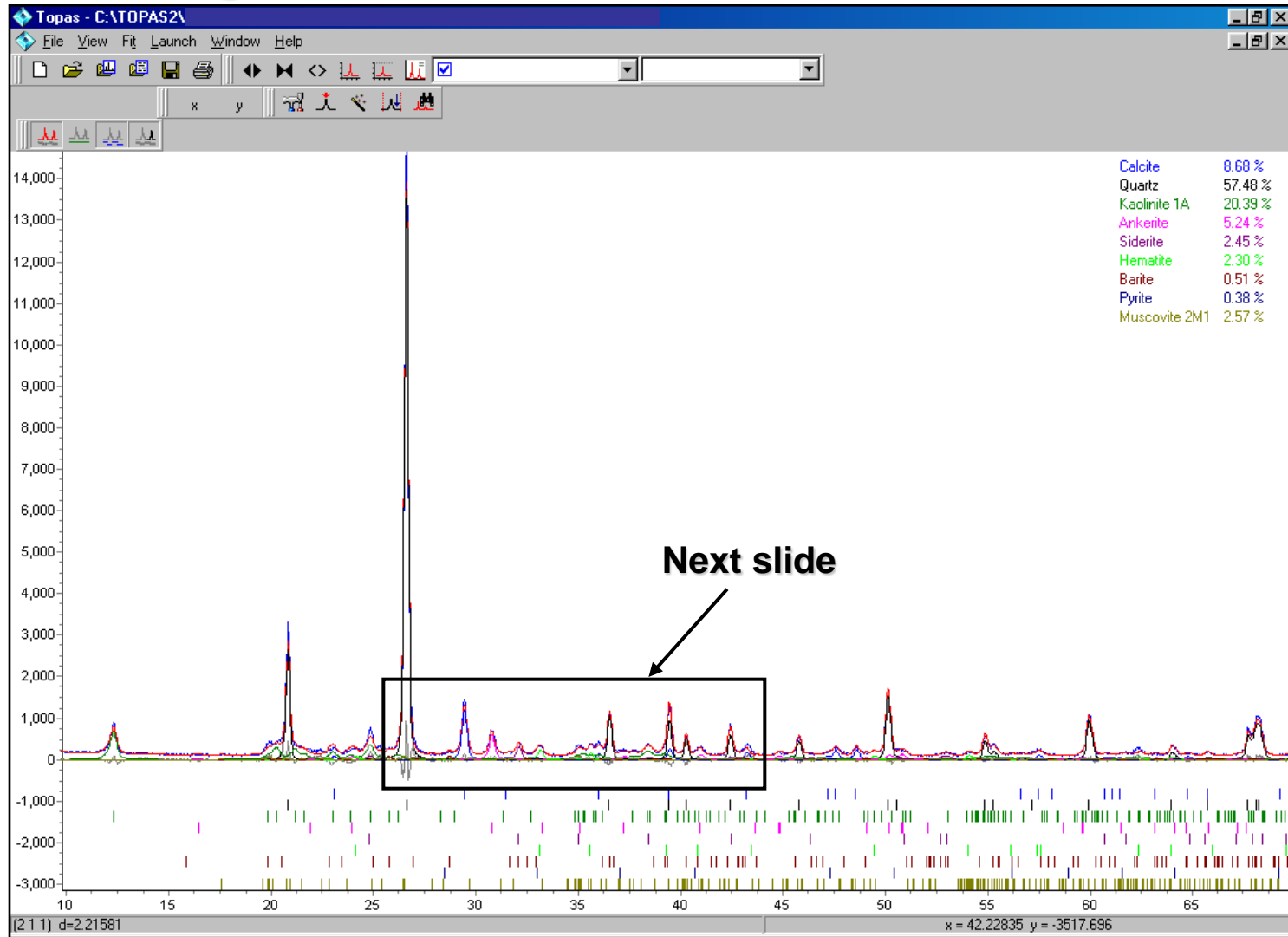## of coexisting calcite, siderite and ankerite in waste rock

- **Step-scan X-ray powder-diffraction data were collected over a range 3-70°2θ with CuKα radiation on a standard Siemens D5000 Bragg-Brentano diffractometer equipped with a diffracted-beam graphite monochromator crystal, 2 mm (1°) divergence and antiscatter slits, 0.6 mm receiving slit and incident-beam Soller slit.**

- **The long sample holder used (43 mm) ensured that the area irradiated by the X-ray beam under these conditions was completely contained within the sample.**

- **The long fine-focus Cu X-ray tube was operated at 40 kV and 40 mA, at a take-off angle of 6°.**

Quantitative phase analysis of coexisting calcite, siderite and ankerite in waste rock
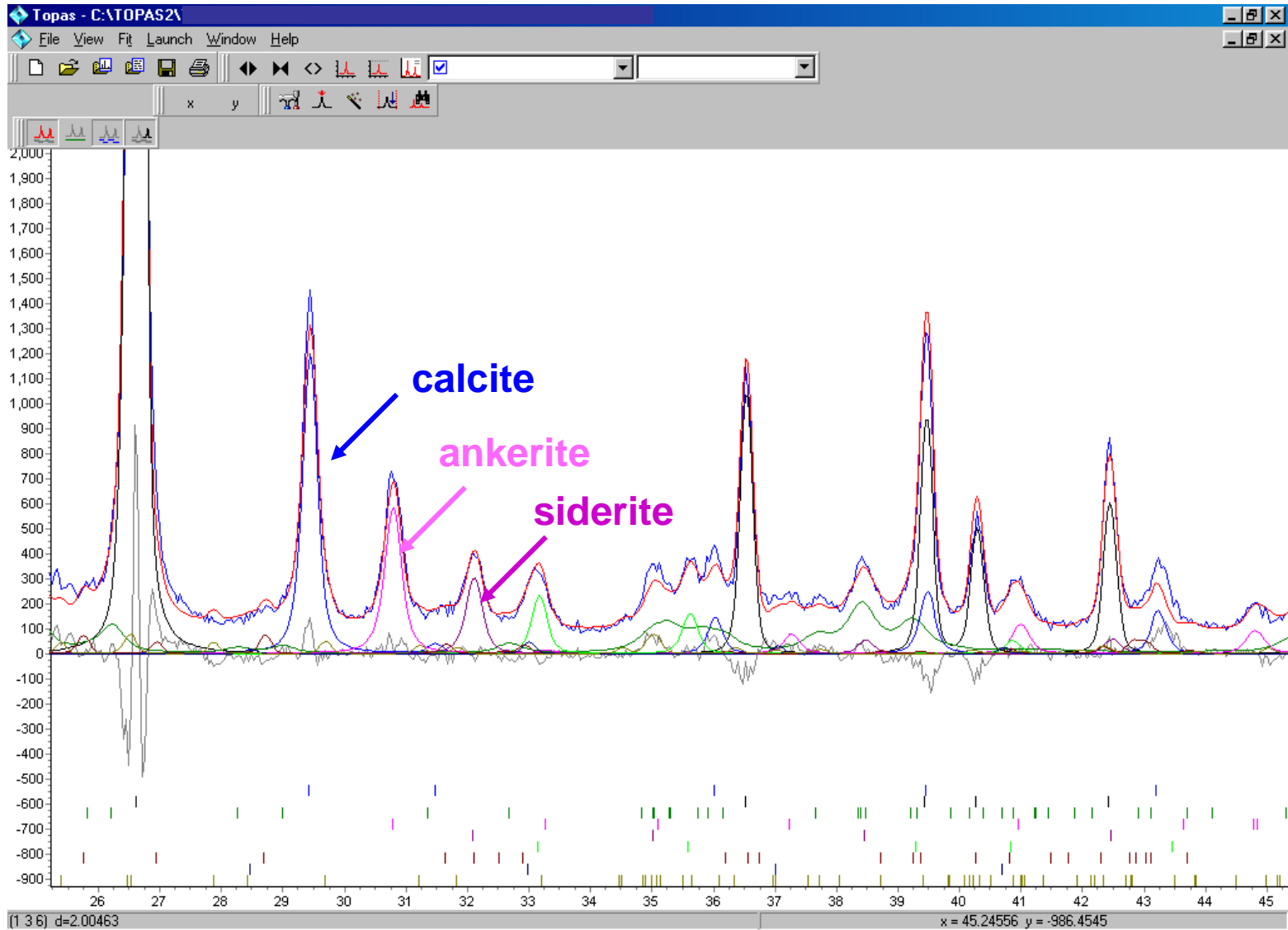
■ **Results of quantitative phase analysis:**

Phase	Wt.%
Calcite	8.7 (0.2)
Siderite	2.5 (0.2)
Ankerite	5.2 (0.2)
Quartz	57.4 (0.4)
Muscovite	2.6 (0.3)
Pyrite	0.4 (0.1)
Kaolinite	20.4 (0.4)
Hematite	2.3 (0.2)
Barite	0.5 (0.1)
Total	100.0

Quantitative phase analysis
of coexisting calcite, siderite and ankerite in waste rock

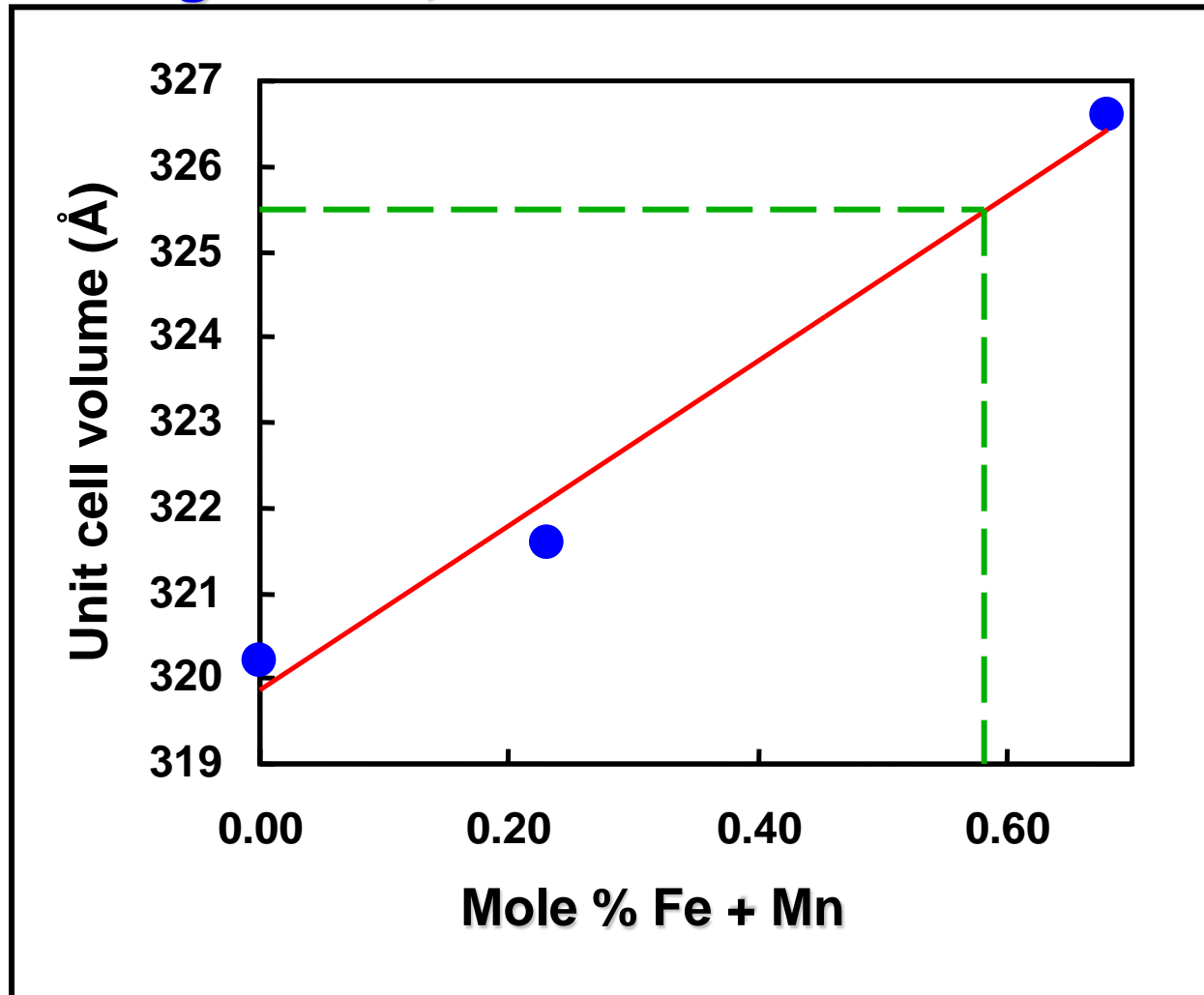**■ Rietveld refinement plot: waste rock from cherty sediments**

Quantitative phase analysis
of coexisting calcite, siderite and ankerite in waste rock

■ **Zoomed Rietveld plot:** **calcite - blue**, **siderite – purple**, **ankerite - magenta**
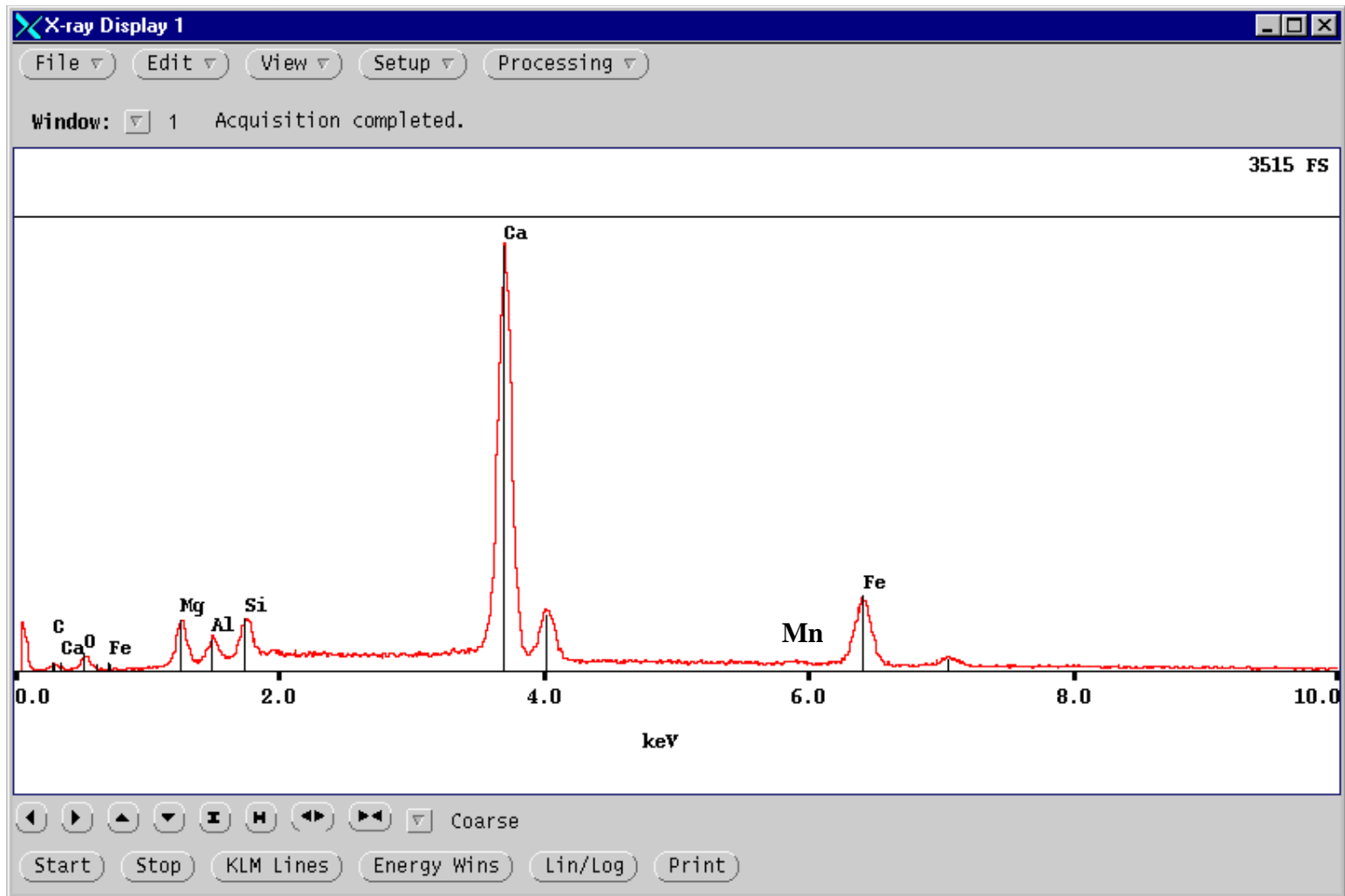
Quantitative phase analysis
of coexisting calcite, siderite and ankerite in waste rock

- Cell volume of ankerite vs. mole% (Fe + Mn). Blue points are from published single-crystal structure studies. (Fe + Mn)(ankerite) = 0.58 mole%.

Quantitative phase analysis
of coexisting calcite, siderite and ankerite in waste rock

■ **Energy-dispersion X-ray spectrum of ankerite. Al and Si are from mineral dust contaminating the carbonate grain.**

Summary

- **X-ray powder diffraction studies are not restricted to simple "fingerprinting" of crystalline phases**

- **The amounts of calcite-group and dolomite-group minerals (calcite, siderite, dolomite, ankerite) may be measured quantitatively using the <u>Rietveld method</u>**

- **The amounts of <u>all other minerals</u> may also be measured simultaneously**

- **Fe and Mn content in minerals cannot be directly distinguished using X-ray diffraction (similar X-ray scattering power)**

- **Specific elemental compositions are best measured using <u>electron-probe microanalysis on polished thin sections</u>**

Software for Rietveld Analysis

- **Two user-friendly (expert user) commercial programs:**
  - **Topas 2.0 (Bruker AXS)**

    http://www.bruker-axs.com/production/products/xrd/software/topas/
  - **Siroquant 2.5 (Sietronics Pty. Ltd) – has refinable clay patterns**
  - **http://www.sietronics.com.au/siroqnt/siroqnt.htm**
- **There are also many good freeware programs (not user-friendly, expert). For a complete list see:**
  - **http://www.ch.iucr.org/iucr-top/comm/cpd/rietveld.html**