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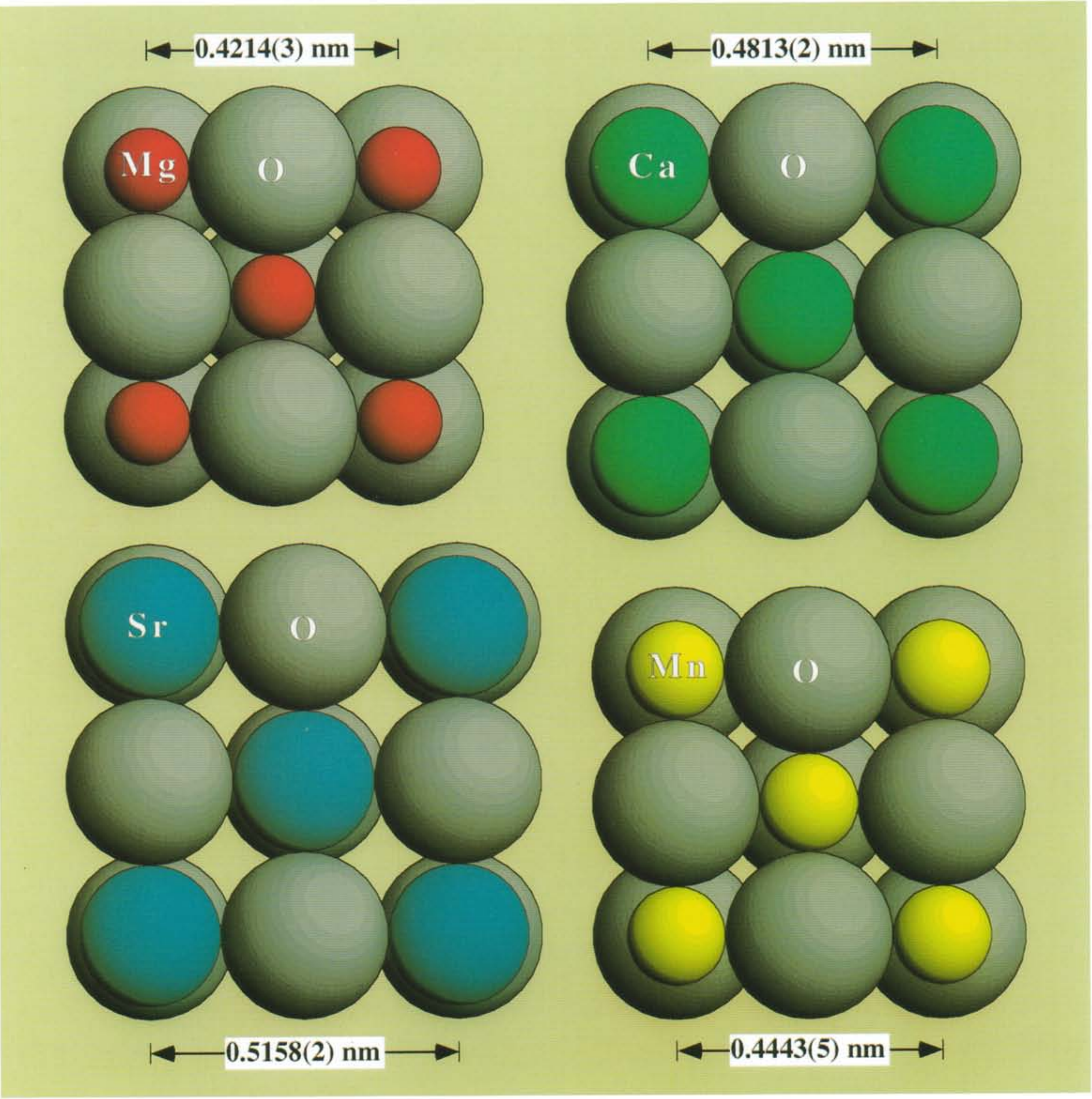

New Uses for Powder X-Ray Diffraction Experiments in the Undergraduate Curriculum

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ABSTRACT

Modern, computer-controlled powder diffractometers have made x-ray diffraction truly accessible to undergraduate students. Rugged, highly accurate goniometers that rarely need alignment, software-directed data acquisition and analysis, and on-screen comparison of data with powder diffraction standards leave sample preparation as almost the only non-keyboard skill required. These advances make it possible for students to concentrate on the information that can be gained from the diffraction experiment, rather than on the mechanics of data collection and analysis. In effect, the x-ray diffractometer has become an instructional aid in our classes. In addition to the usual identification of mineral unknowns and quantitative (modal) analysis of fine-grained rocks, our students have used x-ray diffraction: (1) to measure the ionic radii of cations; (2) to determine the chemical composition of olivine crystals; (3) to monitor the progress of phase transformations; and (4) to determine the clay mineralogy of soil samples. These projects help move mineralogy courses beyond description and into the realm of experimental science.

Keywords: Apparatus; geology – teaching and curriculum; mineralogy and crystallography.

Introduction

Diffraction of x-rays by crystals is one of the most exciting experiments accessible to undergraduate geology students. This is because x-ray diffraction offers very strong evidence that minerals consist of periodic arrays of atoms, with an array spacing close to the wavelength of x-rays. Furthermore, powder x-ray diffraction profiles can be used to identify unknown minerals even if the crystals are too small for many other measurements. These are the major reasons x-ray diffraction has long been included as a topic in mineralogy classes.

Until recently, we found that x-ray diffraction experiments were difficult to do well. Our x-ray equipment was unreliable, often out of alignment, and rarely produced good data. Students used the x-ray equipment only as part of an assignment or a special research project. All of this has changed due to the acquisition of a powerful, precise, computer-controlled, powder diffractometer. We now use x-ray diffraction as an integral part of several courses. Because it is so easy to collect good x-ray data, we find that powder diffraction is no longer an end in itself, but has become a handy tool that can be used to help us explore other topics. What follows is a description of some of the pedagogic uses of x-ray diffraction that we have implemented successfully in our courses.

Measuring the Sizes of Atoms

Many important concepts of crystal chemistry are based on the hypothesis that atoms come in different sizes, depending on the element, charge, coordination number, and so on. It is no longer necessary to ask students to accept this hypothesis on the basis of other people's experiments. Powder x-ray diffraction experiments can be conducted by the students in a mineralogy class to measure for themselves the sizes of atoms.

Data collected by a Smith College mineralogy class on the simple isostructural oxides periclase (MgO), lime (CaO), manganosite (MnO), bunsenite (NiO), and strontium oxide (SrO) are shown in Figure 1. These compounds, although rare as minerals, are readily available from chemical supply companies. All have the periclase/halite structure based on a cubic closest packing of oxygen anions with divalent cations filling all of the octahedral sites. Notice the similarity of the diffraction patterns! The strong peaks have the same Miller indices and relative positions, however, the 2θ angle and, therefore, d-spacing, of peaks with the same Miller index is different for each pattern. If the structure is the same and the anions are the same, then the differences in the patterns must be due to differences in the cations.

These patterns were collected jointly by small groups of students as they learned to use the powder diffractometer. Each group studied only one of the oxides. The students calculated unit-cell dimensions from their data using a least-squares lattice-refinement program that is included with the diffractometer, although it could be done with a calculator for these cubic minerals, with a spread sheet template (Novak and Colville, 1989), or with other software (for example, see Burnham, 1991). The unit-cell edge of the periclase structure has a length equal to the sum of the diameters of the oxygen anion and the divalent cation (see cover photo). Assuming that the oxygen anion has the same radius (0.140 nm) in each oxide, it is possible to calculate the cation radius implied by the size of each unit cell (Table 1). Calculated radii for these rapidly collected data (10° 2θ per minute) are very close to those given by Shannon and Prewitt (1972) based on a much more exacting analysis. The cover photograph shows a view of the oxide structures based on the measured cation sizes and adds

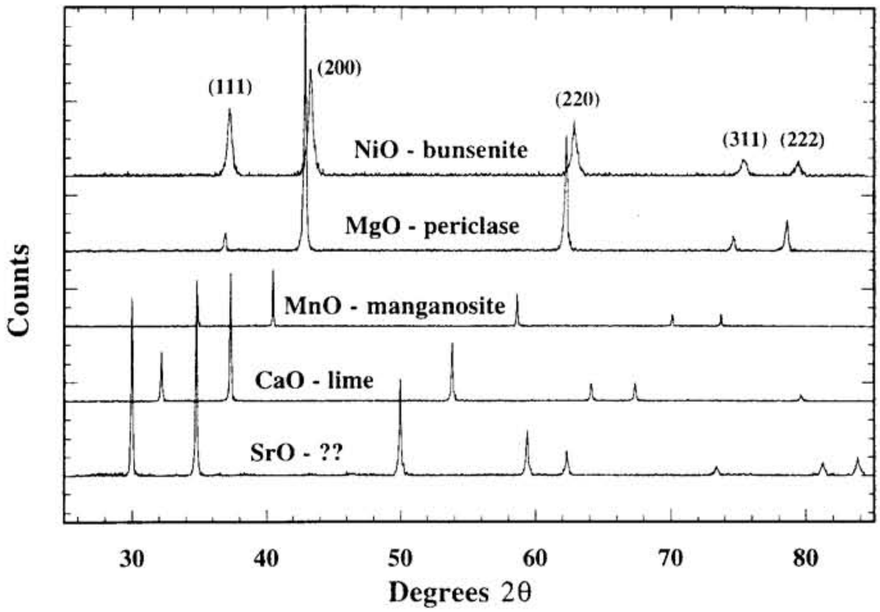

Figure 1. X-ray diffraction profiles for powders of the five, isostructural, cubic oxides NiO, MgO, MnO, CaO, and SrO. Note that the profiles are very similar, but that the positions of the diffraction peaks are systematically shifted. The observed differences in interplanar spacing may be attributed to differences in the effective radii of the cations with $Ni^{+2} < Mg^{+2} < Mn^{+2} < Ca^{+2} < Sr^{+2}$ (Table 1).

Oxide	Unit Cell a (nm)	Unit Cell a (nm)	ICDD Card No.	Oxygen r (nm)	Cation r (nm)	Cation r (nm)	Cation
	measured	ICDD file		assumed	calculated	Shannon	
NiO	0.4178(4)	0.41769	4-835	0.140	0.069	0.069	Ni^{+2}
MgO	0.4214(3)	0.4213	4-829	0.140	0.071	0.072	Mg^{+2}
MnO	0.4443(5)	0.4445	7-230	0.140	0.082	0.083	Mn^{+2}
CaO	0.4813(2)	0.481059(9)	37-1497	0.140	0.101	0.100	Ca^{+2}
SrO	0.5158(2)	0.516	6-520	0.140	0.118	0.118	Sr^{+2}

Table 1. Ionic radii (r) for five divalent cations calculated by mineralogy students from unit cell parameters (a) of the respective oxides that were determined by the class. Unit cell results are compared with the unit cell data compiled in the International Centre for Diffraction Data (ICDD) Powder Diffraction File Computer Data Base. Calculated ionic radii are compared with the ionic radii for 6-coordination compiled by Shannon (1976).

graphical meaning to the concept of ionic "porosity." Additional data might be collected for other minerals to demonstrate the effects on atomic radii of coordination number, valence, or bond type.

Determining the Chemical Compositions of Mineral Solid Solutions

Once students have seen that different atoms have different diameters, they are primed to accept x-ray evidence for mineral solid solutions. Olivine is a good candidate for these measurements because its lattice parameters are linear functions of composition, Fe^{+2} being larger than Mg^{+2}. Other minerals that might be used include orthopyroxene, alkali feldspar, and cummingtonite. None of these is uniquely binary, so some error is likely if additional components are present.

A collection of rocks containing olivines with a variety of compositions is preferred, but an alternative is a collection of powdered olivines that can be reused. Students collect x-ray powder patterns from the olivines separated from their rock. They determine the olivine composition by one of several methods. They may use the position of the (130) peak relative to an internal standard peak along with the calibration of Schwab and Kustner (1977), or they may determine the unit cell volume of their sample and use a linear standard curve to extract the composition from the tabulated unit cell values for pure forsterite and fayalite. Results can be compared with specific-gravity or refractive-index measurements or, better still, with electron microprobe compositions. Juxtaposition of the diffraction patterns from several olivines emphasizes the effect of composition on peak positions (Figure 2).

Monitoring Phase Transformations

Solid-state phase transformation is an important topic in mineralogy that is likely to seem rather abstract to students. We have used the powder diffractometer to detect phase transformations that occur when students heat minerals in a simple box furnace (1100°C maximum temperature, approximate cost $1300). For example, the first "lime" diffraction pattern obtained for the ionic-radius experiment described in a preceding section showed that the old stockroom CaO had hydrated and carbonated on the shelf to become portlandite ($Ca(OH)_2$) and calcite ($CaCO_3$). Heating this mixture to 800°C for one hour caused dehydration and decarbonation reactions and yielded excellent lime (CaO). Superimposing the diffraction patterns of the reactants and products convincingly demonstrates the phase changes (Figure 3).

Silica polymorphs are commonly used in discussions of phase transformations. We have tried a number of experiments with silica to explore these transformations with interesting results that can be evaluated by powder diffraction. Quartz is a very stable mineral and will survive at high temperatures metastably for days (at least). More response is obtained by heating silicic acid, an amorphous form of silica

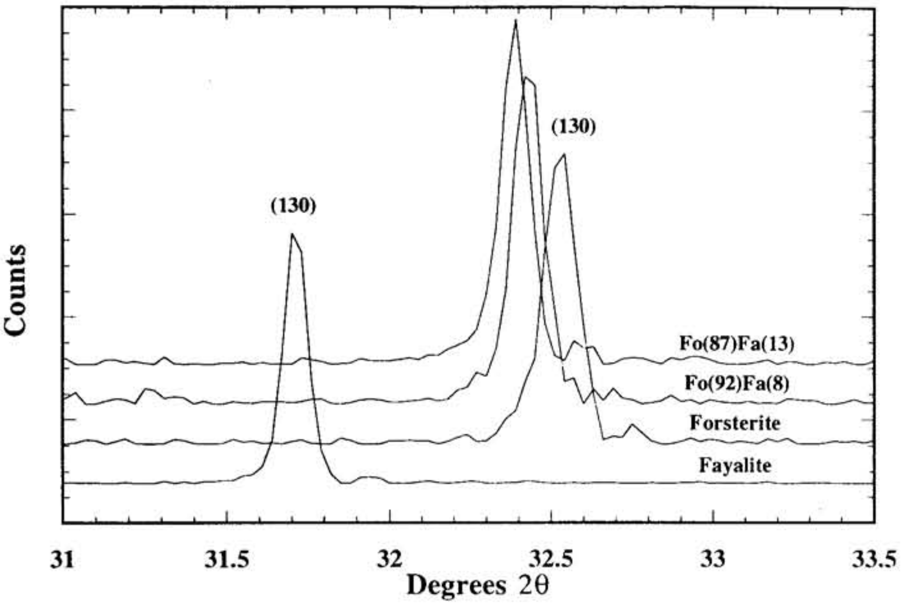

Figure 2. Portions of the x-ray diffraction profiles for powders of 4 olivines. The samples include a synthetic fayalite and three natural olivines. Note that the position of the (130) peak varies with olivine composition. More iron-rich olivines have larger values of $d_{(130)}$ and, therefore, smaller values of $2\theta_{(130)}$ than more magnesian olivines.

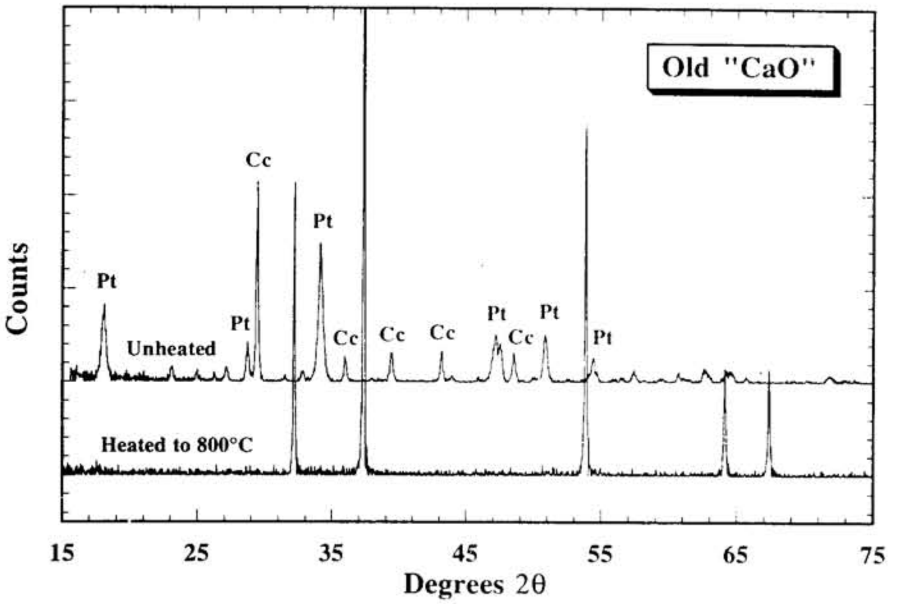

Figure 3. X-ray diffraction profiles for powders of an old sample of "CaO" and the same sample after heating for one hour at 800°C. Peaks on the profile of the old sample match portlandite (Pt), $Ca(OH)_2$, and calcite (Cc), $CaCO_3$. After heating all the peaks match lime, CaO.

available from chemical supply catalogs. A powder-diffraction pattern (Figure 4) of silicic acid has no sharp peaks, only a "glass hump" due to short-range order in the glass with a spacing (0.394 nm), which is related to the size of the SiO_4 tetrahedra. Silicic acid heated at 1500°C for one hour crystallizes to a powder of cristobalite that gives an excellent diffraction pattern (this requires a more expensive high-temperature furnace). Heating for various times and temperatures in the more accessible tridymite "stability" field yields changes in the shape and position of the broad glass peak and even "metastable" cristobalite.

Heating experiments give students tangible evidence of phase transformations and provide excellent opportunities to discuss topics ranging from mineral stabilities to experimental petrology to kinetics. Many similar experiments are possible and we have as a goal trying at least one new experiment each year. For example, in future classes we plan to disorder an alkali feldspar, homogenize some exsolution lamellae, and conduct a time-temperature-transformation (TTT) study. Rapid, accurate powder x-ray diffraction makes this sort of laboratory experimentation accessible to undergraduate students.

Clay Mineralogy

Clay minerals receive little attention in many mineralogy classes, perhaps because it's difficult to do a hardness test or collect optical data on clay minerals. This neglect is especially unfortunate in light of the number of our students destined for careers in environmental geology. Good x-ray diffraction equipment makes clay minerals fair game for undergraduate students. In fact, the preparation of clays for diffraction is in some ways a logical extension of the experiments in mineral "behavior" discussed in the previous section.

We ask small groups of students to analyze the mineralogy of a clay-sized soil, till, weathered granite (grus), or lake sediment that were collected on a class field trip (if possible). In lab, the samples are disaggregated in a sonic dismembrator and a <2μm fraction is separated by spinning the resulting slurry in a centrifuge (Moore and Reynolds, 1989). Two strongly-oriented samples (to strengthen the (001) peaks) of each fraction are prepared by covering glass slides with the clay suspension and drying overnight. One sample of each fraction is held for 24 hours over a solution of ethylene glycol in a closed container.

X-ray diffraction patterns of the "coarse" and fine (<2μm) fractions are compared with patterns of the glycolated samples to look for expandable clays. The glycolated samples are then heated to 350°C for one hour and x-rayed again to see if the clay minerals will "collapse" due to the loss of interlayer volatiles (Figure 5). In some cases, the samples are also exposed to potassium-rich solutions to check for clays with a high interlayer charge (vermiculite). These clay-mineral experiments are reasonable because the x-ray data collection is fast and simple.

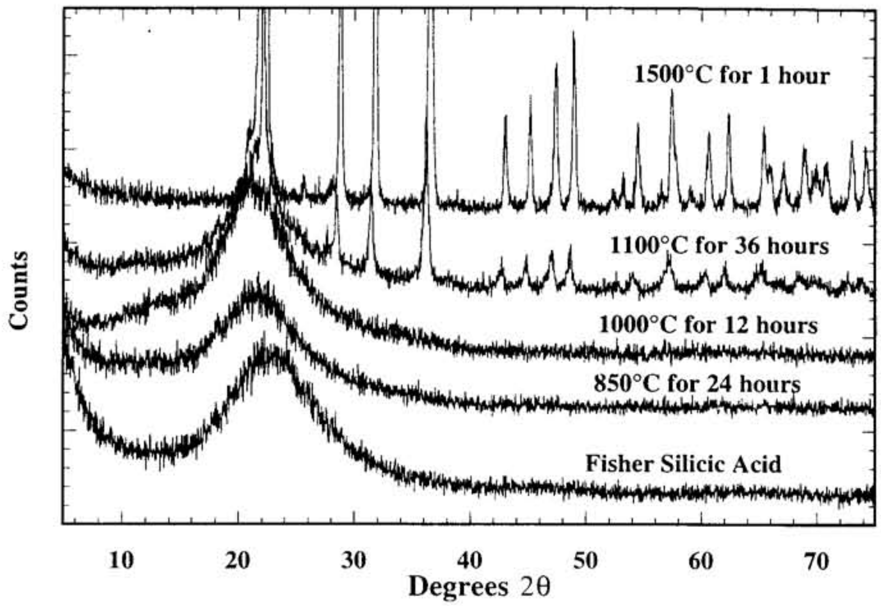

Figure 4. X-ray diffraction profiles for powders of Fisher silicic acid unheated and after heating at several temperatures. The profile of the unheated sample shows only a single, broad, glass peak at 22.6° 2θ, which corresponds to a d-spacing of 0.394 nm. Heating at 850° and at 1000°C caused only minor changes in the glass peak. Heating at 1100° and at 1500°C caused crystallization of cristobalite. Interestingly, the 1100°C "metastable" cristobalite has broader peaks, each at a higher d, than the equivalent peaks for the 1500°C "stable" cristobalite.

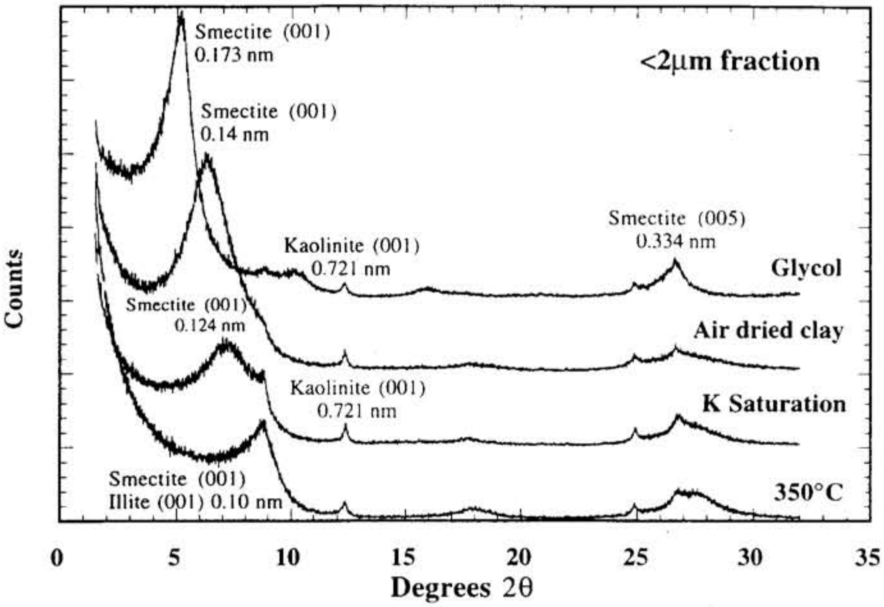

Figure 5. X-ray diffraction profiles for the fine fraction (<2μm) of a B-horizon soil developed on a Colorado end moraine. Shifting of the 0.14 nm peak to 0.173 nm upon exposure to ethylene glycol and its collapse to 0.10 nm upon heating demonstrate the presence of smectite. The absence of change in the 0.721 nm and 0.357 nm peaks after the same treatments confirms the presence of kaolinite.

Once the mineralogy of the samples has been determined, students can answer questions concerning the origin of the sediment. Is the till clay-rich because it incorporated a preglacial soil? What mineralogical changes occurred during the grussification of the granite? Questions like these help relate mineralogy to the material learned in other courses.

Discussion

X-ray diffraction is useful as a tool in mineral identification. Indeed, a computer-controlled diffractometer with a 2 kw generator and on-line access to a file of reference diffraction data makes x-ray mineral identification simple enough and fast enough for routine use by students. Powder x-ray diffraction is also useful in modal analysis of fine-grained rocks (Rosenberg and Barth, 1994). Our students use x-ray diffraction for these purposes. However, our interest in x-ray diffraction has increased considerably as we have learned to use it as a tool that permits us to include in our courses a variety of topics in an active, experimental fashion.

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Cover Photo

Solid-sphere models of one unit cell for each of the oxides MgO, MnO, CaO, and SrO. The unit cell dimensions and effective ionic radii depicted are those determined by mineralogy students (and listed in Table 1 of the article by John Brady and Robert Newton beginning on page 466). Note the increase in "porosity" as the size of the cation increases. This image was created with *ATOMS*, a computer program sold by Shape Software.