MAKING SOLID SOLUTIONS WITH ALKALI HALIDES (AND BREAKING THEM)

John B. Brady
Department of Geology
Smith College
Northampton, MA 01063
jbrady@science.smith.edu

INTRODUCTION

When two cations have the same charge and a similar radius, a mineral that contains one of the cations may contain the other as well, thus forming a *solid solution*. Common examples include Mg^{+2} and Fe^{+2} as in olivine, Na^{+1} and K^{+1} as in alkali feldspar, Al^{+3} and Fe^{+3} as in garnet. Some solid solutions are complete, so minerals may occur with the similar cations present in any proportion (e.g. olivine). In other cases, the solid solution is limited (e.g. alkali feldspar) so that some intermediate compositions cannot be formed, at least at low temperatures. Solid solutions are important because the physical properties and behavior of a mineral depend on its chemical composition.

In this exercise, the class will grow a variety of crystals of the same mineral, but with different chemical compositions. These crystals will be made from mixtures of halite (NaCl) and sylvite (KCl) that are melted and cooled. Because K^{+1} is significantly larger than Na^{+1}, the unit cell is larger in sylvite than in halite. Intermediate compositions have intermediate unit cell sizes. Thus, a measurement of the lattice spacing of the crystalline products of your experiments can be used to determine their chemical composition. The principle goal of these experiments is to demonstrate that solid solutions do occur and that their physical properties vary with their chemical composition. Additional goals include studying the effect of composition on melting, exploring the process of exsolution as a function of temperature, and seeing the effect of fluids and deformation on crystallization kinetics.

SAMPLE PREPARATION

- The class should work together in small groups to prepare a series of ten-gram mixtures of NaCl and KCl in simple molar proportions, say every 10 or 20 mole percent KCl depending on the number of groups. Ten grams is much more sample than you will need, but the reagents are inexpensive and weighing larger quantities will improve the accuracy of the resulting mixes (Why?). Because the gram formula weights of these compounds differ (NaCl = 58.4428 g/mole, KCl = 74.555 g/mole), some calculation is required to determine the appropriate mass proportions. Both NaCl and KCl are hygroscopic, so for the most accurate results you should use dry reagents that have been heated above 100°C and cooled in a dessicator.
- Be sure to record your calculations and reagent weights in your lab notebook.
- Mix the measured NaCl and KCl thoroughly.

PART I. MAKING SOLID SOLUTIONS BY CRYSTALLIZING FROM A MELT

Many minerals grow by crystallizing from a magma. The compositions of the minerals generally reflect the compositions of the melt from which they have grown. Granites are rich in potassium and the feldspar that grows from granitic liquids is orthoclase. Gabbros are rich in calcium and the feldspar that grows from gabbroic liquids is Ca-rich plagioclase. By cooling quickly from a NaCl-KCl melt, you should be able to grow alkali halide crystals that have the same composition as the melt.

- Place a modest amount (1-2 grams) of your mixture in an inexpensive porcelain crucible with a shiny glazed finish.
- Wearing heat-resistant gloves and using tongs, carefully place the crucible with your sample in a box oven set at 800°C. Although the melting temperature varies with composition, this temperature should be hot enough to melt any sample except pure NaCl, which melts at 801°C. (You can put a sample of pure NaCl in the oven if you want to check the temperature. If any melting occurs, the sample and oven have reached temperatures of 801°C or higher. In fact, melting points of pure substances like NaCl are so consistent that they are used to calibrate thermocouples and other high temperature thermometers.)

- When your sample has melted (5-10 minutes), carefully remove the crucible (it's now at 800°C!) from the oven with the tongs and gloves. Set the crucible on a heat-resistant surface and let it cool. Initially, the NaCl-KCl mixture should be molten. However, it will crystallize in a few seconds, cooling rapidly because the sample is small -- much more rapidly than most igneous rocks. Crystallization is very fast in this system and the crystals will have grown from the melt at high temperatures (probably above 600°C). The sample and crucible will contract upon cooling, making cracking sounds.
- Be sure to wear eye protection if you want to watch the crystals grow.
- After the crucible has cooled, the alkali halide crystals can be easily removed from the crucible with a spatula.

X-RAY DIFFRACTION

The easiest way to examine the crystals you have grown is with powder x-ray diffraction -- if you have an x-ray diffractometer. The ionic radius of potassium (0.138 nm) is considerably larger than the ionic radius of sodium (0.102 nm), if both are in six coordination with chlorine. Halite (NaCl) and sylvite (KCl) have the same crystal structure (they are isostructural) based on a cubic closest packing of large Cl- anions (radius = 0.181 nm) with the smaller cations (Na^{+1} or K^{+1}) filling all the six-coordinated (octahedral) sites. In sylvite the chlorine atoms are farther apart, to accommodate the larger K^{+1} ions, than they are in halite with its smaller Na^{+1} ions. Thus, the d-spacing of each lattice plane (hkl) in sylvite is larger than the d-spacing of the same plane (hkl) in halite. If a crystal has a composition intermediate between that of NaCl and KCl, the d-spacing for any plane (hkl) should be intermediate between that of the same plane (hkl) in halite and sylvite. If the solid solution is ideal, then there is no ΔV of mixing and a graph of the d-spacing vs. molar composition should be a straight line.

- The crystals you have grown are surprisingly unstable at room temperature. Therefore, crush the sample lightly in a mortar. **Grind as little as possible!**
- Because of the high symmetry of halite, very few planes (hkl) give strong diffraction peaks. To speed the analysis, scan a small range of diffraction angles (2θ) from 27° to 33°. This range of 2θ should include the (111) peak for your samples. Remembering Bragg's Law ($n\lambda = 2\, d \sin \theta$), which mineral, halite or sylvite, would you expect to have the larger 2θ value for each peak?
- A scan rate of $1°2\theta$ per minute is normally sufficient. Slower or faster scan rates may give you more or less accurate peak positions, respectively.

DATA ANALYSIS

- Also, measure the position of the (111) peak on diffraction patterns for halite and pure sylvite.
- Draw a graph with d-values on the y-axis and molar composition (from NaCl to KCl) on the x-axis.
- Plot $d_{(111)}$ for each sample at the appropriate composition on this graph.

- Connect the data points for pure halite and pure sylvite with a straight line. Do the data points for the other samples fall on the line? If not, are they distributed randomly about the line or do they fall systematically above or below the line? Do these data demonstrate that you have grown crystals of composition between NaCl and KCl?

PART II. OTHER EXPERIMENTS

Precipitation from an Aqueous Solution

- Both halite and sylvite are highly soluble in aqueous solutions. Dissolve 1-2 grams of your NaCl-KCl reagent mix in 10-20 cc of distilled water, stirring well.
- Evaporate the solution and collect powder x-ray diffraction data on the precipitate that remains.
- Explain your results.

Effects from Grinding

- Prepare a solid solution sample from an alkali halide melt as described in Part I and collect x-ray data after a light crushing.
- Grind the sample vigorously in a mortar and then collect x-ray data.
- Explain your result.

Effect of Water

- Prepare a solid solution sample from an alkali halide melt as described Part I and collect x-ray data after a light crushing.
- Grind the sample gently, but add a few drops of water to the mortar.
- Collect x-ray data and explain your result.

Melting Temperature

- Measure the melting temperature for a series of alkali halide crystals ranging in composition from pure NaCl to pure KCl.
- Graph the measured melting temperatures as a function of composition in the NaCl-KCl system.
- Your answer may differ if you start with a halite-sylvite mixture or with an alkali halide solid solution crystal prepared as in Part I. Why?

Breaking Solid Solutions

- Prepare a suite of solid solution samples from an alkali halide melt, as described Part I, and collect x-ray data after a light crushing.
- Anneal the samples in a 450°C oven (for 15 minutes?).
- Collect x-ray data on your sample and explain what your see.
- Repeat this experiment at other temperatures (350-500°C ?).
- Graph your data.
- Compare your results to the alkali feldspar phase diagram.

REFERENCES

Barrett, W.T., and Wallace, W.E. (1954) Studies of NaCl-KCl solid solutions. I. Heats of formation, lattice spacings, densities, Schottky defects and mutual solubilities: Journal of the American Chemical Society, 76, 366-369.

Levin, E.M., Robbins, C.R., and McMurdie, H.F. (1964) Phase Diagrams for Ceramists: The American Ceramic Society, Columbus, 601p.

NOTES TO THE INSTRUCTOR

These experiments are quite easy and satisfying to perform. The kinetics of crystallization, nucleation and growth, exsolution, and diffusion are quite rapid in the NaCl-KCl system, so quite a few experiments can be performed during one lab session. Because x-ray diffraction data is needed only for a 6° range in 2θ, characterization of the run products also can be completed quickly. The first part of the exercise as I have described it is very structured. Part II is less structured and more open-ended. Alternatively, you can design an exercise that gives the students less guidance and lets them discover for themselves the details of the NaCl-KCl phase diagram. However, because alkali halide crystals of intermediate composition are notoriously unstable at room temperature, I suggest that you at least warn students of this fact and give them guidance in preparing their samples for x-ray diffraction. When I first tried these experiments, I had some puzzling results due to grinding and also due to getting the sample damp while trying for a more rapid quench (hot ceramic crucibles crack if you set them in a pan of water!). Then I read that some of the chemists trying similar experiments (e.g. Barrett and Wallace, 1954) worked in a dry box to get consistent results! The following figures are the results of experiments with two different classes. The data are surprisingly good with minimal effort and care.

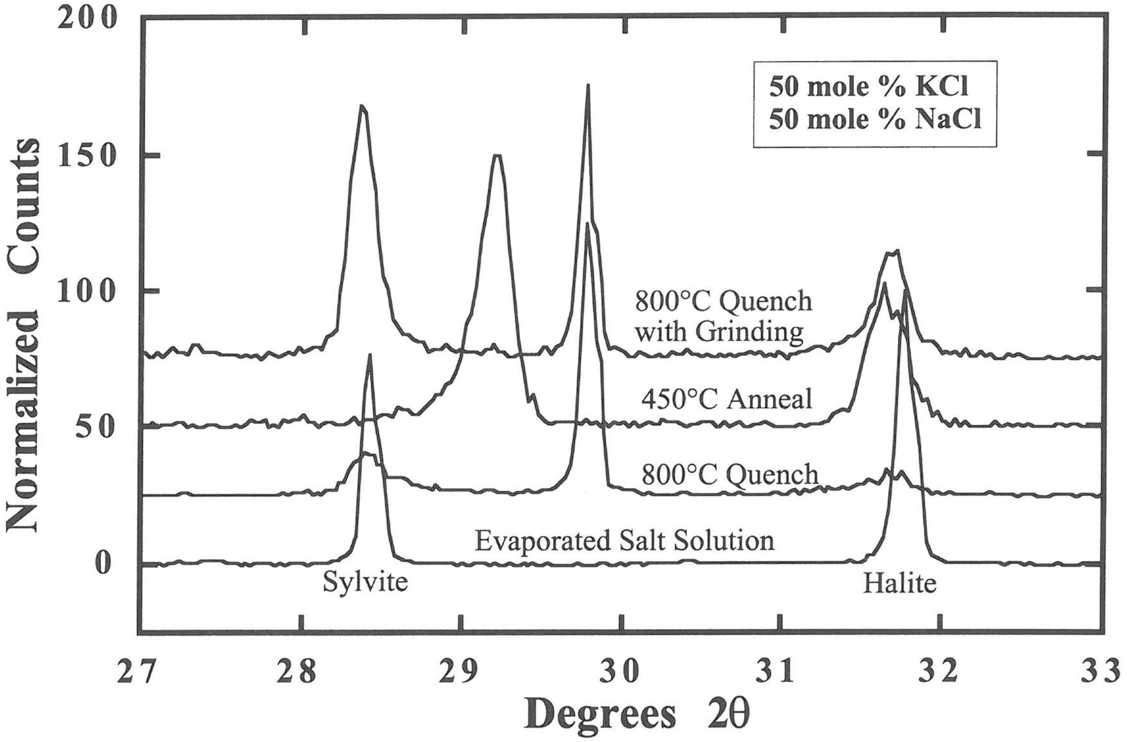

Figure 1. Class x-ray diffraction data for four experiments with a 50:50 KCl-NaCl mix. All peaks are for the (111) plane of sylvite, halite, or an alkali halide solid solution. The bottom line, which shows the location of the (111) peak for halite and sylvite, was obtained from a sample preciptated from an aqueous solution upon evaporation. The second line is for a nearly homogeneou solid solution sample quenched from an 800°C molten salt solution. The third line is for a sample that was first quenched from a melt and then held at 450°C for 24 hours. The two peaks show that both a potassium-rich and a sodium-rich alkali halide phase are present. The top line is for the quench sample of the second line that has been ground a short time in a mortar. Sylvite and halite peaks have appeared due to recrystallization during grinding.

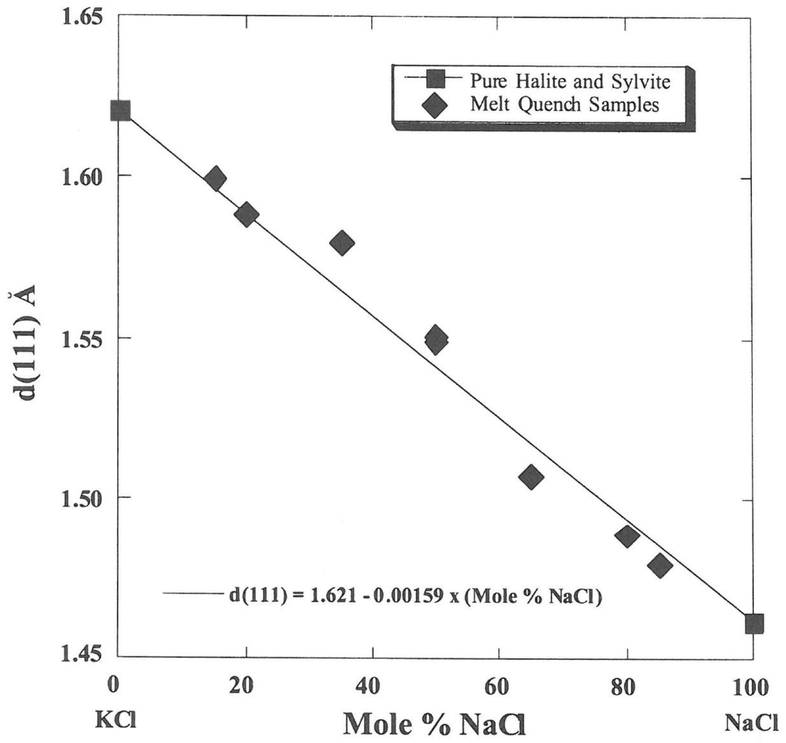

Figure 2. Class x-ray diffraction data for alkali halide solid solution samples quenched from alkali halide melts. The chemical composition of the melt mixture is given on the horizontal axis. The measured $d_{(111)}$ of the quenched products is given on the vertical axis. The line connects the observed $d_{(111)}$ values for sylvite and halite.

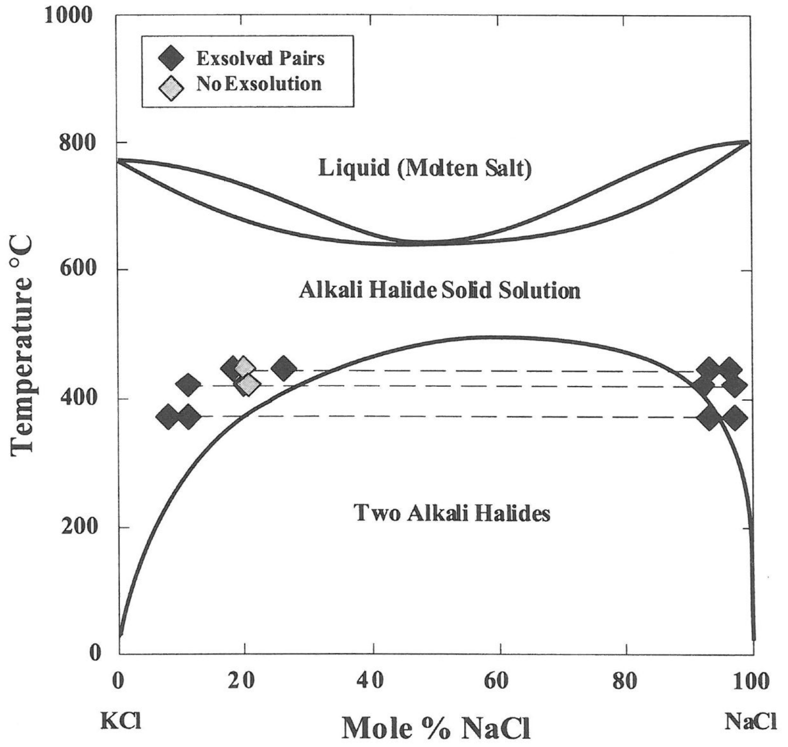

Figure 3. Class exsolution data for annealing of samples quenched from alkali halide melts. The dashed lines connects the observed alkali halide pairs. Two samples that did not exsolve are also shown. Compositions are based on measured $d_{(111)}$ values and the line in Figure 2. The solvus is from Barrett and Wallace (1954). The liquidus and solidus are schematic, but are based on the melting points of sylvite and halite and Figure 1258 in Levin et al. (1964).