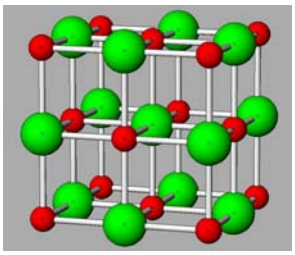
[1]Synthetic Alkali Halides



A Model for Crystallization from a Magma

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. Normal granites are rich in potassium (K), so feldspar that grows from granitic liquids is orthoclase (K-feldspar). Some magmas, however, contain significantly more sodium (Na) than potassium (K); they crystallize albite (Na-feldspar) instead. Magmas of intermediate composition may crystallize intermediate-composition feldspars under some, but not all conditions.

We would like to do experiments on feldspars to determine how they crystallize, but they melt at high temperatures – really too high for us to work with in the lab. So, we will use alkali-halides as surrogates.

Common salt is almost pure NaCl (halite). Sylvite, sometimes used as a salt substitute for people who are on high sodium diets, has composition KCl. For this project, we are going to melt NaCl, KCl, and mixtures of both, to make magmas. We will the crystallized the magmas and X-ray them to see what we get.

We are testing three hypotheses:

1. It is possible to crystallize alkali-chloride salts from a magma with any composition between NaCl and KCl.

2. Because K^+ and Na^+ do not have the same ionic size, the atomic spacing in alkali chlorides will vary systematically with composition.

3. Alkali chlorides are equally stable at high (just below liquidus) and low (subsolidus) temperatures.

<u>Procedure</u>

You will work in groups. Each group will mix up appropriate amounts of KCl and NaCl to produce some of the molar mixtures listed in the box on the next page. (The TA will determine which compositions should be made by which group.)

Note the table lists molar, not weight percents. You will have to convert from mole% to weight % before you weigh. FYI, the (gram) molar weight of NaCl is 58.4428; the molar weight of KCl is 74.555.

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[1]Exercise based on an article by J. Brady (in Brady, Mogk and Perkins, Teaching Mineralogy, Mineralogical Society of America, 1997)

Note 1: Both NaCl and KCl are hygroscopic, so: use the KCl and NaCl that are in the drying oven. You will have to use a mitten to take them out of the oven. Weigh them quickly to avoid burning your fingers.

Record all calculations and reagent weights in your notebook.

Target compositions

mix	mole % halite	mole % sylvite
Ha100	100	0
Ha90	90	10
Ha80	80	20
Ha70	70	30
Ha60	60	40
Ha50	50	50
Ha40	40	60
Ha30	30	70
Ha20	20	80
Ha10	10	90
Ha0	0	100

Part 1: Synthesizing Alkali Halides

1. For each composition, weigh out the reagents and mix well in a mortar with acetone. Mix up about 6 grams. This is more than you need, but sufficient in case you have to redo some experiments.

2. Place about 2 grams of your mixture in a porcelain crucible with a shiny glazed finish.

3. Wearing heat resistant gloves and using tongs, carefully place the crucible with your sample in the oven set at 850^{o}C. Although the melting temperature of alkali halides varies with composition, this is hot enough to melt any mixes in this experiment.

4. When your sample has melted (5-10 minutes) remove it quickly. Take care – it is very hot. Quickly pour it on the aluminum slab, and place the smaller piece of aluminum on top – press very gently or not at all. You have to do all this before the "magma" crystallizes – not much time. Be careful and speedy!

5. After 30 seconds remove the top piece of aluminum. After another 30 seconds, the sample will be cool enough to touch. Carefully affix to a glass slide as demonstrated by the TA. Then X-ray the sample.

Note 2: The crystals you grow are very unstable. That is why we do not grind them for X-ray. The technique given above yields good results most of the time – but may take a few tries to get figured out.

6. We are going to X-ray from 27^{o} to 33^{o} 2**2** only. In this range we will see a peak, called the (111) peak. Recall that X-ray peak angles depend on atomic spacing. For alkali halides, the angle (2$\mathbf{2}_{111}$) varies with composition because of the different sizes of Na^{+} and K^{+}. The appropriate equation relating distance to angle is Braggs Law:

$\lambda = 2\, d_{111} \sin\theta_{111}$

where λ is the wavelength of the X-radiation we are using (in this case copper K_α with a wavelength of 1.5418Å). d_{111} is the distance between layers of atoms causing the diffraction, and θ_{111} is <u>half</u> the angle measured with the X-ray goniometer.

As a class, we are going to share data. For each of your samples, collect an X-ray scan, use Jade to determine the angle of the (111) peak. Print off a copy of your diffraction pattern. Record your angles on the blackboard and give the copy of your X-ray pattern to the TA (who will distribute all the patterns to the rest of the class).

7. Look at all the X-ray scans – if some look bogus for some reason, make a note so you can ignore the results later if need be. Draw a graph with d-values on the y-axis and molar compositions (from NaCl to KCl) on the X-axis. Plot d_{111} for each sample (your's and everyone else's). If possible, draw a line or curve through the data and discuss what your graph shows. Do these data demonstrate that you have grown crystals having compositions between NaCl and KCl? How close do the data fit to your line/curve? What is the accuracy of your experiments? What is the precision of your experiments? Make sure you know the difference between accuracy and precision!

Note 3: Carefully preserve all specimens after X-raying. Put them in a vial and put the vial in the drying oven. No plastic caps on the vials, please!

<u>Part 2: What happens at lower temperature?</u>

8. Take your specimens (that is why you saved them after X-ray) and anneal them by putting them in the oven for 15-30 minutes (at a subsolidus temperatures determined by the TA). Your samples will go in in several batches – all will be annealed, but temperatures will vary between 350 and 500°C.

9. After your samples come out of the oven, repeat the X-ray measurements and share data as before.

10. Graph the results of the experiments as before. Interpret your results and compare them with the alkali feldspar phase diagram.

<u>Part 3: The Report</u>

Now, write up all results, complete with relevant graphs. Turn in a well constructed paper, following guidelines given by the TA. Evaluate each of the three hypotheses that we started with.

Additional Information: Alkali Feldspars and Alkali Halides

Alkali feldspars can have any composition between albite and orthoclase.

However, not all compositions are stable under all conditions.

The diagram at the right shows that all compositions are melted at high temperatures. There is a eutectic at about 1000 C - that is the lowest temperature at which there can be a melt.

Below 1000 C, down to around 600 C, any composition feldspar is stable.

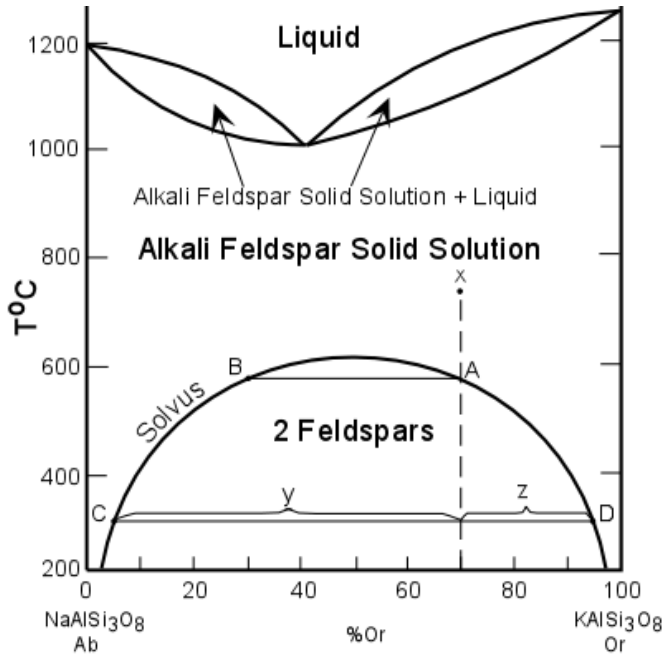

Figure 4

Beginning about 600 C, some compositions fall in the 2-feldspar field. We say there is a "miscibility gap." The curve that outlines the gap is called the "solvus."

Consider a happy feldspar of composition x. Let it cool and just below 600 C, it hits the solvus. Now, with further cooling it "unmixes." For example, when it gets to 300 C, it will have unmixed to form two distinct feldspars having compositions shown by the letters C and D. One is close to albite in composition, the other is close to orthoclase. If they are intergrown, they may form a compound mineral grain called "perthite." The relative amounts of the two feldspars can be determined by measuring the length of line segment y and z. (But, the calculation seems backwards.)

At 300 C:

y/(y+z) is the fraction of feldspar D.
z/(y+z) is the fraction of feldspar C.

For our experiments, we studied alkali halides instead of alkali feldspars. First we tried to synthesize all compositions at high temperature. We hoped we were above the solvus. Then we put the feldspar in an oven at lower temperature to see if they would unmix.

Your job, then is to look at the X-ray data and determine whether the alkali halide system is a good analog for feldspars. You have to evaluate and interpret all results.

Note: to analyze the alkali halides, we only looked for one X-ray peak. The (111) peak gives a direct measure of composition. If you X-ray one, homogeneous alkali halide, you get only one peak. If you analyze a mix, you may see several.