PHASE FUN WITH FELDSPARS: SIMPLE EXPERIMENTS TO CHANGE CHEMICAL COMPOSITION, STATE OF ORDER, AND CRYSTAL SYSTEM

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INTRODUCTION

Alkali feldspars form solid solution series ranging in chemical composition from $KAlSi_3O_8$ to $NaAlSi_3O_8$. In addition to K-Na chemical substitution, these minerals vary in the way aluminum (Al) and silicon (Si) ions are distributed among the symmetrically nonequivalent tetrahedral sites that make up their structures (Figs. 1 and 2). Two distinctly different kinds of distributions can be found. In low albite ($NaAlSi_3O_8$) and microcline ($KAlSi_3O_8$), both of which have triclinic symmetry, Al and Si are distributed among four symmetrically distinct tetrahedral sites (named T10, T1m, T20, and T2m), and most of the Al ions are concentrated in only one of these, Si filling the other three (a so-called "ordered" distribution). In analbite ($NaAlSi_3O_8$) and sanidine ($KAlSi_3O_8$), however, Al and Si are more-or-less randomly distributed ("disordered") between just two tetrahedral positions, T1 and T2 (the "0" and "m" positions having become symmetrically equivalent through mirror plane and rotational symmetry). Moreover, analbite and sanidine possess "topochemically monoclinic" Al-Si distributions, i.e., tetrahedral site occupancies consistent with monoclinic symmetry; this is not the case for low albite and microcline.

Despite the fact that analbite and sanidine have topochemically monoclinic Al-Si distributions, only the unit cell of sanidine has true monoclinic geometry at room temperature (although analbite can be converted to monoclinic geometry by heating to about 980°C). Relative to K-rich sandine, the smaller sodium ion in analbite causes a so-called displacive phase transformation that converts the structure to triclinic symmetry. Low albite and microcline, therefore, are triclinic for a different reason than analbite. The former minerals have Al-Si distributions that are inconsistent with monoclinic symmetry. The unit cell of analbite, on the other hand, is metrically triclinic due to Na.

In addition to the end members, some natural alkali feldspars have intermediate chemical compositions and Al-Si distributions. Virtually no naturally occurring "potassium feldspar" is devoid of sodium. And the potassic feldspar "orthoclase" has a monoclinic Al-Si distribution similar to that of sanidine, but with Al more abundant in the T1 site than in T2. For the purposes of this exercise, however, we shall focus only on the four end members: Low albite, microcline, analbite, and sanidine.

Sodium feldspars (low albite and analbite) can be converted to potassium feldspars (microcline and sanidine, respectively), or vica versa, through simple short-term "ion-exchange" experiments. This chemical conversion can be achieved easily by immersing feldspar grains in molten salts such as KCl, NaCl, KBr, or NaBr. In such experiments the feldspar grains exchange alkali ions with the molten salt according to reactions such as

$$NaAlSi_3O_8 + KCl \;\text{<--->}\; KAlSi_3O_8 + NaCl$$

Ordered feldspars, such as low albite and microcline, can be converted to disordered ones

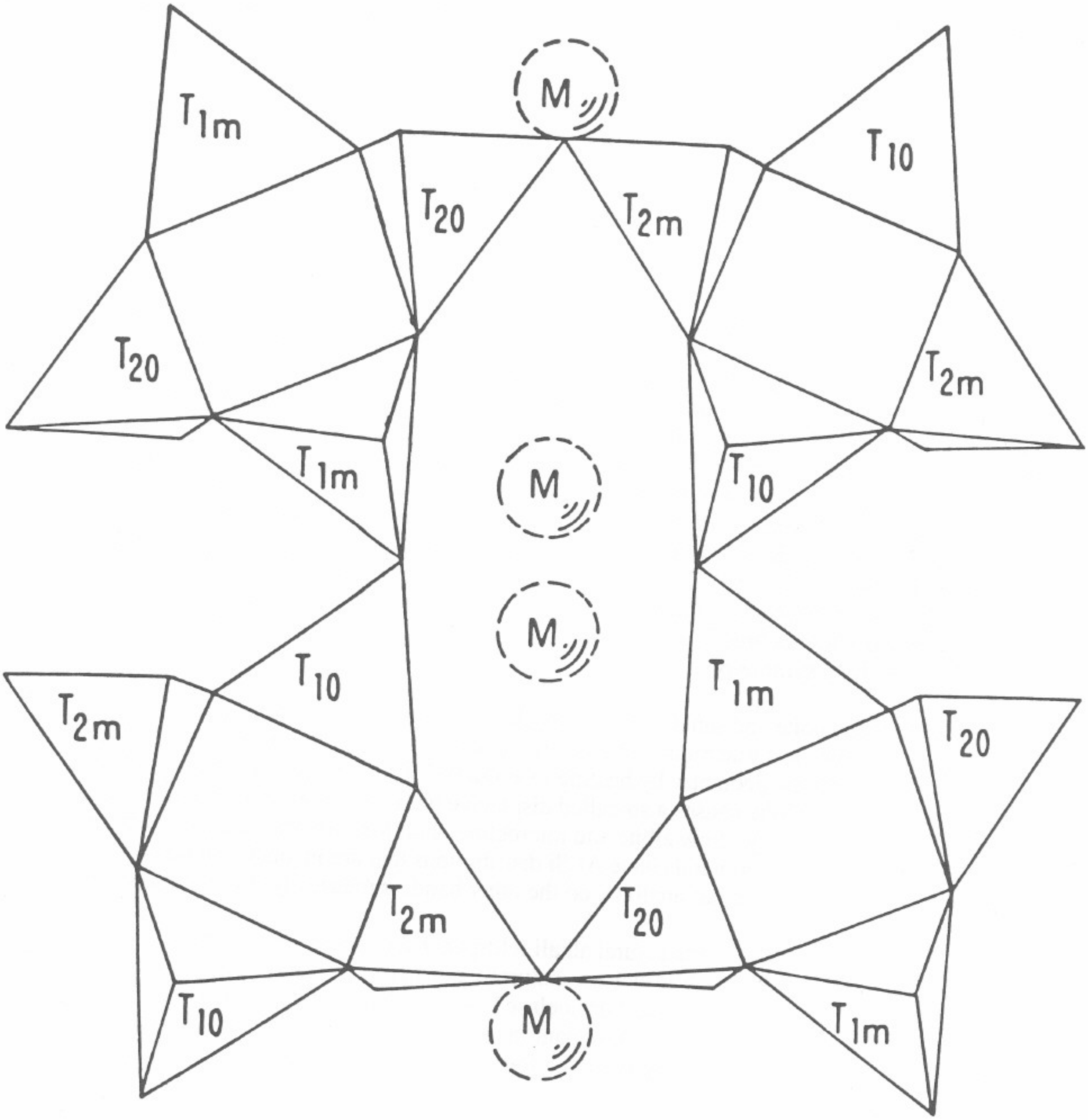

FIGURE 1. A portion of the triclinic alkali feldspar structure projected onto the ($\bar{2}01$) crystallographic plane. Symmetrically distinct tetrahedra are indicated by T10, T1m, T20, and T2m labels. The positions of alkali ions are designated "M."

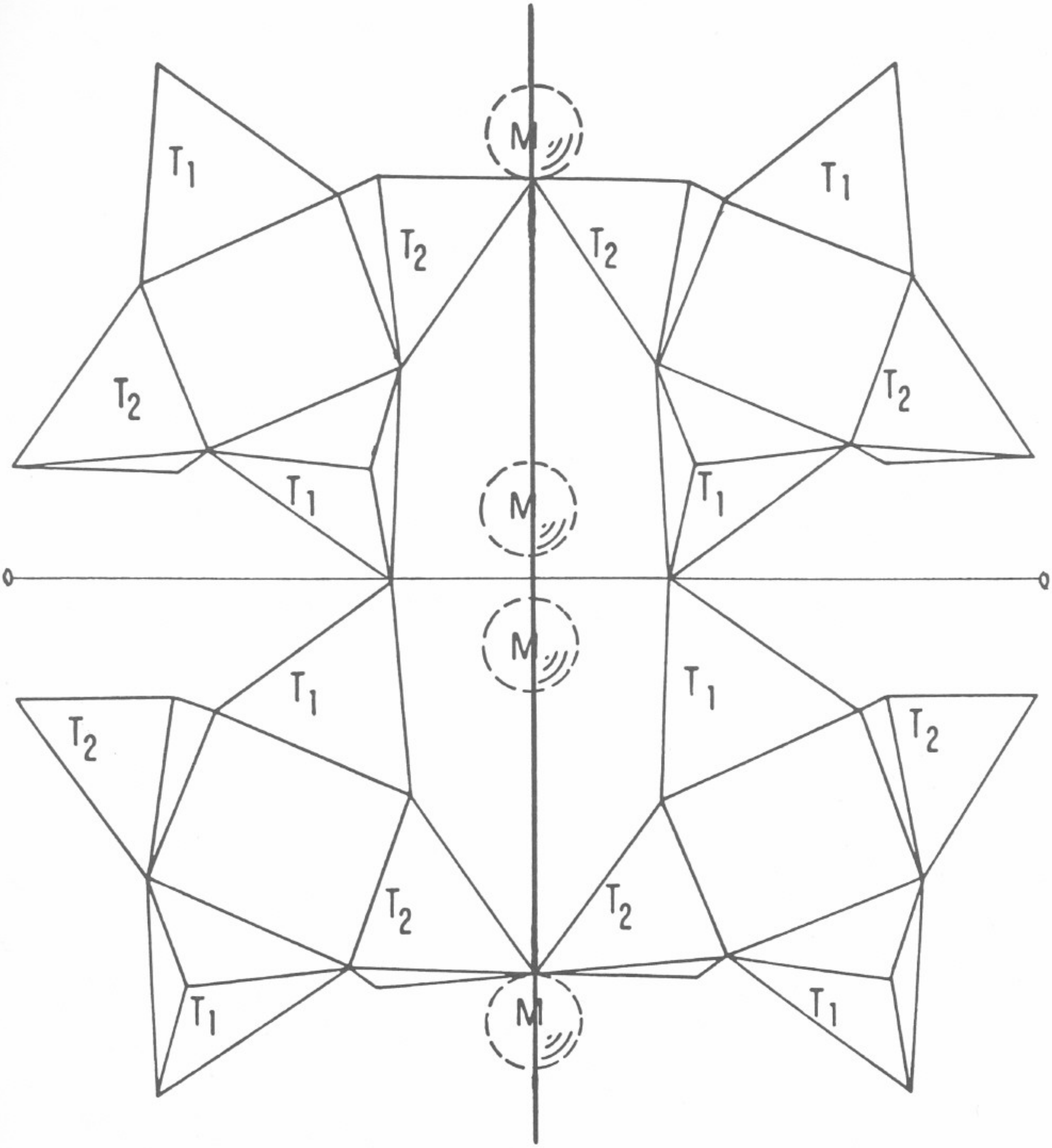

FIGURE 2. A portion of the monoclinic alkali feldspar structure projected onto the ($\bar{2}01$) crystallographic plane. Symmetrically distinct tetrahedra are labeled T1 and T2. Tetrahedra that had "0" and "m" designations as triclinic feldspars are symmetrically related in monoclinic feldspars by a mirror plane (heavy line) and a two-fold rotational axis (light line) perpendicular to the mirror plane. Thus, the number of distinct tetrahedral sites is reduced from four to two.

(analbite and sanidine, respectively) through long-term heating experiments that cause Al and Si to exchange places among the tetrahedra. Remember, even though analbite is metrically triclinic, its Al-Si distribution is disordered and consistent with monoclinic symmetry, so it can easily be transformed to true monoclinic geometry through potassium-exchange and conversion to sanidine. Relationships among the four end members are summarized as follows:

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                        ORDERED ALKALI FELDSPARS
                (TOPOCHEMICALLY AND METRICALLY TRICLINIC)

      LOW ALBITE *****************************MICROCLINE
      (TRICLINIC)                              (TRICLINIC)
           *                                        *
           *                                        *
           *                                        *
           *                                        *
SODIUM     *                                        * POTASSIUM
FELDSPARS  *                                        * FELDSPARS
           *                                        *
           *                                        *
           *                                        *
           *                                        *
           *                                        *
      ANALBITE ********************************SANIDINE
      (METRICALLY TRICLINIC)                     (METRICALLY MONOCLINIC)

                       DISORDERED ALKALI FELDSPARS
                        (TOPOCHEMICALLY MONOCLINIC)
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DATA COLLECTION

Each student should obtain an "unknown" feldspar end member from her/his instructor. Prepare the specimen for X-ray diffraction analysis, then collect X-ray data over a 2θ range from about 18° to 60° (if you are not using CuK_α radiation, your instructor will adjust these values).

X-Ray Data Analysis: There are significant differences among the X-ray diffraction patterns of the four alkali feldspar end members. Data for these can be found in Borg and Smith (1969; note that these authors refer to analbite as "high albite"). To become familiar with the differences among the patterns, you might first compare end-member X-ray data for the low-angle 2θ region (18° to 35°). Figures 1 and 2 in Hovis (1989) also can be helpful.

Composition Determination: Alkali feldspar composition is expressed by N_{Or}, the mole fraction of K in the mineral (e.g., if $N_{Or} = 0.9$, the feldspar formula is $K_{0.9}Na_{0.1}AlSi_3O_8$). The $(\bar{2}01)$ X-ray peak position varies nearly linearly with N_{Or} (Fig. 3) between 2θ values of about 21° for K-feldspars (N_{Or}=1) and 22° for Na-feldspars (N_{Or}=0). Find this peak and record its position.

A. Use Figure 3 to graphically approximate the chemical composition of your specimen from the position of its $(\bar{2}01)$ X-ray diffraction peak (or calculate composition from the equation given in the figure caption). Is your feldspar sodic or potassic?

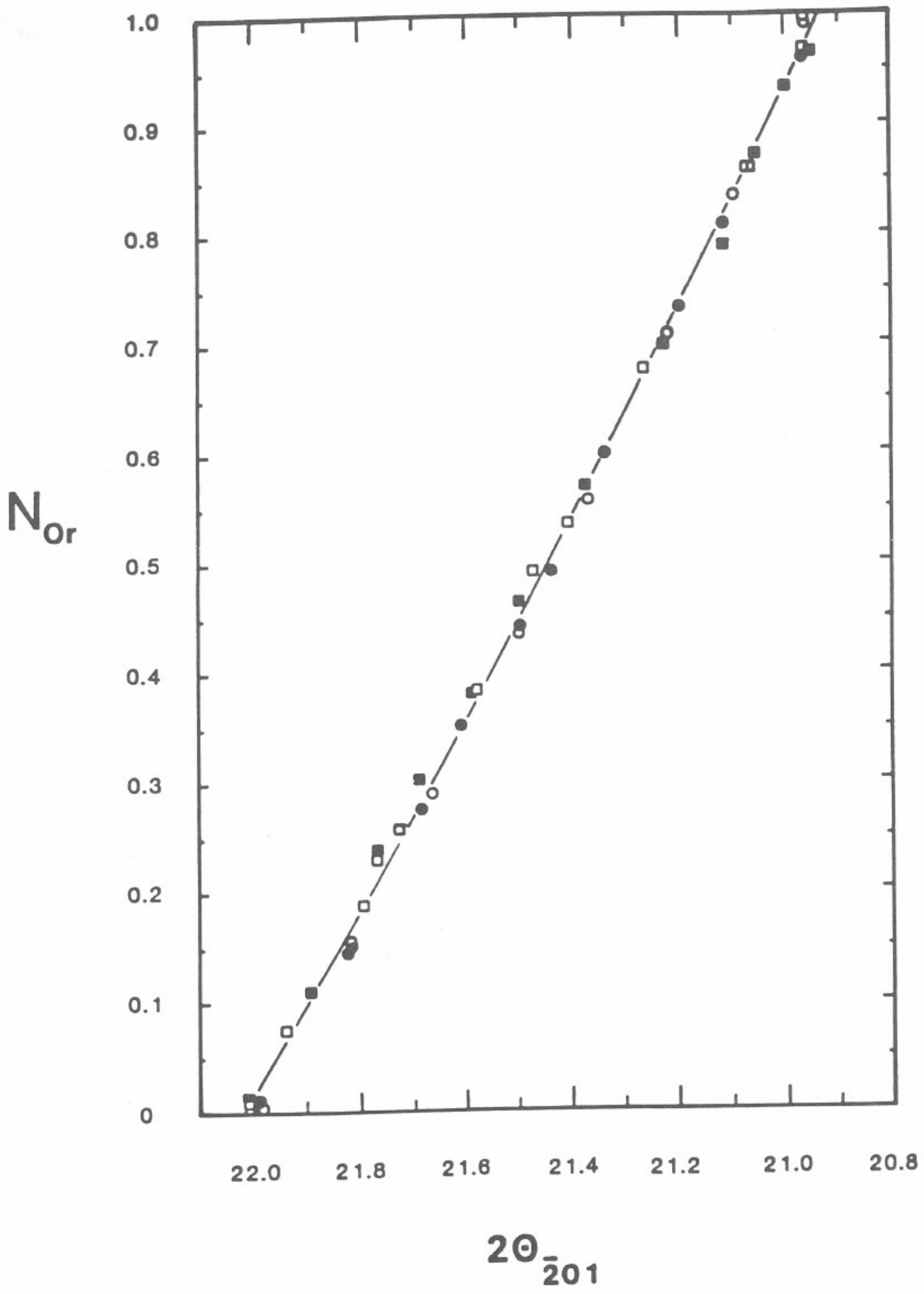

FIGURE 3. Plot of N_{Or} against 2Θ for the $(\bar{2}01)$ X-ray diffraction maximum (CuK_α radiation; Hovis, 1989). Data points are for feldspars with a wide range of Al-Si distributions. Compositions may be determined either graphically or by using the equation for the curve above: $N_{Or} = 70.726 - 5.6200\,(2\Theta) + 0.10936\,(2\Theta)^2$.

State of Al-Si Order: You can obtain an estimate of the Al-Si distribution in your alkali feldspar by comparing your X-ray data to those for the pertinent end members. You know from Part A whether your feldspar is sodic or potassic. Now compare your X-ray pattern to those of the appropriate end members in Borg and Smith (1969), low albite and analbite if your specimen is sodic, or microcline and sanidine if your specimen is potassic.

B. Which of the end-member X-ray patterns comes closest to matching your data?

Another measure of Al-Si distribution is based on the difference in the positions (2θ's) of the (131) and $(1\bar{3}1)$ X-ray peaks. Kroll and Ribbe (1983) have summarized $\Delta(2\theta)$ $[(131) - (1\bar{3}1)]$ values for the four alkali feldspar end members as follows: Low albite (+1.10°), analbite (+2.00°), microcline (-0.81°), sanidine (0.00°). [Sanidine is monoclinic, so its (131) and $(1\bar{3}1)$ peaks are equivalent.]

C. What is the difference in the 2θ positions of these peaks for your feldspar?

D. From this peak separation, and taking into account the chemical composition determined in Part A, what is the state of Al-Si order in your feldspar, "ordered" or "disordered?"

Experiments: Once you have obtained this baseline of information, try one or more of the experiments below and collect X-ray data from 18° to 60° on each product to see how the X-ray pattern has changed. After each experiment, determine the identity of the product by measuring the positions of the $(\bar{2}01)$, (131) and $(1\bar{3}1)$ peaks. Also note whether there are other differences in the diffraction patterns that help in determining chemical composition and Al-Si distribution.

EXPERIMENTAL PROCEDURES

Low Albite ---> Microcline

1. Grind low albite into a powder (fine enough to pass through a 200-mesh sieve).

2. Place the powder in a crucible appropriate to the temperature of this experiment (Pt works well but others may work also) containing a large excess of KCl. (Use a molar ratio K:Na > 100:1. Three grams of chloride for every 0.1 gram of feldspar will accomplish this.)

3. Mix the feldspar powder with the KCl.

4. Place a lid on the crucible.

5. Place the crucible in a box oven and increase the temperature to 30° above the melting point of the KCl (776°C + 30°C = 806°C). [**Warning:** Do not use research-grade equipment for this, because to a small degree evaporating KCl will contaminate the oven.]

6. Leave the crucible in the oven for 24 hours.

7. Remove the crucible from the oven (either at high temperature or after it has cooled). Cool to room temperature.

8. Place the resulting feldspar and chloride in distilled or deionized water (if the outside of the crucible is clean, you can simply place the entire crucible in a beaker and fill it with water). After some chloride has dissolved, pour off the solution (be careful not to lose feldspar), and add more water. Several rinsings will be required to remove all chloride; if you do not succeed in doing so, you will get both feldspar and chloride peaks in the X-ray spectrum.

9. Discard the final solution and dry the feldspar.

Microcline ---> Low Albite

1. Use the same procedures as above, but with microcline as the starting material, NaCl (melting temperature of 801 °C) as the exchange medium, and an oven temperature of about 830°C.

2. One difference between this ion exchange and the one above is that conversion of low albite to microcline cracks the feldspar (from expansion), whereas this reaction will not. So in the first case, if you do not grind the feldspar fine enough, the ion exchange will likely go to completion anyway. But in the microcline ---> low albite conversion, a coarse initial sample probably will result in an inhomogeneous final product (K-rich grain cores).

Low Albite ---> Analbite

1. Anneal low albite powder or a crystal at 1050°C. Several days (five) is probably enough time for conversion to analbite, but two or three weeks will guarantee success.

Microcline ---> Sanidine

1. Use the same procedure as low albite ----> analbite. In this case, however, you really will need three weeks at 1050°C to guarantee success, since this transformation is more sluggish than for the sodic analogs.

Analbite ---> Sanidine and Sanidine ---> Analbite

1. Use the same procedures as for low albite ---> microcline and microcline ---> low albite, respectively.

"Around the World"

1. If you want to be bold, try making all four phases starting with a single mineral. First convert microcline to low albite, then disorder the low albite to form analbite, then potassium-exchange the analbite to make sanidine! Or use the reverse route: low albite ---> microcline ---> sanidine ---> analbite. [Note: You will not be able to complete the circuit to the ordered phase, since disordered feldspars cannot be made to "reorder" in reasonable periods of time under dry conditions.]

Intermediate Compositions

1. You also can make intermediate compositions between low albite and microcline or between analbite and sanidine. Combine powders of the end-member phases in the molar proportions desired to synthesize the composition you want. [To do this you will have to think about how weights of the samples are related to moles.]

2. Mix the powders well (doing it in a fluid such as acetone helps), then pack the dry powders tightly into a crucible. [It helps to make a pellet using a pelletizer or to tamp down the powders with a bent spatula to promote as much grain-to-grain contact as possible.]

3. Place the crucible in a box oven and increase the temperature to 930°C.

4. The feldspar grains will chemically homogenize after about five days. It will help if you remove the crucible from the oven every 24 to 48 hours and remix the sample. This will aid ion exchange of K and Na between grains.

5. Remove the crucible from the oven while at high temperature. [This will require a pair of long-handled temperature-resistant tongs.] Allow the crucible to cool on a well-insulated bench top. A homogeneous K-Na feldspar should result.

6. Since K-Na substitution causes all X-ray peaks to shift positions, it will be difficult to compare X-ray data for intermediate compositions to those of end-member feldspars. However, even for these feldspars chemical composition can easily be determined through use of the $(\bar{2}01)$ peak/line (Fig. 3). Once composition has been established, data for additional peaks can be matched to those in Figures 1 and 2 of Hovis (1989).

FURTHER ANALYSIS OF STRUCTURAL STATE

For topochemically monoclinic feldspars a number of peak separations, some largely independent of composition [e.g., $(\bar{2}04)$-(060) and (060)-$(\bar{1}13)$], can be used to measure the degree of Al-Si order-disorder (see Figs. 3 through 6 of Hovis, 1989). Unit-cell dimensions also can be utilized to characterize composition and Al-Si distribution (see Hovis, this publication).

REFERENCES CITED

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NOTES TO THE INSTRUCTOR

For starting materials you can use natural low albite, microcline, or sanidine. If you want to use analbite, you will have to synthesize it using techniques described in the text. Sanidine also can be synthesized from either microcline or orthoclase through disordering experiments.

If your students are confused by the details of order-disorder relationships, do not be discouraged from running the lab; there are still lots of things you can do. It is enough for them to understand that there are differences among alkali feldspars in Al-Si distribution and that these are related primarily to temperature of equilibration.

There are a variety of ways that you can run this lab. For example, you could give different end members to different class members and have each identify the initial specimen. Then, you could assign each student (or group) an experiment, either ion exchange or disordering, and have them identify the final products. Note, however, that you will not be able to reorder disordered specimens.

Or you could give all class members the same initial mineral (preferably an ordered one), then have different students (groups) perform different experiments on it. Some students may want to do the whole "Around the World" tour.

Dexter Perkins has told me that he has students do time-based experiments to demonstrate kinetics. So one could run ion-exchange experiments for shorter periods of time (or with larger grain sizes) to demonstrate inhomogeneity of the final product (broad, or double, $(\bar{2}01)$ peak). One could do the same thing with disordering experiments. Dexter also indicated that he has his students do comparative chloride melt experiments using $CaCl_2$ as an exchange medium, then asks them to figure out why virtually no ion exchange with the feldspar took place.

You also can try ion exchange in mixed salts [e.g., (K,Na)Cl], but you should be forewarned that the resulting feldspar will not have the same composition as the initial salt, even if you swamp the system with salt. The alkali feldspar - (K,Na)Cl system forms a "reciprocal ternary," but the tie lines do not connect feldspar-salt pairs having the same K:Na ratio. A class project might be to figure out the configuration of the reciprocal ternary tie lines. A word of warning, though: the achievement of equilibrium in such experiments takes significantly longer than 24 hours. One thing you can try here also is to approach the equilibria from both directions (reversed equilibria) using sodic and potassic feldspars and various salt mixtures as starting materials in different experiments.

Along the same lines as above, you can try ion exchange experiments between feldspars and salt below the melting point of the salt. Yes, feldspars and salts do exchange ions under these conditions, providing the temperature is not too low. If you do this below the critical temperature of the feldspar solvus, you could wind up with two feldspars and salt as a final product!

Let your imagination run wild. There are lots of possibilities. Have phase fun with feldspars!