

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

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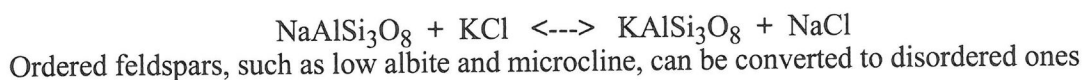
## INTRODUCTION

Alkali feldspars form solid solution series ranging in chemical composition from  $\text{KAlSi}_3\text{O}_8$  to  $\text{NaAlSi}_3\text{O}_8$ . 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 ( $\text{NaAlSi}_3\text{O}_8$ ) and microcline ( $\text{KAlSi}_3\text{O}_8$ ), 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 ( $\text{NaAlSi}_3\text{O}_8$ ) and sanidine ( $\text{KAlSi}_3\text{O}_8$ ), 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  $980^\circ\text{C}$ ). Relative to K-rich sanidine, 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 vice 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



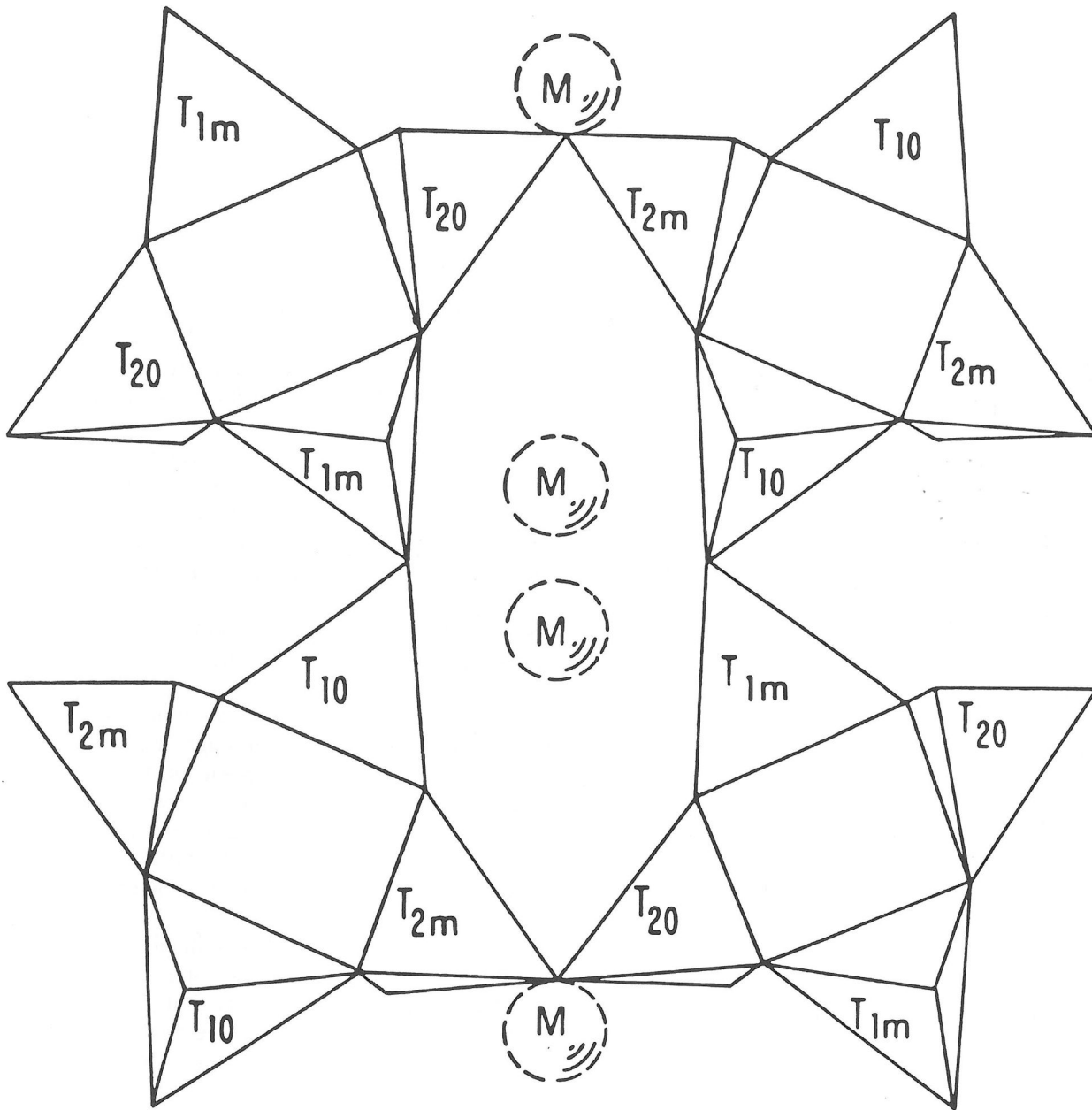


FIGURE 1. A portion of the triclinic alkali feldspar structure projected onto the  $(\bar{2}01)$  crystallographic plane. Symmetrically distinct tetrahedra are indicated by T10, T1m, T20, and T2m labels. The positions of alkali ions are designated "M."

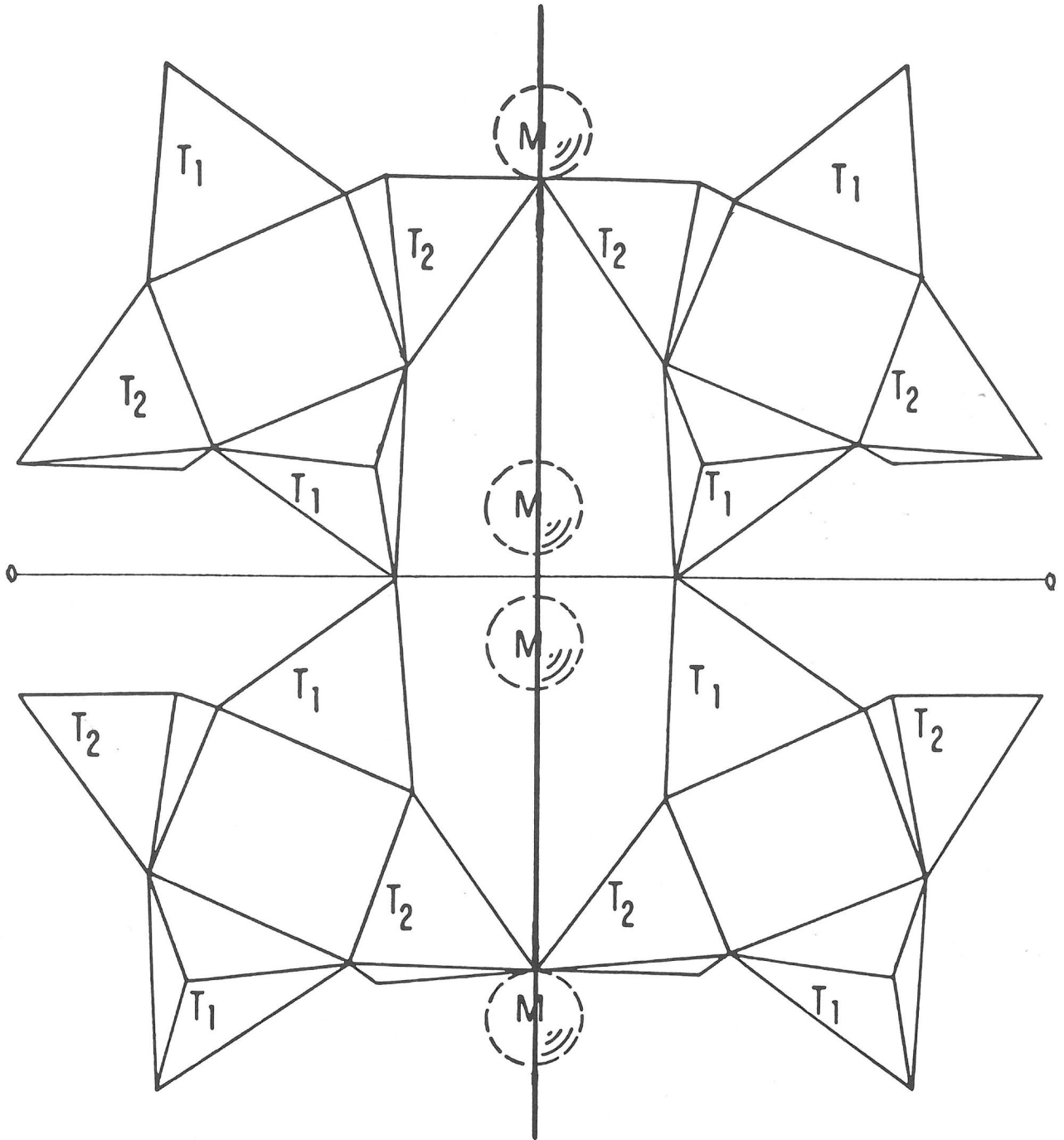
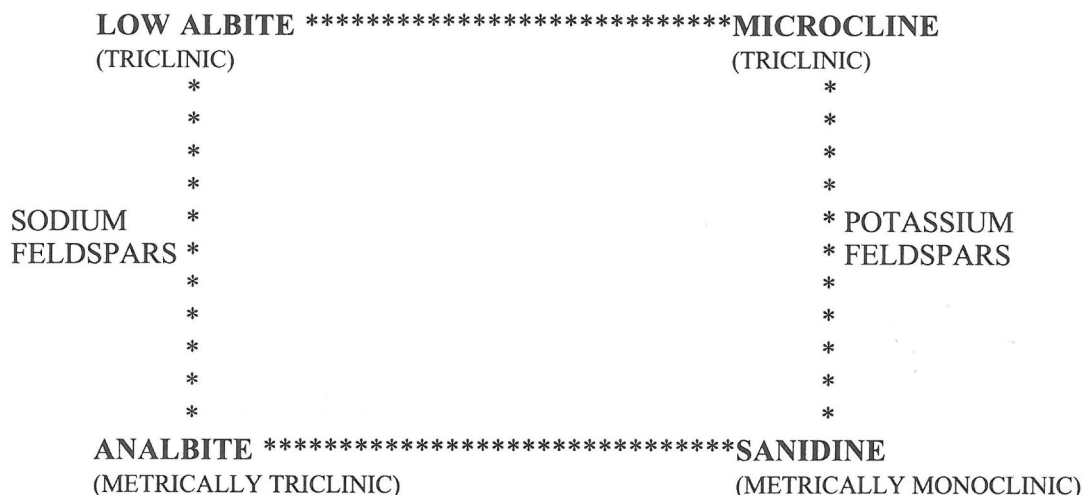


FIGURE 2. A portion of the monoclinic alkali feldspar structure projected onto the  $(\bar{2}01)$  crystallographic plane. Symmetrically distinct tetrahedra are labeled T1 and T2. Tetrahedra that had "0" and "m" designations as triclinic feldspars are symmetrically related in monoclinic feldspars by 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:

**ORDERED ALKALI FELDSPARS**  
(TOPOCHEMICALLY AND METRICALLY TRICLINIC)



**DISORDERED ALKALI FELDSPARS**  
(TOPOCHEMICALLY MONOCLINIC)

**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<sub>α</sub> 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 (201) 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 (201) X-ray diffraction peak (or calculate composition from the equation given in the figure caption). Is your feldspar sodic or potassic?



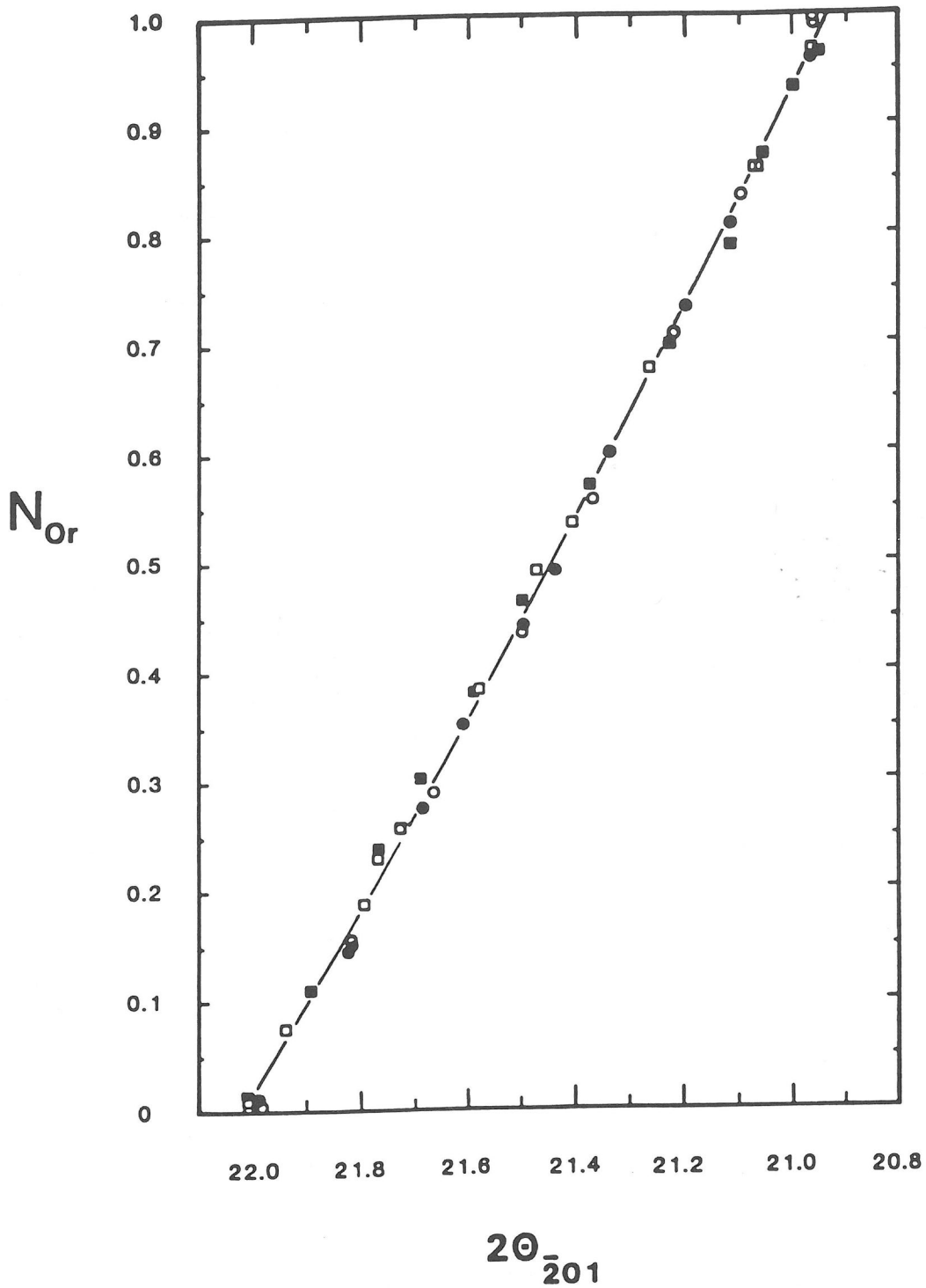


FIGURE 3. Plot of  $N_{Or}$  against  $2\theta$  for the  $\bar{2}01$  X-ray diffraction maximum (CuK $_{\alpha}$  radiation; Hovis, 1989). Data points are for feldspars with a wide range of Al-Si distributions. Compositions may be determined either graphically or by using the equation for the curve 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 ( $2\theta$ '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  $2\theta$  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 (201), (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

- Borg, I.Y., and Smith, D.K. (1969) Calculated X-ray powder patterns for silicate minerals. Geological Society of America Memoir 122, 896 pp.
- Hovis, G.L. (1989) Effect of Al-Si distribution on the X-ray powder diffraction maxima of alkali feldspars and an easy method to determine T1 and T2 site occupancies. *Canadian Mineralogist*, 27, 107-118.
- Kroll, H., and Ribbe, P.H. (1983) Lattice parameters, composition, and Al,Si order in alkali feldspars. In P. H. Ribbe, Ed., *Feldspar Mineralogy*, 57-99. Mineralogical Society of America Reviews in Mineralogy, 2 (2nd edition).

## 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, (201) peak). One could do the same thing with disordering experiments. Dexter also indicated that he has his students do comparative chloride melt experiments using  $\text{CaCl}_2$  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.,  $(\text{K},\text{Na})\text{Cl}$ ], 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 -  $(\text{K},\text{Na})\text{Cl}$  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!



# DETERMINATION OF CHEMICAL COMPOSITION, STATE OF ORDER, MOLAR VOLUME, AND DENSITY OF A MONOCLINIC ALKALI FELDSPAR USING X-RAY DIFFRACTION

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## INTRODUCTION

Alkali feldspars (commonly referred to as “potassium feldspars”) are among the most abundant minerals in the Earth’s crust. As such, they have the potential to provide important information about the rocks in which they occur. Using X-ray data, it is possible to characterize both the chemical composition and state of order of an alkali feldspar, and in some instances to approximate the temperature at which the feldspar equilibrated. Molar volume and density, fundamental properties of any mineral, also can be determined.

Although many chemical substitutions occur in these minerals, the replacement of K by Na is the most common. Thus, as a first approximation, alkali feldspars can be thought of as solid solutions varying from potassium-rich to sodium-rich end members, that is, from  $\text{KAlSi}_3\text{O}_8$  to  $\text{NaAlSi}_3\text{O}_8$ . Mineralogists characterize alkali feldspar composition by a parameter called  $N_{\text{Or}}$ , which is simply the “mole fraction” of potassium in the mineral. If  $N_{\text{Or}} = 0.7$ , for example, a formula of  $\text{K}_{0.7}\text{Na}_{0.3}\text{AlSi}_3\text{O}_8$  is implied (note that Na and K always add to 1.0). Both the  $a$  unit-cell dimension and the (201) X-ray diffraction peak of an alkali feldspar are quite sensitive to K:Na ratio. In this exercise both will be used to estimate the composition of an alkali feldspar.

In addition to chemical composition, alkali feldspars are characterized by their state of “order” or “disorder.” Ordering phenomena can occur in any crystalline material in which two or more ions compete for symmetrically nonequivalent crystallographic sites. In monoclinic alkali feldspars it is aluminum (Al) and silicon (Si) ions that occupy both of the crystallographically distinct tetrahedral sites (named T1 and T2; see Fig. 2 of Hovis, this publication). Ordering relationships, however, are found in many other mineral series, including pyroxenes, amphiboles, and micas, and in sites other than tetrahedral ones. Because these relationships are temperature- and/or pressure-dependent, they can give important information about the conditions under which a mineral has equilibrated.

The state of order in monoclinic alkali feldspars is defined by the distribution of Al and Si between the two tetrahedral sites. To illustrate, let us suppose that there are a total of 2000 tetrahedra in a tiny feldspar crystal. Since there are equal numbers of T1 and T2 sites, 1000 of these would be T1 sites and 1000 would be T2 sites. Because of the 1:3 Al:Si ratio, 500 Al ions and 1500 Si ions would occupy these sites. The most “ordered” possible monoclinic feldspar crystal would have all 500 Al ions in one site (the T1). The 1500 Si ions would fill the remaining 500 T1 sites and all 1000 of the T2 sites. Thus, the fraction of Al ions in the T1 site (symbolized  $N_{\text{Al}(T1)}$ ) of such a crystal would be 0.50 (500/1000), and the fraction of Al in T2 ( $N_{\text{Al}(T2)}$ ) would be 0.00. On the other hand, a “perfectly disordered” crystal would have a “random” distribution of Al and Si between the two sites (that is, the same occupancy in both sites). In such a case, 250 Al

ions and 750 Si ions would fill each site. In this case,  $N_{\text{Al}(T1)} = N_{\text{Al}(T2)} = 0.25$  (250/1000).

A convenient way to express the Al-Si distribution of an alkali feldspar is with a single parameter,  $Z$ , defined as twice the difference of the atom mole fractions of Al in the two tetrahedral sites (Thompson, 1969 and 1970):

$$Z = 2 [N_{\text{Al}(T1)} - N_{\text{Al}(T2)}] \quad \text{Eqn. (1)}$$

Substituting into this equation the above mole fractions of Al, we see that a perfectly ordered monoclinic feldspar would have a  $Z$ -value of 1.0 (2 times 0.50), whereas a perfectly disordered one would have a value of 0.0 (2 times zero). Although we can relate the  $Z$ -values of any natural sample to this range (samples with  $Z$ -values closer to 1.0 being more ordered, and those closer to 0.0 more disordered), bear in mind that naturally occurring alkali feldspars seem to possess  $Z$ -values in a range from about 0.8 to 0.2; even synthetically disordered ones have  $Z$ -values of only 0.07 or so (Hovis, 1986). We can use X-ray data to estimate the  $Z$ -value of any monoclinic alkali feldspar.

Just as  $Z$  can be calculated from site populations, site populations can be calculated from  $Z$ . Considering Eqn. (1) above, and the fact that  $N_{\text{Al}(T1)} + N_{\text{Al}(T2)}$  must sum to 0.5 in the simple K-Na alkali feldspar system, one can use these two simultaneous equations to demonstrate that

$$N_{\text{Al}(T1)} = (1 + Z) / 4 \quad \text{Eqn. (2)}$$

$$N_{\text{Al}(T2)} = (1 - Z) / 4 \quad \text{Eqn. (3)}$$

So, just as site populations can be used to calculate  $Z$ ,  $Z$ -values can be converted to the fractions of aluminum (and silicon) in each of the tetrahedral sites. Whether one chooses a  $Z$ -value or the individual site populations to express the state of order is arbitrary; the two are equivalent.

For alkali feldspars, the state of order is almost solely dependent on the temperature of equilibration, ordered samples having equilibrated at lower temperatures (e.g., hydrothermal veins) than disordered ones (e.g., volcanic phenocrysts). Because geologists are interested in the conditions to which a rock has been exposed, the temperature information that a feldspar-bearing rock might provide is potentially valuable. One must remember, however, that feldspars can re-equilibrate (become more ordered) as they cool; the environments most likely to have preserved temperature information are either those in which cooling occurred rapidly under relatively dry conditions, or ones in which temperatures never were very high.

## DATA COLLECTION

Each student should obtain a monoclinic alkali feldspar from the instructor and prepare the sample for X-ray analysis. If students have been instructed on the use of an "internal standard" (silicon makes a good one), include it in the sample, otherwise ignore the internal standard. If you do not use an internal standard, however, your X-ray system must be relatively well aligned, because errors in  $2\theta$  will produce errors in both peak positions and unit-cell dimensions.

1. If using  $\text{CuK}\alpha$  radiation, collect X-ray data from  $18^\circ$  to  $60^\circ$   $2\theta$ . If using another type of radiation, adjust these values appropriately. If using a diffractometer, a scan rate of  $1^\circ/\text{min}$  produces better data, but rates up to  $5^\circ/\text{min}$  may be employed.



2. Measure and record the positions and intensities of as many peaks/lines as possible. If an internal standard was mixed with the sample, correct all peak positions using data from the standard.
3. Identify the Miller Indices of each peak/line. The data in Borg and Smith (1969) for adularia, orthoclase, and sanidine will be helpful. If you cannot determine which of the latter data sets is most closely comparable to yours, index peaks using the data for orthoclase. Peaks also can be indexed using information in the JCPDS data base.
4. Using a lattice constant refinement program such as LCLSQ (Burnham, 1962), or the "electronic spreadsheet" of Novak and Colville (1989) or software included with an automated X-ray system, compute the unit-cell dimensions of your sample. In making this calculation, you should ignore "overlapping" peaks/lines (i.e., those for which there is more than one set of Miller Indices) should be ignored. Remember to refine the unit-cell dimensions in the monoclinic crystal system.
5. Record the position of the ( $\bar{2}01$ ) peak, found in the general vicinity of  $21^\circ 2\theta$  for  $\text{CuK}\alpha$  radiation.

### PART I: COMPOSITION DETERMINATION

Remember that the principal chemical substitution in alkali feldspars is  $\text{K} = \text{Na}$ . As larger potassium ions replace smaller sodium ions, the interplanar spacings ( $d_{hkl}$ ) generally increase, and as a result all three of the unit-cell axes ( $a$ ,  $b$ ,  $c$ ) expand. Of these  $a$  is the most sensitive to composition (Fig. 1). Furthermore, as any one interplanar spacing increases, the corresponding  $2\theta$  decreases (a function of the Bragg equation). As an individual peak/line, the ( $\bar{2}01$ ) is especially sensitive to  $\text{K} = \text{Na}$  substitution, changing from about  $22^\circ 2\theta$  for pure-Na feldspar to  $21^\circ$  for pure-K feldspar ( $\text{CuK}\alpha$  radiation; see Fig. 3 of Hovis, this publication).

- A. Use the ( $\bar{2}01$ ) peak of your feldspar and the equation below (Hovis, 1989) to compute  $N_{\text{Or}}$ . (Values of  $2\theta$  should be for  $\text{CuK}\alpha$  radiation.)

$$N_{\text{Or}} = 70.726 - 5.6200 (2\theta) + 0.10936 (2\theta)^2 \quad \text{Eqn. (4)}$$

- B. Substitute the  $a$  unit-cell dimension of your feldspar into the equation below (Hovis, 1986) as a second method of computing  $N_{\text{Or}}$ ; this should produce a value similar to that in Part A.

$$N_{\text{Or}} = -366.3261 + 129.2335 a - 15.42053 a^2 + 0.6232109 a^3 \quad \text{Eqn. (5)}$$

- C. The two methods will not compare perfectly, but they should be close. How well do the two  $N_{\text{Or}}$  values agree?
- D. If they do not agree well, what might be the reason(s)?

### PART II: DETERMINATION OF STATE OF ORDER

Just as with composition, peak positions and unit-cell dimensions are affected by the interchange of Al and Si ions between T1 and T2 tetrahedral sites. At any one composition, disorder causes the  $c$  dimension to shorten and the  $b$  dimension to lengthen. A plot of  $c$  against  $b$

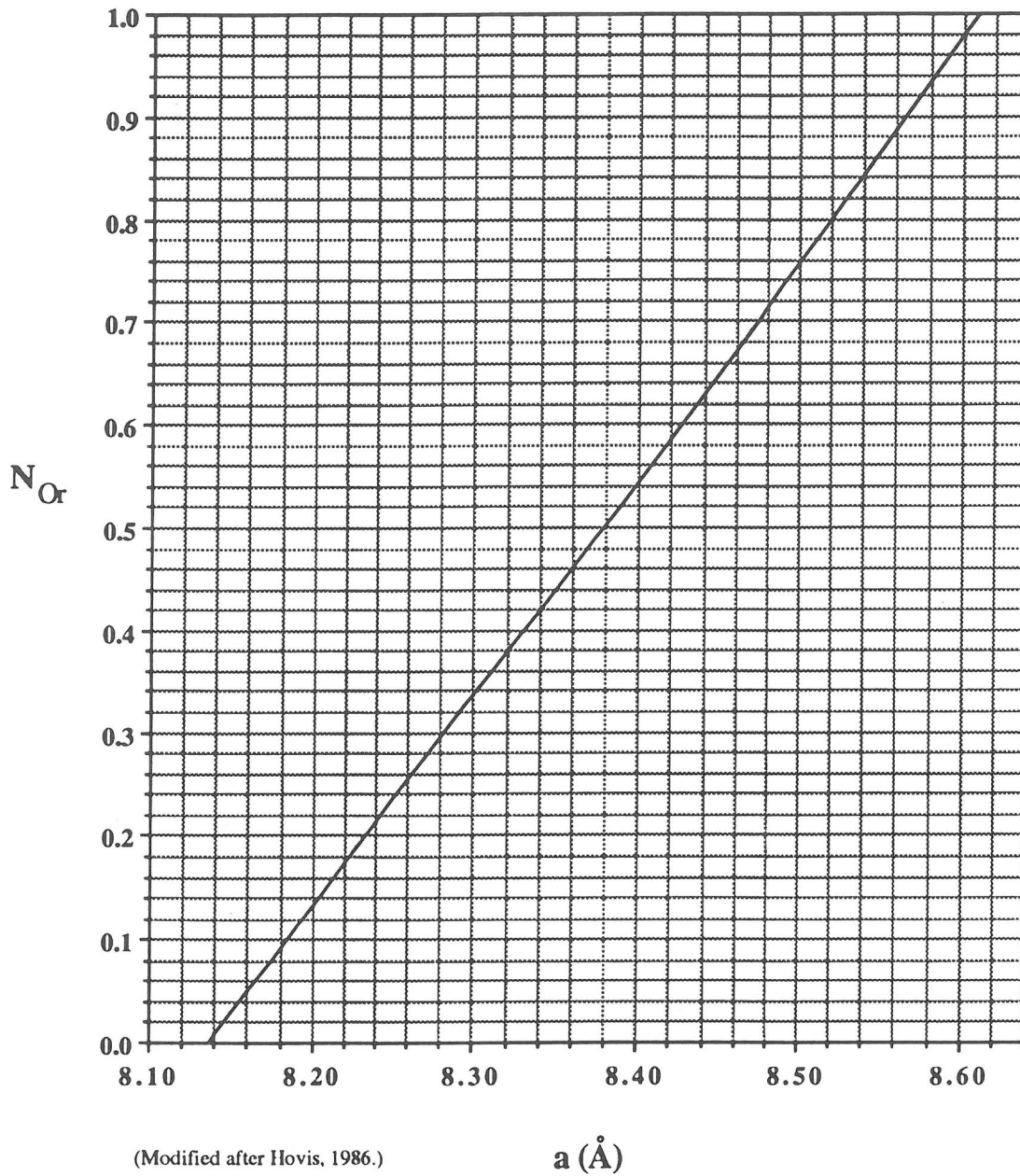
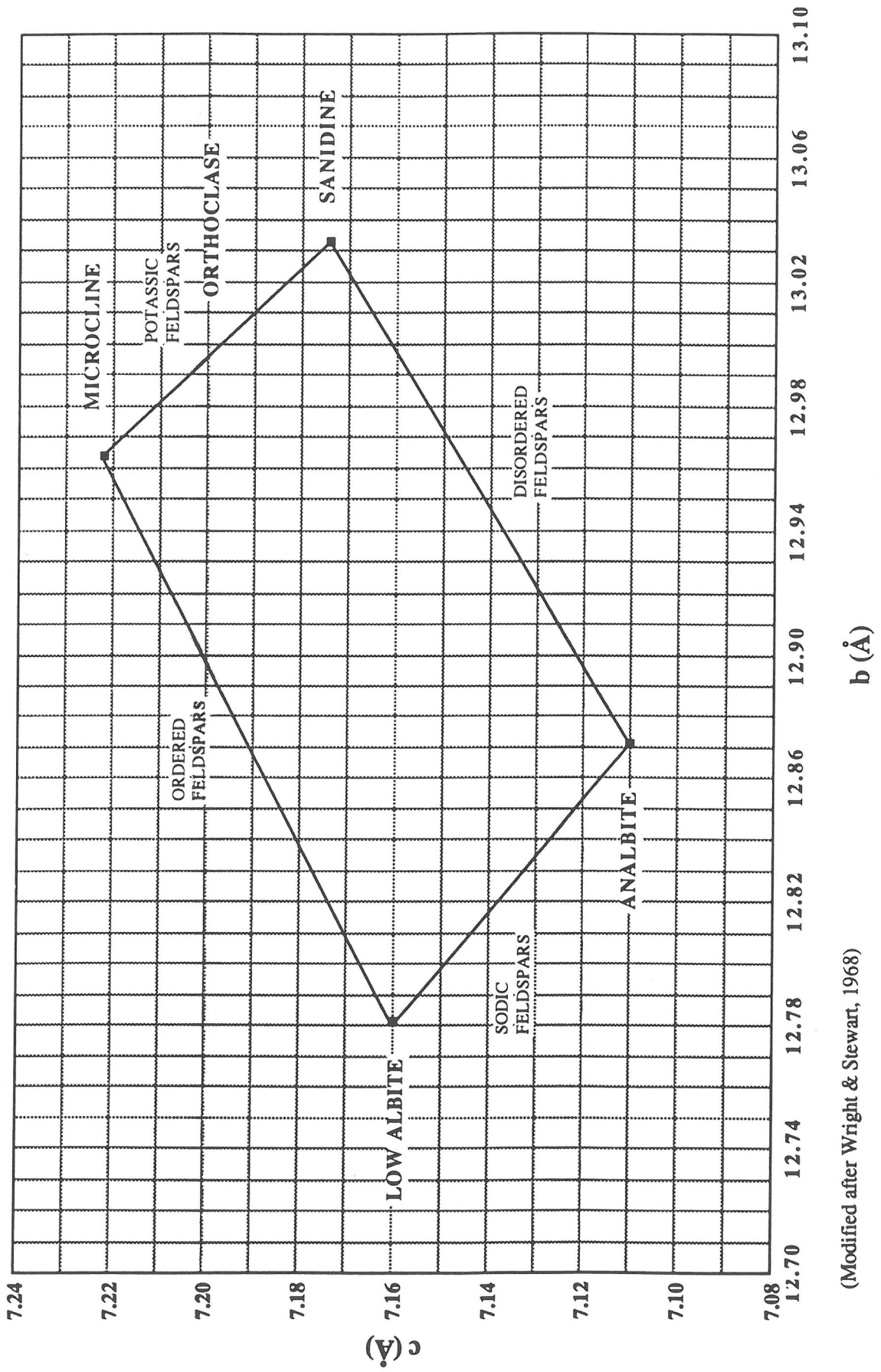


FIGURE 1. A plot of  $N_{Or}$  against the  $a$  unit-cell dimension. The  $a$  unit-cell dimension is affected to a small degree by ordering. Although slightly different curves should be used for different Al-Si distributions, the curve above [Eqn. (5)] is an “average” relationship that does not take state of ordering into account.

FIGURE 2



(Modified after Wright & Stewart, 1968)

(Fig. 2; similar to Wright and Stewart, 1968, and Kroll and Ribbe, 1983) illustrates this point well; note, for example, the changes of  $\underline{b}$  and  $\underline{c}$  for pure-K feldspars in the conversion of orthoclase (relatively ordered) to sanidine (disordered).

You will see from Figure 2 that  $\underline{b}$  and  $\underline{c}$  also are affected by composition; both parameters expand with increased potassium content in the feldspar. Because  $\underline{b}$  and  $\underline{c}$  are functions of both ordering and composition, neither can be used alone to determine either the state of Al-Si order or composition. Nevertheless, it is relatively easy to obtain the information we need. We shall take advantage of the fact that we now have compositional information determined in Part I.

We shall illustrate two methods that can be used to determine state of order. In Parts A-G below, the  $\underline{c}$  unit-cell dimension alone is utilized. In Part A we “subtract out” the effects of composition on the observed value of  $\underline{c}$  ( $\underline{c}_{\text{obs}}$ ). This is done by taking  $\underline{c}_{\text{obs}}$  of your sodium-bearing feldspar and sliding it along an “iso-order” line in Figure 3 to the pure-potassium end of a K-Na “ion-exchange series.” The resulting parameter,  $\underline{c}_{\text{K}}$ , is the  $\underline{c}$ -value that your feldspar would have had if it had contained no sodium.

- A. To compute  $\underline{c}_{\text{K}}$ , use Eqn. (6) below (Hovis, 1986). Employ the  $\underline{c}$  unit-cell value determined from your X-ray data ( $\underline{c}_{\text{obs}}$ ) and the  $N_{\text{Or}}$  from Part IB above.

$$\underline{c}_{\text{K}} = \underline{c}_{\text{obs}} + 0.038 (1 - N_{\text{Or}}) \quad \text{Eqn. (6)}$$

- B. Since  $\underline{c}_{\text{K}}$  is sensitive to Al-Si distribution (see Fig. 4), it may be used to determine  $Z$ . The equation below (Hovis, 1986) expresses the line on Figure 4 that relates these two parameters. Calculate  $Z$  using the  $\underline{c}_{\text{K}}$  from Part A above.

$$Z = -144.962 + 20.2032 \underline{c}_{\text{K}} \quad \text{Eqn. (7)}$$

- C. Next compute  $N_{\text{Al(T1)}}$  and  $N_{\text{Al(T2)}}$  using Eqns. (8) and (9) below (Hovis, 1986).

$$N_{\text{Al(T1)}} = (1 + Z) / 4 = -34.3939 + 4.82884 \underline{c}_{\text{K}} \quad \text{Eqn. (8)}$$

$$N_{\text{Al(T2)}} = (1 - Z) / 4 = +34.8939 - 4.82884 \underline{c}_{\text{K}} \quad \text{Eqn. (9)}$$

[As a check on your calculations, note that for any monoclinic K-Na feldspar  $N_{\text{Al(T1)}}$  and  $N_{\text{Al(T2)}}$  should sum to 0.50.]

- D.  $N_{\text{Si(T1)}}$  and  $N_{\text{Si(T2)}}$ , the mole fractions of Si in T1 and T2, also may be computed. This is very simple, because the mole fractions of Al and Si add to 1.0 in each site. Thus:

$$N_{\text{Si(T1)}} = 1 - N_{\text{Al(T1)}} \quad \text{Eqn. (10)}$$

$$N_{\text{Si(T2)}} = 1 - N_{\text{Al(T2)}} \quad \text{Eqn. (11)}$$

- E. Given the fact that natural and synthetic feldspars have  $Z$ -values ranging from about 0.8 (most ordered) to 0.07 (most disordered), rank the state of order of your feldspar:

Highly ordered? Highly disordered? In between?

- F. Using Figure 5 (Hovis, unpublished), employ the  $Z$ -value of your feldspar to approximate the temperature at which it equilibrated.

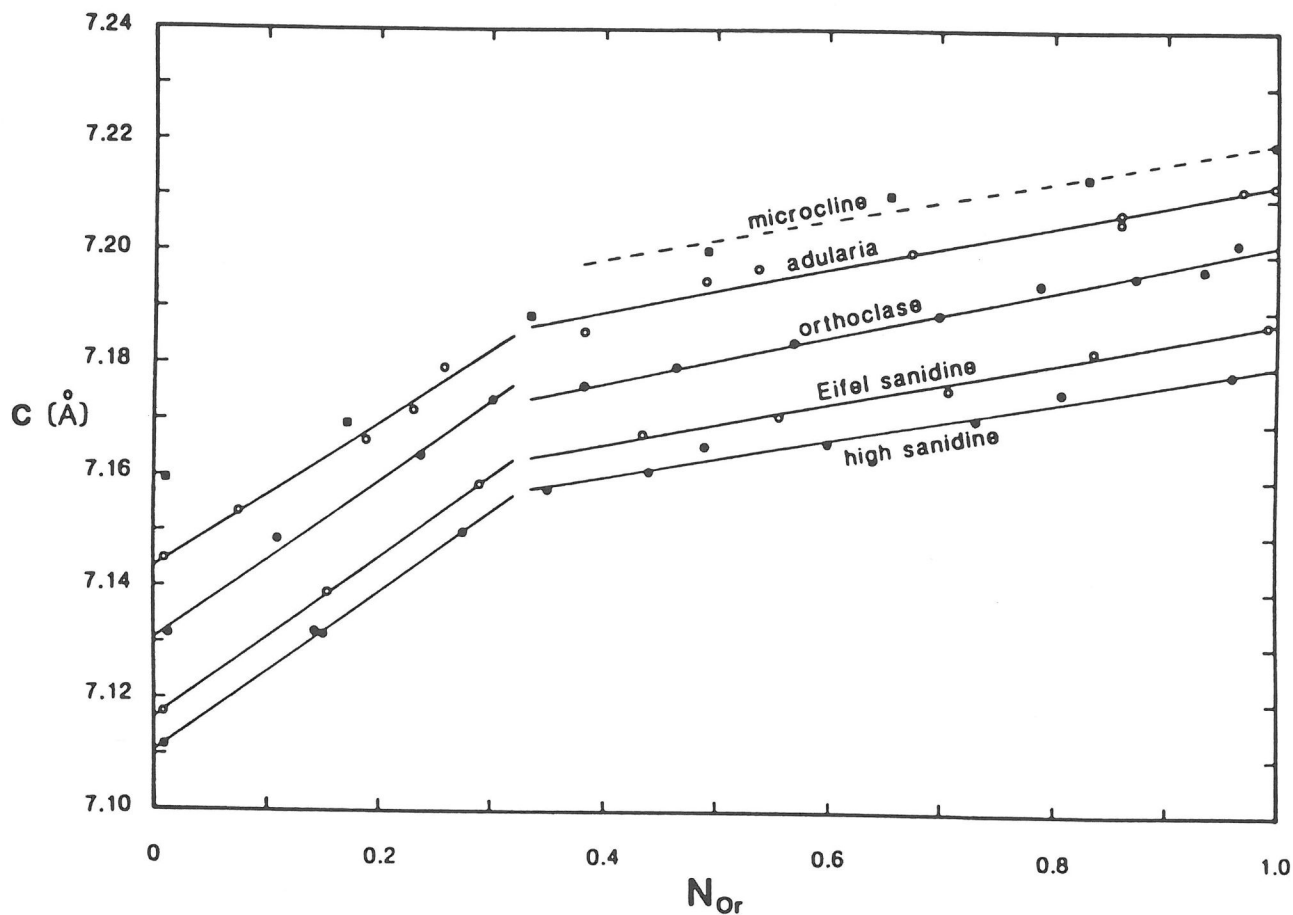


FIGURE 3. The  $c$  unit-cell dimension plotted against  $N_{Or}$  for several iso-structural series of alkali feldspars (Hovis, 1986). Note that  $c$  is a function of both chemical composition and Al-Si distribution. One can “correct” the observed  $c$ -value of an alkali feldspar for Na by sliding it along a line of “constant Al-Si order” (e.g., the “adularia,” “orthoclase,” or “sanidine” lines) to the pure-K end of a series ( $N_{Or} = 1$ ). This produces the value  $c_K$ , which is the  $c$ -value for the pure potassium end member of the series. Such a feldspar would have the same Al-Si distribution as its Na-bearing analog.

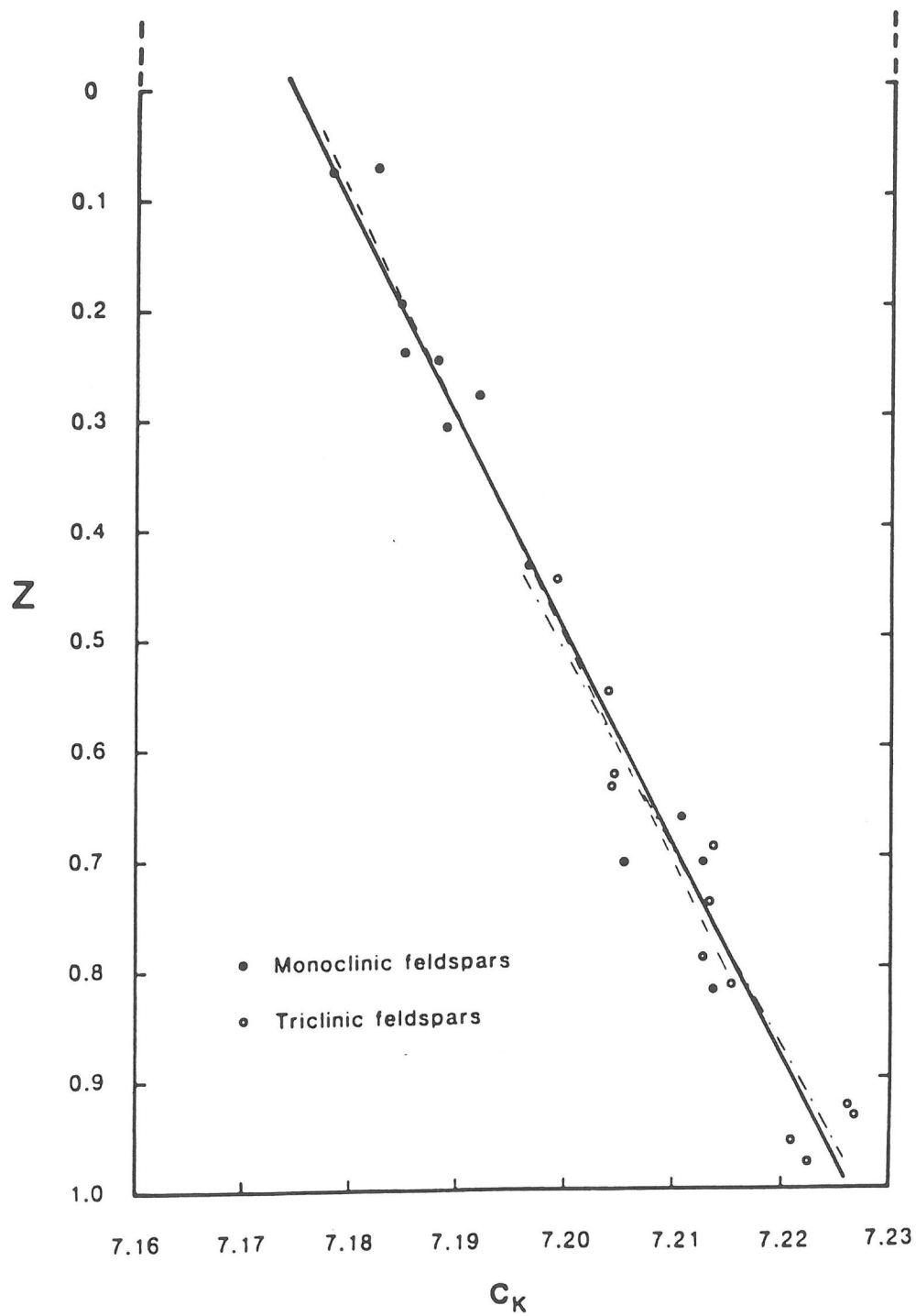


FIGURE 4. Plot of  $Z$  against  $c_K$  for alkali feldspars having various degrees of order (Hovis, 1986). Separate (light dashed) lines represent data for feldspars with triclinic and monoclinic Al-Si distributions; however, these have virtually the same slope. The heavy line is based on data for all feldspars and is expressed by Eqn. (7).

- G. Is it more likely that your alkali feldspar came from a (a) hydrothermal vein, (b) pegmatite, or (c) high-temperature lava?

Research on the use of unit-cell dimensions to estimate Al-Si distribution in alkali feldspars has been pioneered by a number of workers, including Wright and Stewart (1968), Stewart and Ribbe (1969), and Kroll and Ribbe (1983). A commonly used method for simultaneously estimating both the composition and state of order of an alkali feldspar is to plot its  $c$  unit-cell dimension (that is,  $c_{\text{obs}}$ ) against its  $b$  dimension:

- H. Plot on Figure 2 the  $b$  versus the  $c$  ( $c_{\text{obs}}$ ) unit-cell dimension of your feldspar.
- I. Does the position of the plotted point make sense for the  $N_{\text{Or}}$  and Al-Si distribution computed above for your feldspar? Briefly discuss.

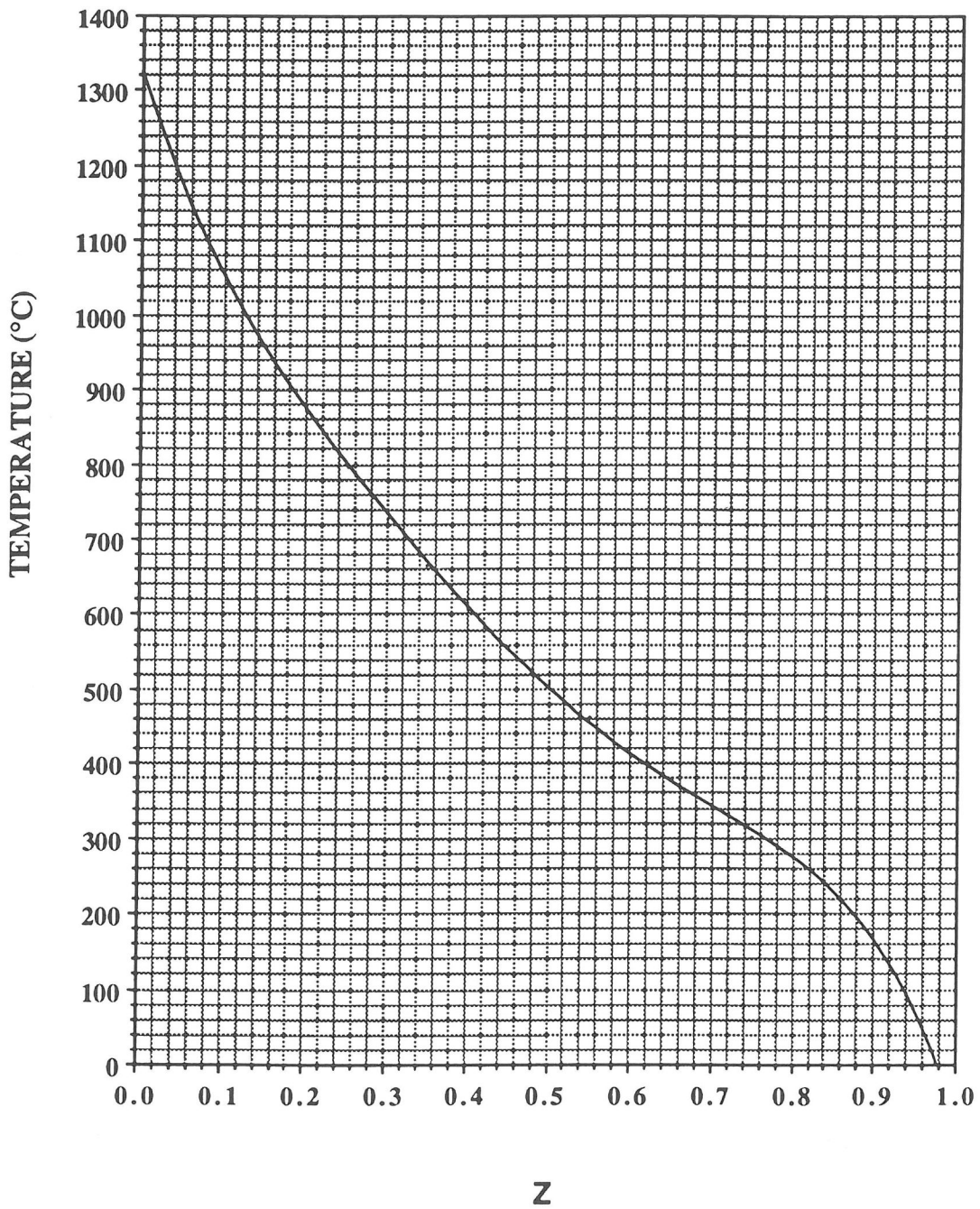
### PART III: MOLAR VOLUME AND DENSITY DETERMINATION

Volume and density are important properties of minerals and rocks. Molar volume, the space occupied by one "mole" of a substance, relates closely to the conditions of stability of a mineral; as pressure increases with depth in the Earth, materials that occupy less volume are favored. Density too is a fundamental property of any material and an important parameter to which geophysicists relate both gravity and seismic data. It is density differences among materials that help geologists interpret the structure and composition of rocks that exist below the Earth's surface. The molar volume of a mineral can be determined directly from X-ray data, and with accompanying chemical information density also can be estimated.

The output from the unit-cell dimension calculations should include information on unit-cell volume, that is, the volume occupied by one unit cell of your feldspar. Since there are four formula units in each unit cell, you can easily compute how much volume one formula unit takes up. If you multiply the latter number by Avogadro's constant ( $6.022 \times 10^{23}$ ), you would know how much volume one mole of your feldspar occupies (molar volume). All that remains, then, is to convert volume in  $\text{\AA}^3$  to volume in more familiar units of  $\text{cm}^3$  (a conversion factor of  $10^{-24}$ ). All these conversions can be accomplished simultaneously by multiplying unit-cell volume by 0.15055. Then, once you know molar volume, you can take advantage of chemical information to compute density. Just follow the instructions below.

- A. Multiply the unit-cell volume ( $\text{\AA}^3/\text{unit cell}$ ) by 0.15055 to convert to molar volume in  $\text{cm}^3/\text{mole}$ .
- B. Write out the chemical formula determined in Part IB above, based upon eight oxygens. Now take the atomic weights of chemical elements in the formula (K, Na, Al, Si, and O) and multiply each by the relevant subscript, then add the resulting five numbers. This sum is the gram formula weight, that is the weight of one mole, of your feldspar.
- C. You now know both the volume (Part A) and the weight (Part B) of one mole of your feldspar. In order to compute its density, simply divide the gram formula weight (g/mole) by the molar volume ( $\text{cm}^3/\text{mole}$ ). Note that the resulting units will be in  $\text{g}/\text{cm}^3$ .





[This graph will produce approximate temperatures; it is still in a developmental stage (Hovis, unpublished).]

FIGURE 5. Temperature plotted against Z for alkali feldspars having various degrees of order.



D. Check the density (or specific gravity) of alkali feldspar (or microcline, orthoclase, or sanidine) in an appropriate reference book, such as your Mineralogy textbook. What value is given?

How does your value compare? [It should be close; if it isn't, check your calculations.]

E. How does the density of an alkali feldspar compare to those of minerals such as forsterite (olivine), enstatite (pyroxene), and pyrope (garnet)?

F. Based on the comparison made in Part E, would you expect alkali feldspars to be more abundant in the Earth's crust or the Earth's mantle?

### REFERENCES CITED

- Borg, I.Y., and Smith, D.K. (1969) Calculated X-ray powder patterns for silicate minerals. Geological Society of America Memoir 122, 896 pp.
- Burnham, C.W. (1962) Lattice constant refinement. Carnegie Institution of Washington Year Book 61, 132-135.
- Hovis, G.L. (1986) Behavior of alkali feldspars: Crystallographic properties and characterization of composition and Al-Si distribution. *American Mineralogist*, 71, 869-890.
- Hovis, G.L. (1989) Effect of Al-Si distribution on the X-ray powder diffraction maxima of alkali feldspars and an easy method to determine T1 and T2 site occupancies. *Canadian Mineralogist*, 27, 107-118.
- Kroll, H., and Ribbe, P.H. (1983) Lattice parameters, composition, and Al,Si order in alkali feldspars. In P. H. Ribbe, Ed., *Feldspar Mineralogy*, 57-99. Mineralogical Society of America Reviews in Mineralogy, 2 (2nd edition).
- Novak, G.A., and Colville, A.A. (1989) A practical interactive least-squares cell-parameter program using an electronic spreadsheet and a personal computer. *American Mineralogist*, 74, 488-490.
- Stewart, D.B., and Ribbe, P.H. (1969) Structural explanation for variations in cell parameters of alkali feldspar with Al/Si ordering. *American Journal of Science*, 267-A, 444-462.
- Thompson, J. B., Jr. (1969) Chemical reactions in crystals. *American Mineralogist*, 54, 341-375.
- Thompson, J. B., Jr. (1970) Chemical reactions in crystals: Corrections and clarification. *American Mineralogist*, 55, 528-532.
- Wright, T.L., and Stewart, D.B. (1968) X-ray and optical study of alkali feldspar: I. Determination of composition and structural state from refined unit-cell parameters and 2V. *American Mineralogist*, 53, 38-87.

## NOTES TO THE INSTRUCTOR

1. It is important that the feldspar you give each student is monoclinic. To differentiate orthoclase and sanidine (monoclinic) from microcline (triclinic), compare X-ray data between  $18^\circ$  and  $35^\circ$   $2\theta$  ( $\text{CuK}_\alpha$  radiation) using Borg and Smith (1969) or other data.
2. It also is important to give students single-phase specimens. To identify perthitic samples, look at the (201) peak; for two-phase specimens the latter will be double, or very broad.
3. The best material for highly ordered K-feldspar is probably “adularia,” such as the Swiss vein deposits. Be careful, though, in some cases these are triclinic.

Single-phase intermediately-ordered orthoclase can be hard to find, because in plutonic (including pegmatitic) environments it often re-equilibrates to microcline during cooling. The Benson pegmatite in New York provides good material, and the yellowish or greenish orthoclases from Madagascar pegmatites are excellent. As highly potassic materials, these feldspars beat mother nature by hitting the solvus at a temperature that was too low for exsolution to occur.

Highly disordered sanidine can be obtained from phenocrysts in lavas, or you can synthesize it yourself by cooking K-rich feldspar at  $1050^\circ\text{C}$  for about three weeks.

4. If your X-ray system is out of alignment, the resulting unit-cell dimensions will be in error. Obviously, this will adversely affect the results.
5. In addition to (or in place of) the equations given, you also can have your students graphically determine parameters such as  $N_{\text{Or}}$ ,  $c_K$ , and  $Z$  from the figures.
6. Obviously, this exercise is fairly sophisticated. However, my students have done well with it. One place you might have to help them is with inspection of the X-ray data once the unit-cell dimensions have been calculated, showing them what to look for in the way of mistakes. If in calculating unit-cell dimensions a student has made a mistake in typing a  $2\theta$  value (e.g.,  $21.148^\circ$  instead of  $20.148^\circ$ ), or in indexing a peak, it is likely to have very significant consequences on the results. So, it would be good to check on quality somewhere along the line, or to give students an idea of how to identify mistakes, e.g., by looking at “residuals” (calculated versus observed peak positions), or by inspecting the magnitudes of the “standard errors” that the calculations produce).
7. Remember that some feldspars re-equilibrate as they cool, especially in slow-cooling environments. Therefore, I have been careful to communicate the concept that Al-Si distribution represents the temperature of “equilibration” as opposed to the temperature of “formation.”