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 $KAlSi_3O_8$ to $NaAlSi_3O_8$. Mineralogists characterize alkali feldspar composition by a parameter called N_{Or}, which is simply the "mole fraction" of potassium in the mineral. If $N_{Or} = 0.7$, for example, a formula of $K_{0.7}Na_{0.3}AlSi_3O_8$ is implied (note that Na and K always add to 1.0). Both the <u>*a*</u> unit-cell dimension and the $(\bar{2}01)$ 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 <u>fraction of Al ions in the T1 site</u> (symbolized $N_{Al(T1)}$) of such a crystal would be 0.50 (500/1000), and the <u>fraction of Al in T2</u> ($N_{Al(T2)}$) 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, $N_{Al(T1)} = N_{Al(T2)} = 0.25$ (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):

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

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 $N_{Al(T1)} + N_{Al(T2)}$ must sum to 0.5 in the simple K-Na alkali feldspar system, one can use these two simultaneous equations to demonstrate that

$$N_{Al(T1)} = (1 + Z) / 4 \qquad \text{Eqn. (2)}$$
$$N_{Al(T2)} = (1 - Z) / 4 \qquad \text{Eqn. (3)}$$

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 2θ will produce errors in both peak positions and unit-cell dimensions.

1. If using CuK_{α} radiation, collect X-ray data from 18° to 60° 2θ. If using another type of radiation, adjust these values appropriately. If using a diffractometer, a scan rate of 1°/min produces better data, but rates up to 5°/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° 2θ for CuK_α radiation.

PART I: COMPOSITION DETERMINATION

Remember that the principal chemical substitution in alkali feldspars is K = 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 2θ decreases (a function of the Bragg equation). As an individual peak/line, the $(\bar{2}01)$ is especially sensitive to K = Na substitution, changing from about 22° 2θ for pure-Na feldspar to 21° for pure-K feldspar (CuK_α 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_{Or}. (Values of 2θ should be for CuK_α radiation.)

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

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

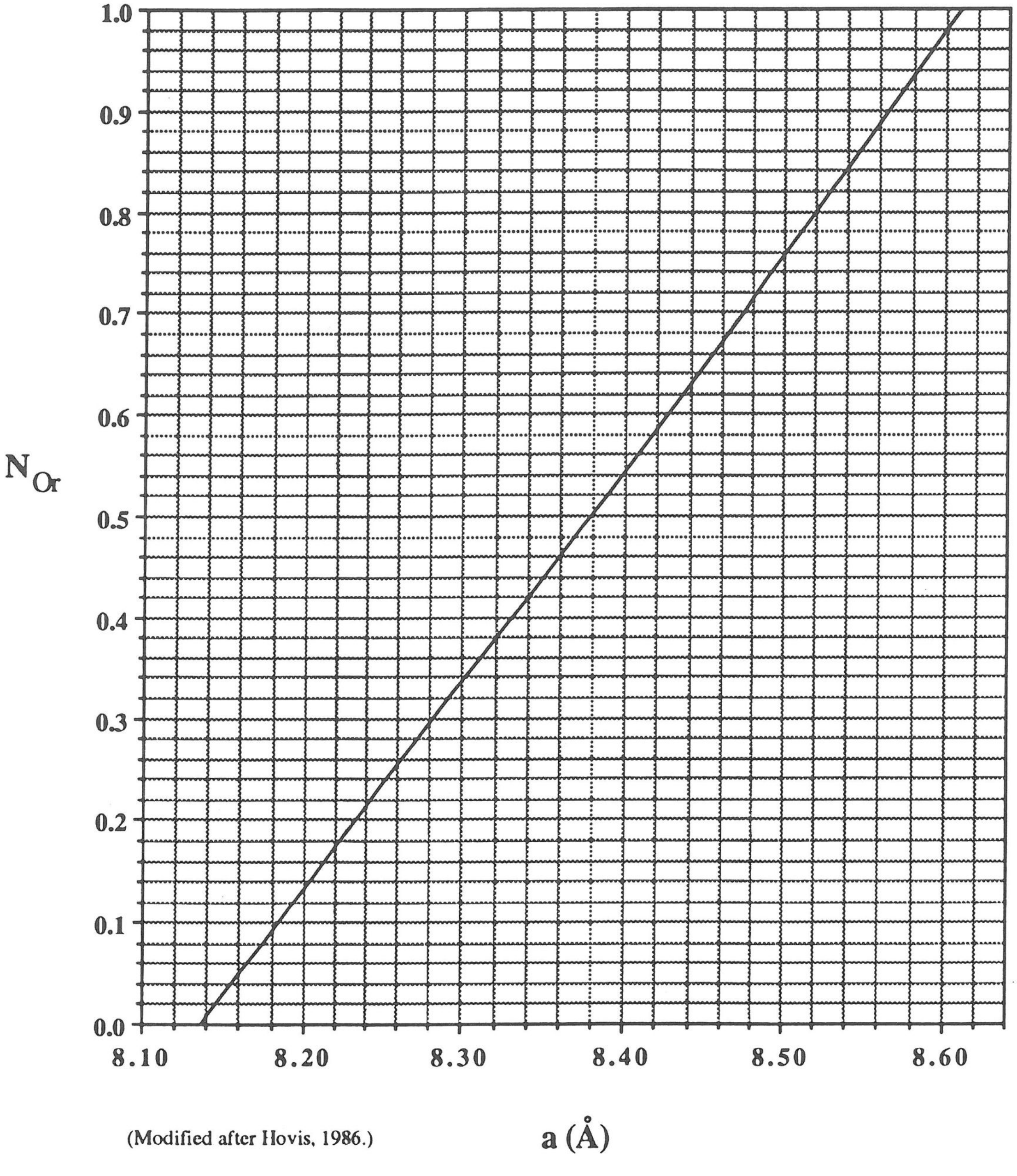
$$N_{Or} = -366.3261 + 129.2335\,\underline{a} - 15.42053\,\underline{a}^2 + 0.6232109\,\underline{a}^3 \qquad \text{Eqn. (5)}$$

C. The two methods will not compare perfectly, but they should be close. How well do the two N_{Or} values agree?

D. If they do not agree well, what might be the reason(s)?

PART II: DETERMINATION OF STATE OF ORDER

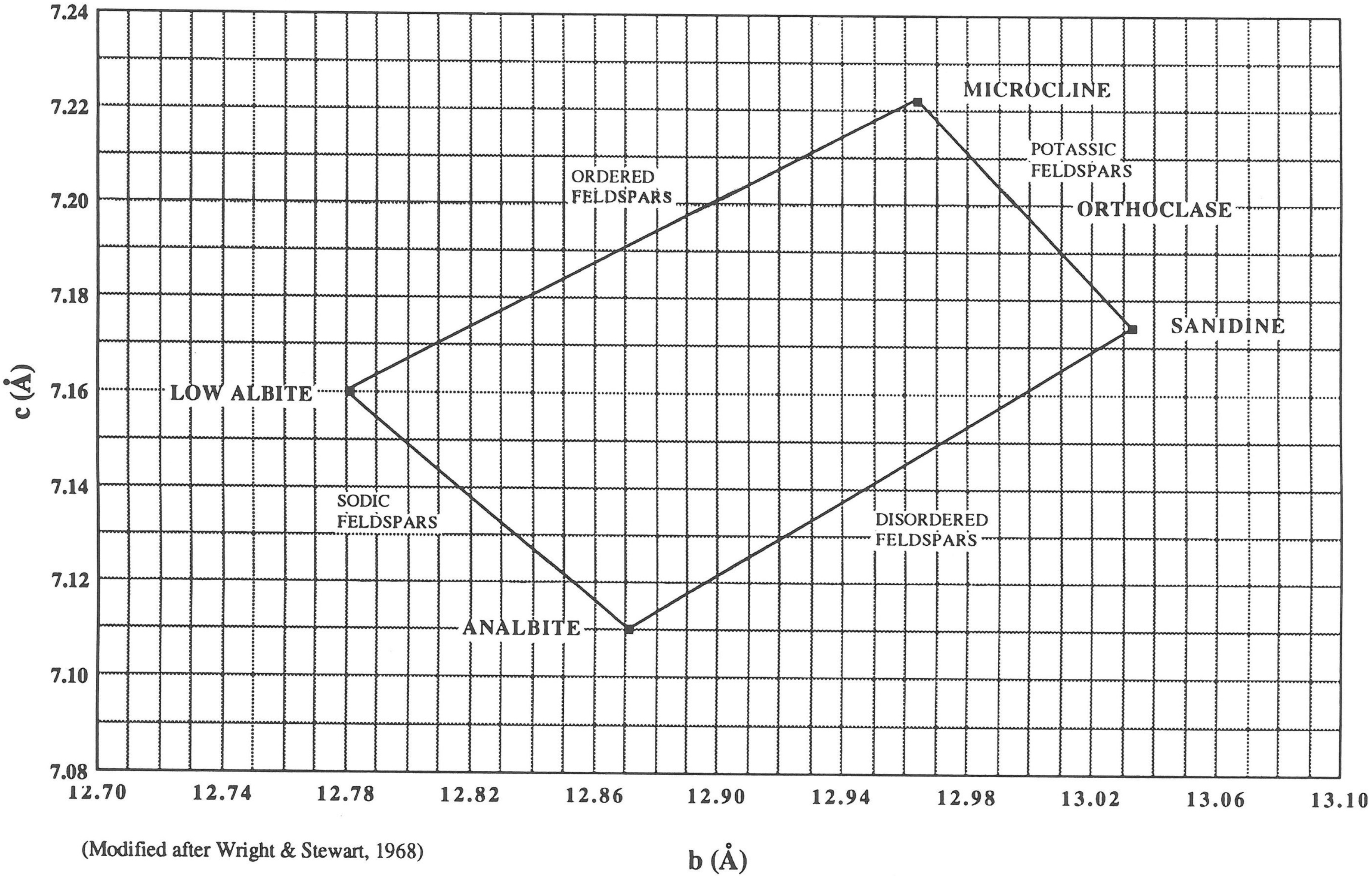
Just as with composition, peak positions and unit-cell dimensions are affected by the interchange of Al and Si ions between T1 and T2 tetrahedral sites. At any one composition, disorder causes the c dimension to shorten and the b dimension to lengthen. A plot of c against b



(Modified after Hovis, 1986.)

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 $\underline{c}$ ($\underline{c}_{\mathrm{obs}}$). This is done by taking $\underline{c}_{\mathrm{obs}}$ 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, $\underline{c}_{\mathrm{K}}$, is the $\underline{c}$-value that your feldspar would have had if it had contained no sodium.

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

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

B. Since $\underline{c}_{\mathrm{K}}$ 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 $\underline{c}_{\mathrm{K}}$ from Part A above.

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

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

$$N_{\mathrm{Al(T1)}} = (1 + Z)/4 = -34.3939 + 4.82884\,\underline{c}_{\mathrm{K}} \qquad \text{Eqn. (8)}$$
$$N_{\mathrm{Al(T2)}} = (1 - Z)/4 = +34.8939 - 4.82884\,\underline{c}_{\mathrm{K}} \qquad \text{Eqn. (9)}$$

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

D. $N_{\mathrm{Si(T1)}}$ and $N_{\mathrm{Si(T2)}}$, 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:

$$N_{\mathrm{Si(T1)}} = 1 - N_{\mathrm{Al(T1)}} \qquad \text{Eqn. (10)}$$
$$N_{\mathrm{Si(T2)}} = 1 - N_{\mathrm{Al(T2)}} \qquad \text{Eqn. (11)}$$

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.

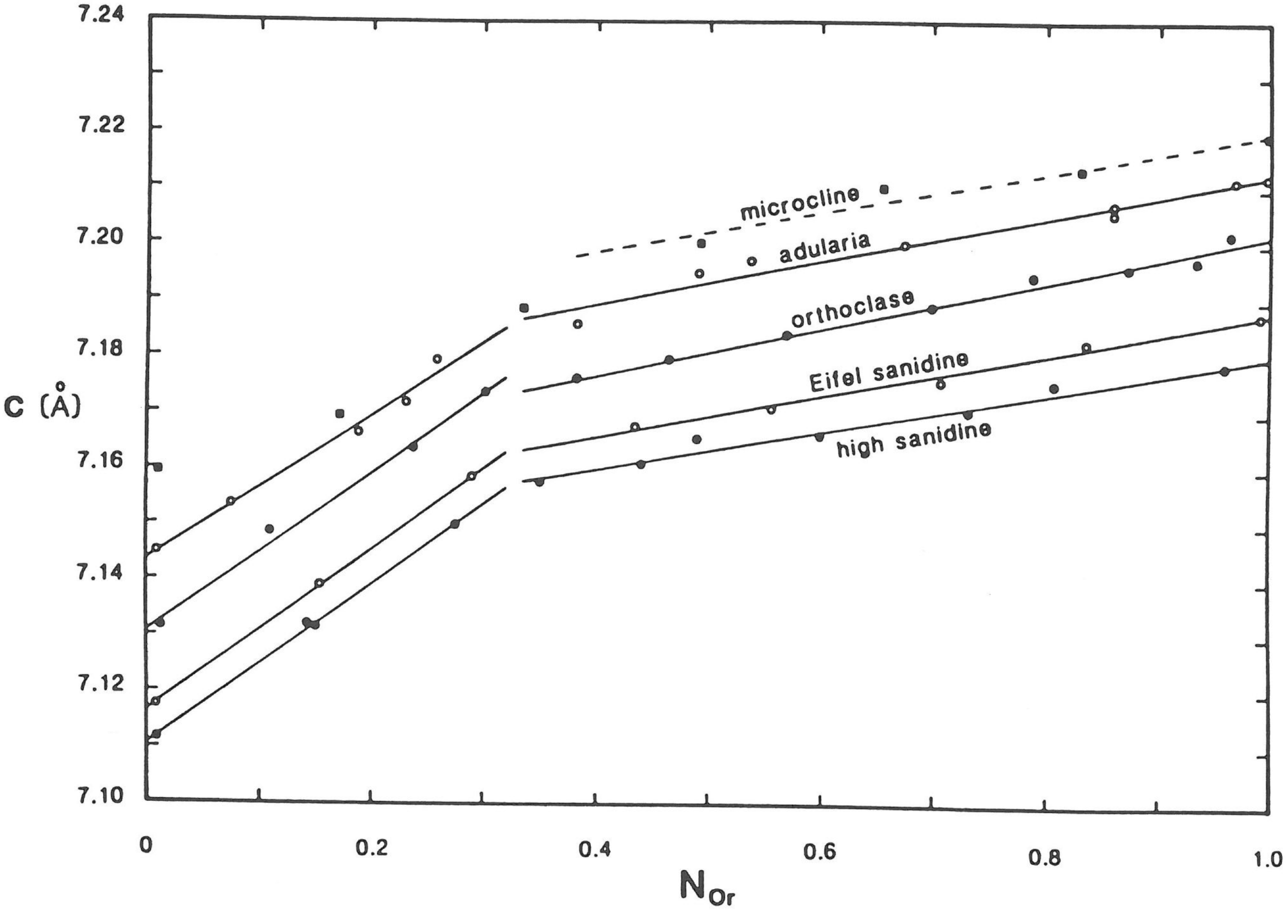


FIGURE 3. The c unit-cell dimension plotted against N_{Or} for several iso-structural series of alkali feldspars (Hovis, 1986). Note that c is a function of both chemical composition and Al-Si distribution. One can "correct" the observed c-value of an alkali feldspar for Na by sliding it along a line 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.

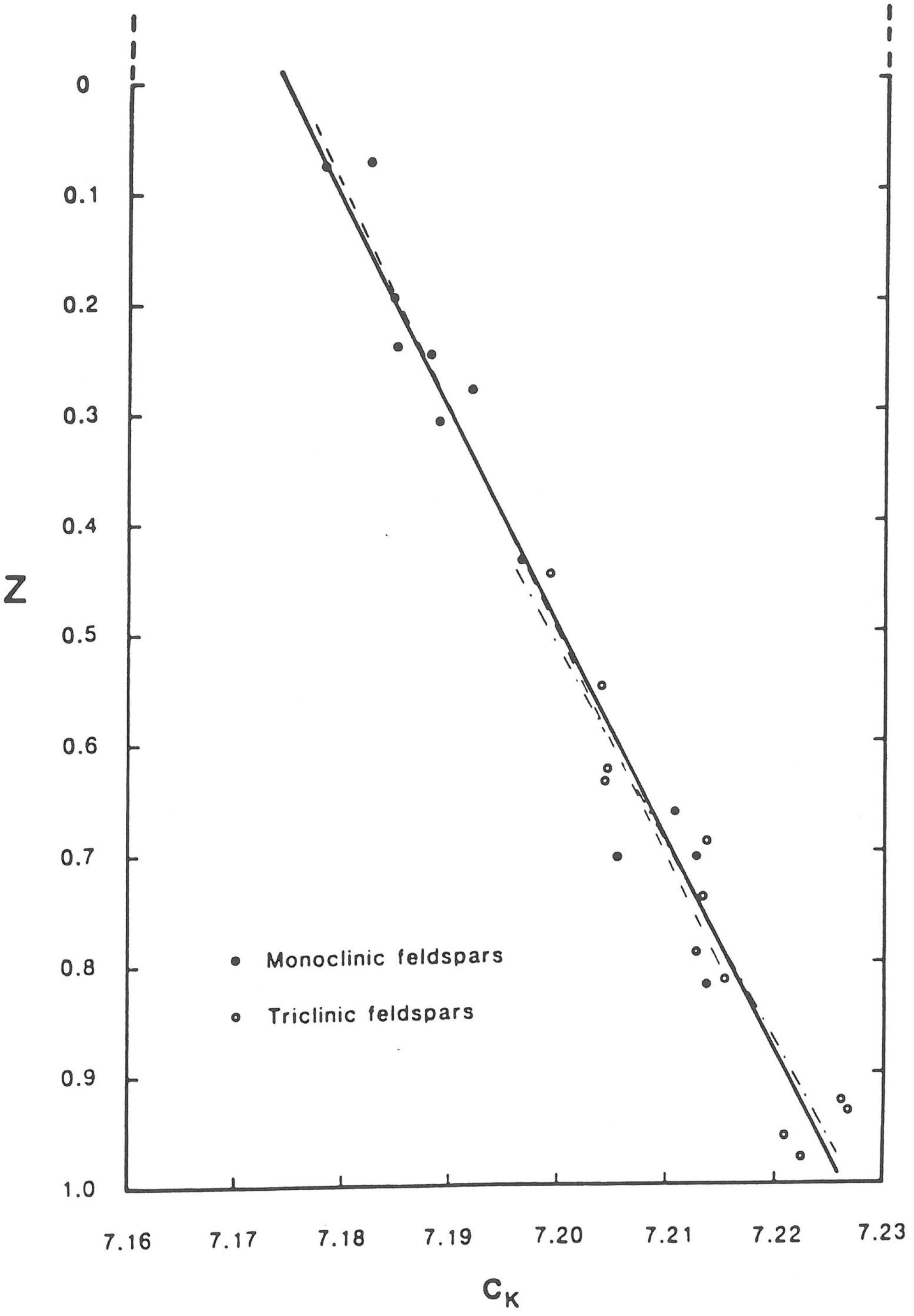


FIGURE 4. Plot of Z against $\underline{c}_K$ for alkali feldspars having various degrees of order (Hovis, 1986). Separate (light dashed) lines represent data for feldspars with triclinic and monoclinic Al-Si distributions; however, these have virtually the same slope. The heavy line is based on data 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 $\underline{c}$ unit-cell dimension (that is, $\underline{c}_{obs}$) against its $\underline{b}$ dimension:

H. Plot on Figure 2 the $\underline{b}$ versus the $\underline{c}$ ($\underline{c}_{obs}$) unit-cell dimension of your feldspar.

I. Does the position of the plotted point make sense for the N_{Or} and Al-Si distribution computed above for your feldspar? Briefly discuss.

PART III: MOLAR VOLUME AND DENSITY DETERMINATION

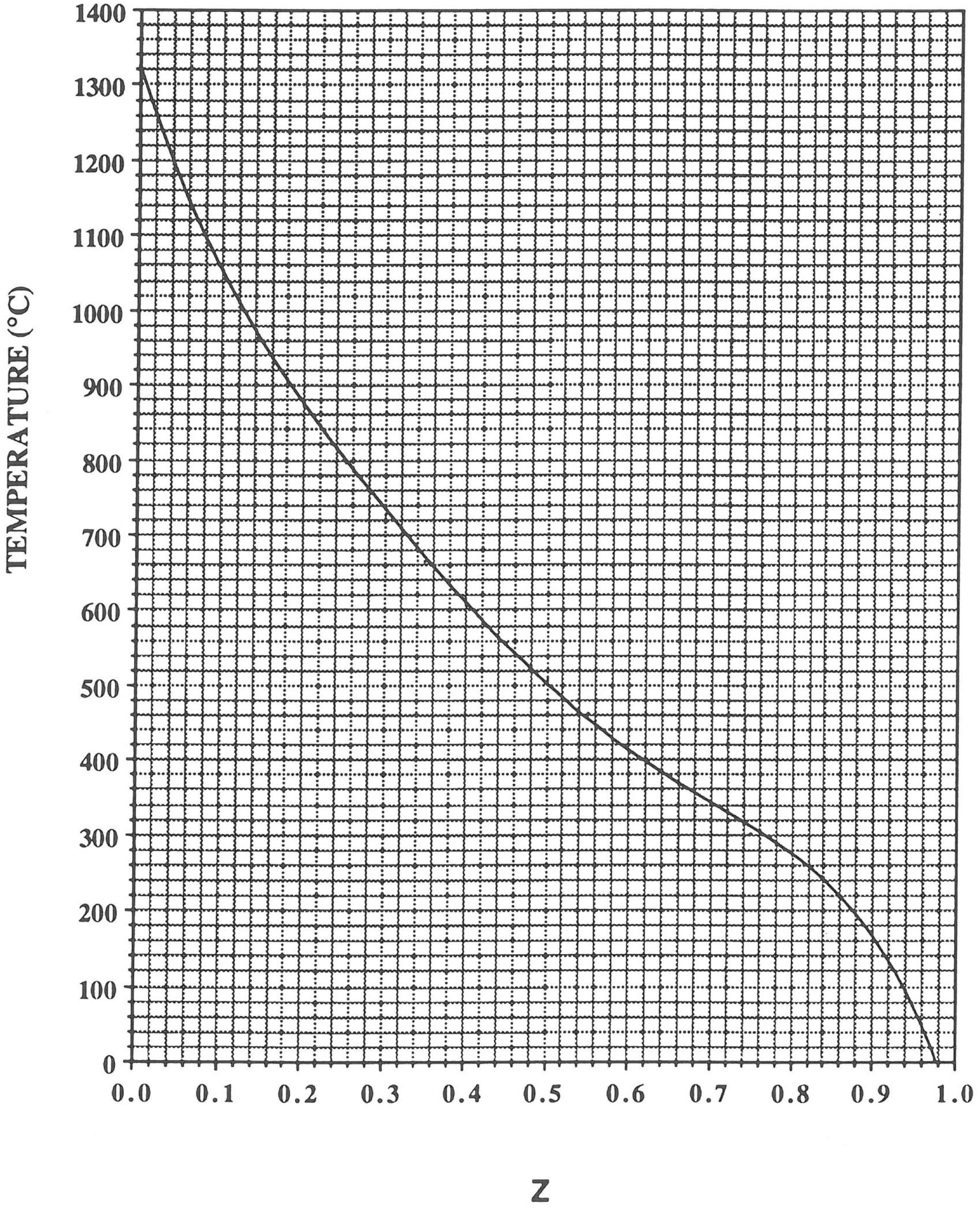
Volume and density are important properties of minerals and rocks. Molar volume, the space occupied by one "mole" of a substance, relates closely to the conditions of stability of a mineral; as pressure increases with depth in the Earth, materials that occupy less volume are favored. Density too is a 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 (6.022×10^{23}), you would know how much volume one mole of your feldspar occupies (molar volume). All that remains, then, is to convert volume in $Å^3$ to volume in more familiar units of 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 ($Å^3$/unit cell) by 0.15055 to convert to molar volume in cm^3/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 (cm^3/mole). Note that the resulting units will be in g/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?

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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° and 35° 2θ (CuK_α 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 ($\bar{2}01$) 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°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_{Or}, $\underline{c}_K$, 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 2θ value (e.g., 21.148° instead of 20.148°), 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."