

Balancing complex mineral reactions with basic algebra

Balancing reactions in first year chemistry class was usually a simple matter of inspection. For example, if asked to write out the balanced reaction between the reactants hydrochloric acid and calcite (calcium carbonate), and the products calcium chloride, water and carbon dioxide, most students would probably have little difficulty coming up with:



Indeed, for those students with an aptitude for chemistry, being told the products (in deep blue) were calcium chloride, water and carbon dioxide wouldn't even be necessary: the reactants (in green) are simple enough to figure out what the products would likely be.

A comparable chemistry problem in a mineralogy or petrology class, however, could be quite a bit more challenging. Although the calcite in the previous is of course a mineral, it's obviously a very simple one; in contrast, the formulas for many rock-forming silicates can often be much more complex (consider amphibole or tourmaline, for example). And in the real-life situation of deriving a balanced mineral reaction by modeling the observed mineral assemblage identified in an actual rock, it may not even be entirely obvious which minerals are the reactants and which minerals are the products!

In this situation, asked to write out a balanced reaction between, for example, K-feldspar, biotite, chlorite, muscovite and quartz, just by inspection and without knowing *a priori* which minerals are the reactants and which are the products, even an accomplished chemistry student might feel totally stumped.

Fortunately, however, there is a simple algebraic technique that can be used to balance these sorts of reactions, and as an added bonus, which minerals go on one side of the equation and those which go on the other side comes out in the math. As an example, let's take a look at the assemblage described above. In fact, that particular reaction is an important one that marks the transition between the "chlorite zone" and the "biotite zone" in the Barrovian-style metamorphism of pelitic rocks. The preceding description is actually an inadvertent hint, as it implies that chlorite and biotite should be on opposite sides of the reaction. But as we'll see, that hint is entirely unnecessary.

The following numbered steps go through this full metapelite example, from initial set-up to final results. Ancillary explanatory notes are included along with each step for more detail. Following the last step, I've offered some additional mineral assemblages to practice writing reactions with (these are of varying difficulty... the answers are on the last page). So good luck, and happy balancing:

(1) To begin, let's start with the formulas for the minerals of interest:

K-feldspar: $K[AlSi_3O_8]$

"biotite": $KMg_3[AlSi_3O_{10}(OH)_2]$

"chlorite": $(Mg_2Al)[AlSi_3O_{10}(OH)_2]Mg_3(OH)_6$

muscovite: $K(Al_2\Box)[AlSi_3O_{10}(OH)_2]$ (the \Box means a vacancy)

quartz: SiO_2

The formulas I've used here are basic "structural" formulas. Unlike "empirical" formulas, which lump all *like* components together for simplicity (for example, the "chlorite" above could be empirically written as simply $Mg_5Al_2Si_3O_{18}H_8$), structural formulas break out individual components into the separate building blocks which make up the mineral. Of course, it's not necessary to use structural formulas for this exercise, and arguably, it might actually result in the accounting being a bit more cumbersome. But I believe students should become familiar with, and comfortable with, basic structural formulas. So I'm always going to use them.

Also with regard to formulas, the compositions here for biotite and chlorite have been greatly simplified from what you might find on mindat.org or in a mineralogy textbook. This is necessary to make balancing the reactions manageable. If you're curious as to why and how we get from the typical complex solid solution formulas for a general biotite family mineral and a general chlorite family mineral to these simple particular end-members [the simplified "biotite" here is really phlogopite, and the "chlorite" here is really clinocllore], check out the detailed appendix near the end of this tutorial. The generalized solid solution expressions can normally be added back in at the end, if desired.

(2) Set up the following table:

	K-feldspar (F)	biotite (B)	chlorite (C)	muscovite (M)
K =	1F	1B		1M
Mg =		3B	5C	
Al =	1F	1B	2C	3M

This is how the table is set up: Only multi-component minerals are included in the top header row. Single component minerals (such as quartz) can be ignored here, because we'll be able to add them back in at the very end. Likewise, only the elements in the multi-component minerals appear in the left-most header column. So for example, because quartz is omitted in the mineral list in the top row, Si is similarly omitted in the element list in the left-most column. Although quartz (and also H_2O and CO_2) are probably the most common single-component minerals treated this way (along with their constituent Si, H and C), sometimes

rutile (with its Ti), corundum (with its Al), and other simple oxides are similarly omitted. Note that in this example, Al must be included in the table because corundum is *not* a part of the observed mineral assemblage, and so it can't be used to balance the reaction later. Also, oxygen is never included in the element list (except in some very rare odd cases), although if an element like Fe changes oxidation state, extra oxygen may be needed during the final reaction balancing.

More about the table: each table entry (in blue) represents the molar amount of the element (row) present in the specified mineral (column). The mineral abbreviations provide the basis for the algebraic formulation, so they should be included. Hence, the 3B entry means there are 3 Mg atoms in the biotite formula unit, and the blank cell at the intersection of K and chlorite indicates that chlorite contains no potassium. Also important is that the table has one more column than row (that is, columns = rows + 1).

Regardless of how many columns are needed (that is, how many minerals are included in the initial balancing), the table always has to have one more column than row. One very important rule is that if a particular element is given its own row, then *every* mineral that contains that element must have its own column.

(3) Each row in the table becomes its own equation. So we end up with:

$$K = 1F + 1B + 1M$$

$$Mg = 3B + 5C$$

$$Al = 1F + 1B + 2C + 3M$$

where F, B, C, and M are the unknowns, and actually represent the stoichiometric coefficients of the respective minerals in the final balanced reaction! (nifty, huh?)

And what are the values for K, Mg and Al? Well, each one has to be 0! Why is this? Using the K equation as an example, all of the potassium in the reactants has to be exactly balanced out by all of the potassium in the products (otherwise there would be excess potassium unaccounted for). Thus the K equation above ($1F + 1B + 1M$) has to be equal to a net of 0. The same must be true for the Mg equation and the Al equation, since we can't have excesses of those elements either. Obviously, this means that one or more of the variables will have to turn out to be a negative number.

So we end up with:

$$0 = 1F + 1B + 1M$$

$$0 = 3B + 5C$$

$$0 = 1F + 1B + 2C + 3M$$

(4) Still with me here? Great, because that's the end of the set up... not too complicated, huh? The rest is just the math.

So, on to the math... One mathematical concept that comes into play here is that to solve for a set of n unknowns, you have to have n independent equations. For example, if you have only the equation $X + Y = 5$, what are the values of X and Y ? The answer, it turns out, is a bit unsatisfying: there are an infinite number of solutions. However, if you add in another condition (that is, another equation), so for example you had the equations $X + Y = 5$ and $X - Y = 3$, then there is only one solution which will satisfy both equations simultaneously... $X = 4$ and $Y = 1$.

Math whizzes might notice a slight problem, however. In our mineral reaction example, we have three equations, but we have four unknown variables (F , B , C and M). This is unsolvable, and it seems like perhaps we must have made a mistake somewhere along the way. But there's no mistake, and in fact we only have to use a simple trick to solve the set of equations. The trick is that we pick any one of the variables (it doesn't matter which one, although which you choose could make the math a little easier or a little harder), and we assign it a value of 1.

For this example, I'm going to assign $B = 1$.

You might wonder how this can be possible? Well, the trick works because the coefficients in a chemical reaction are *relative* numbers, not *absolute* numbers. Looking back at the $\text{HCl} + \text{calcite}$ example on the first page, the reaction can be rearranged as follows (remember, $[+]$ numbers are products and $[-]$ numbers are reactants):

$$0 = 1 (\text{HCl}) + 1 (\text{H}_2\text{O}) + 1 (\text{CO}_2) + -2 (\text{HCl}) + -1 (\text{calcite})$$

But equally true would be:

$$0 = 4 (\text{HCl}) + 4 (\text{H}_2\text{O}) + 4 (\text{CO}_2) + -8 (\text{HCl}) + -4 (\text{calcite})$$

or:

$$0 = -0.5 (\text{HCl}) + -0.5 (\text{H}_2\text{O}) + -0.5 (\text{CO}_2) + 1 (\text{HCl}) + 0.5 (\text{calcite})$$

or an infinite number of other possibilities (note, however, that in this last version, the change of sign switches the products with the reactants. But of course this switch doesn't really matter; the reaction is equally valid going to the right or to the left. Just flip all the signs if you prefer to reverse the reaction direction).

So again, whatever value is assigned to B is inconsequential; all the other variables (F , C and M) will simply end up appropriately proportioned to B .

By the way, although one could pick any of the four variables to assign a value of 1 (or 10, or whatever number you want), a bit of quick inspection shows that choosing B or C first is probably the best choice in this example. Why is that?

Because the equation $0 = 3B + 5C$ can then be quickly and easily solved for the other variable. Hence:

$$B = 1 \text{ (by assignment)}$$

then solving for C, gives

$$C = -3/5$$

Don't worry about the fractional value of C... we'll get rid of fractions later.

With values for B and C now known, and two remaining unknown variables left, use either linear combination (usually easier) or substitution (usually a bit messier) and the two remaining equations to solve for F and M.

$$M = 3/5$$

and

$$F = -8/5$$

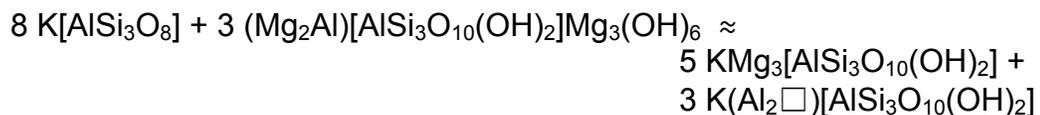
(5) At this point, the *partially* balanced reaction can be written as (where I've replaced the F, B, M and C with their mineral names):

$$0 = -8/5 \text{ K-feldspar} + 1 \text{ biotite} + 3/5 \text{ muscovite} - 3/5 \text{ chlorite}$$

Rearrange the equation so that minerals with negative coefficients are treated as reactants (on the left side), and minerals with positive coefficients are treated as products (on the right side). Multiplying through by 5 will clear out the fractions:

$$8 \text{ K-feldspar} + 3 \text{ chlorite} \approx 5 \text{ biotite} + 3 \text{ muscovite}$$

or, in chemical nomenclature:



Note the use of an "almost equal" sign (\approx) instead of an equal sign ($=$). That's because although we're almost finished, we're still not quite done yet.

(6) Inspection of the partially balanced reaction shows that K, Mg, and Al are balanced on both sides of the reaction (there are 8 K, 15 Mg and 14 Al on each side). This should be expected, because these are the three elements that were the basis of the 3 independent equations we derived in step 3. If any of these three elements don't balance, then you've likely made a math error.

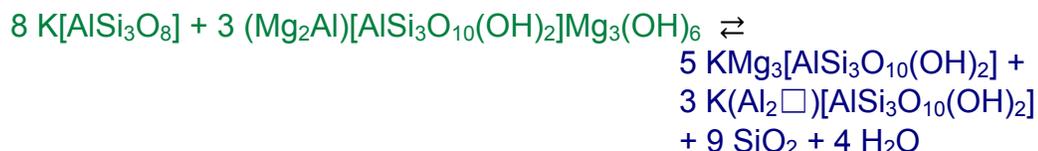
(7) Next we examine the remaining elements... the ones that were *not* included in the table. How do the number of Si and H (and also O) atoms compare on both sides of the reaction?

For Si, there are 33 on the left side, but only 24 on the right side, so an extra 9 SiO₂ need to be added to the right side. Because SiO₂ is a single component mineral that wasn't included in the tabular element balancing (that is, SiO₂ doesn't include K, Mg or Al), adding it here at the end of the balancing process doesn't affect any of the previous calculations we worked on. And because quartz almost certainly occurs in this rock, it's an allowable mineral to include.

For H, there are 24 on the left side, but only 16 on the right side, so again an extra 4 H₂O need to be added to the right side. As with the previous SiO₂, because H₂O is a single component mineral, it can be added here at the end without affecting any of our earlier calculations. Also, again, because water is ubiquitous in most geologic systems, it too is an allowable component to include.

For O, note that because none of the elements changed oxidation state, the O has to end up balanced by default. Count up the oxygen atoms on each side of the reaction to satisfy this for yourself. Had any elements changed oxidation state (typically when a reaction has minerals and/or gases with both Fe²⁺ and Fe³⁺, C⁴⁺ and C⁴⁻, or H⁺ and H⁰), then the oxygen would also need to be balanced separately at the end.

(8) The complete reaction, with water and quartz included, is now fully balanced:



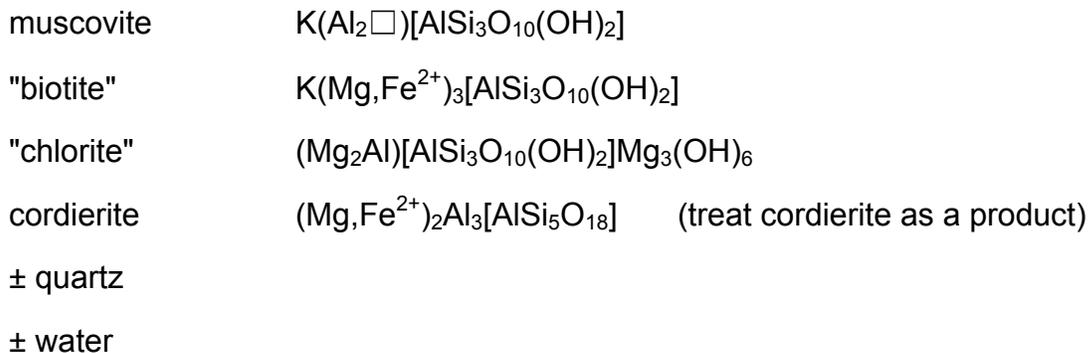
And that's all there is to it.

Perusal of this reaction shows that K-feldspar and chlorite, both common constituents in sedimentary rocks, might therefore be expected to react under the appropriate P and T conditions to form biotite, muscovite, quartz, and water. As written, this reaction follows a prograde path, with chlorite dehydrating to two micas, each with lower water content (and the newly-formed water free to leave the system). Although this particular reaction describes one potential path to transition between the chlorite zone and biotite zone in the Barrovian-style metamorphism of pelitic rocks, it's not necessarily the only path possible. Variations in the initial bulk rock chemistry, or in prevailing physio-chemical conditions such as oxygen fugacity, all play a role in what reactions might be favored to occur. Deciphering these complexities in an actual rock can often be a major challenge. Ultimately, however, predicting and balancing a plausible mineral reaction can also be a very rewarding achievement... and pretty fun too.

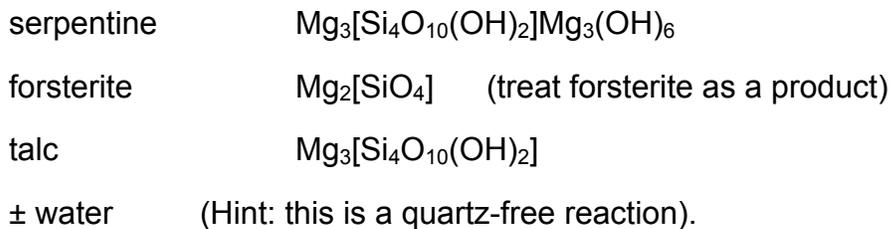
Additional practice with more reactions:

Try writing a balanced reaction for each of the five metamorphic mineral assemblages listed below. For consistency, one mineral in each set is identified as either a reactant or a product, chosen so that the final balanced reaction will generally represent the prograde path (that is, the higher T [sometimes higher P] set of minerals should end up on the right-hand side of the reaction), except where otherwise noted. A basic structural formula for each mineral is given (but be aware, however, that these are *not* necessarily end-member formulas, nor are all of any potential Fe^{2+} and Fe^{3+} substitutions explicitly listed... so, one or more simplification steps may still be warranted!) The five assemblages are arranged roughly in order of increasing difficulty. For your geologic interest, additional information about the general bulk rock composition and the typical P and T conditions, applicable to each reaction, are included. Answers are on the last page. As before, good luck, and happy balancing!

(1) A reaction within the albite-epidote hornfels metamorphic facies (low to moderate T; low P), in a pelitic sedimentary rock:

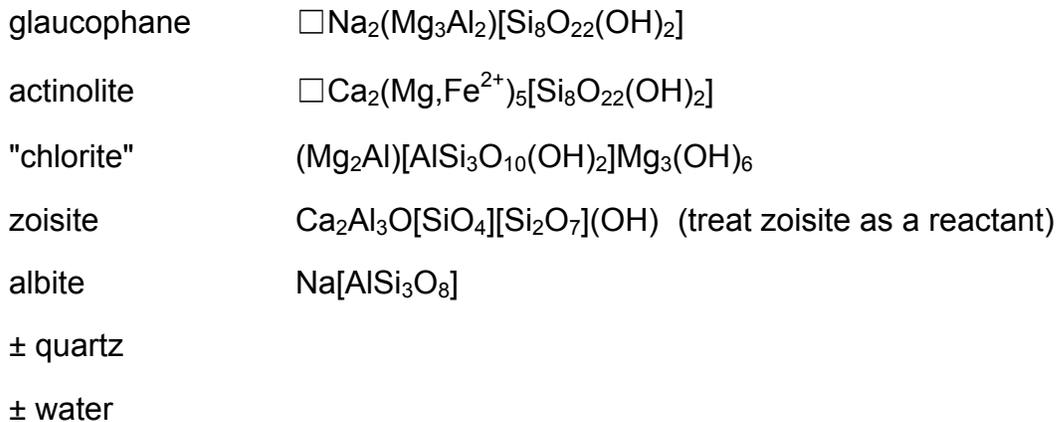


(2) A prograde reaction from the albite-epidote hornfels metamorphic facies (low to moderate T; low P) to the greenschist metamorphic facies (low to moderate T; moderate P), in a serpentinite:

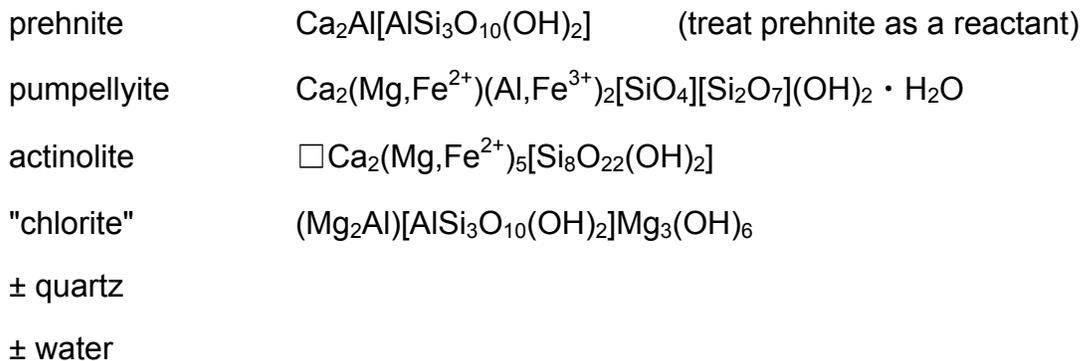


(By the way, this reaction in the other direction [that is, when forsterite is a reactant rather than a product] is one example of the alteration of peridotite).

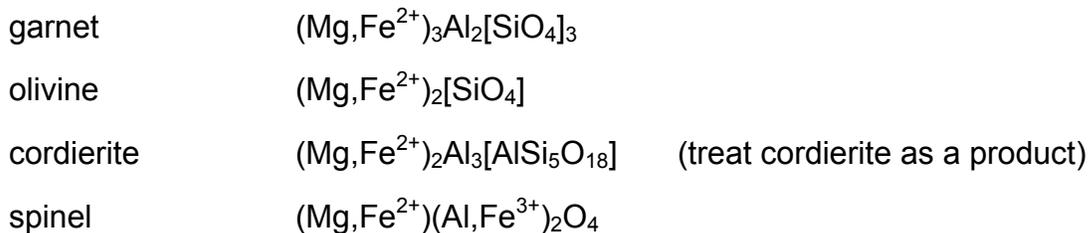
(3) A retrograde reaction from the blueschist metamorphic facies (low to moderate T; high P) to the greenschist metamorphic facies (low to moderate T; moderate P), in a spillitized (seawater-altered) meta-basalt:



(4) A reaction within the prehnite-pumpellyite metamorphic facies (low T; low to moderate P), in a meta-basalt:



(5) A reaction within the sanidinite metamorphic facies (very high T; low P), in a pelitic sedimentary rock:



(Hint: this is a quartz-free reaction).

[APPENDIX 1] Recasting solid solutions as simple end-members:

In the first metapelite example, three of the five minerals are end-member compositions (that is, there are no commas in the formulas):

K-feldspar: $K[AlSi_3O_8]$

muscovite: $K(Al_2\Box)(AlSi_3O_{10}(OH)_2)$

quartz: SiO_2

The other two "minerals" are actually group names of related species, and are represented as solid solutions of two or more end-members (notice the commas):

"biotite": $K(Mg,Fe^{2+})_3[AlSi_3O_{10}(OH)_2]$

"chlorite": $(Mg,Fe^{2+},Al,\Box)_3[(Si,Al)_4O_{10}(OH)_2](Mg,Fe^{2+},Al,\Box)_3(OH)_6$

This concept that biotite and chlorite are not actually minerals *per se*, but are in fact names of mineral groups can sometimes be confusing to students, many of whom were probably not taught the distinction in their introductory classes. Still, in order to effectively use this algebraic method, we first have to re-cast the complicated solid solution formula represented by the group name, to a simple specific composition we can more easily work with. These specific compositions need not necessarily be end-members, but using end-members usually makes the math so much easier!

For this example, the Mg-Fe²⁺ pair is easiest to deal with, because there are no minerals in this assemblage that have Mg but *can't* contain Fe, or have Fe but *can't* contain Mg. If this is the case (and thankfully it usually is), we can just pick just one element (either Mg or Fe²⁺) to simplify the more complex solid solution. In this case, I'll choose Mg, so:

"biotite" becomes $KMg_3[AlSi_3O_{10}(OH)_2]$ (this is actually phlogopite, an end-member of the biotite family)

"chlorite" becomes $(Mg,Al,\Box)_3[(Si,Al)_4O_{10}(OH)_2](Mg,Al,\Box)_3(OH)_6$

In the uncommon case where in addition to any combined (Mg,Fe²⁺) mineral(s) there's also one or more minerals with Mg, but which can't take Fe (this is rare), or with Fe, but which can't take Mg (for example, if epidote, hematite or pyrite is included), then the (Mg,Fe²⁺) cannot be replaced with Mg or Fe alone, but rather must be replaced with a discrete combination of both, for example (Mg_{0.5}Fe²⁺_{0.5}). The comma is gone, so this can now be numerically balanced. Incidentally, solid solutions involving Al and Fe³⁺ can normally be simplified in an analogous way as how Mg and Fe²⁺ are treated. In this case, it's usually easiest to just replace Fe³⁺ with Al.

Another feature to notice that while "chlorite" is indeed now simpler, it still isn't an end-member (there are still a bunch of commas in the formula). To further simplify "chlorite", however, we probably wouldn't want to just replace (Mg,Al) with all Mg, and (Si,Al) with all Si. Because Al occurs in orthoclase and muscovite *without* Mg, because there is a coupled substitution in distributing Al between the Mg and Si cation sites, and because Al will be one of the elements we'll end up using to balance the full reaction, we have some (but not unlimited) flexibility in choosing an acceptable chlorite formula. Even so, we'll want to pick a chlorite formula that is plausible for the system we're trying to model. Here are our five main choices:

"chlorite"-1: Mg₃[Si₄O₁₀(OH)₂]Mg₃(OH)₆ (here I have simply replaced all the Al+□ with Mg, and then appropriately charge balanced the Si site. Although written in the T-O-T O format of a chlorite, it turns out a chlorite with this composition isn't actually known as a mineral. Instead, this formula should be slightly re-written to Mg₃[Si₂O₅(OH)₄], a T-O type serpentine group sheet silicate. But since we want a chlorite for this example and not a serpentine, we won't pick this choice).

chlorite-2: (Mg₂Al)[AlSi₃O₁₀(OH)₂]Mg₃(OH)₆ (this is the chlorite end-member clinocllore, a common mineral with one Al in one of the Mg-sites charge-balanced by one Al in the Si-site. This may be a good choice for our metapelite).

"chlorite"-3: (MgAl₂)[Al₂Si₂O₁₀(OH)₂]Mg₃(OH)₆ (oddly enough, this also doesn't occur as a T-O-T O chlorite, but again should be re-written as (Mg₂Al)[AlSiO₅(OH)₄], a T-O serpentine family mineral known as amesite. While chemically it might not be a bad choice for our rock, we want a chlorite and not a serpentine for this example).

chlorite-4: (Mg₂Al)[AlSi₃O₁₀(OH)₂](Al₂□)(OH)₆ (this is the chlorite end-member sudoite, with a somewhat more complex coupled substitution than that in clinocllore. Again, chemically, this seems like it could be an acceptable choice for our Barrovian metapelite reaction).

chlorite-5: (Al_{2.33}□_{0.67})[AlSi₃O₁₀(OH)₂](Al₂□)(OH)₆ (this is the chlorite end-member donbassite. This is a poor choice for our reaction because it leaves biotite as the only mineral with Mg. That means we'd be unable to balance the desired reaction without requiring Mg to either leave or enter the system as an aqueous species (Mg²⁺_(aq)), or alternatively, we'd have to include an extra Al-free

Mg mineral, which is not likely plausible for this Al-rich bulk rock composition. $\text{Mg}^{2+}_{(\text{aq})}$ as a product or reactant might be OK if there's geologic evidence to support that assumption, but in this example, we want to consider a system where only H_2O is allowed to move in or out of the system... not additional ions.

Among the five choices and based on the aforementioned criteria, only the clinocllore (chlorite-2) and the sudoite (chlorite-4) would be appropriate for the metapelite example, and either end-member could be used (although with somewhat different final results, of course). For the original exercise, clinocllore was selected, because it is the more common and more well known species. However, for additional practice balancing reactions, the exercise could be repeated using sudoite instead (or even trying the amesite).

One final note with regard to the simplification of solid solutions to discrete or end-member compositions: if there are only two minerals with, for example, $(\text{Mg},\text{Fe}^{2+})$, it is a mathematical necessity that in a closed system, both must be simplified the same way. Hence, for example, if only biotite and chlorite are considered, both must be treated as Mg or Fe end-members, or as the same Mg_xFe_y intermediate composition. Alternatively, if one or more additional Fe and/or Mg minerals are included, or if Fe and/or Mg is allowed to leave or enter the system (as an aqueous species, for example), then the requirement that Mg_xFe_y be the same for each mineral can be relaxed. Nonetheless, calculations in this latter case can be very unwieldy, and in fact may require numerical methods rather than simple algebra to solve. In most cases, it is advantageous to simplify the system as much as possible.

ANSWERS to practice reactions:

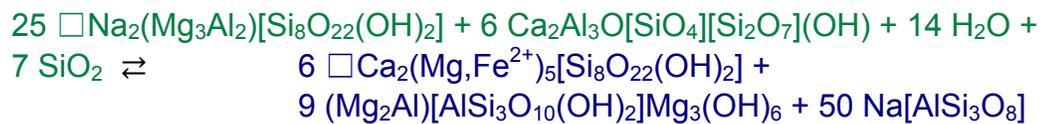
reaction (1):



reaction (2):

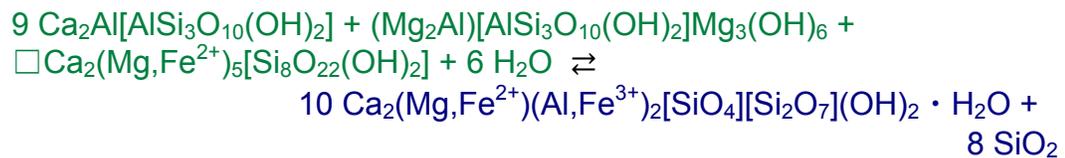


reaction (3):



(Here's a question: why don't the vacancies need to balance on each side?)

reaction (4):



reaction (5):

