MINERAL SYNTHESIS AND X-RAY DIFFRACTION EXPERIMENTS

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GENERAL INSTRUCTIONS, COMMENTS AND NOTES

Purpose:

- give students a better understanding of how and why mineralogical reactions occur
- give students a practical introduction into the use of an X-ray diffractometer
- teach students to be creative, critical and analytical in the face of confusing or ambiguous data
- give students an understanding of, and appreciation for, the way scientists think and work

Philosophy:

These labs are based on experimentation, but if they are to be valuable learning experiences, instructors should avoid the "cook book" approach to science. We give students assignments/problems with only a minimum of instruction. The goals are clearly set out, but the means are not. Sometimes, experiments may not "succeed," no matter what students do. In others, the results depend on the techniques used or on student ingenuity. Ambiguous results are common. It is tempting for instructors (especially graduate students teaching assistants) to try to put students on the "right path" by explaining too much. If you do that, it stifles student creativity and thinking and leads to student boredom. If you let them operate on their own, they will amaze you.

Although we may give individual students individual assignments, we encourage them to work in groups--one way to do this is to have half their grade come from their own work, and the other half from the group's work as a whole. We often have groups of 3-4 students, with each working on their own individual mineral. We group them by mineral chemistry.

Although students are sometimes confused or uncertain, after completing the mineral experiments, most of our students give "a big thumbs-up." Some really excel at this sort of exercise. Sometimes the best students are ones who only receive mediocre scores on traditional labs or exams. At the other extreme, we have found that a few students cannot handle the uncertainty involved in true experimentation. No matter how we explain and encourage, they are frustrated at not knowing how to do things, and at not getting what they think is the "right" answer. They seem unwilling to make, or incapable of making, meaningful interpretations. Most of the frustration seems to stem from lack of confidence.

Specific Projects:

We have had our students try to synthesize many different minerals in many different chemical systems. It really makes no difference which minerals students try to make, because it does not matter if their experiments succeed. In fact, the students often gain more from these

exercises if they have to explain why things apparently "failed." But, if you want experiments that give the expected results, have them try making spinel minerals (spinel, galaxite, etc.)--just about any spinel mineral will yield good results. (You can incorporate Fe as Fe_2O_3--it will partially reduce to produce some spinels.) Pyroxene, olivines and calcium silicates (wollastonite, larnite, etc.) usually work out, but do not react as completely as oxides. They can also synthesize alumino-silicates and related minerals such as anorthite, grossular or andradite at one atmosphere, but recycling is normally required to get large amounts of reaction. If you want to confuse/challenge students, have them try to make something that melts at relatively low temperatures--incongruent melting is the best if maximum confusion is what you are after. To avoid melting and some other problems, we recommend avoiding minerals containing K_2O or Na_2O.

As a variation on these labs, we have had students react two or three minerals to make another, or decompose a mineral and analyze the products. For example, they can react calcite with quartz to get a $CaSiO_3$ polymorph, or periclase with gibbsite to produce spinel. And, tremolite decomposes nicely to diopside+enstatite+quartz. In summary: try anything you feel like, just to see if it will work. Once you instill the right attitude in the students, all experiments become successful.

Library and Computer Resources:

Synthesis experiments have been done before, and if students poke around in a library they will find appropriate papers. Curiously, few students even think about going to the library. When they ask if it is OK, we encourage them to use library resources--some do, most do not.

Many good X-ray diffraction data bases and search programs are available. We find it better to have students use hard copies of X-ray reference files--even if that means that they are not doing "complete" searches. We use search manuals sometimes. Other times we print out 30-50 patterns and make copies available in the laboratory.

Some recommended chemicals to use as starting materials (reagent grade):

$CaCO_3$	Zn-acetate
MgO	Al-hydroxide
Fe_2O_3	MnO_2
TiO_2	silicic acid

Equipment Needed:

mortars/pestles	1000° oven
many small vials	ceramic crucibles
airplane glue	spatulas, scoops
balance scale (±0.01 grams)	long handled crucible tongs
weighing paper	heat resistant glove
pelletizer	X-ray diffractometer
Teflon spray to lubricate pelletizer	

Handouts:

Attached to this write-up are lab handouts we used in 1997. Many variations are possible, and we make changes every year. In 1997, the students did their experiments over a six

week period; they were doing other things in mineralogy lab at the same time.

Week #1: We instruct students about the need to write everything down in a lab book. This need cannot be overemphasized--students generally do not record things well enough so that they can go back later and figure out what they have done. We tell them to take care--especially with weighing--but inevitably they make mistakes. It is up to each instructor whether to point out the mistakes or let them go on and figure things out later.

We tell the students that, at high temperatures, compounds release H_2O and CO_2 and that simple reagents become oxides. We give them ceramic crucibles which they load with various pure reagents, weigh, and fire over night. After cooling, they reweigh the reagents and calculate the percent weight loss that each experienced. They compare results with theoretical ones based on chemical formulas. (These calculations are not trivial. Students may require a good deal of help and explanation. One problem is that the compositions of reagents such as Al-hydroxide and silicic acid usually do not correspond to those in books--as the students will find out! In addition, metal oxides such as MnO_2 may or may not be completely oxidized. And, calcium oxide picks up water from the atmosphere very quickly--actually gaining weight while it sits on a scale.) After everyone in the lab agrees on the "correct" weight loss percentages, students calculate the amounts of reagents they need to mix to synthesize their mineral. In the process they learn about converting moles to grams, etc.

Week #2: Students make their reagent mixes and collect X-ray patterns. They also X-ray each reagent individually, and the reagents that they fired at 1000^{o}C the previous week. By comparing patterns, they can decide which peaks in their reagent "mix" pattern correspond to which reagents. Although not in the lab write-up this year, we also usually give them unlabeled X-ray patterns of natural samples of calcite, lime, periclase, gibbsite or diaspore, any Mn-oxide, and quartz to try to match with the patterns they collect. We ask them why the X-ray patterns for the reagents and the natural materials of similar composition do not match exactly. As reference materials, we give them copies of data from the JCPDS or another X-ray diffraction data base. Some results will be ambiguous. Students may need some guidance. They may need to be told how well peaks should match, how much attention to pay to peak intensities, and other practical things. But, as much as possible, they should be left alone to figure out what they think the best criteria are to establish a good match.

Week #3: Students grind their reagent mixes, make a pellet, and then put the pellet in a high-T oven. We use acetone to wet the powders, so the grinding is done under a hood or near an open window. They must be encouraged to grind for a long time (30 minutes is not unreasonable). Fine grinding is a key to good reaction! (The grinding process will result in big messes, and lots of spilling. That is one reason students started with a gram of material.) We make pellets by binding the powders (with airplane glue) in a homemade pelletizer made of tool steel. We have to go to the machine shop once a semester to get our pelletizer turned on a lathe because tool steel is easily galled. Although in a real research lab, researchers make pellets at high pressures, for student exercises high pressures should be avoided because of possible danger, and because the students will destroy cheap homemade pelletizers.

Students weigh empty crucibles, place their pellets inside, and then weigh the loaded crucibles. They place the crucibles into a cool oven which slowly heats to 800°C. Some samples partially crepitate on heating, which causes no problems. After cooking, students remove samples from the oven, reweigh them, and grind a small amount for X-ray diffraction. It is likely that students will get their samples mixed with someone else's!

Week #4: After students remove their pellets from the oven, they collect an X-ray pattern and identify the phases present. The amount of reaction depends on the compound they were trying to make and may not be great. They should compare their scan with the ones they collected for the dehydrated and decarbonated reagents--some peaks will likely match.

Week #5: Students now regrind their material, make new pellets, reweigh them, and recook them at 1000°C. For best results, they should repeat this process several times, but time may be a factor. In 1997 we did no repeats. Fine grinding is extremely important and often determines success or failure. After each cooking, a small amount of sample is reserved for X-ray diffraction. For some attempted syntheses, students obtain nearly complete reaction after one 1000 °C cycle. But for many compounds, recycling or higher temperatures are needed to get good reaction.

Normally we do not heat our ovens above 1000°C for several reasons. Hotter temperatures pose serious safety risks (but even 1000°C can give a bad burn if students do not take care); 1000°C ovens are not prohibitively expensive and are indestructible if treated reasonably; and most compounds do not melt at 1000°C. As a final "bonus" we sometimes have students submit their samples for cooking in a higher temperature oven (1300 or 1400 °C). This leads to much better reaction, and sometimes to melting (students never seem to think about melting as a possibility and are often confused when they get back a glass) with, perhaps, destruction of a ceramic crucible (which fortunately is not expensive).

Week #6: As a final report, we have each student group prepare an 8-10 page paper. Usually they include an additional 8-10 pages of X-ray diagrams. We ask them to analyze the diffraction patterns one-by-one, starting with the original mix and ending with the last attempted synthesis. We do not want students to get bogged down writing a "book," but we want them to be able to summarize cogently what they have done and what happened. Students should, of course, be analyzing the results of their experiments at every step of the process. But, they will not without MUCH prodding. X-ray patterns should be collected and peaks identified after each cooking, because students should not go on if things are hopelessly confused or mixed up. Sometimes students may wish to start over. But, starting over is pointless if they are going to follow the same procedure, unless they made some fundamental error (e.g., weighing). They must, therefore, be encouraged to analyze their results and to figure out why they got what they did. Some experiments will not yield successful syntheses--they must understand that and explain why.

MINERAL SYNTHESIS PROJECT

Step 1: Formulas and Reagents

What are we doing for this lab?

For this lab you should do the following:

1. Start a lab notebook where you write down everything you do. Never throw anything away. Keep all notes and scribbles. Note any strange things that happen. Write it all down! When you do calculations or weigh things, have someone else check what you do and initial your notebook. This may sound hokey, but it pays off when things get confusing later on. I can't emphasize this enough. If you make errors or fail to write things down at the beginning, everything you do later will be worthless. Check and double check! I could tell you some embarrassing (but true) stories about times I didn't...don't write your own stories.
2. For each of the reagents you need to make your mineral, figure out how much oxide is in the reagent (see method below).
3. For your mineral, calculate how much of each reagent you need to mix to make a 1 gm equivalent mixture (see method below).

The easiest way (plan A) to make "synthetic minerals" might be to mix up pure elements, cook them together, and voila ===> a mineral. Unfortunately there are a zillion problems with this approach. The first one is that some elements are unstable or unavailable in their pure states. And, some of them are available but cost too much. So we consider plan B.

Plan B is to synthesize mineral from oxides. For example, hedenbergite has the formula $CaFeSi_2O_6$. We can write the following formula:

$$CaO+FeO+2SiO_2 = CaFeSi_2O_6.$$

So, we could mix up 1 part CaO, 1 part FeO and one part SiO_2 (molar parts, not weight parts) and react them to get hedenbergite. But, guess what? CaO and FeO aren't available or stable.

So, we go to plan C. Your mission (plan C) is to synthesize your mineral from reagents available in the mineralogy lab. You will mix the appropriate amounts of TiO_2, MnO_2, $CaCO_3$, Fe_2O_3, $Al(OH)_3$, MgO, silicic acid, and Zn acetate. Then you will pelletize your mix and fire it at high temperature. Today we will get you started on your mission, but it won't be completed for a while.

This is your project, but you have a partner and the final grade depends on both of your performances. Work with your lab partner, and consult with others in the lab as you go along. Maybe they have figured out some things you don't know. One important thing, however, is to remain skeptical. Don't believe anything anyone tells you unless you are convinced yourself. Figure things out for yourself because experimentation is not always like cook book chemistry labs. Things that are true for one student may not be true for others doing different experiments.

On the next page is a table with your starting ingredients listed. Note on reagents: they are never what they say they are. Unless you buy the most expensive reagents and store them in the best way, they will contain impurities. Absorbed water from the atmosphere is especially significant for some of them.

Table 1. Elements, oxides, and reagents in the Mineralogy Lab

element	oxide	reagent
Ti	TiO_2	TiO_2
Mn	MnO_2	MnO_2
Ca	CaO	$CaCO_3$
Fe	Fe_2O_3 (or FeO)	Fe_2O_3
Al	Al_2O_3	$Al(OH)_3$
Mg	MgO	MgO
Si	SiO_2	silicic acid
Zn	ZnO	Zn acetate

Calculations

First, you need to figure out what to mix up. The way to think about this is first to consider your mineral as made of oxide components. One mole of hedenbergite, our example, contains one mole of CaO, one mole of FeO, and two moles of SiO_2. We need to convert the molar values to weight percents. I have done this in the table below. The results (right hand column) are that a 1 gm mix of hedenbergite composition contains 0.22604 gm of CaO, 0.28959 gm of FeO, and 0.48436 gm of SiO_2. Now we just have to figure out how much CaO, FeO and SiO_2 are in the reagents we have available, and we can figure out how much reagent to use.

oxide	A= # moles oxide	B=formula weight of pure oxide (g/mole)	C=mass of oxide in our mix (AxB) (g)	X=weight % of oxide in our mix	W=weight of oxide in 1 gm of mix
CaO	1	56.08	c_1=56.080	$X_1=c_1/\Sigma c$=22.604	W_1=0.22604 g
FeO	1	71.847	c_2=71.847	$X_2=c_2/\Sigma c$=28.959	W_2=0.28959 g
SiO_2	2	60.084	c_3=120.168	$X_3=c_3/\Sigma c$= 48.436	W_3=0.48436 g
TOTAL			Σc=248.095	ΣX=99.999	ΣW=0.99999 g

Procedure for determining the oxide content of reagents

Warning: A 1000° oven is very hot! You can get burned easily. Use the long handled tongs and try to hide off to the side of the door. Wear the fire proof glove or you are a (burned) idiot. If you are intimidated, let the TA's do the hot work. That's why they make the big bucks.

Another Warning: Be sure to figure out (with a scratch or something) a way to identify your crucible. They all look the same after they come out of the oven.

Write all weights down in your lab notebook. Don't make mistakes! Carefully weigh an empty clean crucible. Add about 0.5 grams of reagent and weigh again. Calculate the weight of the sample in the crucible. Place crucible in oven for several hours or more. Remove and weigh as

soon as it has cooled enough to handle and not hurt the scale. Now calculate the weight of the sample after firing (subtract the weight of the empty crucible). Assume that all the reagent has reacted to the oxide (listed in Table 1). You can now figure out how much oxide is in the reagent:

oxide % in reagent = 100 x (final weight of sample) / (starting weight of sample)

Iron poses a special problem. If we want reduced iron oxide (FeO) in our mix (as we do for hedenbergite), we need to make a correction if we start with oxidized iron oxide (Fe_2O_3). When we fire any iron oxide in air we get Fe_2O_3 (=$FeO_{1.5}$). The extra oxygen will (we hope) go away when we make our mineral. So, we need to put extra Fe_2O_3 in our mix to get the correct amount of FeO. The difference in the atomic weight of $FeO_{1.5}$ and FeO is 11.13%. Hence, if we want FeO at the end, we need to add 11.13% extra Fe_2O_3. *Note: if we wanted Fe_2O_3 in our final product we would not add an extra 11.13%.* Its possible that the Fe_2O_3 will gain weight when fired. This could occur if some of the Fe is reduced. No problem. Do the calculation the same way.

For the sake of this example, we will assume that silicic acid contains 90.51wt% SiO_2, $CaCO_3$ contains 56.18 wt% CaO, and the Fe_2O_3 really contains 96.67 wt% Fe_2O_3. (These are typical values.) So, we calculate the amount of reagents in a 1 gm "hedenbergite" mixture:

oxide	grams of oxide needed = A	% of oxide in reagent/100 = B	Fe correction = C	total amount of reagent needed = A x C / B
CaO	W_1=0.22604 g	0.5618		0.40234 g
FeO	W_2=0.28959 g	0.9667	1.1113	0.33290 g
SiO_2	W_3=0.48436 g	0.9051		0.53514 g
TOTAL	ΣW=0.99999 g			1.27038 g

So, our mix will weigh 1.27038 gm total. After firing we should have 1.00000 gm of product. But, since there is always some loss, we probably won't. But it should be close.

Step 2: Mixing Reagents and X-ray Analysis

What are we doing for this lab?

For this lab you should do the following:
1. Continue to write everything in your lab notebook.
2. Recheck your calculations and then mix up the appropriate reagents needed to make your mineral.
3. X-ray (and interpret the X-ray results):
    a. reagents right out of the bottle
    b. the dehydrated/decarbonated reagents (from last week)
    c. your reagent mix prior to putting in the oven

Mixing Reagents

Once you have determined the amounts of reagents needed to make your mineral, it is time to mix them up. So here is the process I recommend. Determine how much of each reagent you need to make 1 gram of your mineral (you were supposed to do this last week, but you may want to redo it).

1. Zero the scale (no tare). Then weigh a piece of weighing paper without anything on it.
2. For each reagent: Put a different piece of weighing paper on the scale and tare to zero. Carefully weigh out the appropriate amount of reagent. Then carefully dump it onto the weighing paper you weighed in step 1. Do not spill. Don't make dust that blows away. Slowly, carefully, completely. ***Do not put anything back into a reagent bottle--EVER!*** Use small spatulas and go slowly.
3. When you get done weighing each reagent and combining them on one piece of weighing paper: zero the scale (no tare), weigh the loaded weighing paper, subtract the empty weight determined in step 1, and you will have the total weight of reagents in your mix. Check this total against your theoretical total. It should be close. If not, figure out why or do it all over again.

All weights, whether right or wrong, and all steps should be written down in your lab book! Have someone else check your weights at every step of the way!

Grinding that Mix

Now take your mix and put it into a mortar. Wet it with lots of acetone--so it is really swimming, not just damp--and grind for at least 10 minutes. 30 minutes is better. Make sure lab windows are open. Work under the hood with the fan on whenever you can. Add acetone as needed during the grinding process. Be careful when you first add acetone or you will "blow away" some of your mix and mess up the composition.

A description of what you mixed up and how you ground it should go in your lab notebook.

X-raying

The TA's will instruct you on the use of the X-ray machine. Please do it their way and don't break the machine or X-ray yourself. You should X-ray each of the reagents you are using (take sample right out of the bottle), the dehydrated reagents that you made last week, and your mix.

A description of how you prepare the samples and how you X-ray them should go in your lab notebook.

Analyze the Results

For the reagents: compare your X-ray results with reference data and scans provided by the TA's.
For the dehydrated reagents: compare your results with reference data and scans provided by the TA's.
For your mix: Compare your scan with the scans for each individual reagent. Use colored pencils and color the various peaks that belong to each reagent.

Copies of your X-ray charts and data, and your interpretation go in your lab notebook.

Step 3: Pelletize and Start Cooking; Analyze X-ray Patterns of Initial Mixes

What are we doing for this lab?

For this lab you should do the following:
1. Continue to write everything in your lab notebook.
2. Grind your mix of reagents VERY well and then bind to make a pellet. Put the pellet in the 800°C oven and leave it there for a week.

Making Pellets

Once you have mixed the appropriate reagents, and ground the mix VERY well, it is time to make a pellet. To do this, put your powders in a mortar, add enough acetone to make it very wet, and then add a drop of glue. Mix well. Let it dry until just a bit moist. Put it in the pellet die and squeeze it between the two pistons. The TA's will show you how. Take care, the pellet die can be destroyed if you get the pistons in wrong or are sloppy about how you apply pressure. Depending on how moist your sample was, pressing of the powder should be real quick. Remove (or push out) one of the pistons. Then use the pushing tools (bolts) to push out the other piston and the pellet.

Cooking the Pellet

Place the pellet in a clean ceramic crucible and put it into the 800°C oven for a week. (Or get someone else to put it in there for you.)

A description of how you mixed and pelletized your sample and when and how you put it in the oven should go in your lab notebook.

Step 4: X-ray Products of 800° Oven

What are we doing for this lab?

For this lab you should do the following:
1. Continue to write everything in your lab notebook.
2. X-ray the products out of the 800° oven
3. Analyze X-ray pattern

Now is the time to start taking real care -- try not to lose any more of your sample or you will be in trouble later on!

Catch Up!

This week there is not a lot to do, so you can catch up if you are behind.

X-ray Product

Remove your pellet from the oven. Take your pellet and crush it. Probably you can do this in a mortar but maybe you will have to use a steel piston/cylinder. Grind your sample extremely well. Put a small amount on a glass slide for X-ray. Save the rest so you can make a new pellet later on.

X-ray your sample. Analyze the peaks. Compare the starting X-ray diffractions charts (for your mix and for the reagents separately) with your 800° chart. Also, be sure to compare the charts of the dehydrated/decarbonated reagents with your 800° chart. You should be able to match just about all peaks. If the reagents reacted to produce new phases, you may have to look up some peaks in the Search Manuals. The TA's will show you how. Of course, the goal was to synthesize your mineral--so be sure to check reference data for your mineral and compare to your experimental products. Good Luck! This can be confusing. Be patient and persistent and you will become enlightened.

Make sure copies of all diffractograms are in your notebook. And, also the details of your analysis of the pattern.

Step 5: Put Your Mineral in the 1000° Oven

What are we doing for this lab?

For this lab you should do the following:
1. Continue to write everything in your lab notebook.
2. Grind (very well) and repelletize your sample; put it in the 1000° oven

Hey-- It is even more important now to take real care -- try not to lose any more of your sample or you will be in trouble!

Make Another Pellet and Cook It

OK, now you have cooked your reagents at 800°. You have also X-rayed the products. Now, we want to recycle your stuff in a 1000° oven. So, take your products and crush them in a mortar. Take care not to lose any material. Grind extremely well and make a new pellet. Put it into the oven and relax.

Just as a reminder, you should now have the following X-ray patterns:
(a) individual reagents
(b) individual reagents after firing at 800°
(c) starting mix of reagents
(d) mix of reagents after firing at 800°

So, you can compare (a) with (b) to see what happens when reagents are cooked--you should be able to figure out what they change into. You can compare (a) with (c) to identify the X-ray peaks in your starting mix pattern. You can compare (b) with (d) to identify the X-ray peaks in your reagents after the first firing, and to identify what phases are present. You can also check to see if the mineral you are trying to make did indeed form.

Now, after we regrind, repelletize, and refire at 1000°, we will analyze the pattern again to see what happened. If we still aren't getting what we want, we may take new pellets over to the EERC and have them cooked at 1200°.

Step 6: X-ray Products of 1000° Oven

What are we doing for this lab?

For this lab you should do the following:
1. Continue to write everything in your lab notebook.
2. X-ray the products out of the 1000° oven
3. Analyze X-ray pattern

X-ray Product

Remove your pellet from the oven. Take your pellet and crush it. Probably you can do this in a mortar but maybe you will have to use a steel piston/cylinder. Grind your sample extremely well. Put a small amount on a glass slide for X-ray. Save the rest so you can make a new pellet later on. X-ray your sample. Analyze the peaks as you did for the products of the 800° oven.

Make sure copies of all diffractograms are in your notebook. And, also the details of your analysis of the pattern.

Prepare a Final Report as Instructed by the TA's.