

GEO 475L/ CHE 475L -- Solid Earth Geochemistry
Laboratory #3 9/27/07

Geological Sample Preparation II: Remaining Sample Preparation and Acid Digestion

Last week we discussed rationale and difficulties involved in sampling of geological materials. Today we will carry out a series of tasks, culminating with acid digestion of mineral separates. First, we will rough-crush our rocks with the tool steel mortar and pestle and then sieve the grains to arrive at a desired grain size population. Next we will use techniques at our disposal to separate fractions enriched with our minerals of interest. In a future lab we will examine samples under the microscope to ensure purity, and then grind them powder with the alumina ceramic ball mill and digest them, in preparation for chemical analysis. To speed things along today, each student will perform a digestion with a CRM (certified reference material). *Record all pertinent information in your laboratory notebook.* You may be asked to repeat any of these procedures, and will have to rely entirely on your notes for this. Be particularly certain to record any measurement that is made. Make your notes clear and explicit, so that you can go back to them and understand what was done.

Overview of Acid Rock Digestion Considerations

Carbonate rocks can be largely brought to complete dissolution with HCl or similar medium. Most silicate rocks, on the other hand, will not completely dissolve in HCl, HClO₄, HNO₃ or H₂SO₄ at Earth surface pressure and the temperatures on a typical electrical hot plate (80-180°C). The most widely used and effective acid for decomposing silicates is hydrofluoric acid (HF). This works according to the general reaction:



This reaction progresses even at low temperature, but, like most chemical reactions, is much more efficient at higher temperature (e.g., 220°C). Nevertheless, HF vaporizes at relatively low temperature, so unless the container is unusually well sealed, you will steadily lose HF while the rock digests on the hot plate. As you have read, HF, particularly in concentrated form, is a dangerous substance, so we cannot use it unless we use great care to avoid contact with it as a liquid or vapor. While handling HF you will wear safety eyewear, vinyl or PVC gloves, and a Tyvek jacket.

If we try this kind of digestion in a container made of glass, polyethylene, polypropylene, polycarbonate, or polymethylpentene the acids or the high temperature destroy our container. The solution to this problem is in the use of containers fabricated from fluorinated polymer resins (Teflon). The bottles in which we keep concentrated acids are FEP (fluorinated ethylene propylene) and the vials we use for digestion are made of PFA (perfluoroalkoxy). Both are largely inert to acids and are usable above 200°C (204-260°C). Items made from these materials have the downside of being bloody expensive (each 7 ml vial is about \$10), so we dare not melt or otherwise damage our Teflonware!

We will go over together the necessary points on laboratory etiquette (in particular the use of pipettes and the scientific balance). Please refer to the syllabus for a reminder on the consequences of not following the established rules for laboratory behavior.

In preparing samples for dissolution we typically mix HF with another acid (we will use concentrated HNO₃) in order to keep the residual solution acidic as HF molecules react or volatilize. We will use a volume ratio of 5:1 HF:HNO₃. Each student will prepare a digestion of one CRM (rock standard in powder form). Note that these are precious (again: expensive and hard to get, in many cases) materials that must never be contaminated. Consider ways of avoiding contamination before opening the jar or vial containing the standard. We will aim for 0.05 g of each standard -- getting this exact weight is unimportant, as long as the precise result is recorded. After samples are treated with HF + HNO₃, I will shepherd them through complete digestion during the coming week. This typically equates to monitoring samples on a hot plate at c. 100oC, periodically agitating. When all solids have disappeared, concentrated HCl is added while the solution progressively evaporates. In the process any residual HF is lost as vapor and samples conclude the process as Cl-based solutions, with reasonable shelf-life.

student	CRM ID	sample type
Cunningham	SCo-1	shale
Grade	SDC-1	mica schist
Kauffman	NBS-99a	Na-feldspar
Smith, S	BHVO-2	basalt
Stringer	AGV-2	andesite
Teeter	GSP-2	granodiorite
Williams	RGM-2	rhyolite

Questions to Ponder -- written and calculated solutions due at beginning of 10/4 lab:

- (1) You need to digest a clinopyroxene (CaMgSi₂O₆) sample but you are running out of HF in your lab. Hence, you would like to use as little HF to dissolve a given sample as possible. Concentrated HF is 49% HF by weight. Seeing as digestion is seldom stoichiometric, presume complete dissolution will require a molar ratio of 10:1 H:Si.
 - a. Using this rationale, how much pyroxene could you reasonably hope to dissolve with 1 ml HF?
 - b. You estimate that your pyroxene contains 40 ppm Li, and you want to analyze Li isotopes in the sample. For the measurement, you will need at least 20 ng Li. Determine the mass of pyroxene to dissolve, and from that the volume of HF to use for the minimalist digestion.
- (2) Consider that Teflon vials are essentially infinitely re-usable--after dissolving a sample, we can boil them in concentrated acid, and eventually we have a perfectly clean vial. Teflon is chemically resistant but it is soft and can be scratched. What are the potential consequences of scratching the interior of a Teflon vial relative to this otherwise infinite reuse? Be specific.
- (3) We want to determine the Si isotopic composition of the clinopyroxene from question #1. In order to make this measurement, we need to purify Si from an aqueous solution, so the sample must be dissolved. What pitfalls might be encountered in this process? How might they be avoided?