

**GEO 475L/ CHE 475L -- Solid Earth Geochemistry
Laboratory #5 10/11/07**

Introduction to Ion Exchange Chromatography

At the end of Lab #4 we were left with a set of completely dissolved samples in dilute (~1M) HCl. At this stage the samples are not so stable to remain in this form indefinitely—the high proportion of dissolved solids, even after the Fe-coprecipitation, will ultimately lead to some part of the elemental budget of the solution forming a solid. Hence, we need to do something with the solutions quickly.

As we considered in the last exercise, in order to isolate the REE (or just Sm and Nd, as needed for Nd isotope analysis), some additional steps need to be undertaken beyond simple digestion. This is where ion exchange chromatography comes in. This method was developed in more primitive forms in the first half of the 20th century but reached new levels of sophistication with the development of commercially available exchange polymers in the 1960's. Since then the selectivity and diversity of ion exchange resins has continued to improve to the point that ion-specific resins for a number of elements are now in wide use. Smash open a commercial purification cartridge from a standard kitchen water purifier and you find a vast number of little glistening spheroids: a mixture of cation and anion exchange resin, very much like we will use.

Theory

Ion exchange occurs as a result of natural processes, as well as in the laboratory. In short, ions in solution can bind with surface and crystallographic sites in minerals and other solids during water-rock interaction, dominantly at submagmatic temperatures. In this process, less energetically favorable bound ions are released, effecting a selection to the process. In nature, this process has major implications for the transport of contaminants in groundwater systems. The same fundamental principles underpin the use of ion exchange chromatography in the laboratory. Using synthetic solids (mainly sulfonated polystyrenes) we can demonstrate that elements will have predictable preference for the resin (referred to as “the stationary phase” in some chemistry literature) or the coexisting solution at equilibrium. By systematically varying the solvent medium (HCl, HNO₃, etc.) and its concentration, we see systematic changes in the resin/solvent partitioning behavior of the elements--this is the same concept as the crystal-liquid partitioning we have been modeling in lecture this week. Thus, if we seek to separate element X from a complex ionic solution (like our solutions after flux fusion, or any digested rock sample or natural water), we can develop a protocol for this extraction, selecting a combination of resin type and solvent for maximum separation of the element of interest from the matrix. The most important variables we can control in this process include resin type and volume, aspect ratio of the exchange column, solvent composition, and flow rate.

Ion exchange partition coefficients (essentially distribution coefficients, as we have calculated for geological systems) have been determined empirically for many such combinations, so finding the right recipe is a matter of combing the literature. Attached is a list of coefficients for this resin, using HCl.

Ion Exchange Columns

We will use prefabricated 10 ml exchange columns. The “column” refers to a tube that retains the stationary phase (resin) by way of a porous disk (these are commonly constructed from either pressed organic material or fibrous silica). It is important to avoid loading solids on the resin (especially if we hope to reuse it, as is common)--note that our flux fusion samples will contain plenty of solids. Liquids added to the column spend some length of time passing through (and hence reacting with) the

stationary phase. By gravity, solutions ultimately flow out the bottom of the column. We can either discard these solutions or collect them, depending on what we predict is being removed from the resin by addition of any given volume of liquid (referred to as the eluant).

Exchange Capacity

- wet capacity of this resin [AG 50W-x8, 100-200 mesh] = 1.7 meq/ml
- simplifying assumption: “rock” = $\text{CaAl}_2\text{Si}_2\text{O}_8$
- 40 mg/mmol (Ca) + 26 mg/mmol (Al, x2) + 28 mg/mmol (Si, x2) = 100 mg cations /mmol “rock”
- 200 mg “rock” = 2 mmol cations
- “rock” = 16 meq/mmol (add up positive charge equivalents), so 200 mg “rock” yields 32 meq cations
- if coprecipitation eliminates ~50% by mass, 1 mmol solid = 16 meq
- since columns are small, we split each sample into 3 subsamples; 1/3 yields ~8 meq per split
- applying the wet resin capacity from above, this means we require ~4 ml resin per column

Procedures

- waste cup in place under each set of 3 columns
- rinse each column with ~10 ml DI H_2O
- equilibrate resin with 2 ml 2.5M HCl
- load samples (remember, these are in ~1M HCl)
- elute 12 ml 2.5M HCl
- elute 2 ml 6M HCl
- transfer waste into appropriate accumulation bottle
- place labeled beaker under each set of 3 columns
- elute 10 ml ~6M HCl
- cover with Parafilm (I will evaporate these)

Question to Ponder -- written and calculated solutions due at beginning of 10/18 lab:

- (1) Use Table 1 in the paper by Strelow to predict the following:
- a. What abundant elements are likely to be strongly enriched in the 2.5M HCl elution?
 - b. What abundant elements are likely to be strongly enriched in the 6M HCl elution (with the lanthanides)?