EXTRACTION OF BERYLLIUM-10 FROM SOIL BY FUSION

Summary

This method is used to separate Be from soil and sediment samples, for AMS analysis. After adding Be carrier, the sample is fused with KHF_2. Be is extracted from the fusion cake with hot water. K is removed by precipitation, the sample is dried to expel fluoride, and Be is recovered as $Be(OH)_2$. Yields are typically 70-80 %, but can be increased by additional leaching of the fusion cake.

Version

Written by John Stone, 1996-2002. This version revised May 2004 by Greg Balco. Available at:

http://depts.washington.edu/cosmolab/chem.html

References

If you use this method, please cite:

Stone, J.O.H. (1998). A rapid fusion method for the extraction of Be-10 from soils and silicates. *Geochimica et Cosmochimica Acta* (Scientific comment) 62, 555-561.

Sampling and grinding

Mix and grind an unbiased $\sim$ 50-100 g sample of the material. If possible, mix the original sample bag before opening and take representative proportions of coarse and fine material. Fine soil, carbonate nodules, clay lumps, rock fragments, etc., all have different ^{10}Be concentrations. Grinding homogenises the sample and ensures that these components are evenly represented in the small subsample used for the analysis. If the sample is wet, you will need to dry it before grinding.

Initial sample drying

Samples are best run in batches of four. This is because we currently have four Pt crucibles. Given more crucibles and sufficient hotplate space, batches of 8 or even 12 are equally feasible.

Label and tare four disposable aluminum foil drying dishes and transfer a few grams of ground sediment to each with a steel spatula.

Weigh them on the top-loading balance and record the weights. The only purpose of this step is to determine the water content of the sample; if this is not important to you (e.g., old drillcore samples), skip this step.

Dry overnight at 95°C in the small soils oven.

Weighing and carrier addition

Remove soils from the oven, cool ($\sim$ 30 minutes), and, if you are interested in the water content, weigh on the top-loading balance. Record the dry weight.

Tare four clean platinum crucibles on the 4-figure balance. Record the crucible number against its sample name in your notebook or on a spreadsheet. It is easier to transfer the crucibles to the oven for later drying if you set them up in a square baking pan at this point. Remember that the entire crucible will be immersed in the leaching solution later; handle it only with clean plastic tongs or with clean gloves.

Place each crucible on the top-loading balance and tare the balance. Using the soils spatula, transfer 0.5 g of sample into each crucible. If you expect the sample to have less than $\sim 5 \times 10^7$ atoms $\cdot$ g^{-1} ^{10}Be (e.g., river sediment in the Cascades) use 1 g of sample. More than 1 g of sample makes the fusion more difficult and decreases the Be yield.

Weigh sample plus crucible on the 4-figure balance. Record the weights.

Take the current bottle of "high-level" Be carrier (usually a commercial AA or ICP standard solution with a Be concentration near 1000 mg/l) and zero it on the 4-figure balance.

Using the 1-ml Eppendorf pipettor with a clean tip, remove the desired amount of Be carrier solution and transfer it to the crucible. For 0.5 g of sample, use 0.3 ml carrier. For 1 g of sample, use 0.4 ml carrier. Be sure the pipette tip drains fully, and **take care not to touch the sample**. Re-cap the bottle tightly and return it to the balance. Record the weight removed. Re-zero the balance for the next sample.

If you are preparing a blank, it seems to improve the yield to add 1 ml Al standard solution to the crucible as well.

After adding carrier to all the samples, return the samples to the soils oven and dry for 1-2 hours. Drying at a low temperature (45°- 50°C) reduces the tendency of the sample to form an unbreakable "brick," and makes it easier to break up later.

Fusion

Remove the samples from the oven. Place them on the top-loading balance and, using the "Fusion reagents" spatula, add a weight of anhydrous Na_2SO_4 equal to the sample weight to each crucible. Clean the spatula. Transfer the crucibles to the fume hood and add 5 times the sample weight of anhydrous KHF_2 flux to each crucible.

CAUTION! KHF_2 is toxic and, when handled, produces dust. Handle it in the fume hood only. It is probably best to bring a portable balance into the hood for this step. Clean up any spilled KHF_2 with a wet kimwipe before proceeding.

Mix the contents of each crucible using a separate clean plastic rod for each sample. Try to break up and dislodge any caked soil from the bottom of the crucible. It is critical that the sample and flux are well mixed and that the sample is broken into small (< 1-2 mm) pieces, else the fusion will be time-consuming and possibly unsuccessful. Put the plastic rods aside into a beaker of DI water for later cleaning.

Set up the MAPP gas torch in the hood. Place a clean ceramic slab near the torch to hold the hot crucible later. Place a baking tray under the flame to catch spatter from the fusion. Light the torch.

CAUTION! Nearly everything that might be in or near the fume hood is flammable or meltable. Securely affix the MAPP torch to a ring stand. Test it before proceeding to make sure there are no objects within reach of the flame. Also, you are about to produce a red-hot pool of one of the most corrosive substances known. Wear full protective gear.

Hold the crucible with Pt-tipped tongs. Warm it over the flame, gradually at first until the initial foaming ceases, then increase the heating until the sample and flux evolve into a clear, fluid melt. At this point the bottom of the crucible will be red-hot. Keep the melt hot until there are no refractory nodules left and the entire sample has dissolved. Once this stage is reached, continue heating for a further 30-60 seconds. The whole operation should take less than 5 minutes.Try not to prolong the fusion unnecessarily, as this appears to reduce the Be yield. Remove from the flame, turn the torch off, and roll the sample around the crucible walls as it cools to obtain a thin coat rather than a large lump in the bottom of the crucible. When it has solidified, place the crucible on the ceramic slab to cool fully.

CAUTION! NEVER allow hot platinum to touch other metals. DON'T hold hot platimum with ordinary steel tongs. Iron will alloy with the platinum and reduce its melting point. NEVER heat platinum in an orange (carbon-rich) flame. Hot carbon depositing on the crucible will also alloy with the platinum, weakening it and lowering the melting point.

Be extraction

During the fusion, Be forms a water-soluble compound K_2BeF_4. Al, Fe, and Ti, the most problematic contaminants for our purposes, form insoluble fluorides. Hot water leaching releases Be, leaving the Al, Fe, and Ti in the solid residue.

Place the cold crucible into a 125 ml Teflon beaker. Record the number of the beaker. Cover it with 100 ml DI water, then cover the beaker with a white PTFE Teflon watch "glass."

Put the beaker on the hotplate at setting 3.5 (Corning hotplates) for at least several hours. Leaving it overnight is convenient.

Take the beaker off the hotplate and put the watch glass aside into a beaker of DI water for later cleaning. Holding the crucible with clean plastic forceps, pulverize the fusion cake with a flat-ended plastic rod, aiming to dislodge as much of the material as possible. The cake should break away cleanly from the sides of the crucible, as a fairly brittle material after only a few hours of heating, but as a soft paste if heated overnight. Often a few bits of residue (usually on the sides of the crucible) cannot be dislodged. Don't worry about them. Rinse any remaining paste off the crucible into the beaker with a little DI water, then put the crucible aside in a beaker of DI water for later cleaning.

Separation from fusion residue

Put the beaker back on the hotplate at setting 4.5 (for Corning hotplates. **Careful...any hotter than this will soften the Teflon**) until the liquid volume has reduced to approximately 30 ml. If there is more than 30 ml, it is hard to carry out the next steps in a single 50 ml tube; if you reduce the volume much below 25 ml you risk saturating the solution and precipitating fluorides. Evaporating from 100 ml down to 30 ml takes 4-5 hours.

Label a clean 50 ml centrifuge tube. Cool the contents of the beaker and transfer them to the tube. Rinse the fusion cake into the tube with a little DI water if necessary. Try not to exceed 40 ml total volume in the tube. Put the beakers aside for cleaning.

Centrifuge the tube at 2500 RPM for 5 minutes. Label a second clean 50 ml centrifuge tube. Decant the supernatant into the fresh tube. Add 10 ml DI water to the first tube that contains the fusion cake, and put it aside: if you later discover that you had a poor Be yield you may be able to recover more from the fusion cake later.

This is a good place to stop if necessary.

Potassium removal

In the fume hood, add full-strength perchloric acid in 1 ml increments to the supernatant from the previous step. A heavy, white, granular precipitate ($KClO_4$) will form and sink to the bottom of the tube. Keep adding $HClO_4$ until no further precipitate forms. This may require as much as 10 ml of $HClO_4$. When you are sure that no addtional precipitate is forming, add an additional 1-2 ml of $HClO_4$ to the tube, cap the tube, and put it aside for several hours to ensure that you have precipitated the maximum possible amount of $KClO_4$.

CAUTION! Perchloric acid is dangerous. Use appropriate precautions. Work only in the perchloric acid hood in the prep lab.

Centrifuge the tube at 2500 RPM for 5 minutes. Pour off the supernatant into another 125 ml Teflon beaker. Record the beaker number. Add 1 ml of 8M HNO_3 to each beaker. Place the beaker on the hotplate **IN THE PERCHLORIC ACID FUME HOOD** at setting 4-4.5 (Corning hotplates). Dry overnight. The beakers will fume towards the end of the drydown and a small white cake of excess $KClO_4$ will form (sometimes tinged pale yellow-green).

The centrifuge tube containing the $KClO_4$ precipitate can be reused in the next step. Rinse the $KClO_4$ into a waste bottle with a couple of rinses of DI water. Rinse the tube repeatedly with DI water into the sink. Fill the tube with DI water, cap it, and put it aside until the next step.

Be recovery

Turn off the hotplate and cool the beakers. Add 25 ml of 1 % HNO_3 to each beaker. Turn the hotplate back to a low setting ($\sim$ 3-3.5). The $KClO_4$ cake should dissolve within 10-15 minutes.

When the cake is fully dissolved, rinse the centrifuge tubes that you reserved from the previous step (or use new tubes) and pour the solutions into the appropriate tubes. Rinse the beaker into the tube with a little DI water. You should end up with 25-30 ml of solution in each tube. Don't worry if a small amount of $KClO_4$ precipitate (a few grains) forms as the solutions cool; however, if a large amount forms you may need to centrifuge and transfer the sample to a new tube.

CAUTION! Perchloric acid is highly involatile and will have condensed all over the Teflon beakers during the dry-down. Handle the beakers with disposable nitrile gloves and, when you are done with them, immerse them in a beaker of DI water and rinse them thoroughly.

Make up a bottle of fresh NH_3 solution by adding approx. 1 part AR grade ammonia to 2 parts DI water.

Using a disposable pipette, add 1-2 drops of methyl red pH indicator solution to each tube. Using another disposable pipette, add NH_3 solution drop by drop to the tube, mixing the solution as you

go. When the solution changes color from red, through orange, to yellow, add a couple more drops of NH_3 solution, cap and mix, and put the tube aside. With luck, a small precipitate of $Be(OH)_3$ will appear. This may take several hours. Once the precipitate has flocculated and begun to settle, centrifuge at 2500 RPM for 5 minutes. Discard the supernatant into the same waste bottle you used for $KClO_4$ earlier.

Add 5 ml of 1 % HNO_3 to each tube and mix to redissolve the hydroxide precipitate. Transfer the resulting solution into a clean, labeled 15 ml centrifuge tube and store to await AMS measurement.

Cleaning labware

Platinum crucibles. Rinse the crucibles with DI water repeatedly. Heat below boiling overnight in a 10% sodium hydroxide solution. This will convert the hard fluoride encrustations into a soft hydroxide paste. Return the sodium hydroxide solution to its bottle and rinse the crucibles repeatedly with DI water. Scour them with a wet kimwipe, removing any remaining hydroxide paste. Heat them overnight below boiling, or boil them for at least 30 minutes, in the 5% HNO_3 solution marked "Fusion-ware rinsing acid." Rinse 3x with DI water and dry in the oven. Remember, unlike beakers, both the inside and outside of the crucibles need to be equally clean.

Teflon beakers and PTFE watch glasses. Rinse repeatedly with DI water and scour with an alcohol-soaked kimwipe. Rinse again with DI, then heat overnight in the 5% HNO_3 solution marked "Fusion-ware rinsing acid." Rinse 3x with DI water and dry in the oven.

Plastic forceps and spatulas. Rinse with DI water. Sonicate in Alconox/DI water for an hour or two. Rinse again to get rid of the suds. Soak overnight (don't heat) in in the 5% HNO_3 solution marked "Fusion-ware rinsing acid." Rinse 3x with DI water and dry in the oven.