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U-Pb Age Results

Rock samples were crushed to mineral size under clean conditions using a jaw crusher and disc pulverizer, and minerals were separated using a Wilfley table, disposable sieves, heavy liquids and a Frantz magnetic separator at The University of Texas at Austin. Zircons were characterised using a binocular reflected-light microscope, transmitted light petrographic microscope (with condenser lens inserted to minimize edge refraction.

Multiple or single grains of each population were selected for analysis on the basis of optical and magnetic properties to ensure that only the highest quality grains were analysed. All mineral fractions analysed were strongly abraded (Krogh, 1982), subsequently re-evaluated optically and then washed successively in distilled 4N nitric acid, water and acetone. They were loaded dry into TEFLON capsules with a mixed $^{205}Pb/^{235}U$ isotopic tracer solution and dissolved with HF and HNO_3. Chemical separation of U and Pb from zircon using 0.055 ml columns (after Krogh, 1973) resulted in a total Pb procedural blank of approximately 1 pg over the period of analyses. The U procedural blank is estimated to be 0.25 pg. Pb and U were loaded together with silica gel and phosphoric acid onto an outgassed filament of zone-refined rhenium ribbon and analyzed on a multi-collector MAT 261 thermal ionization mass spectrometer operating dynamic mode with all masses measured sequentially by the secondary electron multiplier - ion counting system. Ages were calculated using decay constants of Jaffey et al. (1971). Errors on isotopic ratios were calculated by propagating uncertainties in measurement of isotopic ratios, fractionation and amount of blank. Results are reported in Table 1 with 2σ errors. Linear regressions were performed using the procedure of Davis (1982). The goodness of fit of a regressed line is represented as a

probability of fit, where 10% or better is considered acceptable and corresponds to a Mean Square of Weighted Deviates (MSWD) of 2 or less.

Table 5.1. Uranium-lead data for zircons extracted from the Red Hills intrusion.

	Concentration				Corrected atomic ratios*			
Fraction	Weight (mg)	U (ppm)	Pb^T (ppm)	Pb^{rad} (ppm)	$^{206}Pb/^{204}Pb$	$\pm 2\sigma$	$^{238}U/^{204}Pb$	$\pm 2\sigma$
Z1 med sub-euh	0.0140	464.48	6.30	4.76	249.2	0.8	22912.3	137.5
Z2 clr clrls	0.0034	458.42	6.35	4.80	285.8	0.9	26495.5	159.0
Z3 clr clrls	0.0045	434.80	5.04	4.47	1267.9	3.8	124709.2	748.3
Z4 med	0.0188	496.22	5.72	5.11	605.9	1.8	58577.5	351.5

Code for fraction numbers is: Z, zircon.

Abbreviations are: clr, clear; clrls, colorless; sub-euh, subhedral to euhedral; med, medium (80-160 microns).

*Corrected ratios: corrected for fractionation (0.10 and 0.07%/amu for Pb and U, respectively), laboratory blank (3 and 1 pg for Pb and U, respectively) and spike. Two-sigma uncertainties on isotopic ratios are reported as absolute error.

All fractions abraded.

Re-Os Age Results

Concentrations of Re and Os in all of the minerals analyzed were obtained through isotope dilution. Detailed explanation of isotope dilution can be found in Faure (1986) and Dickin (1993). Samples were loaded by the carius tube method (Shirey and Walker, 1995). Os was extracted from the solutions by a two-stage distillation process similar to Frei et al. 1998, and Roy-Barman et al. 1997. Re was purified from the distilled solutions by column chemistry. Samples were analyzed on a negative thermal ionization mass spectrometer in the Keck lab at the University of Arizona. Loading procedures are described in Chesley and Ruiz (1998).

The most difficult part in this procedure is extraction of very low concentrations of Os from the solutions in the carius tube. Problems arise because the samples are sulfides, thus dissolved sample solutions are very reduced due to large quantities of sulfur in solution. Theoretically, this can inhibit spike and sample equilibration. Therefore, we use a reverse aqua-regia (one that has more parts nitric then hydrochloric) and peroxide solutions in the carius tube to increase the amount of O in the solution. Our experiments show that use of these extra oxidizing agents enhances spike/ sample equilibration. We have also found that addition of peroxide during distillation improves the quality of the beams during analysis.

Due to the low concentration of Os in the samples analyzed, the concentration of the Os blank has a profound effect on the data. For instance, if a sample has 10ppt, and we dissolved 1 gram of sample with the blank varying from 1 to 1.5 picograms, the measured ratios will have at least a 10% correction. This error is an order of magnitude or more then the counting statistics of the machine. Therefore, all reported values take account for this error by reporting the deviation of the isotopic ratios when the change of the blank is considered. The Re blank is not significant since the concentration of the blank has remained relatively constant at 20-35 picograms, and the samples analyzed normally contain > 400 picograms Re.

Over the three years of analyzing Os, the blanks have dropped considerably because improved cleaning procedures and overall chemistry. Table C. 1 illustrates the total procedural blanks (addition of spike in the carius tube) for the three years. Regardless of the concentration of Os, the measured $^{187}Os/^{188}Os$ remained constant through time between 0.175-0.18. In order to isolate where the blank resides, Os was measured in various amounts of acid, different parts of the distillation process, and the platinum filaments used. None of the individual tests provided a clear-cut source for the blank. Thus, the blank could reside in the carius tube, or could represent the cumulative effect of the whole process.

Table H.1- Total procedural blanks for all of the Re-Os studies

Date	**Os (pg)**	**Re (pg)**
Dec. 1997	6	31
Apr. 1998	4	38
Aug.1998	3	37
Oct. 1998	2	29
Apr. 1999	2	38
Jun. 1999	2	39
Oct. 1999	2	36
Feb. 2000	0.9	
Feb. 2000	1.3	25

Since we modified the procedure slightly for analyzing sulfides for Re-Os the following is a protocol for loading the carius tubes, running the distillations, and cleaning the savellix. The materials needed are listed and the processes are described in detail below.

Loading Carius Tubes:

Materials and procedure for loading carius tubes:

Carius tube		
3 times distilled nitric acid	Re, Os spikes	Snap lid 5 ml vail
pipette and tips	glass funnels	liquid nitrogen
3 times distilled hydrochloric acid	hydrogen peroxide	alcohol
flask for freezing ct	12 ml falcon tubes	4 x 4 weighing paper
torch and lighter	oven	metallic pipe bomb

The first step in loading carius tubes is labeling each tube. Normally six tubes are used, and glass funnels are placed in the nose of the tube to facilitate addition of acids and samples. Weigh out the sample by placing it on the weighing paper. Gently pour the sample in the glass funnel by slowly tapping the sides of the weighing paper. Prepare the nitric, hydrochloric, and peroxide in 12 ml falcon tubes. The amounts of acid used depends on the sample size (table C. 2). The maximum amount of acids used without exploding the carius tubes is about 30ml of total fluid (or about half of the carius tube is full), which limits the amount of sulfide sample to a maximum of two grams. Some attempts of greater then two grams of sample did not yield the amount of predicted Os, thus indicating that sample and spike did not equilibrate at any point during the procedures. When attempting samples of greater then 0.5 grams, use larger carius tubes. The

amount of pressure in tube increases drastically when dissolving more sample, since additional sulfur gas is produced in the tube.

Table H.2- Estimated amount of sample and acid needed

Amount of Sample (g)	**HCl (ml)**	**HNO_3 (ml)**	**H_2O_2 (ml)**
0.01 – 0.5	6	2	2
0.5- 1.5	12	4	4
1.5- 2.0	18	6	6

After samples are in the carius tube freeze the alcohol bath by adding liquid nitrogen into the flask for freezing carius tubes. Add enough liquid nitrogen until the alcohol comes to a slurried state, then put the carius tube in the bath. Weigh the Os spike in the snap lid 5 ml vail, then the Re spike in the same vial. For spiking amounts refer to (Table C. 3). In order to reduce contamination, the spikes used for loading are kept in 7 ml threaded vials, rather then taking the spike from the 1 liter bottle.

Table H.3- Estimated amount for spikes for various types of ore deposits

Deposit type	**sample (g)**	**Approx. Os**	**Os spike (g)**	**Approx. Re**	**Re spike (g)**

Low concentration	1 to 2	6-50 ppt	0.007 0.009	to	200-10000 ppt	0.2 to 1

Porphyry

Copper

- Concentration of Os spike is 1.11 nanograms per gram, the spike is enriched in ^{190}Os

- Concentration of Re spike is 6.72 nanograms per gram, the spike is enriched in ^{185}Re

*- Molybdenite spikes are higher concentrations of similar spikes of Os milligrams

per gram and Re milligrams per gram

Pipette the spikes into the carius tube via the funnels, then pour the hydrocholric acid in the 5 ml snap lid to rinse the savillex. Pippette at least 2ml of hydrochloric acid (using the same pipette tip) into the carius tube to ensure that the spike is in the carius tube. Completely freeze spikes, and hydrochloric acid, you can add more liquid nitrogen if the mixture is not cold enough. After frozen add the nitric and peroxide and freeze these.

Once the acids are frozen, seal the nose of the caius tube with the torch by warming the nose of the tube with a blue flame and then seal by increasing the temperature of the flame and focusing on the opening of the carius tube. Rotate the tube at a constant pace throughout the sealing procedure. Immediately place the carius tube in the hood after sealing. If the seal was not good enough or the sample becomes very reactive the seal can break and acid will flow out of the tube.

After the samples have warmed to room temperature (which is about 2 hours after sealing), put the samples in a metallic pipe bomb (size of the pipe bomb depends on the size of the carius tube). Place pipe bombs in the oven overnight at 200°C.

Distillation

Materials and procedure for distillation

6- 64ml threaded teflon vials with distillation caps	6 medium, threaded 120ml teflon jars
6- threaded 17ml teflon flat bottomed vials	10 feet FEP heavey walled tubing 1/8
teflon boiling chips	aluminum foil
6 Falcon tubes with 5 ml 3 times 8N nitric acid	hydrogen peroxide
Nalgene tubing 1/41D, 3/8 OD, 1/16 W	6 10cc popropylene glass syringe
HBr	Stand-two types (Picture 2)
Tupperware rectangular box at least 5 inches deep	6 Falcon tubes (with punctured lids)
12 Twisty ties	
metal rod to score carius tubes	
liquid nitrogen and flask with alcohol	ice
6 1-22ul pipette tips	Exacto knife and scissors
Nitrogen tank and regulators	Flat thermomenter
Aluminum block (machined to fit distillation sav.)	Chem. Wipes
Y connectors	Hot plate
1000ml Beaker for carius tubes to warm	

The key to a successful distillation is to have all of the material prepared and assemble them slowly. This protocol will highlight each step thoroughly. First, prepare the 6-64 ml distillation savillex by threading the tubes with enough tubing (FEP heavy walled), so that when closed the tubing nearly touches bottom of savillex tube. Since the fit of the tubing can be very tight, cut the tubing on an angle and slightly wet it (with MQ) so as to ease the process of threading the tubes. Set the distillation savellix in the aluminum block and put it on the hot plate.

Next prepare the 6 glass syringes with peroxide that will be added to the distillation. Put about 12ml of peroxide into a falcon tube. Grab the syringe (plunger completely compressed), and tilt the falcon tube to nearly horizontal to the lab counter. Slowly draw 3-5 ml of peroxide from the falcon tube to the syringe. After all six syringes are filled, cut 6 one-inch pieces of Nalgene tubing. Connect the syringe to a branch on the Y connection. Next, connect the one-inch tubing to the stem of the connection put a 1-200µml pipette tip in the end of the Nalgene tubing. Connect the last branch of the Y connection to the nitrogen flow. Use the twisty ties to attach the syringes to the post in an upright position. Put the nose of the pipette tip in the tubing of the distillation savellix.

Now finish making the connections for the distillation by preparing the HBr. Puncture the lids of 6 falcon tubes with scissors. Place these flacon tubes in the custom made tupperware bin, and set this on a stand. Cut 6 1-foot long pieces of FEP heavy walled tubing with the exacto knife. Connect tubing with the other end of the distillation savellix and the punctured lid of the falcon tubes that are in the custom made tupperware. Take the lid off of the tupperware and fill the bin half full with ice and water mixture (add enough ice to keep water cold for at least three hours). Carefully add 8-9 ml of HBr to the Falcon tubes that are sitting in the ice bath. After all six are filled, turn the nitrogen and slowly bleed the nitrogen gas until the HBr in the Flacon tubes is bubbling.

Next, open the carius tubes. Prepare a bath in 1000 ml beaker for the carius tubes to warm in, get the beaker and fill with ice and water mixture about 2/3 full. Freeze the carius tubes, this can be done two ways, either directly emerging the tubes in liquid nitrogen, or freezing the alcohol bath. After the tube is completely frozen, score the nose around the perimeter of the carius tube. Place carius tubes in the hood and break the nose of the tube along the place where it is scored. Place the cracked tubes in the water bath in order to warm them. Some samples tend to be reactive when opening, so watch the tubes warm. While the carius tubes warm to room temperature (usually 10 minutes or so) place 10-20 small teflon boiling chips in the bottom of the distillation beaker.

Once the tubes have warmed take carius tube out of the bath with a chem. wipe and carefully pour contents in the distillation savillex. In order to reduce contamination, place a chem. wipe on the tops of the other distillation savillex. Then, place the lid of the savillex which you are adding the sample on the chem wipe. Proceed with this process quickly as to ensure that no Os has become a volatile and lost. Rinse the carius tube with 5 ml 8N nitric in the falcon tube, and swirl acid in the tube and pour the contents into the distillation beaker. In order to add the nitric without spilling acid, pour slowly. After loading six tubes, check each HBr falcon tube to assure that they are receiving nitrogen and bubbling, and then wait for at least 10-15 minutes. During this time the HBr might become slightly discolored to an almost chocolate brown. After 15 minutes slowly add the peroxide. Some solutions become very reactive during this step, so proceed with care and be prepared to change the nitrogen flow with each one of the regulators. Wait another 10-15 minutes after adding peroxide before raising temperature. Raise temperature of the aluminum block to about 110°C. At about 30-40°C the solutions become reactive again because of O release so be careful when regulating the nitrogen flow. Let the experiment distill for at least 1 hour at 110°C. Watch the experiment to make certain that nitrogen flow is constant

throughout the experiment, condensation commonly occurs on the lids of distillation beakers and inhibits proper flow of nitrogen and potentially OsO species

Prepare the savellix for the Re and Os solutions. Record and label the Os (17ml threaded teflon vial) and Re (medium 120ml jar) savillex. Wrap teflon tape around the lids of the Os savillex. After 1 hour at 110°C turn the temperature off and take the HBr solutions out of the Falcon tube and place in Os savillex and wait until block cools completely before placing Re solution in Re beaker. Place the Os savillex under heat lamp at 80°C for at least 3 hours, then remove lid and dry down overnight. Uncap the cooled Re solutions and dry down overnight.

Microdistillation

Materials and procedures for microdistillation

Conical sav.	1 time distilled HBr	Pipettes and tips
Chromerge(CrO_3)	Aluminum foil	Thermometer

We follow the method in Roy-Barman et al. (1998). Open the conical savillex and piptte about 0.015 to 0.016ml of Hbr into the tip of the conical. Open the Os (17ml) savillex and pipette in about 0.025-0.028ml of chromerge in the base of the savillex. Pipette the chromerge out of the 17ml Os beaker and place on the lid of the conical savillex. Carefully screw the conical part to the lid (have the lid facing up so as not to move the chromerge). Wrap aluminum foil around the conical, and place conical savillex on hot plate and turn heat to 80°C. Let the experiment sit at temperature for at least 2 hours. After two hours take foil off and carefully unscrew lid. Place the conical part of the savillex in the dry box and wash the chromerge on the lid with MQ.

Cleaning Procedures:

All savillex experience a four stage cleaning procedure. After use all saveillex are rinsed with MQ water, and then nitric acid is added in the containers. They are placed on a hot plate and heated for at least two days. The exception to this part of the cleaning is the Os conicals,

HBr is used in this step rather then nitric. After two days or more, the acid is discarded and the savillex is placed in a sulfuric bath (this bath also has a one package of NoChromix added). Savillex are kept in the sulfuric bath for 2 days or more.

Next the savillex are taken out of the sulfuric acid and thoroughly rinsed with MQ water and placed in a bath of nitric acid. This bath is heated and they are kept in the bath for a few days. Finally, the savillex are taken out of the nitric and rinsed with MQ water and placed in a MQ bath. Once out of the MQ water the savillex are wrapped in Saran Wrap for storage.

Provided by R. Mathur of University of Arizona Re-Os lab.