REPORT OF THE INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY (ICP-MS) FACILITY, UNIVERSITY OF NOTRE DAME 1993-1996

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http://www.nd.edu:80/~cbpc/ICPMS.html
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INTRODUCTION

The University of Notre Dame ICP-MS facility (Fig. 1 and cover) is operated through the Center of Bioengineering & Pollution Control and the Department of Civil Engineering & Geological Sciences. Strong ties between these two entities have allowed the facility to grow through varied research and the analysis of samples from industry, particularly from the environmental company Phytotech of New Jersey.

FIGURE 1: North view of the ICP-MS Laboratory

The ICP-MS facility was purchased using a combination of money from the Academic Research Infrastructure program of the National Science Foundation along with matching funds furnished by the University of Notre Dame. Over a period of 4 months in 1993 demonstrations and quotes were solicited from three vendors: Perkin Elmer, Turner Scientific, and FISONS Instruments. Sensitivity, technical support, sample introduction techniques available, and value for money were the main criteria used in evaluating these systems. The order finally went to FISONS Instruments at a price of $390,000 for the following items:

1 PlasmaQuad II ICP-MS with standard interface (Fig. 4)	1 Isotope Dilution Software Package
1 LaserProbe with enlarged sample chamber (Fig. 5)	1 Three year Full Service Contract
1 CETAC Ultrasonic Nebulization Unit (Fig. 6)	1 Consumables Package
1 Hydride Generator (Fig. 7)	1 IBM Computer with 17" Monitor
1 Eletrothermal Vaporization Unit (Mark IIIa) (Fig. 8)	1 Autosampler (Fig. 10)
1 Flow Injector (Fig, 9)	1 Peristaltic Pump

CLEAN LABORATORY, 106 CUSHING

The ICP-MS Facility is housed in a modular Class 1000 clean laboratory built by Clean Air Technologies, Inc., of Michigan at a cost of $32,295. In this laboratory we have custom built polypropylene cabinetry and workbenches, as well as a HEPA-filtered flow bench (Fig. 2) for ultra-trace element sample preparation, from PolyDesign of Richardson,

FIGURE 2: PolyDesign HEPA-filtered Laminar Flow Work Bench

Texas at a cost of $27,225. Ultrapure water is supplied by a Barnstead-Thermolyne Nanopure water system which supplies 1.5-2.0 liters of 18 mega-ohm water a minute (Fig. 3). The laboratory is kept under positive pressure to reduce contamination.

CLEAN LABORATORY, 112 CUSHING

A Class 1000 clean laboratory was custom-built by Notre Dame in 1991 for the purpose of being a sample preparation facility. Again, all work benches and cabinetry were custom-made by PolyDesign of Richardson, Texas. Also, a fume hood capable of handling perchloric and hydrochloric acids was installed to allow open vessel rock digestions (in teflon beakers) to be conducted. All fumes are neutralized via a water-based scrubber before being vented to the atmosphere. An ultrapure water system furnished by Culligan,

FIGURE 3: The Barnstead-Thermolyne 18 Mega-Ohm Ultrapure Water System

supplies 18 mega-ohm water to two polypropylene sinks at a rate of 3-5 liters per minute. As with the 106 facility, this laboratory is kept under positive pressure.

As the ICP-MS is an ultra-sensitive analytical facility, potential sources of contamination must be eliminated from the laboratories (hence the HEPA-filtered air, positive pressure, and 18 mega-ohm water supply) such that any signal detected by the ICP-MS is then from the sample, not from "blank" contamination. To this end, we distill the acids used in the sample preparation procedure (HCl, HNO_3, and Hydrofluoric), buying them at reagent grade before using quartz stills for nitric and hydrochloric and teflon stills for the hydrofluoric acids. We do not distill the potentially explosive perchloric acid, it being bought from Fisher Scientific in its purest form.

While the ICP-MS facility was installed in the summer of 1993, the first 18 months of operation were spent getting to know the system and fully testing it's capabilities. One Master's thesis was completed during this time by Jonathan Noris on Selenium contamination of groundwater.

FIGURE 4: The Plasma-Quad II ICP-MS

LABORATORY OPERATION & MANAGEMENT

The University of Notre Dame ICP-MS facility operates under the direction of Dr. Clive R. Neal with Dr. Jinesh C. Jain, the ICP-MS Lab manager, co-ordinating the day-to-day running and maintenance of the facility. Dr. Jinesh C. Jain was hired as the ICP-MS Laboratory Manager on May 1, 1995. Initially, his efforts were devoted to familiarizing himself with the PlasmaQuad and its software, as well as publicizing the facility to potential users within and outside Notre Dame. Now his duties are to co-ordinate users of the facility, train new users, assist in sample preparation and data reduction, and develop new analytical techniques. There are regular meetings of the principal users to discuss progress, problems of the laboratory, new directions, priorities, and improve the efficiency of the lab. The ICP-MS facility is available on a priority basis to University of Notre Dame researchers. Non-university research and industrial work is accepted to help defer the maintenance costs of the facility.

PROCEDURES IN USE

The procedures (newly developed and published) which are routinely being used in our laboratory include: (1) HF/HNO_3 digestion procedure for trace element analysis in rock

FIGURE 5: The Laser Ablation Microprobe now capable of generating three wavelengths of laser radiation: 1064 nm (IR), 532 nm (visible), 266 nm (UV). This allows micro-sampling of solid samples including petrographic thin sections.

powders; (2) sodium peroxide fusion procedure for determination of rare earth elements, Zr, Hf, Nd, Ta, and Th in refractory minerals; (3) Determination of trace elements in superconductors; (4) HNO_3/H_2O_2 digestion procedure for multi-element analysis in plant

and resin samples; (5) Determination of low level platinum group elements in rock samples; and (6) determination of Cesium and uranium in water samples. Full Details can be found in Appendix A.

FIGURE 6: The CETAC Ultrasonic Nebulizer for ultra-trace element analysis (pico-gram/gram detection).

PROBLEMS

A major problem, which was related to a design flaw, which occurred during the first two years of operation was the failure of the auto-shutdown mechanism on the plasma when coolant supply was interrupted. This was rectified by replacing the fail safe flow switch and cleaning the filter in the main chiller on a monthly basis.

During the first 4 months of 1995, a number of problems were encountered with the Plasma Quad II. This grew progressively worse between May and August, 1995. The problem was found to be associated with a faulty breaker which was fixed only by replacing the Mains Distribution Unit (MDU). This shutdown process affected resolution   on all

mass numbers and peak duplication which were corrected by replacing the circuit boards in STE unit. The solenoid valve did not function because of inadequate voltage supply and resulted in back pressure of argon flows. The inadequate voltage supply to STE system controller also resulted in the failure of communication between the computer and the ICP-MS. Lack of power to peristaltic pump and autosampler caused the sample introduction system to fail. Also, there was a problem with one turbo pump and one roughing pump which were replaced by FISONS. The problems related to closing of slide valve and tripping of detector (PC to Analog mode) during the run resulted in interruption of counting cycle. Several replacements were necessary, including the torch, nebulizer, sampler and skimmer cones, tubes, and the RF coil. Total machine down-time during the period was about 50%. These were fixed by the manufacturer under our extended warranty. A letter was written to Fisons to seek a compensation for the loss of time resulting from the breakdown and they responded positively by extending the warranty on the instrument for one more year (monetary value $39,000).

FIGURE 7: The FISONS VGS 200 Hydride Generator for analysis of elements which form gaseous hydrides at ambient temperatures (i.e., As, Bi, Ge, Pb, Sb, Se, Sn, & Te), as well as elemental Hg.

FIGURE 8: The Mark IIIa Electrothermal Vaporization Unit for the ultra-trace element analysis of micro-liter samples.

ANALYTICAL FEE

General acid digestion of solid samples (HF/HNO$_3$) and water samples are rated at $15 for the first element and $3 for each additional element up to a maximum of $75. For fusion and brine, analyses are rated at $20 for the first element and $3 for each additional element up to a maximum of $80. Sample preparation for Platinum Group Elements, Brines and Plant/Animal Tissue is precise, time-consuming, and requires a lot of consumables - hence the higher cost. Discounts are given depending upon the number of samples to be analyzed and whether the customer is willing to be involved in the sample preparation.

PROCEDURE	CONTRACT	COLLABORATIVE
Trace Element (Acid Digestion) (41 Elements)	$75	$60
Trace Element (Fusion) (41 Elements)	$80	$65
REE (Acid Digestion) (14 Elements)	$50	$30
REE (Fusion) (14 Elements)	$55	$35
High Field Strength Elements (Acid Digestion) (9 Elements)	$40	$25
High Field Strength Elements (Fusion) (9 Elements)	$45	$30
Platinum Group Elements (6 Elements)	$120	$60
Waters (up to 55 Elements)	$50	$35
Brines (up to 55 Elements)	$75	$50
Plant/Animal Tissue (up to 55 Elements)	$75	$50

About sixty percent of the machine time was used for research purposes and remaining 40% percent time was utilized for outside work. The machine is equipped with an autosampler which allows us to operate the instrument outside normal hours. The analytical fee charged to users varied from $15-$120/sample depending on the nature of sample preparation, number of elements, and whether the research is collaborative. These rates are estimated from laboratory expenses over the past 12 months (standards, standard reference materials, acids, gas, ICP-MS consumables, computer accessories, water filters, bottles, test-tubes, etc.). Total income from analytical fees to ICP-MS laboratory during the past year months was about $43,865.

FIGURE 9: The VGS 100 Flow Injector for use in analyzing samples containing high total dissolved solids (e.g., seawater, brines, etc.).

BREAKDOWN OF INCOME TO THE ICP-MS FACILITY

UNIVERSITY OF NOTRE DAME:

Chemical Engineering	$1,100
Biological Sciences	$260
CE/GEOS*	$2,700
Clive R. Neal	$13,650
Dean's Office*	$4,200
CBPC*	$2,700

OTHER UNIVERSITIES:

University of Tennessee	$2,000
University of Quebec, Canada	$800
University of Saskatchewan, Canada	$5,000

INDUSTRIES:

Phytotec	$20,655
Sherwin Williams	$400

TOTAL	**$53,465**

* Money for Equipment Match

This income allowed:

1) the completion of an unfunded Master's thesis on the analyses of the platinum group elements and gold (PGEs + Au) in geological samples;

2) the development of a technique to analyze high-field strength elements in geological samples;

3) partial funding of a project to analyze the PGEs + Au in sediments across the Cretaceous-Tertiary boundary.

Total expenditures from January 1st 1995 until August 30th, 1996, was $56,218.31, making a lab deficit of $2,753.31. However, these figures do not reflect income during September which should reduce this to a zero balance.

FIGURE 10: The Gilson Autosampler which allows automated runs of up to 150 samples with a wash procedure in-between each individual sample tube.

ADDITIONS
- The current laser sampler has only a infra red laser set at 1064 nm. Upgrade of the existing is planned to include visible (532 nm) and ultra-violet (266 nm) capabilities which will extend its applications to solids deficient in the transition elements and allow us to better control the ablation process.
- A larger vacuum pump will be attached to the expansion chamber of the ICP-MS to lower the vacuum and obtain higher sensitivity.

FUTURE IMPROVEMENTS
- A microwave sample preparation system will enhance sample preparation throughput. This will greatly reduce the dissolution time for organic and mineral/rock samples.
- Overhaul of the air handling system in 112 Cushing, the sample preparation clean lab will be carried out in the Fall of 1996.
- A concentric nebulizer will be added in order to analyze small volume samples.

USE OF THE NOTRE DAME ICP-MS FACILITY

The following research projects have been undertaken in the ICP-MS lab:

Solutions from the differential dissolution of the meteorite Orgueil.

Ontong Java Plateau Basalts from Malaita, Solomon Islands.

Ontong Java Plateau Basalts from Makira, Solomon Islands.

Ontong Java Plateau Basalts from Leg 130 of the Ocean Drilling Project.

Hafnium and barium abundances in semi-conductors.

Scavenging of trace metals in lake water.

Apollo 12 lunar basalts.

Apollo 16 lunar highlands samples.

Russian kimberlite samples.

Characterization of NIST standard reference glasses 610 & 612.

Characterization of new USGS standards BIR-2, DTS, AGV-2 and BHVO-2.

Groundwater samples from Juday Creek.

Fe contents in liver samples.

Platinum group elements (+Au) in samples across the Cretaceous-Tertiary boundary.

The following industrial analyses have been conducted:

Uranium and cesium contents in groundwater - PhytoTech, New Jersey.

Fe contents in paint - Sherwin Williams, Chicago.

The following analytical procedures have been or are being developed:

Platinum group element (& Au) in geological samples.

High field strength element determinations in geological samples.

Trace element analysis of minerals in thin section using Laser Ablation ICP-MS.

Trace element analysis of Ceramics using Laser Ablation ICP-MS.

Develop Electrothermal vaporization (ETV) technique for analysis of Cadmium and other toxic elements in durum wheat.

The following Masters projects have been completed or are in progress:

Treatment of High-Selenium Waste Waters - Jonathan Noris, 1994.

Development of an ICP-MS Analytical Technique for the Quantification of the Platinum Group Elements (PGEs) and Gold in Geological Samples using Cation Exchange Pretreatment - James A. O'Neill, Jr, 1996.

Development of an ICP-MS Protocol for Analyzing the High Field Strength Elements (HFSEs) in Geological Samples - Cathleen McGinnis, 1997.

The following Ph.D. projects are currently in progress:

Characterization of the Sub-Lithospheric Mantle in Venezuela, South America, and its Influence upon Arc Magmatism in the Lesser Antilles - Cathleen McGinnis.

Growth of the Large Igneous Provinces: A Case Study of the Ontong Java Plateau, SW Pacific - Amy Birkhold-VanDyke.

Using Platinum Group Elements (PGEs) to Characterize the Nature of K-T Boundary Extinctions - James C. Ely.

MAIN USERS OF THE NOTRE DAME ICP-MS FACILITY

University of Notre Dame:
1. Dr. C. Neal, Civil Engineering & Geological Sciences
2. Dr. S. Silliman, Civil Engineering & Geological Sciences
3. Dr. J.K. Rigby, Civil Engineering & Geological Sciences
4. Dr. L.H. Ketchum, Civil Engineering & Geological Sciences
5. Dr. J.B. Fein, Civil Engineering & Geological Sciences
6. Dr. P. McGinn, Chemical Engineering
7. Dr. D. McAbee, Biological Sciences
8. 8 graduate students

Outside Users/Collaborators:
1. Dr. B. Ensley, Phytotech, New Jersey
2. Dr. N. Jain, Sherwin Williams paint Company, Chicago
3. Dr. S. Wilson, USGS
4. Dr. P. Jauhar, USDA, Fargo, North Dakota
5. Dr. S.J. Barnes, University of Quebec, Canada
6. Dr. S. Jana, University of Saskatchewan, Canada
7. Dr. A.R. Mermut, University of Saskatchewan, Canada
8. Dr. J. Mahoney, University of Hawaii
9. Dr. J. Brannon, Washington University, St Louis
10. Dr. F.A. Podosek, Washington University, St Louis
11. Dr. K. Johnson, University of New Orleans
12. Dr. L.A. Taylor, University of Tennessee
13. Dr. G.A. Snyder, University of Tennessee
14. Dr. J-F. Gaillard, Northwestern University

PUBLICATIONS & CONFERENCE ABSTRACTS REPORTING DATA FROM THE
NOTRE DAME ICP-MS FACILITY

PAPERS:

Neal C. R. , Davidson J. P., and McKeegan K. D. (1995) Geochemical analyses of small samples - microanalytical techniques for the nineties and beyond. *Reviews of Geophysics, Supplement.U.S National Report to the IUGG* (1991-1994), 25-32.

Mahoney J. J., White W. M., Upton B. J. G., Neal C. R., and Scrutton R.A. (1996) Beyond EM-1: Lavas from Afanasy-Nikitin Rise and the Crozet Archipelago, Indian Ocean. *Geology* **24**, 615-618.

Neal C. R., Mahoney J. J., Duncan R.A., Kroenke L.W., Petterson M.G., and Jain J. (1996) The Rise and Fall of the Ontong Java Plateau. *AGU Monograph on Large Igneous Provinces* (J.J. Mahoney & M. Coffin, eds) (submitted).

O'Neill J. A., Neal C. R., and Jain J. C. Quantifying the Platinum Group Elements (PGEs) and Gold in geological samples using cation exchange pretreatment and Ultrasonic Nebulization Inductively Coupled Plasma-Mass Spectrometry (USN-ICP-MS). *Chem. Geol*. (submitted).

Pearce N. J. G., Perkins W. T., Westgate J. A., Gorton M. P., Jackson S. E., Neal C. R., and Chenery S. P. New data for the National Institute of Standards and Technology 610 and 612 glass reference materials. *Geostandards Newsletter* (submitted).

Podosek F. A., Ott U., Brannon J. C., Bernatowicz T. J., and Neal C. R. Pervasive Cr anomalies in Orgueil. *Meteoritics* (submitted).

Jain J.C., McGinnis C., and Neal C.R. Minimization of memory effects in the measurement of low-level high field strength elements by ICP-MS (*in preparation*).

EXTENDED ABSTRACTS:

Podosek F. A., Ott U., Brannon J. C., Bernatowicz T. J., and Neal C. R. (1995) ^{54}Cr anomalies in the Orgueil carbonaceous Chondrite. *Annual Meeting of the Meteoritical Society Meeting*, Washington D.C.

Snyder G. A., Neal C. R., and Taylor L. A. (1995) Mantle sources of lunar volcanism in the Ocean of Storms: Evidence from trace-element and Nd isotopic chemistry of fine-grained basalts at Apollo 12. 26th Lunar & Planetary Science Conference

Chambers J. G., Snyder G. A., Taylor L. A., and Neal C. R. (1995) Dichotomy of major-element and trace-element chemistry of some KREEPy to super-KREEPy Mg-rich highland lithologies: Revitalization of REEP-fraction metasomatism. 26th Lunar & Planetary Science Conference

Podosek F. A., Ott U., Brannon J. C., Bernatowicz T. J., Neal C. R., Alexander C., and MacPherson G. J. (1994) Distribution of Cr anomalies in carbonaceous chondrites. *Annual Meeting of the Meteoritical Society*, Prague, Czech Republic.

Neal C. R. and Taylor L. A. (1994) Utilization of ICP-MS analytical techniques for determination of siderophile-element abundances: Potential uses for the planetary geochemist. *Lunar Planet. Sci.* **XXV**, 983-984.

Ott U., Podosek F. A., Brannon J. C., Bernatowicz T. J., and Neal C. R. (1994) Chromium isotopic anomalies in stepwise dissolution of Orgueil. *Lunar Planet. Sci.* **XXV**, 1033-1034.

ABSTRACTS:

Jain J. C., Neal C. R., and O'Neill J. A. Jr. (1996) Origin of the Ontong Java Plateau (OJP) at the Core-Mantle Boundary: Platinum Group Element (PGE) and Gold (Au) Evidence. AGU Fall Meeting, San Francisco.

Birkhold-VanDyke A. L., Neal C. R., Jain J. C., Mahoney J. J., and Duncan R. A. (1996) Multi-Stage Growth for the Ontong Java Plateau (OJP)? A Progress Report from San Cristobal (Makira), Solomon Islands. AGU Fall Meeting, San Francisco.

McGinnis C. E., Neal C. R., and Jain J. C. (1996) Development of an Analytical Technique for the Accurate & Precise Determination of the High Field Strength Elements (HFSEs), Cs, & Mo by ICP-MS with Geological Applications. AGU Fall Meeting, San Francisco.

O'Neill J. A. Jr., Neal C. R**.**, and Jain J. C. (1996) Addressing Heterogeneous Distribution & Trace Abundances of Platinum Group Elements (PGEs) and Gold (Au) in Silicate Rock Matrixes: Quantitative Analyses using Ultrasonic Inductively Coupled Plasma-Mass Spectrometry (USN-ICP-MS). AGU Fall Meeting, San Francisco.

Ely J. C., Neal C. R., and Rigby J. K. Jr. (1996) Platinum Group Elements (PGEs) and Gold (Au) Abundances Using Ultrasonic Nebulizer- Inductively Coupled Plasma-Mass Spectrometry (USN-ICP-MS) From a Volcanic Ash Sequence Spanning the K-T Boundary, McCone Co., MT. AGU Fall Meeting, San Francisco.

Sivanandan S., Jain J., McGinnis C., and Neal C.R. (1996) Limiting factors in the determination of low level rare earth and high field strength elements (REE & HSFE) by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). *42nd International Conference on Analytical Sciences & Spectroscopy*, August 10-13, 1996, Univ. Western Ontario, London, Ontario, Canada.

O'Neill J. A. Jr., Neal C. R., and Jain J. C. (1995) Determination of Platinum Group Element (PGE) and gold abundances by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) following separation by cation exchange. *AGU Fall Meeting*, San Francisco, *EOS* **76**, 663.

Jain J. A. Jr., O'Neill J. A., Neal C. R., Mahoney J. J., and Petterson M. G. (1995) Siderophile elements in Large Igneous Provinces (LIPs): Origin of the Ontong Java Plateau at the core-mantle boundary? *AGU Fall Meeting*, San Francisco, *EOS* **76**, 700.

Petterson M. G., Neal C. R., Saunders A. D., Babbs T. L., Mahoney J. J., and Duncan R. A. (1995) Speculations regarding the evolution of the Ontong Java Plateau. *AGU Fall Meeting*, San Francisco, *EOS* **76**, 693.

O'Neill J. A. Jr., Neal C. R., and Jain J. C. (1995) Determination of platinum group elements and gold by inductively coupled plasma mass spectrometry following separation by cation exchange. *Geological Society of America Annual Meeting*, New Orleans.

Neal C. R. (1995) Matrix-matched standardization of garnet and clinopyroxene REE profiles using LA-ICP-MS: Developing a technique for analyzing petrographic thin sections. *V.M. Goldschmitt Conference*, Penn State University.

Pearce N. J. G., Perkins W. T., Westgate J. A., Groton M. P., Jackson S. E., and Neal C. R. (1995) Trace element data for the NIST synthetic glass reference materials 610 and 612. *V.M. Goldschmitt Conference*, Penn State University.

Neal C.R., Mahoney J.J., Saunders A.D., and Babbs T.L. (1994) Trace element characteristics of a 3.5-4km thick section of OJP basalts, Malaita, Solomon Islands. AGU Fall meeting, San Francisco, *EOS* **75**, 727.

Neal C. R. (1993) Using LaserProbe ICP-MS to analyse petrographic thin sections for trace elements: A preliminary report. AGU Fall Meeting, San Francisco, *EOS* **74**, 626.

PROTOCOLS

1) ICP-MS LAB PROTOCOLS

1) CLEAN CONES IN THE EMP LAB;

2) ALWAYS WIPE DOWN BENCH TOPS, TOPS OF THE MACHINERY, DESKS, ETC., WITH 18 MEGAOHM WATER WHEN YOU ARE ABOUT TO HAND OVER TO ANOTHER USER;

3) MEET WITH THE NEXT USER BEFORE HANDING THE MACHINE OVER TO DISCUSS PERFORMANCE, PROBLEMS, ETC.;

4) MAKE SURE CLEAN CONES AND GLASSWARE ARE INSTALLED AFTER YOU HAVE RUN YOUR LAST SAMPLE AND BEFORE HANDING OVER TO THE NEXT MACHINE (YOU WILL HAVE TO OBTAIN THE NEXT USERS CONES);

5) DO NOT STORE SAMPLES IN THE AUTOSAMPLER RACKS. ALL SAMPLES LEFT IN THESE RACKS AFTER USER CHANGE OVER WILL BE DISCARDED;

6) ALL SAMPLES LEFT OUTSIDE A USERS DESIGNATED CUPBOARDS SPACE AFTER THAT USER HAS HANDED THE MACHINE OVER WILL BE THROWN OUT;

7) THE USER OPERATING ON THE FIRST OF EACH MONTH HAS TO CLEAN THE TACKY MAT;

8) MAKE SURE THE ARGON AND CHILLER ARE TURNED OFF AFTER LEAVING FOR THE DAY - FOLLOW THE PROCEDURE ATTACHED TO THE AR TANK FOR TURNING THE ARGON OFF;

9) WHEN USING THE ETV, MAKE SURE THE VALVE IN THE AR LINE IS OPEN TO ALLOW AR TO FLOW TO THE ETV. **MAKE SURE YOU CLOSE IT AGAIN AFTERWARDS - IF NOT, A LOT OF AR IS LOST.**

10) INFORM CLIVE/JINESH WHEN NEW ARGON IS NEEDED AT LEAST TWO DAYS PRIOR TO IT RUNNING OUT (IF YOU CAN EASILY TILT THE TANK, IT'S TIME FOR NEW ARGON!);

11) **ALL BREAKAGES AND/OR MISHAPS TO BE REPORTED IMMEDIATELY!!!!**

2) SAMPLE PREPARATION CLEAN-LAB PROTOCOLS

- Always wear a lab coat and overshoes in the lab;

- When handling acids, wear safety goggles and plastic gloves;

- NO OPEN BEAKERS OUTSIDE THE FUME HOOD;

- Before handling hydrofluoric acid (HF), make sure you know where the antidote cream is;

- IF YOU SPILL "HF" ON YOURSELF, PUT THE ANTIDOTE CREAM ON THE AFFECTED AREA AFTER QUICKLY RINSING THE AREA WITH WATER. CONTACT SECURITY IMMEDIATELY FOR TRANSPORT TO THE INFIRMARY OR EMERGENCY ROOM.

- When handling "HF", always wear to full face mask and always keep open containers of "HF" well inside the fume hood;

- When using the pipettes, always use a new pipette tip for each new solution.

- When using the balance, remove static from Teflon containers using the "anti-Static" gun provided;

- Always use container that have been cleaned following the "Cleaning Protocol".

3) WHOLE-ROCK SAMPLE PREPARATION (POWDERING) PROTOCOL

This protocol is designed to minimize the contamination of the whole-rock powder during the preparation procedure. Potential contaminants are weathered surfaces, coolant oil from the rock saw, and in the case of the platinum group elements, the rock saw, hammer, splitter, jaw crushers, and personal jewelry.

By following this procedure, the resultant powder will be able to be analyzed for any element or isotope in the knowledge that the powder is free of contamination and it is the fresh whole-rock that is being analyzed.

1) **REMOVE ALL JEWELRY FROM HANDS AND WRISTS and WASH HANDS**

2) **SAWING AND GRINDING**

(a) Use the water-cooled rock saw to trim off the weathered surfaces of the larger samples.

(b) Use the 75µ disk (diamond impregnated) to grind off the sawn surfaces; to ensure that the surface is ground far enough, grind until the striations from the disk are parallel on the surface, then turn the sample 90˚ and repeat until the original striations have been removed. This disk may also be used to remove weathered surface remaining on the sawn large samples and from samples too small to saw.

(c) Make sure that all surfaces have been ground using the 75µ disk such that fresh surfaces are now exposed.

(d) After each sample has been ground, remove the disk from the grinding wheel and rinse thoroughly under the tap in order to avoid cross contamination between samples. Replace for the next sample.

(e) Wash the ground sample under the tap and dry.

3) **SPLITTING THE SAMPLE**

(a) Place the sawn/ground sample in a heavy duty freezer bag and then put this inside a second. Place on a sturdy flat surface (NOT a bench or desk top).

(b) The sample will be split into peanut-sized chips (or smaller) by using a hammer, but in order to eliminate contact with metal, the metal hammer is covered with cloth duct tape. A new layer is added for each sample in order to avoid cross contamination between samples.

(c) As the sample has flat surfaces, hitting the sample with the duct tape-covered hammer should not split the bags unduly.

(d) Gather the peanut-sized chips (or smaller) and place in a Pyrex beaker and cover with 18 megaohm (ultra-pure) water and ultrasonic for 30 minutes.

(e) Air dry the sample and pick out any chip with a weathered surface.

4) **POWDERING THE SAMPLE**

(a) Put the chips in the agate mill so that they fill the gap between ball and the chamber so that it is **HALF FULL. DO NOT OVERLOAD OR PUT LARGE CHIPS IN THE MILL.**

(b) Put in the mill and start - check after 5-10 minutes the consistency of the powder by putting on a clean pair of plastic gloves (a new pair for each sample) and feeling the consistency. It should feel like talcum powder when the grinding is complete. If it still feels "gritty", grind some more.

(c) Tip the milled powder onto a clean piece of paper then pour into a clean, new ziplock plastic bag and label accordingly.

(d) Wash the mill under the tap using a kitchen scouring pad to remove all powder. Rinse thoroughly water and then with acetone. Use the compressed air unit to dry the mill. Before adding the bulk of the chips of the next sample, add a small amount (to cover the bottom of the mill) and grind to ensure the mill is "cleaned out" of the previous sample. Remove and discard this powder, wash as before and dry. Then add the bulk of the sample chips to the mill.

REMEMBER TO:

(A) CLEAN EQUIPMENT/UTENSILS THOROUGHLY BETWEEN SAMPLES IN ORDER TO AVOID CROSS CONTAMINATION;

(B) AVOID CONTACT OF THE SAMPLE WITH METAL TO AVOID ANY POTENTIAL PGE CONTAMINATION.

4) TUNE-UP PROTOCOLS

- Always wear overshoes or socked feet in the ICP-MS Lab;

- Always do a Fine Mass Calibration before starting;

- Always do a short term stability test and ensure RSD ≤ 2% for all elements before starting;

- Always fill out the log book each time you use the machine;

1) Check coolant level in main chiller;

2) Make sure main chiller and gas are turned on;

3) Check that the rotary switch on the side of the machine is set to "Normal";

4) Check that the sampler and skimmer cones, glassware, and tubes are clean and undamaged;

5) Check the initial Expansion Pressure (E3), Intermediate Pressure (E-4) and Analyzer Pressure (E-8) - enter values into log book;

6) Turn on mini-chiller to spray chamber;

7) Start the peripump after extracting the nebulizer and manually start the gas flows - check that the spray is constant (let spray hit a tissue). If it is not (i.e., it is pulsing), adjust tension in pipes at peripump. If that does not fix it, seek help. Switch pump off after this procedure;

8) Go from "Pumping" mode to "Stand-By" mode (computer) and ensure that the cool gas flow rate is $\approx 14 \, l \, sec^{-1}$;

9) Let machine purge for about 15 seconds more than the minimum indicated by the computer;

10) Light the plasma;

11) After stabilization, switch to "Operate" mode;

12) The running pressures should be approximately: Expansion Pressure (E0), Intermediate Pressure (E-4), Analyzer Pressure (E-6) - enter values in log book;

13) Start the peripump;

14) Have the machine set at mass 115 (Indium) - can be set using the computer;

15) Let the machine stabilize for ≈ 1 hour;

16) Then check that the torch is centered - adjust horizontal and vertical settings checking cps read out on screen at the left of the machine;

17) To begin with, the lenses should be set to their default settings (i.e., Extraction = 2.0; Collector = 7.8; L1 = 7.7; L2 = 5.4; L3 = 5.0; L4 = 3.8). RF power should be 1350 Watts.

18) Gas Flows: Nebulizer $\approx 0.85 \, l \, min^{-1}$; Cool Gas $\approx 14 \, l \, min^{-1}$; Auxiliary $\approx 1.5 \, l \, min^{-1}$. Gas flows may be adjusted slightly during the tuning procedure, but do this under supervision. Do not touch any other knob on the front panel.

19) Run a quick 30 second scan to check the resolution;

20) Then start tuning on mass 115 in the following order of lens stack controls: Extraction, Collector, L1, L3, L2, L4. Need to maximize counts at best stability.

21) Once the tuning procedure has been conducted once, adjust Auxiliary and Nebulizer flows to maximize counts at best stability;

22) Repeat steps 20) & 21);

23) Set the machine at mass 156 = Cerium Oxide - adjust gas flows (Auxiliary & Nebulizer) to minimize oxides;

24) Re-set to mass 115 and repeat step 20);

25) Set machine to mass 9 (Beryllium) and repeat step 20);

26) Set machine to mass 238 (Uranium) and repeat step 20);

27) Once the tuning procedure is complete, enter lens settings and gas flows in the log book;

28) Run short term stability test - only acceptable if elements are $\leq 2\%$ standard deviation and oxides $< 10\%$ of element (preferably $< 5\%$);

29) If stability test is OK, you are ready to run samples. If not, repeat tuning procedure.

5) SAMPLE PREPARATION AND MACHINE SET-UP
USING FULL TRACE ELEMENT ANALYSIS PROTOCOL

This procedure allows data to be reduced using both a modified standard addition protocol as well as using external calibration. It allows an independent check of the data, if it is questioned, or if the spike may have been made up incorrectly.

1) Dissolution of sample. After HF/HNO$_3$ treatment, dissolve 50mg of rock in 100 ml of 2%/5% HNO$_3$ (depending on the matrix you are using - we will change to 5% HNO$_3$) - gives 0.05% of rock in solution.

2) Make up a stock solution of As, Rh, In, Re, & Tl at 40 ppb in 5% HNO$_3$. These will act as Internal Standards.

3) Prepare stock solutions of Matrix Standards A & B in DOUBLE the concentrations (ppb) shown in the table. Each Matrix Standard is prepared by adding 3 g of a stock solution to a test tube followed by 3 g of the Internal Standard stock. The Matrix Standard concentration for each element in the final solution should be close to those given in the table. Internal Standards are again at 20 ppb.

4) Prepare a stock solution of the Spike shown in the table (concentrations are again in ppb). In this stock solution should be the Internal Standards at 40 ppb concentration. 3g of this solution is added to 3 g of sample or concentration standards, such that the concentrations are half those in the table and the Internal Standards are again at 20 ppb.

5) **SAMPLE PREPARATION**: Prepare two sets of tubes for each concentration standard, each standard reference material, and each unknown sample:

   (a) Prepare Concentration Standards of 1, 5, 10, 50, 100 ppb - prepare two test tubes each containing 3 g of Concentration Standard solution of double the concentration required (i.e., 2, 10, 20, 100, or 200 ppb) to one add 3 g of the Internal Standard stock solution, to the other add 3g of the spike stock solution containing the internal standards at 40 ppb. This will give you Concentration Standards of 1, 5, 10, 50, & 100 ppb, the former unspiked (except for the internal standards) and the latter spiked with all elements listed in the table (plus the internal standards). Throughout this and the next two steps, the former is the unspiked aliquot and the latter the spiked aliquot;

   (b) Add 3 g of each Procedural Blank to each tube; to one tube then add 3 g the Internal Standard stock solution, to the other add 3 g of the Spike containing the internal standards;

(c) Add 3 g of the standard reference material/unknown sample (<u>0.05% concentration</u>) to each sample; to one tube then add 3 g of the Internal Standard stock solution, to the other add 3 g of the spike containing the internal standards. The former is the unspiked aliquot and the latter the spiked aliquot.

(d) For each acid blank, add 3 g of 5% HNO_3 to 3g of the Internal Standard stock solution.

6) **ANALYSIS**: Set up the Matrix Standard, Concentration Standards, Standard Reference Materials, Acid Blanks, and Unknown Samples as follows:

1)	Matrix Std A	21)	Procedural Blank Unsp
2)	Matrix Std B	22)	Procedural Blank Sp
3)	2%/5% HNO_3 Acid Blank	23)	2%/5% HNO_3 Acid Blank
4)	1ppb Conc Std Unsp	24)	Matrix Std A
5)	1ppb Conc Std Sp	25)	Matrix Std B
6)	2%/5% HNO_3 Acid Blank	26)	2%/5% HNO_3 Acid Blank
7)	5ppb Conc Std Unsp	27)	Std Ref. Material Unsp
8)	5ppb Conc Std Sp	28)	Std Ref. Material Sp
9)	2%/5% HNO_3 Acid Blank	29)	2%/5% HNO_3 Acid Blank
10)	10ppb Conc Std Unsp	30)	Unknown Sample 1 Unsp
11)	10ppb Conc Std Sp	31)	Unknown Sample 1 Sp
12)	2%/5% HNO_3 Acid Blank	32)	2%/5% HNO_3 Acid Blank
13)	Matrix Std A	33)	Unknown Sample 2 Unsp
14)	Matrix Std B	34)	Unknown Sample 2 Sp
15)	50ppb Conc Std Unsp	35)	2%/5% HNO_3 Acid Blank
16)	50ppb Conc Std Sp	36)	Matrix Std A
17)	2%/5% HNO_3 Acid Blank	37)	Matrix Std B
18)	100ppb Conc Std Unsp	38)	2%/5% HNO_3 Acid Blank
19)	100ppb Conc Std Sp	ETC., ETC.!
20)	2%/5% HNO_3 Acid Blank	

7) Between each test tube, a 3 stage wash sequence is run: (a) 10% HNO_3 + 1 drop of HF per 150 ml of nitric; 2) 10% HNO_3; 3) 2%/5% HNO_3 (depending on which is used as the matrix for your standards and samples). Each wash is run for 90 seconds.

8) Run a Standard Reference Material (unspiked and spiked) at the beginning, middle, and end of your run.

9) At the end of your run, end up with Matrix Std A, Matrix Std B, then the concentration standards of 1, 10, 100 ppb (unspiked and spiked). Again, run the wash sequence between each test tube.
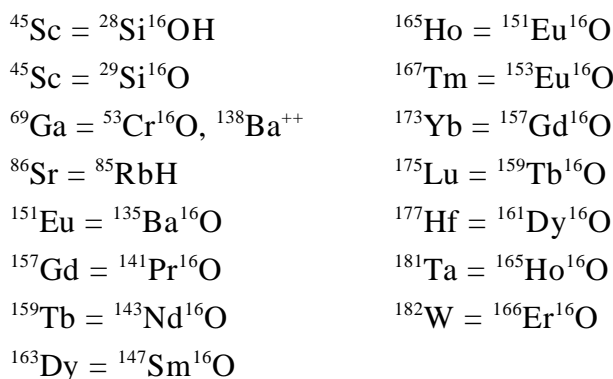
10) Do not run more than 12 unknown samples in one run.

DATA REDUCTION

1) **BLANK CORRECTION**: *Sample Counts - Acid Blank Counts* (nearest acid blank to where sample was analyzed in the sequence).

2) **INTERFERENCE CORRECTION**: *Blank-Corrected Sample Counts - % of Interference Counts* (calculated from Matrix Standards A & B directly above and below the sample in the analysis sequence outlined above)

The following interferences are corrected for:

$$^{45}Sc = {}^{28}Si^{16}OH \qquad\qquad {}^{165}Ho = {}^{151}Eu^{16}O$$
$$^{45}Sc = {}^{29}Si^{16}O \qquad\qquad {}^{167}Tm = {}^{153}Eu^{16}O$$
$$^{69}Ga = {}^{53}Cr^{16}O, {}^{138}Ba^{++} \qquad {}^{173}Yb = {}^{157}Gd^{16}O$$
$$^{86}Sr = {}^{85}RbH \qquad\qquad {}^{175}Lu = {}^{159}Tb^{16}O$$
$$^{151}Eu = {}^{135}Ba^{16}O \qquad\qquad {}^{177}Hf = {}^{161}Dy^{16}O$$
$$^{157}Gd = {}^{141}Pr^{16}O \qquad\qquad {}^{181}Ta = {}^{165}Ho^{16}O$$
$$^{159}Tb = {}^{143}Nd^{16}O \qquad\qquad {}^{182}W = {}^{166}Er^{16}O$$
$$^{163}Dy = {}^{147}Sm^{16}O$$

3) **CALCULATION OF "MATRIX FACTORS"**: These corrections are required to account for fluctuations in sensitivity (counts per ppb) due to signal suppression/enhancement. This can be conducted in two ways:

(a) Signal fluctuation in the regularly spaced Matrix Standards: Look at the counts on each element in these standards. Not only can you calculate the % of interferences on certain elements, but you can see the change in signal intensity on all elements. The assumption is that the change is linear between each set of Matrix Standards, and the counts on the samples/standards in between can be corrected on the basis of position in the analytical sequence.

(b) Signal fluctuation on each element in the spike: Using the spiked samples/standards, the change in counts per ppb for each element in the spike can be monitored and corrected for:

[(Spiked Sample or Std Counts - Unsp. Sample or Std Counts)/ppb in spike]*Dilution Factors

Dilution Factors are those incurred by the dilution of the spike by the sample.

(c) The "Matrix Factor" applied to the analysis is basically (b)/(a). As matrix factors are consistent over a range of masses, the correction

applied to unspiked elements is that of the closest element, or can be calculated assuming linear change between matrix factors of elements bracketing these unspiked elements.

4) **MACHINE DRIFT CORRECTION**: This corrects for changes in machine response across the mass range during the time of analysis. It is related to 3), but is used to look at drift between spiked and unspiked samples. This allows a better (more precise) determination of the counts per ppb of elements in you spike because we use elements that are NOT included in the spike. Therefore, ASSUMING THAT EXACTLY THE SAME AMOUNT OF SAMPLE/STANDARD HAS BEEN ADDED TO EACH TEST TUBE (or you know the EXACT amount of sample in each tube), we should have the same number of counts from each test tube. Elements to be used: Li, Rb, Ce, Bi - these are not in the spike.

5) **FINAL CALCULATION**:
> **(Corrected Unknown Counts/Corrected Std Counts per ppb)* Drift Factor*Matrix Factor*Dilution Factor**

Elements	Standard A	Standard B	Spike
^{7}Li	40	--	--
^{9}Be	40	--	40
^{45}Sc	40	--	80
^{51}V	40	--	80
^{53}Cr	--	100	--
^{59}Co	40	--	80
^{60}Ni	40	--	80
^{65}Cu	40	--	80
^{66}Zn	40	--	80
^{69}Ga	--	40	80
^{85}Rb	40	40	--
^{86}Sr	100	--	200
^{89}Y	20	--	20
^{90}Zr	40	--	80
^{93}Nb	20	--	20
^{95}Mo	20	--	20
^{118}Sn	20	--	20
^{121}Sb	20	--	20
^{133}Cs	20	20	20
^{137}Ba	200	--	400
^{139}La	20	--	40
^{140}Ce	20	20	--
^{141}Pr	20	--	40
^{145}Nd	--	40	80
^{147}Sm	--	40	80
^{151}Eu	--	40	20
^{157}Gd	--	40	40
^{159}Tb	40	--	20
^{163}Dy	20	--	40
^{165}Ho	20	--	20
^{167}Er	40	--	80
^{169}Tm	20	--	40
^{173}Yb	20	--	20
^{175}Lu	--	40	20
^{177}Hf	--	20	40
^{181}Ta	--	20	20
^{182}W	--	20	20
^{206}Pb	40	--	40
^{207}Pb	40	--	40
^{208}Pb	40	--	40
^{209}Bi	20	--	--
^{232}Th	20	20	20
^{238}U	20	--	20

Concentrations in ppb

6) WASHING OF TEFLON AND GLASSWARE (REFERRED TO AS *ITEM*)

- rinse used *item* in 18 MΩ H_2O
- Place rinsed *item* in 50% HCl on hot plate (medium) in rear of laminar flow fume hood for 5 days

    -place date on glass beaker with tape and marker
- remove *item* using teflon tongs and rinse in 18 MΩ H_2O
- Place rinsed *item* in 50% HNO_3 on hot plate (medium) in rear of laminar flow fume hood for 5 days

    -place date on glass beaker with tape and marker
- remove *item* from 50% HNO_3 using Teflon tongs
- rinse used *item* in 18 MΩ H_2O
- place *item* in 18 MΩ H_2O bath on hot plate (med.) in rear of laminar flow fume hood for 3 days
- discard 18 MΩ H_2O and rinse *item*
- air dry *item* under laminar flow fume hood
- After *item* is dry:

    -cap screw top Teflon beakers with correct cover

    -cover glassware with parafilm
- place clean *item* in appropriate cabinet

Discard used 50% HNO_3 & HCl after 3-5 uses (depending upon batch sizes)

7) PGE (+ Au) ION EXCHANGE COLUMN PROTOCOLS

CLEANING

- place column in 10% HNO_3 bath for 24 hours (room temperature)
- rinse column in 18 MΩ H_2O
- place column in 10% HCl bath for 24 hours (room temperature)
- rinse column in 18 MΩ H_2O
- air dry

PACKING RESIN

- fill columns with 18 MΩ H_2O
- spatula desired amount of resin into column reservoir
- allow to settle
- adjust resin depth if needed

CLEANING COLUMN/RESIN AFTER USE

- fill reservoir (~20 ml) with 6M (50%) HCl
- collect and discard effluent
- repeat
- fill 50 ml Teflon beaker with 5% HCl
- place column in Teflon beaker containing 5% HCl
- fill column (not reservoir) with 5% HCl
- using 5 ml pipette, draw resin up column and into pipette
- decant resin into reservoir and allow to settle
- add 10 ml of 5% HCl to re-equilibrate column

STORING COLUMNS

- clean columns using cleaning protocol
- add 10ml 5% HCl to reservoir
- seal with parafilm
- place column in 4 L beaker containing ~ 1 L of 5% HCl
- Cover beaker with Saranwrap
- Place under fume hood