APPENDIX D
LEAD ISOTOPE DATA

Data Report:
Pb Isotope Compositions and
Backscatter Electron Image Analyses

RE: Pakootas, et al. v. Teck Cominco Minerals, Ltd.

for

Environment International Ltd.

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Introduction

This report includes all data obtained for Environment International Ltd. (EI) by the Isotope Geochemistry Laboratory at the University of Washington (UW) associated with the litigation *Pakootas, et al. v. Teck Cominco Minerals, Ltd*. It comprises the data obtained for all analytical requests made by EI from January 18, 2010 through July 31, 2010.

The analyses consist of two types: high-precision isotope ratio mass spectrometry to determine Pb isotope ratios, and backscatter electron imaging (BSE) using an electron microprobe to quantitatively determine the content of slag particles in selected samples.

The analyses are grouped into three different sample suites. The first two groups are a set of eight samples, informally termed the "ecology samples", that were analyzed once following removal of magnetic material by a hand magnet, followed by a weak acid leach, and then analyzed a second time without any pre-analysis processing. The third set, informally called the "core samples", consists of 31 sediment samples and five slag concentrates. Two of the slag concentrates (BSB3A slag and UCR-10 slag) were produced by magnetic gradient separation and hand-picking under binocular microscope at the UW, and three of the slag concentrates (BSB5A, OC#8C and SCB12A slags) were provided by Dr. Joe Ryan, University of Colorado.

All of the samples were analyzed for Pb isotope ratios ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$). The eight ecology samples and five slag concentrates were analyzed by BSE imaging to determine slag proportions by volume.

In addition to this report, all data and images are also provided in Excel format and image files on the accompanying CD. The seven data tables are in a single Excel file, each table on an individual sheet. The EDS spectra, backscatter images and photomicrograph originals are in a separate folder. A pdf version of this report is also included on the CD.

The analyses were performed by Dr. Bruce Nelson, professor and Dr. Scott Kuehner, laboratory technician. Overall project supervision, quality control and data reduction was done by Bruce Nelson.

Pb Isotope Analyses

Sample Processing: Samples were provided as unprocessed sediment. In the case of the ecology sample suite, for one aliquot from each sample we removed magnetic grains by hand magnet and then subjected the sample to a weak (2M) HCl acid leach. We did no processing to a second aliquot of each sample. The standard operating procedure for the weak acid leach is given in Appendix A.

From two of the ecology samples (BSB3A and UCR-10) we made a slag concentrate using magnetic gradient separation with a Frantz Isodynamic Magnetic Separator. This

was followed by hand-picking under binocular microscope to remove all non-slag grains. The standard operating procedure for the separation process is given in Appendix B.

Dr. Joe Ryan, University of Colorado, provided the remaining three slag separates (BSB5A, OC#8C and SCB12A). We analyzed these samples as received.

We received 109 samples in the core sample suite (Table 1). All of these samples contained varying amounts of water, ranging from damp to free water. Prior to any analysis, they were all processed in the following manner:

1. Any free water was poured off through a filter paper so as to not loose any solid material.
2. An acid-cleaned 15 ml plastic centrifuge tube was filled to 10-15 ml with a representative aliquot of the sample.
3. This aliquot was dried at 90°C in a vacuum oven.
4. From the dried aliquot, a fair split of approximately 4 ml was transferred to an acid-cleaned glass vial.
5. The sample was powdered by hand in an agate mortar and pestle. Between samples the mortar and pestle were cleaned by methanol wipe, grinding of pure quartz sand, again cleaned by methanol, and finally "conditioned" by grinding some of the sample that was then discarded.
6. For a few samples that had gravel-sized grains ($\gtrsim$ 2 mm), approximately half of the dried aliquot was powdered in an agate shatterbox that was cleaned between samples as in step 5.
7. The powdered sample was returned to the glass vial, and a representative aliquot removed to Teflon beaker for dissolution and analysis.

Isotopic Analysis: The standard operating procedure for Pb isotope analyses is given in Appendix C. After chemical separation of Pb from matrix by ion exchange columns, we analyzed Pb isotope ratios on a Nu Instruments multi-collector inductively-coupled-plasma mass spectrometer (MC-ICP-MS).

Reproducibility of measured isotope ratios is better than ±250 ppm (±0.025%) at 2-sigma uncertainty (in this report all analytical uncertainties are expressed at 2 standard deviations). This is evaluated in several ways. Many sample solutions were run two or more times over multiple analytical sessions on different days. All samples in the ecology sample suite that underwent magnetic separation and weak acid leach were run twice. In addition, two aliquots of one sample (UCR-8) were processed through the entire procedure in parallel. All of the repeat analyses of solutions agreed to within 300 ppm, and all but one to within 200 ppm, well within the maximum difference of 500 ppm implied by the quoted error of ±250 ppm. The two separate dissolutions of UCR-8 agreed to within 149, 25 and 62 ppm for the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios, respectively.

Of the 31 core samples analyzed, four samples were analyzed twice, and all were reproduced to within 400 ppm.

We also monitor reproducibility by analyzing the international Pb isotope standard NBS 981. Normalization to this standard also allows calibration of our results with those from other laboratories. The standard is analyzed as an unknown every sixth sample. The NBS 981 results for all analytical sessions are given in Table 2 and Fig. 1. Reproducibility is consistent with our quoted error, and measured values are accurate to within 10 ppm or better of accepted values.

Analyzing a pure Pb standard does not take into account all possible analytical variables that might affect reproducibility. These additional variables may include procedural blank, matrix effects, variations in solution concentration and thallium:lead ratio of the spike, and homogeneity of sample aliquots. Consequently, we also analyzed multiple aliquots of an in-house basalt standard (08UW-BCR-1) to account for all factors that could affect sample analysis. We present results (Table 3, Fig. 2) for eight different aliquots of the sample that went through the entire analytical process. Each of the eight solutions was run two or more times. For n=21 we obtain a 2-sigma error of less than ±200 ppm for all ratios.

Results: Final Pb isotope analytical results are presented in three tables (Tables 4 – 6); Table 4 presents the ecology samples processed by hand magnet and weak acid leach, Table 5 presents the same samples without any processing, and Table 6 presents the results for the core samples and five slag separates. The core samples were run blind in two senses. We received no geographic or geologic context for the samples, and once samples arrived at the lab they received a simple sequential number (C-#, Table 6) that was connected to the original sample only after analysis was complete.

Backscatter Electron Imaging

Overview: The objective of obtaining backscatter electron (BSE) images of samples on the electron microprobe is to quantify the volume % of slag in samples. We report results for analyses of the eight ecology samples, and the five slag separates (Table 7).

Principles of the Analytical Technique: The standard operating procedure for obtaining BSE images and Energy Dispersive Spectroscopy (EDS) spectra is given in Appendix D. BSE imaging returns a sample image for which the brightness is correlated to average atomic weight of the phases. The brightness is translated to a 256-level grey scale. All sample grains have an average atomic weight greater than the mounting epoxy, so the surface area of the analyzed sample can be determined. Natural silicates and silicate glasses have average atomic weight less than that of slag, and slag has average atomic weight less than magnetite and barite. For each sample, we identify the range of gray scale that encompasses slag but excludes natural silicates and oxides. The number of pixels in the image that are within this range are counted, and converted to a modal percent of the sample grains.

The identity of grains was established by obtaining EDS spectra. EDS spectra for natural silicates, natural glass and magnetite are unambiguously distinctive from the spectra for slag (see Figs. 3 – 6). Slag identification was based on 1) the unusually large number of elements present at high concentrations compared to natural minerals, 2) the relative proportions of the elements present, and 3) the identity of elements present.

As detection limits on EDS are about 2000-3000 ppm, slag spectra show 8-10 elements with concentrations >1%. Of these, Si, Ca and especially Fe have very high concentrations while Al is low. Nearly all spectra display a peak at the S and Pb energy and occasionally a Cu peak, elements most unlikely to appear in any natural volcanic glass spectra.

During the process of verifying the analytical approach, we discovered that for some samples there was a minor overlap in the grey-scale range for slag and magnetite. It was clearly a minor overlap, but we established a modified procedure to demonstrate that it would not significantly affect the modal results. By increasing the beam current from 8 to 54 nAmp, and increasing the dwell time by a factor of 10, from 0.05 to 0.5 msec, we obtained the increased resolution required to completely separate magnetite from slag in the images. The trade-off was an order of magnitude increase in analytical time. To test the reproducibility of the two analytical conditions, we analyzed approximately 20% of the area of five samples with the higher resolution mode. For all cases, the modal percent of slag was reproduced to within ±4%.

Results: The results of the modal analysis in both lower and higher resolution mode are given in Table 7. BSE images of each sample analyzed are presented as Figs. 7 – 19. In these images, the bright grains correspond to slag.

Table 1: Samples Received by Bruce Nelson, Univ. Washington, from EI on May 19 and *May 25*, 2010

C#		C#		C#		C#		C#	
1	BSB 3A .5-2	24	*DE #8C 0-.75*	43	SCB 3A 1.3-2.1	57	OC 10A 0.4-1.3	81	SL1-grab
2	BSB 3A 2.3-3.1	25	*DE #8C 1.25-2.25*	44	SCB 3A 2.5-3.2	58	OC 10A 1.3-2.3	82	SL2-grab
3	BSB 4A .9-1.4	26	*DE #8C 4.25-5*	45	SCB 6A 0.5-1.5	59	OC 10A 2.3-3.0	83	SL3-grab
4	BSB 4A 1.5-2.5	27	DE #8C 10.0-17.0	46	SCB 6A 2.8-3.4	60	OC 10A 3.0-4.6	84	SL4-grab
5	BSB 4A 2.5-3.2	28	DE #8C 17.0-24.0	47	SCB 6A 3.6-4.3	61	OC 14A 0.5-1.5	85	A1-BS
6	BSB 4A 3.5-4.5	29	*DE #10A 1-2*	48	SCB 7A 1.0-2.3	62	OC 14A 3.3-4.3	86	A2-SGS
7	BSB 5A .75-1.5	30	*DE #10A 2.1-2.5*	49	SCB 7A 2.7-3.6	63	OC 14A 5.5-6.6	87	A3-SGS
8	BSB 5A 3-3.5	31	*DE #11A2 0-1.3*	50	SCB 7A 3.6-4.4	64	OC 14A Deep 8-10.6	88	A4-SGS
9	BSB 6A 0-1	32	*DE #11A2 2-2.5*	51	SCB 7A 4.4-5.0	65	OC 15A 0.5-1.5	89	A5-SGS
10	BSB 6A 1.5-2.5	33	DE #12A 0-1	52	SCB 7A 5.0-5.6	66	OC 15A 4.2-5.2	90	A6-SGS
11	BSB 6A 2.5-3.5	34	*DE #12A 1.5-3.5*	53	SCB 7A 5.6-6.3	67	OC 15 Deep Drill Auger	91	B2-BS
12	BSB 6A 4-5	35	*DE #12A 6-12*	54	SCB 12A 0.5-1.5	68	OC 15 Deep 9.0-9.8	92	B2-PS0
13	BSB 6A Conf 0.5-1.5	36	DE #14A 0-.75	55	SCB 12A 3.1-4.1	69	OC 18A 0.5-2.0	93	B2-PS20
14	BSB 6A Conf 2.4-3.4	37	DE #14A .75-1	56	SCB 907A 1.0-2.3	70	OC 18A 3.3-3.5	94	B2-PS40
15	BSB 15A 0-1	38	DE #14A 1.4-2			71	OC 18A 4.1-5.1	95	B2-PS60
16	BSB 15A 1-2	39	DE #14A 2-3			72	OC 20A 0.5-1.7	96	B2-PS80
17	*BSB 16A .25-.75*	40	DE #15A 0-1			73	OC 21A 0.0-1.0	97	B3-SGS
18	BSB 16A 1.5-2.2	41	DE #15A 1.9-2.7			74	OC 21A 1.0-2.7	98	B4-BS
19	BSB 17A .75-1.3	42	DE #912A 1.5-3.5			75	OC 21A 2.7-4.3	99	B4-PS0
20	BSB 17A 2-3					76	OC 21 Deep 0.0-1.0	100	B4-PS20
21	BSB 17A 3.75-4					77	OC 22A 1.5-2.5	101	B4-PS40
22	BSB 24A 1.2-1.5					78	OC 23A 0.0-1.2	102	B5-SGS
23	BSB 903A .5-2.0					79	OC 921A 1.0-2.7	103	B6-SGS
						80	OC 923A 0-1.2	104	B7-SGS
								105	B8-SGS
								106	B9-SGS
								107	CL1-clam
								108	CL2-clam
								109	CL3-clam
	23 BSB samples		19 DE samples		14 SCB samples		24 OC samples		29 samples
109	**samples total received**								

Table 2: Measured Pb Isotope Composition of NBS 981 Pb Isotope Standard

	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
Accepted NBS values	*16.9356*	*15.4891*	*36.7006*
	NBS 981 run as unknown		
'NBS-981 ukn1'	16.9373	15.4908	36.7058
'NBS-981 ukn2'	16.9360	15.4894	36.7015
'NBS-981 ukn3'	16.9381	15.4917	36.7077
'NBS-981 ukn4'	16.9334	15.4868	36.6948
'NBS-981 unk'	16.9374	15.4911	36.7065
'NBS-981 unk5'	16.9357	15.4896	36.7034
'NBS-981 unk6'	16.9363	15.4898	36.7023
'NBS-981 unk7'	16.9350	15.4878	36.6980
NBS 981 Pb 40ppb #1	16.9371	15.4905	36.7053
NBS 981 Pb 40ppb #2	16.9361	15.4896	36.7025
NBS 981 Pb 40ppb #3	16.9333	15.4870	36.6961
NBS 981 Pb 40ppb #4	16.9358	15.4888	36.6988
NBS 981 Pb 40ppb #5	16.9344	15.4882	36.6984
NBS 981 Pb 40ppb #6	16.9340	15.4875	36.6967
NBS 981 Pb 40ppb #7	16.9341	15.4876	36.6970
NBS 981 Pb 40ppb #8	16.9361	15.4883	36.7017
NBS 981 Pb 40ppb #9	16.9338	15.4875	36.6975
average	**16.9355**	**15.4889**	**36.7008**
2 standard deviations	**0.0030**	**0.0030**	**0.0080**
2 standard deviations ppm	**175**	**195**	**219**
deviation from accepted ppm	**-4**	**-10**	**6**

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Error on Pb analyses is ±250 ppm (2 sigma) or ±0.025%.

Pb normalized to 205Tl/203Tl = 2.38714 and then to NIST 981 = 16.9356, 15.4891, 36.7006 (Todt et al., 1996) for 206Pb/204, 207Pb/204Pb and 208Pb/204Pb, respectively, by sample-standard bracketing.

Table 3: Pb Isotope Composition of Internal Laboratory Rock Standard

	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
	08UW-BCR-1 internal laboratory rock standard		
08UW-BCR-1J'	18.586	15.613	38.469
08UW-BCR-1J'	18.585	15.611	38.466
'08UW-BCR-1L'	18.584	15.610	38.466
08UW-BCR-1L'	18.583	15.610	38.461
08UW-BCR-1L'	18.584	15.610	38.462
08UW-BCR-1M'	18.582	15.611	38.464
08UW-BCR-1N	18.587	15.613	38.470
08UW-BCR-1N'	18.582	15.610	38.462
08UW-BCR-1N'	18.582	15.613	38.468
08UW-BCR-1P'	18.581	15.609	38.459
08UW-BCR-1P'	18.583	15.611	38.463
08UW-BCR-1P	18.583	15.611	38.462
08UWBCR-1 #1'	18.583	15.609	38.462
08UW-BCR-1 (Q) #1'	18.585	15.610	38.461
'08UW-BCR-1 (Q) #2'	18.586	15.610	38.464
'08UW-BCR-1 (Q) #4'	18.584	15.610	38.463
'08UW-BCR-1 (R) #1'	18.582	15.609	38.458
'08UW-BCR-1 (R) #2'	18.582	15.609	38.461
'08UW-BCR-1 (R) #3'	18.584	15.611	38.464
'08UW-BCR-1 (S) #1'	18.585	15.611	38.465
'08UW-BCR-1 (S) #2'	18.587	15.612	38.470
average	**18.584**	**15.611**	**38.464**
2 standard deviations	**0.0034**	**0.0025**	**0.0068**
2 standard deviations ppm	**181**	**162**	**176**

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Error on Pb analyses is ±250 ppm (2 sigma) or ±0.025%.

Pb normalized to 205Tl/203Tl = 2.38714 and to NIST 981 = 16.9356, 15.4891, 36.7006 (Todt et al., 1996) for 206Pb/204, 207Pb/204Pb and 208Pb/204Pb, respectively, by sample-standard bracketing.

Table 4: Pb Isotope Compositions of Ecology Samples - Magnetic Separation and Weak Acid Leach

Sample	Pb Isotope Composition			ppm differences between repeat runs		
	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
'UCR 1*'	18.186	15.598	38.118			
'UCR 1* repeat'	18.183	15.596	38.114	-154	-135	-122
'DM 2*'	17.172	15.505	36.910			
DM 2* repeat'	17.170	15.508	36.914	-86	133	97
BSB South Zone 3A*	17.038	15.492	36.772			
'BSB South Zone 3A rerun'	17.038	15.490	36.771	30	-105	-16
'UCR 4*'	18.198	15.590	38.160			
'UCR 4* repeat'	18.198	15.593	38.163	6	160	77
'UCR 7*'	17.682	15.556	37.551			
'UCR 7* repeat'	17.682	15.556	37.552	3	-1	35
'UCR-7* '	17.687	15.558	37.558	276	69	145
'UCR 8*'	16.985	15.485	36.768			
'UCR 8* repeat'	16.988	15.486	36.771	169	60	90
'UCR 8* duplicate'	16.984	15.487	36.771			
UCR 8* duplicate rerun'	16.984	15.485	36.764	-31	-121	-183
'UCR 9*'	16.957	15.465	36.703			
'UCR 9* repeat'	16.954	15.465	36.700	-171	-50	-66
'UCR-9*'	16.958	15.463	36.702	34	-136	-28
'UCR 10*'	17.254	15.511	37.064			
'UCR 10* repeat'	17.254	15.511	37.065	-5	38	41
UCR 8* average	16.987	15.486	36.770			
UCR 8* duplicate ave	16.984	15.486	36.767			
difference (ppm)	-149	25	-62			

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Error on Pb analyses is ±250 ppm (2 sigma) or ±0.025%.

Pb normalized to 205Tl/203Tl = 2.38714 and then to NIST 981 = 16.9356, 15.4891, 36.7006 (Todt et al., 1996) for 206Pb/204, 207Pb/204Pb and 208Pb/204Pb, respectively, by sample-standard bracketing.

Table 5: Pb Isotope Compositions of Ecology Samples - Unmodified Samples

Sample	Pb Isotope Compositions		
	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
'UCR 1*'	17.836	15.577	37.755
'DM 2*'	17.125	15.504	36.877
BSB South Zone 3A*	17.177	15.508	36.951
'UCR 4*'	17.907	15.583	37.839
'UCR 7*'	18.058	15.604	38.046
'UCR 8*'	17.620	15.555	37.527
'UCR 9*'	17.691	15.562	37.588
'UCR 10*'	17.152	15.510	36.931

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Error on Pb analyses is ±250 ppm (2 sigma) or ±0.025%.

Pb normalized to 205Tl/203Tl = 2.38714 and then to NIST 981 = 16.9356, 15.4891, 36.7006 (Todt et al., 1996) for 206Pb/204, 207Pb/204Pb and 208Pb/204Pb, respectively, by sample-standard bracketing.

Table 6: Pb Isotope Compositions of Core Samples

Sample	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
1SL [BSB5A slag]	17.345	15.524	37.239
2SL [OC#8C slag]	17.113	15.494	36.867
3SL [SCB12A slag]	16.725	15.470	36.436
BSB-3A slag	17.233	15.513	36.993
UCR-10 slag	16.748	15.454	36.464
C03 [BSB4A 0.9-1.4]	17.396	15.530	37.241
C04 [BSB4A 1.5-2.5]	16.951	15.495	36.715
C05 [BSB4A 2.5-3.2	16.836	15.485	36.572
C06 [BSB4A 3.5-4.5]	18.706	15.622	38.773
C06 [BSB4A 3.5-4.5] rerun	18.700	15.621	38.767
C09 [BSB6A 0.0-1.0]	16.932	15.493	36.679
C09 [BSB6A 0.0-1.0] rerun	16.938	15.491	36.678
C10 [BSB6A 1.5-2.5]	18.882	15.630	38.977
C10 [BSB6A 1.5-2.5] rerun	18.877	15.630	38.972
C10 [BSB6A 1.5-2.5] rerun	18.886	15.632	38.980
C11 [BSB6A 2.5-3.5]	18.987	15.637	39.063
C12 [BSB6A 4.0-5.0]	18.981	15.648	39.195
C12 [BSB6A 4.0-5.0] rerun	18.987	15.646	39.195
C13 [BSB6AConf 0.5-1.5]	17.067	15.498	36.867
C14 [BSB6AConf 2.4-3.4]	17.005	15.497	36.785
C15 [BSB15A 0.0-1.0]	17.248	15.504	37.046
C16 [BSB15A 1.0-2.0]	17.175	15.502	36.979
C17 [BSB16A 0.25-0.75]	17.222	15.495	37.015
C19 [BSB17A 0.75-1.3]	17.549	15.531	37.413
C31 [DE#11A2 0.0-1.3]	18.201	15.621	38.239
C32 [DE#11A2 2.0-2.5]	18.471	15.655	38.589
C32 [DE#11A2 2.0-2.5] rerun	18.474	15.651	38.586
C36 [DE#14A 0.0-0.75]	17.615	15.555	37.510
C37 [DE#14A 0.75-1.0]	18.217	15.622	38.270
C38 [DE#14A 1.4-2.0]	18.904	15.639	38.974
C39 [DE#14A 2.0-3.0]	19.010	15.647	39.012
C48 [SCB7A 1.0-2.3]	17.151	15.513	36.941
C49 [SCB7A 2.7-3.6]	16.897	15.490	36.658
C50 [SCB7A 3.6-4.4]	17.451	15.517	37.409
C51 [SCB7A 4.4-5.0]	17.609	15.524	37.589
C52 [SCB7A 5.0-5.6]	18.418	15.604	38.478
C53 [SCB7A 5.6-6.3]	18.290	15.586	38.309
C58 [OC10A 1.3-2.3]	17.058	15.496	36.860
C61 [OC14A 0.5-1.5]	17.972	15.599	37.909
C65 [OC15A 0.5-1.5]	16.989	15.485	36.766
C68 [OC15Deep 9.0-9.8]	17.212	15.515	37.031
C73 [OC21A 0.0-1.0]	17.524	15.549	37.394

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Table 7: BSE Modal Analysis of Ecology and Slag Separate Samples

Sample	Modes from Mosaic Images					Total area imaged
	%silicate	% slag	% magnetite + misc	image frames	magnification	(sq. mm)
UCR-1	99.4		0.6			
DM-2	28.4	71.4	0.2	36	6.1	219.8
BSB-3A	67.9	32.0	0.1	49	6.1	256.5
UCR-4	99.6	0.4	0.0	42	6.1	219.8
UCR-7	98.9	1.0	0.1	40	8.5	209.0
UCR-8	93.5	6.5	0.0	54	7.1	282.7
UCR-9	99.4	0.3	0.3	49	6.1	256.5
UCR-10	83.9	15.7	0.4	54	7.1	282.7
SBC-12A slag sep	14.2	85.8	0.0	30	8.5	157.1
BSB_5A slag sep	31.4	68.5	0.1	36	8.5	209.4
OC_8C slag sep	0.0	99.9	0.1	35	8.5	183.2
UCR-10 slag	9.6	90.2	0.2	28	10.4	146.6
BSB-3A slag	0.0	100.0	0.0	36	7.1	188.4
analytical conditions						
instrument	JEOL 733 microprobe with GELLER digital imaging					
accelerating voltage (kV)	15					
beam current (nA)	8					
dwell time (msec)	0.05					

	Modes from SubSample images					Total area imaged
	%silicate	% slag	% magnetite + misc	image frames	magnification	(sq. mm)
UCR-1						
DM-2	26.3	73.5	0.3	11	42.5	57.8
BSB-3A	68.6	30.5	1.0	11	42.5	57.8
UCR-4						
UCR-7						
UCR-8	89.7	10.1	0.2	10	42.5	57.8
UCR-9	97.9	1.9	0.2	10	89.0	12.0
UCR-10	84.9	13.4	1.7	10	42.5	57.8
analytical conditions						
accelerating voltage (kV)	15					
beam current (nA)	54					
dwell time (msec)	0.5					

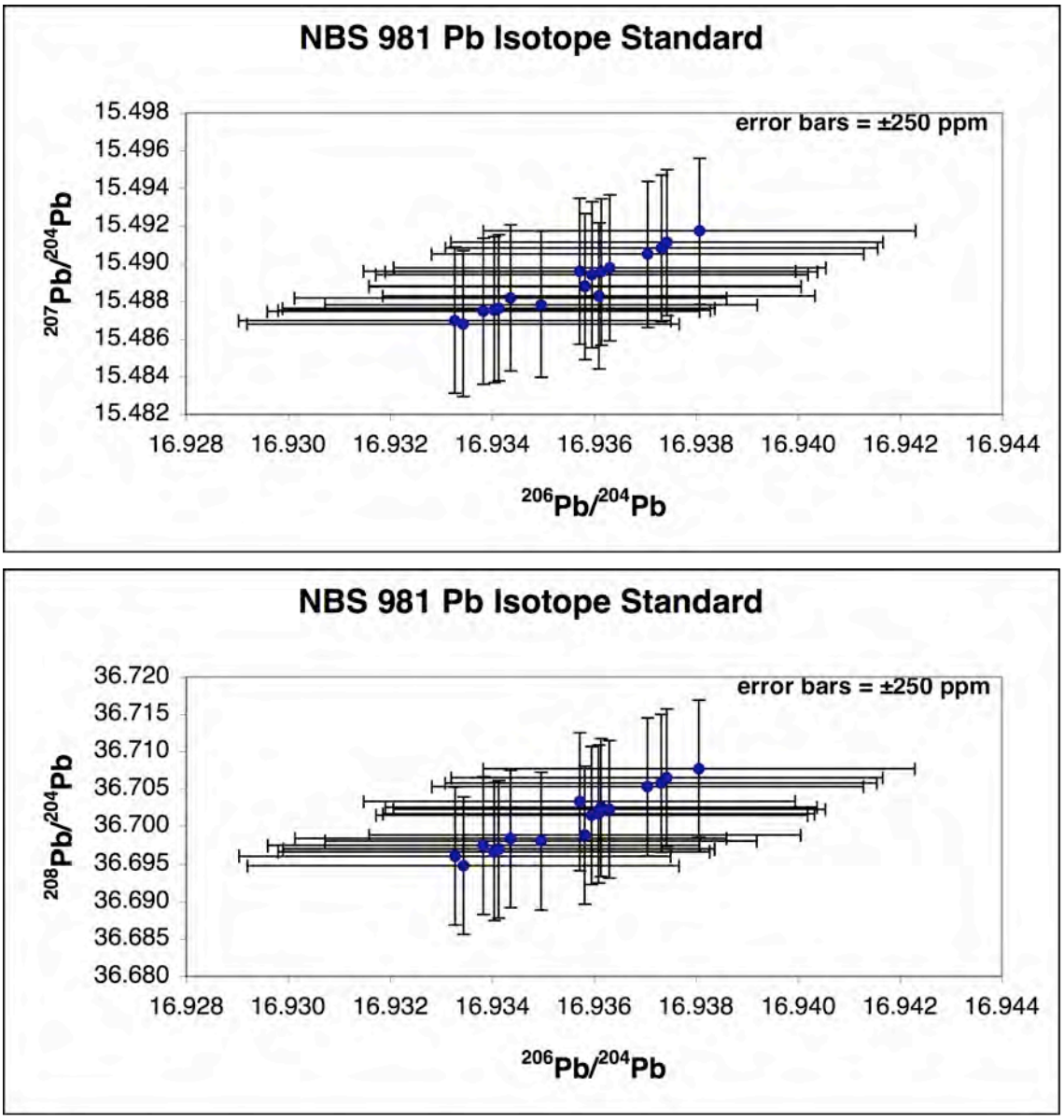

Fig. 1. Measured Pb isotope ratios of NBS 981 Pb isotope standard. Standard was measured every sixth sample as an unknown. Accepted values are 16.9356, 15.4891 and 36.7006 for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ amd $^{208}Pb/^{204}Pb$, respectively (Todt et al., 1996).

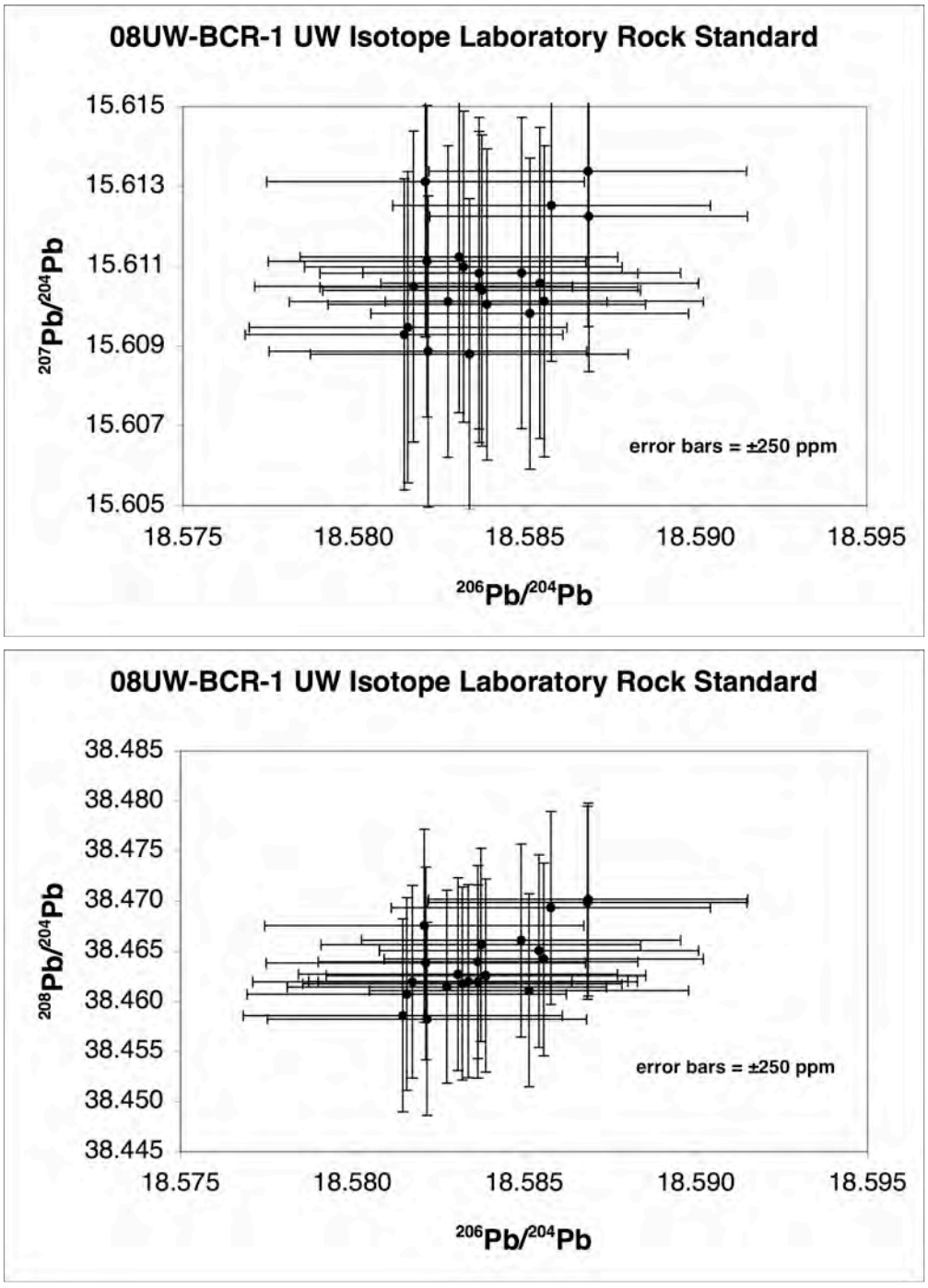

Fig. 2. Measured Pb isotope ratios of internal laboratory rock standard 08UW-BCR-1. Eight aliquots of the standard were measured during the course of the study.

Fig. 3. EDS spectra for a) feldspar, b) rhyolite glass, c) magnetite and d) slag.

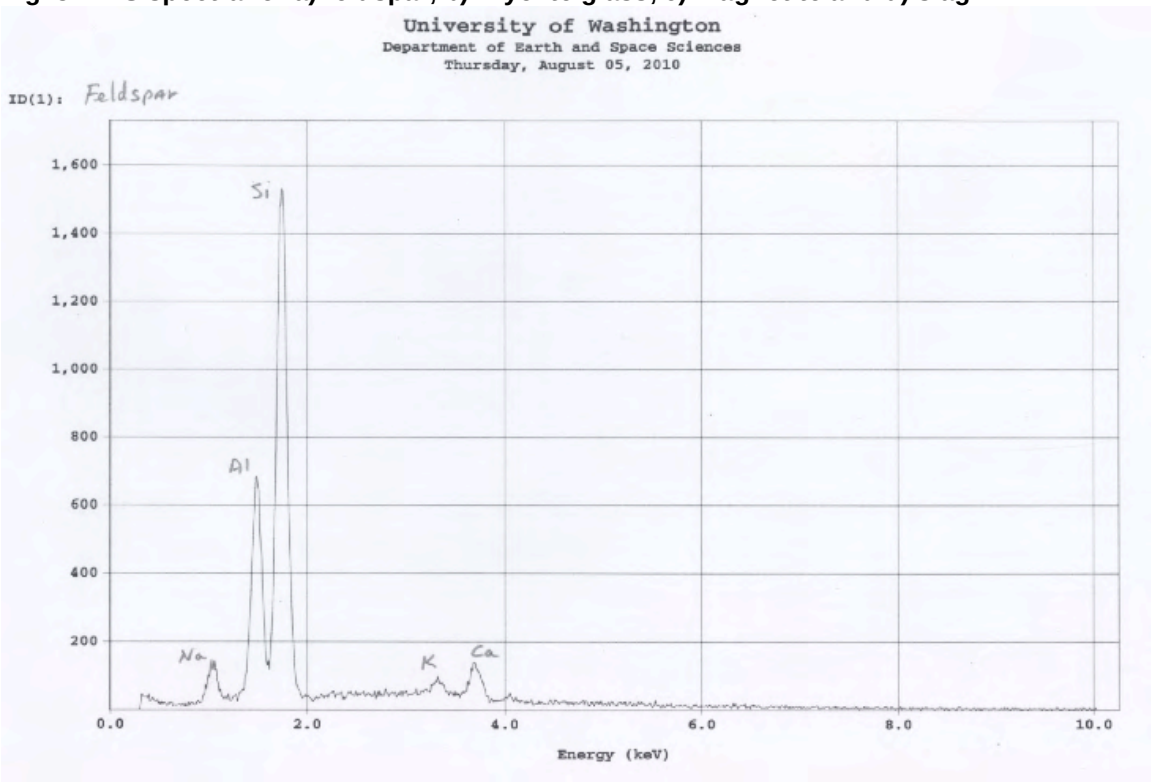

Fig. 3a. Representative EDS spectrum for feldspar.

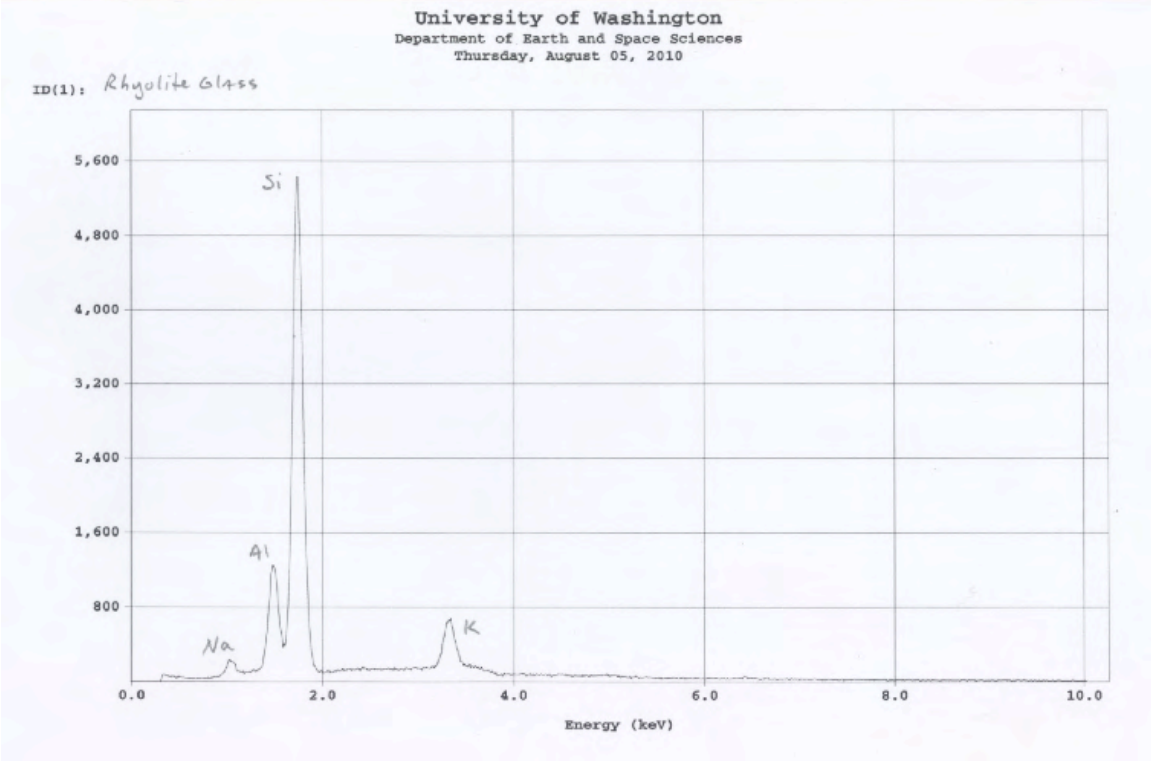

Fig. 3b. Representative EDS spectrum for rhyolite glass.

Fig. 3. Continued

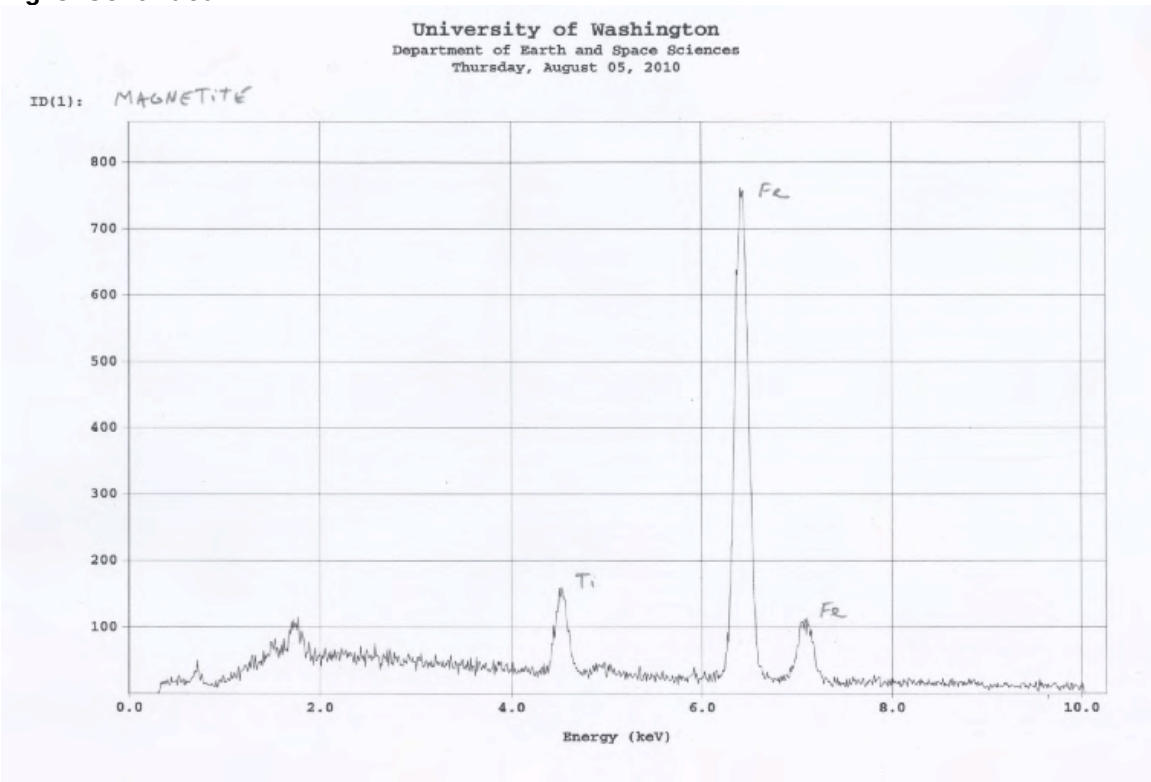

Fig. 3c. Representative EDS spectrum for magnetite.

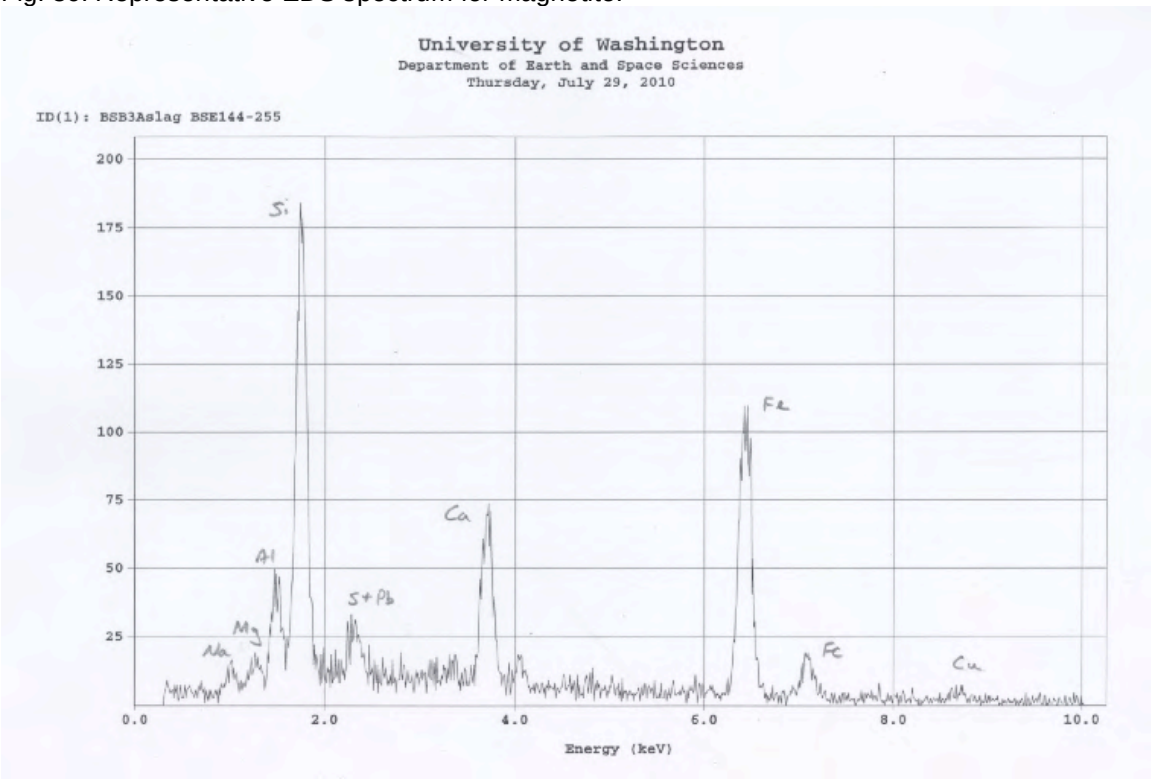

Fig. 3d. Representative EDS spectrum for slag.

Figs. 4-9. Backscatter images with grey-scale range adjusted to identify slag grains. Horizontal field of view (fov) indicated for each image.

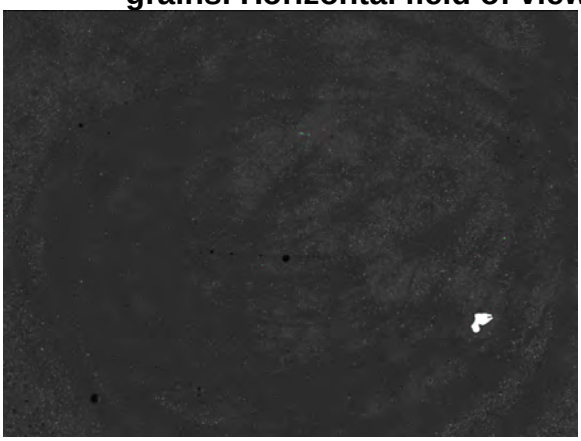

Fig. 4. BSE image of UCR-1; fov = 20mm.

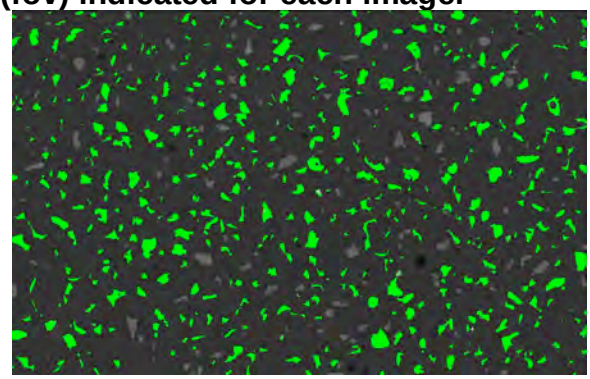

Fig. 5. BSE image of DM-2; fov = 20mm.

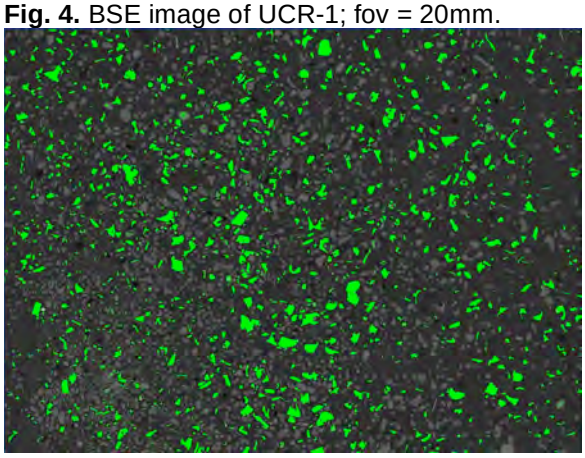

Fig. 6. BSE image of BSB3A; fov = 20mm.

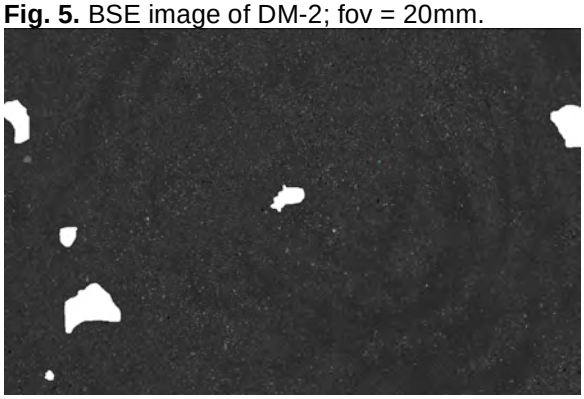

Fig. 7. BSE image of UCR-4; fov = 20mm.

Fig. 8. BSE image of UCR-7; fov = 14mm.

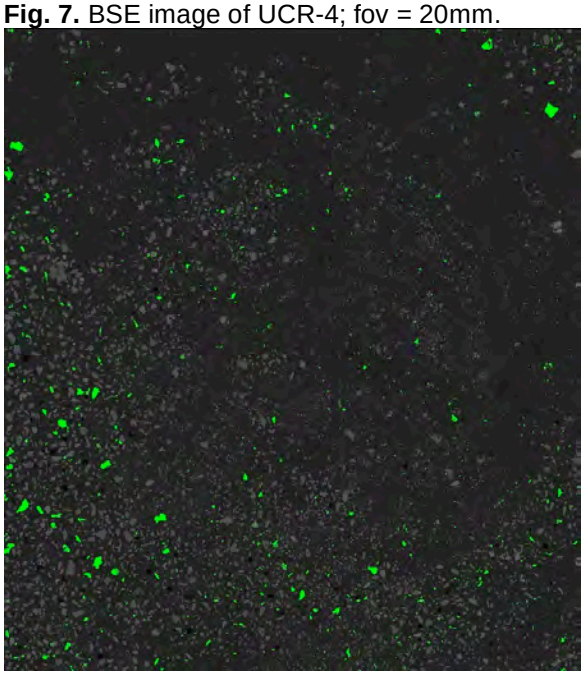

Fig. 9. BSE image of UCR-8; fov = 17mm.

Figs. 10-14. Backscatter images with grey-scale range adjusted to identify slag grains. Horizontal field of view (fov) indicated for each image.

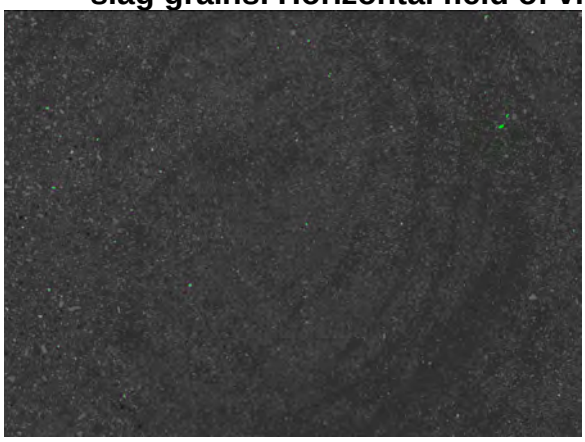

Fig. 10. BSE image of UCR-9; fov = 20mm.

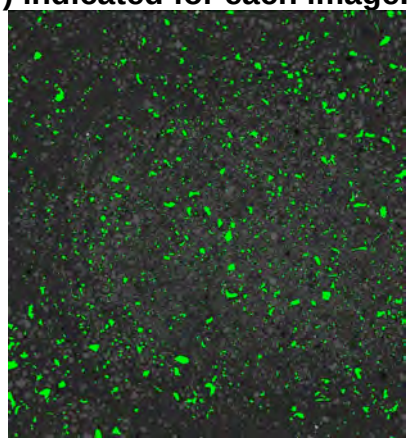

Fig. 11. BSE image of UCR-10; fov = 17mm.

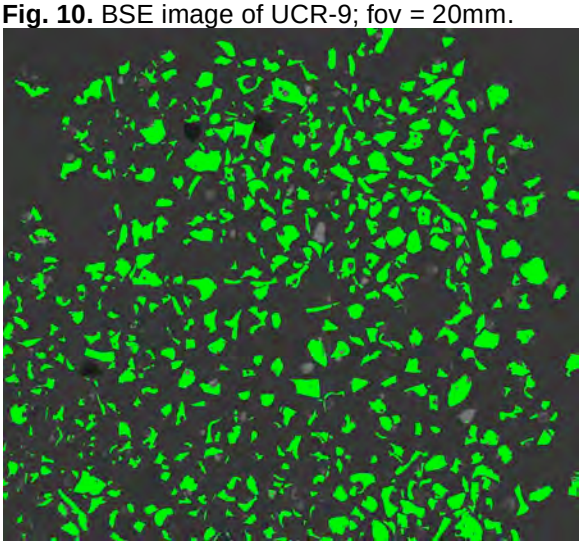

Fig. 12. BSE image SBC12A slag; fov = 14mm.

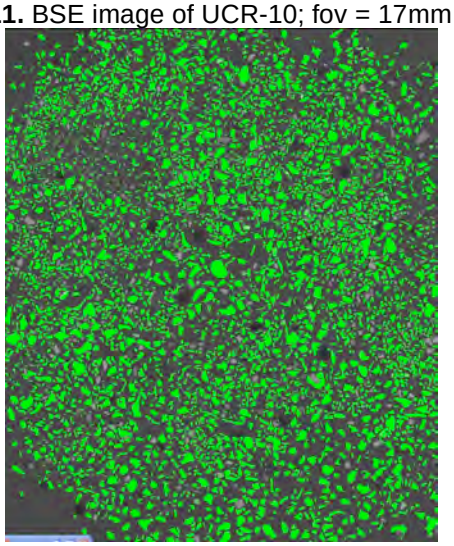

Fig. 13. BSE image of BSB5A slag; fov = 14mm.

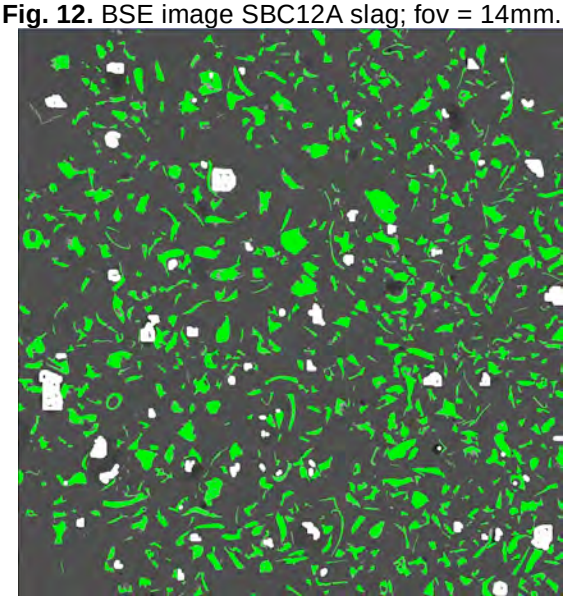

Fig. 14. BSE image of OC8C slag; fov = 14mm.

Note: In several images white shapes are present. These are an artifact of holes in the sample or anomalous electron transmission. These features are ignored by the area calculation software.

Figs. 15-18. Backscatter images and photomicrographs of slag separates prepared at UW, with grey-scale range adjusted to identify slag grains. Horizontal field of view (fov) indicated for each image.

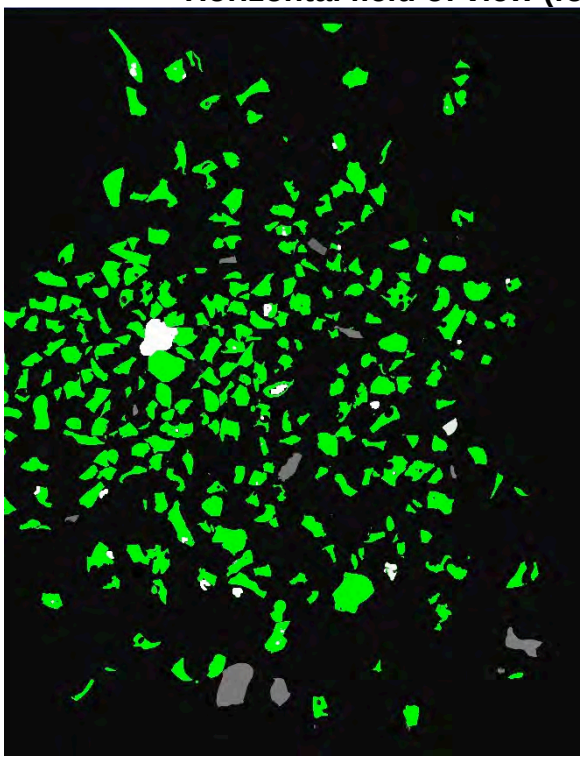

Fig. 15. BSE image UCR-10 slag; fov = 12mm.

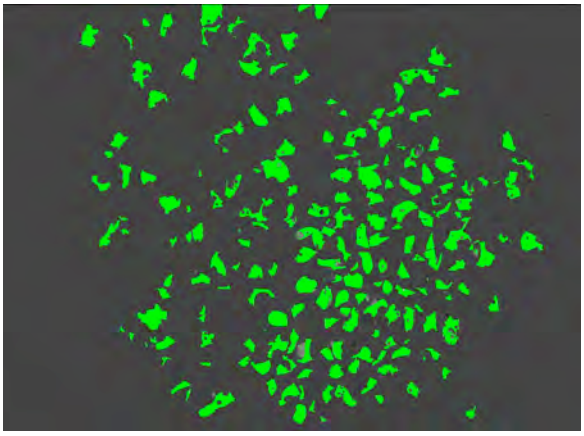

Fig. 16. BSE image of BSB3A slag; fov = 17mm.

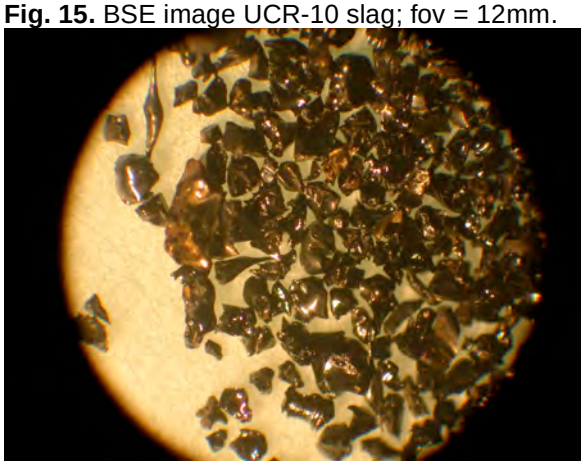

Fig. 17. Photomicrograph of UCR-10 slag; fov = 15mm.

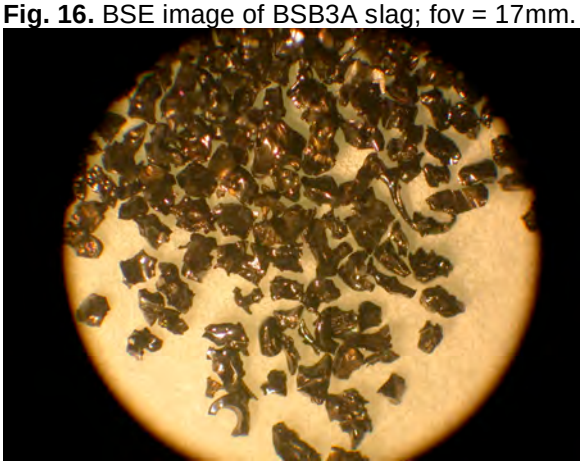

Fig. 18. Photomicrograph of BSB3A slag; fov = 15mm.

Appendix A:
Sample Acid Leach Treatment – Standard Operating Procedure
Dept. Earth & Space Sciences
University of Washington
Isotope Geochemistry Laboratory

Version: March, 2010
Bruce K. Nelson

I. General Conditions

1. This procedure applies to solid samples that require a leaching process prior to dissolution for isotopic analysis.

2. Leached sample and/or leachate may be preserved for isotopic analysis.

3. All sample processing is conducted within HEPA-filtered, positively pressured clean laboratories in Johnson Hall.

4. Analysts must wear lab coats and hats, gloves, eye protection, and observe all lab safety and cleanliness procedures.

5. All acids are distilled in the laboratory, or are ultrapure acids purchased from Seastar. Acids are blank tested prior to use. Acids are stored in Teflon containers.

6. Samples and leach solutions only come in contact with acid-cleaned Teflon containers.

7. Log analyst ID and all steps in sample procedure on prepared log sheets and/or lab notebook.

8. This procedure follows the weighing procedure of the main isotope analysis procedure.

II. Leaching procedures – weak HCl leach

1. Add approximately 3 mL (or minimum of 2 mL/100 mg of sample) 2M HCl to sample; tightly cap and swirl to mix well.

2. Place in ultrasonic bath for 15 minutes at room temperature. Do not submerge caps beneath level of bath.

3. Remove supernate with pre-cleaned pipette tip, preserve in pre-cleaned Teflon Savillex vial if destined for analysis.

4. Rinse sample twice with DI H2O (same amount as HCl added in leach step); add sample rinse to supernate if kept for analysis.

5. Continue with sample dissolution procedure.

Appendix B:
Mineral Separations – Standard Operating Procedure
Department Earth & Space Sciences
University of Washington
Isotope Geochemistry Laboratory

Version: March, 2010
Bruce K. Nelson

I. General Conditions

1. These procedures apply to solid samples with grain size between clay and sand.

2. All separations are performed in HEPA-filtered separation room in the Isotope Geochemistry Laboratory.

3. Separation techniques are adapted to the requirements of each sample. Those separation techniques that are done are performed in the order given in this SOP.

4. Analysts must wear lab coats and hats, gloves, eye protection, and observe all lab safety and cleanliness procedures.

II. Magnetic Mineral Separation

A. Hand Magnet

1. Clean work surface with alcohol and Kimwipe. Lay down clean Techwipe to work on.

2. Spread a fair split of the sample on a large sheet of weigh paper. Agitate so sample forms a single layer.

3. Layout a second sheet of weigh paper to receive sample.

4. Wrap weighing paper or parafilm around large hand magnet.

5. Pass over sample to remove magnetic fraction, transfer to clean weigh paper.

6. Transfer magnetic and non-magnetic fractions to separate, labeled, clean glass vials (label both sides and cap).

7. Record in laboratory notebook.

B. Frantz Magnetic separator

See http://www.sgfrantz.com/labl1.htm for principles of operation.

1. Use dedicated Frantz Isodynamic Magnetic Separator (model L-1) in clean mineral separation room of the Isotope Geochemistry Laboratory.

2. Even if already clean, disassemble Frantz and clean all surfaces with Kimwipes and alcohol.

3. Use part of the sample to adjust flow rate, tilt, inclination and magnetic intensity for optimal separation. Return all of this first pass to the sample reservoir.

4. Pass sample through; use additional passes with modified tilt, flow rate or magnetic intensity if required for further purification.

5. Record all parameters for each pass in laboratory notebook.

6. Store splits in labeled, clean, glass vials. Key split ID to description in notebook.

7. Disassemble and clean Frantz with alcohol and Kimwipes.

C. Hand-picking under binocular microscope

1. Use Nikon SMZ-2T stereoscopic microscope (10–63x magnification) dedicated to mineral separation, located in clean mineral separation room of the Isotope Gechemistry Laboratory.

2. Clean all surfaces with alcohol and Kimwipes prior to use.

3. This step is most effective in removing small amounts of contaminants from a nearly pure separate.

4. Use clean weigh paper or clean Petri dishes or clean watch glass covers upon which to spread out sample.

5. Remove impurities with tweezers, single camel hair taped to brush handle, or single camel hair dipped in mineral oil to extract extraneous grains.

6. Optionally, document appearance of sample split with camera mounted on microscope.

7. Note which split was processed and any relevant photo documentation in laboratory notebook.

8. Clean all surfaces with alcohol and Kimwipe when sample purification completed.

Appendix C:

Pb Isotope Analyses – Standard Operating Procedure
Dept. Earth & Space Sciences
University of Washington
Isotope Geochemistry Laboratory

Version: March, 2010
Bruce K. Nelson

I. General Conditions

1. This procedure applies to solid or dried liquid samples that are ready for total dissolution.

2. All sample processing is conducted within HEPA-filtered, positively pressured clean laboratories in Johnson Hall.

3. Analysts must wear lab coats and hats, gloves, eye protection, and observe all lab safety and cleanliness procedures.

4. All acids are distilled in the laboratory, or are ultrapure acids purchased from Seastar. Acids are blank tested prior to use. Acids are stored in Teflon containers.

5. Beginning with the dissolution step, samples only come in contact with acid-cleaned Teflon containers.

6. Log analyst ID and all steps in sample procedure on prepared log sheets and/or lab notebook.

7. With each batch of samples (maximum of 16) run a procedural blank in parallel.

8. Run a UW-BCR-1 internal laboratory rock standard every 10 to 15 samples.

II. Weighing & Dissolution procedures

A. Obtain an approximate weight of an appropriate split of the sample:

1. Put on new gloves. Clean the worksurface with alcohol and a Kimwipe, then place a fresh Techwipe down as a clean work surface.

2. Label clean glass vial both on cap and on the sides with the sample number, date, and analyst initials using permanent pen.

3. Level and center pan balance. Turn on the pan balance and place large piece of weigh paper on it. On top of this place a pre-folded piece of small weigh paper and then zero the pan balance.

4. If there is excess sample powder, do a fair split to weigh out the desired amount onto the weigh paper.

5. Pour the weighed amount into the vial and cap. Put the capped vial inside a poly glove.

6. Discard gloves and all weigh paper and clean the worksurface. Repeat procedure for each sample.

B. Obtain an accurate sample weight and add acids for dissolution:

1. Label a weighing logsheet or prepare lab notebook.

2. Label pre-cleaned Savillex screw-top Teflon vial with each sample name.

3. Move samples and vials to work surface near the high-precision Metler balance.

4. Thoroughly clean all work surfaces before use and place a Techwpe down as a clean working surface.

5. Turn on the de-ionization unit to decrease static electricity during weighing.

6. Tare the Metler balance, then place the labeled Savillex into the balance. Record to four decimal places the weight of the empty beaker.

7. Remove beaker, replacing it with a piece of weigh paper. Tare the weigh paper.

8. Remove the cap from the sample vial. Weigh out sample onto the weigh paper.

9. Transfer the sample to the labeled empty Savillex.

10. Cap and weigh the sample + Savillex. Record this weight on the sample weigh sheet.

11. If samples will be leached, dropper just enough 2M distilled HCl to wet the sample. Roll the drop around to collect grains that are on the walls of the Savillex.

12. Go to sample leach procedure if required by analysis, then return to next step.

13. Transfer samples to a HEPA-filtered, laminar flow exhaust hood.

14. Add 0.25 mL (~7 drops) of 8N HNO3 to Savillex beaker.

15. Add 2.5 mL (or more) concentrated distilled HF; Swirl to thoroughly mix sample with acids.

16. Tightly recap Savillex vial; Place on hotplate at 50 – 90 C overnight (or until sample completely dissolved)

17. Remove vial from hotplate, let cool, uncap and return to hot plate to dry down completely (~4-6 hours).

18. Add at least 2.5 mL distilled 6N HCl. Swirl.

19. Tightly recap Savillex; return to hotplate overnight (or until sample completely dissolved).

20. Remove vial from hotplate, let cool, uncap and return to hot plate to dry down completely (~4-6 hours).

21. Add 3.0 mL of 1.0N HBr; Tightly recap Savillex; return to hotplate overnight.

22. Remove from hot plate and let cool. Ultrasonicate for 10 minutes.

23. Transfer sample to clean pointy-bottom Teflon Savillex beaker; Centrifuge at 3500 rpm for 5 min. Pipette supernate back into first Savillex beaker.

III. Ion-exchange column procedure

Column preparation:

1. Use dedicated 4 mL Teflon columns and plastic column holders.

2. Charge column with 300 μL of AG-1x8, pre-cleaned ion exchange resin.

3. Place waste beaker under column

4. Pass 3.6 mL of 6N HCl through column (to clean Pb from column/resin)

5. Pass 600 μL of DI H_2O through column (to wash HCl from column/resin)

6. Pass 600 μL of 1.0N HBr through column (to condition resin)

Column pass #1:

7. With clean syringe and pre-cleaned pipette tip, transfer sample from Savillex vial to column. Let acid pass through.

8. Pipette 1.0 mL of 1.0N HBr into Savillex vial that held the sample; transfer HBr rinse to column and let acid pass through.

9. Place sample Savillex beaker under column.

10. Run 2 mL of 6N HCl through column and collect in Savillex (collects sample Pb).

11. Dry down sample completely (~3-4 hours)

Column pass #2:

12. Add 1.2 mL of 1.0N HBr to Savillex beaker (containing dried sample), gently heat for at least 30 minutes and cool.

13. Pass 3.6 mL of 6N HCl through column.

14. Pass 600 μL of DI H_2O thru column.

15. Pass 600 μL of 1.0N HBr through column.

16. Pipette sample solution (with clean pipette tip) from Savillex and onto same column as used in column pass #1.

17. Pipette 400 μL of 1.0N HBr into the sample Savillex vial; transfer to column, let pass through.

18. Pipette another 400 μL of 1.0N HBr into the sample Savillex; transfer to column, let pass through.

19. Place Savillex beaker under column.

20. Pass 2 mL of 6N HCl through column and collect in Savillex vial (to collect purified Pb sample).

21. Dry sample completely for MC-ICP-MS analyses.

22. Remove resin from columns and discard. Store columns in 7N HCl at least overnight before next use.

IV. MC-ICP-MS isotope analysis procedure

A. General Conditions

For documentation of principles and rationale behind analytical procedures followed here, see:

White, W.M., Albarède, F., and Télouk, P., 2000, High-precision analysis of Pb isotope ratios by multi-collector ICP-MS: Chem. Geol., v. 167, p. 257-270.

Kamenov, G.D., Mueller, P.A., and Perfit, M.R., 2004, Optimization of mixed Pb-Tl solutions for high precision isotopic analyses by MC-ICP-MS: J. Anal. At. Spectrom., v. 19, p. 1262-1267.

Weis, D., Kieffer, B., Maerschalk, C., Pretorius, W., and Barling, J., 2005, High-precision Pb-Sr-Nd-Hf isotopic characterization of USGS BHVO-1 and BHVO-2 reference materials: Geochem. Geophys. Geosyst., v. 6, p. doi:10.1029/2004GC000852.

Harkins, S.A., Appold, M.S., Nelson, B.K., Brewer, A.M., and Groves, I.M., 2008, Lead isotope constraints on the origin of nonsulfide zinc and sulfide zinc-lead deposits in the Flinders Ranges, South Australia: Econ. Geol., v. 103, p. 353-364.

1. Samples are analyzed on a Nu Instruments, multiple-collector inductively-coupled-plasma mass spectrometer.

2. Sample dilution, spiking, centrifugation and handling are done within a HEPA filtered laminar-flow bench.

3. Samples are bracketed and normalized to Pb standard NBS-981 international standard.

4. Samples are spiked with NIST-997 Tl standard for mass fractionation correction.

5. Mass 202 is monitored for Hg interference, and the mass 204 corrected for Hg interference using natural Hg isotopic composition.

6. Samples are aspirated in distilled 2% HNO3, via a desolvating nebulizer.

7. The following cup configuration is used for analyses:
H4 (^{208}Pb), H3 (^{207}Pb), H2 (^{206}Pb), H1 (^{205}Tl), Ax (^{204}Pb), L1 (^{203}Tl), L2 (^{202}Hg)

8. Prior to sample analyses, the instrument is tuned for optimal peak shape, peak alignment, intensity and signal stability.

9. The NBS Pb standard is run repeatedly until values stabilize to 200 ppm reproducibility over 60 minutes.

10. Instrumental mass fractionation is corrected using the exponential mass fractionation law. Samples are normalized to accepted NBS 981 values obtained by bracketing standards.

B. Sample Analysis

1. Calculate an initial sample dilution so that it is dissolved in solution in concentration of at least 120 ppb. The initial dilution is in the savillex sample beaker. Use distilled 2% HNO_3 to dilute.

2. Transfer enough sample to pre-cleaned 1.5 mL centrifuge tube so that when diluted to 1.5 mL the concentration is approximately 40 ppb. Compare sample signal intensity to 40 ppb standard signal intensity. Adjust dilution of sample so that signal intensity is within 20% of the standard signal intensity.

3. Add Tl spike. The Pb:Tl ratio should be between 4:1 and 12:1, with the optimal ratio at 8:1.

4. Once samples are diluted and spiked, load centrifuge tubes into the microcentrifuge on the laminar flow bench. Centrifuge at 6000 rpm for 5 minutes.

5. The run sequence is standard-sample-sample-standard.

6. Every sixth sample, run an NBS Pb standard as an unknown to monitor overall precision.

7. Between samples or standards, wash out by aspirating distilled 2% HNO_3 until background levels are obtained.

8. Background values are measured prior to every sample.

9. Records archived include a) hard copy output of calculated results, b) electronic copy of calculated results, c) electronic copy of raw data and backgrounds, d) electronic copy of all instrument parameters during analyses, and e) hard copy log of instrument parameters, plasma time and analyst identity.

Appendix D:
BSE and EDS Electron Microprobe – Standard Operating Procedure
Dept. Earth & Space Sciences
University of Washington
Electron Microprobe Laboratory

Version: March, 2010
Scott Kuehner
Bruce K. Nelson

I. General Conditions

1. These procedures apply to solid samples with grain size between clay and sand.

2. Analyses are performed on a JEOL 733 microprobe, in the department microprobe laboratory.

II. Sample Preparation

A. Mount samples in epoxy:

1. Affix double sided tape to a glass plate and attaché a 1inch inside diameter Al ring.

2. Salt sample grains are inside the Al ring and slightly press into the double-sided tape.

3. Pour a two-component epoxy into the ring and allow to set over night with or without warming.

4. After solidification, press the epoxy plug out of the Al-ring.

5. Polish samples; samples receive a final polish with ¼ micron diamond paste. The steps to the final polish may include lapping with 45 micron diamond, 15 micron diamond and/or alumina, and 6 micron diamond.

6. Carbon coating; the epoxy and included sample grains are made electrically conductive by sublimating a thin 20 nanometer film of carbon onto the surface of each plug.

III. Sample Analysis

A. General Analytical Conditions:

1. Electron beam energy is 15 keV.

2. Beam current is adjusted to 3 – 30 nA to optimize image contrast.

3. Beam diameter is on the order of 10's of nanometers; image resolution is 0.5 micron or better.

B. Backscatter Electron Imaging (BSE):

1. BSE image (brightness is function of average atomic number) is collected digitally.

2. Maximum sample dimension per frame is 3.5 mm.

3. Use digital imaging software to stitch together adjacent images to obtain a mosaic of the entire plug.

4. Optimize contrast and brightness levels of final image to enhance average atomic number contrast.

C. Energy Dispersive Spectroscopy (EDS):

1. Print out gray-scale image (8-bit, 256 grey scale).

2. Acquire a 20-second count of x-ray spectra emitted from identified sample particles.

3. Identify elements present (using associated software) and estimated relative concentrations.

4. Associate identified minerals with characteristic grey level.

5. Estimate modal abundances of phases in sample.

Note: any ambiguities in composition from EDS analysis can be resolved by using the wavelength dispersive spectrometers (WDS).