Evaluation of Bruker's Tracer Family Factory Obsidian Calibration

for

Handheld Portable XRF Studies of Obsidian

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INTRODUCTION

At the request of Bruker AXS, the University of Georgia's Center for Applied Isotope Studies undertook a study to evaluate Bruker's factory-installed obsidian calibration for quantitative analyses of archaeological obsidian by portable/handheld X-ray fluorescence spectrometry (PXRF). Of specific interest here are issues related to accuracy, precision, and reproducibility of data generated using Bruker's Tracer Family PXRF instruments.

Figure 1. Bruker Tracer Handheld PXRF

Over the past decade, PXRF increasingly has been used by scientists, archaeologists, and museum researchers for analysis of widely varied material culture. Among these various material classes, metals, ceramics, silicate rocks, and soils have generated the most interest for archaeologists who routinely incorporate chemical-based studies of material culture (e.g., obsidian, pottery, and chert) to investigate prehistoric social interaction, trade and exchange networks, migration, and the dynamic nature of group identification. Obsidian—a naturally occurring volcanic glass widely used to produce stone tools by prehistoric people—is a material that is ideal for such research because artifacts made from obsidian usually can be linked to their geologic source with a high degree of reliability using analytical techniques, such as XRF.

Since publication of a study by Craig et al. (2007) first demonstrating the feasibility of using portable XRF instrumentation for chemical sourcing of obsidian, the application of this technology to obsidian (and other materials) has grown exponentially. The expansion of PXRF into the archaeological 'tool kit', however, has not been without problems. First and foremost has been the fact that all PXRF instruments sold, until recently (Bruker being the exception here), lacked a matrix-specific factory-installed obsidian calibration, or in the case of two manufacturers, the ability for the

Figure 2. Example of a prehistoric obsidian tool.

user to readily develop their own. Consequently, many of the obsidian PXRF studies that have been published to date, lack accuracy. Although conclusions regarding geological source attribution of obsidian artifacts in these various studies, may be correct or “internally consistent”, this approach amounts to little more than a “trust me” type situation and is not the way that science should be conducted in archaeology or elsewhere. A second fundamental problem has been that PXRF users are not measuring and reporting data for international reference standards. Consequently, it is virtually impossible to assess data in terms of precision, accuracy, and reproducibility—the foundation for valid and reliable science.

Bruker’s obsidian calibration is based on a customized set of forty slab-cut obsidian source samples commissioned from the Archaeometry Laboratory at the University of Missouri Research Reactor (MURR). The set was created specifically to overcome one of the major perceived issues concerning portable-XRF analyses of obsidian—a lack of matrix-specific standards for calibrating instruments[1]. MURR scientists selected samples that would provide a broad range of element concentrations from high-to-low, especially for the elements useful in obsidian sourcing by XRF—

Figure 3. Photograph of the 40 obsidian calibration samples. Each ziplock bag is 5 x 8.5 cm.

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[1] [1] There is some debate among scholars concerning the validity of using pressed international rock standards for empirical calibration of XRF units used primarily for quantitative analyses of solids. The reader is referred to Shackley (2012) for additional details.

primarily Fe, Mn, Zn, Rb, Sr, Y, Zr, and Nb. Most of these elements are particularly useful discriminating elements for obsidian source studies because, as large ions, they are incompatible with crystallizing solids; as magmas evolve the concentrations of incompatible elements will be different for each source.

The 40-sample calibration set, evaluated herein, was analyzed by INAA, LA-ICP-MS, and ICP-MS of solutions at MURR. From those analyses, recommended values were determined for most elements on the Periodic Table. A complete report detailing the reference samples, analytical protocols, and results is available from Bruker (Glascock and Ferguson 2012).

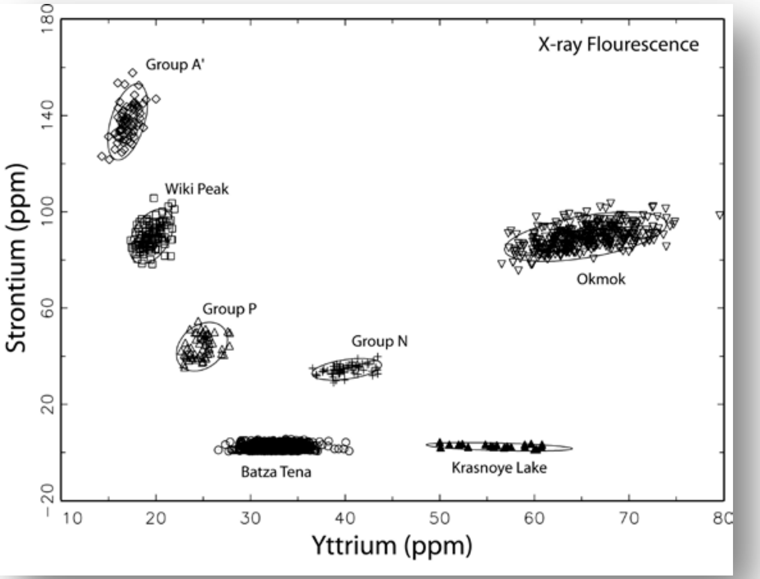

Figure 4. Bivariate plot of Y and Sr concentrations determined for obsidian artifacts from Alaska using a Bruker Tracer Handheld PXRF. Different clusters of data represent distinct compositional groups indicative of specific geological sources of obsidian.

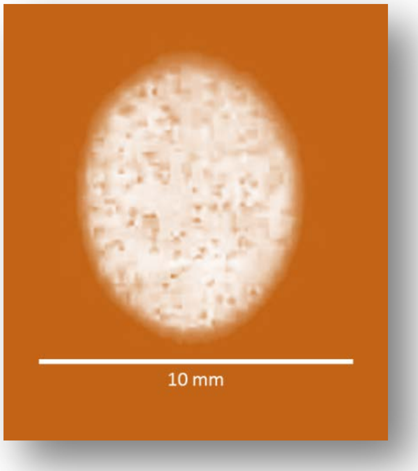

Figure 5. X-ray beam spot size and shape for the instrument used in this study. Image was obtained using Polaroid instant film.

METHODS

Analyses were conducted using a Bruker Tracer III SD handheld XRF spectrometer equipped with a rhodium target X-ray tube and a silicon drift detector with a resolution of ca. 145 eV FWHM for 5.9 keV X-rays (at 200,000 counts per second) in an area 10 mm^2. The spot size on this specific instrument is less than 10 mm diameter.

All samples were measured at 40kV, 25 µA, with a 12 mil Al, 1 mil Ti, 6 mil Cu filter placed in the X-ray path for a 200-second live-time count. Peak intensities for the Kα peaks of Mn, Fe, Zn, Ga, Rb, Sr, Y, Zr, Nb, and Lα peak of Th were calculated as ratios to the Compton peak of rhodium, and converted to parts-per-million (ppm) using Bruker's factory-installed calibration for obsidian.

RESULTS

Instrument stability

As a first step in assessing the Bruker's obsidian calibration and the Tracer's stability, the instrument was set up to analyze XRF standard 08 continuously for 17 hours with spectra being saved every 200 seconds. This resulted in data for 307 analyses (Appendix B) that are summarized in in Table 1, below. Individual data points for these analyses are plotted in Figure 7 (Zn, Ga, Th, Rb, Sr, Y, Zr, Nb) and Figure 8 (Mn and Fe).

Data for these 307 analyses exhibit relatively low variation (%RSD). For Fe, Rb, Y, Zr, and Nb, the %RSD is 2% or lower which is comparable to data generated on most laboratory-based EDXRF instruments. Mn, Zn, and Ga exhibit %RSD values of ca. 3-6% which is typical for these elements. Sr has the highest error, as would be expected given its low concentration in this particular sample (which also approaches the limits of EDXRF detection for Sr in silicate matrices). In other words, the high %RSD for Sr in this sample is entirely due to counting statistics, and in no way a reflection of the instrument itself. A Horwitz Curve (Horwitz et al. 1980) (Figure 6) for the 40 obsidian calibration standards discussed above illustrates this point. Horwitz Curves are commonly used to evaluate upper and lower ends of calibration curves. In this plot, Sr concentrations (x-axis; based on the average value of measurements) are plotted against %RSD (y-axis). A power trendline is fit against all data points. In this plot, however, the x-axis is constrained to samples with less than 100 ppm Sr to facilitate the evaluation of the low end of the curve. The plot shows that as concentration decreases (i.e., lower counting statistics), that %RSD increases; thereby illustrating the point that measurement error is correlated with concentration (counting statistics). The closer one gets to instrument detection limits, the greater the analytical error. At concentrations of about 7 ppm we observe less than 5 %RSD. At concentrations above 15 ppm the error decreases to about 2-3 %RSD. To reiterate, the high %RSD reported in Table 1 is not a reflection of PXRF performance; similar results would be obtained with any properly calibrated EDXRF spectrometer regardless of manufacturer.

Of particular import for Figures 7 and 8 is that the overall trend for each element is "flat" indicating that instrumental drift is not an issue. For researchers conducting analyses under field conditions, reanalysis of samples is oftentimes not possible, and data must therefore be of high quality. An instrument that drifts throughout the day will impart greater analytical error on the experiment and could result in needless reanalyses of samples. For obsidian, this could mean that distinctions among compositional groups could be obscured such that source identification is not possible. Finally, it is important to note in Figures 7 and 8 that the relative deviation between analyses is minimal and that no outliers are present (all analyses are presented in these figures).

Table 1. *17-Hour Stability Test (307 consecutive analyses at 200 seconds each) for sample XRF08*

	Mn	**Fe**	**Zn**	**Ga**	**Th**	**Rb**	**Sr**[1]	**Y**	**Zr**	**Nb**
Average	438.7	7446.2	134.1	27.0	41.7	364.4	1.1	83.9	163.7	237.5
Stdev	23.7	72.6	4.6	1.7	1.5	3.4	0.5	1.6	1.7	2.4
%RSD	5.4	1.0	3.4	6.2	3.5	0.9	41.1	2.0	1.0	1.0

[1] High %RSD (% relative standard deviation) a consequence of low Sr concentration in this sample which results in low counting statistics. In no way is this a reflection of instrument used for the analysis (all XRF instruments would exhibit similar errors at this concentration and matrix). For samples containing more than 15 ppm Sr, 2-3 %RSD is the norm.

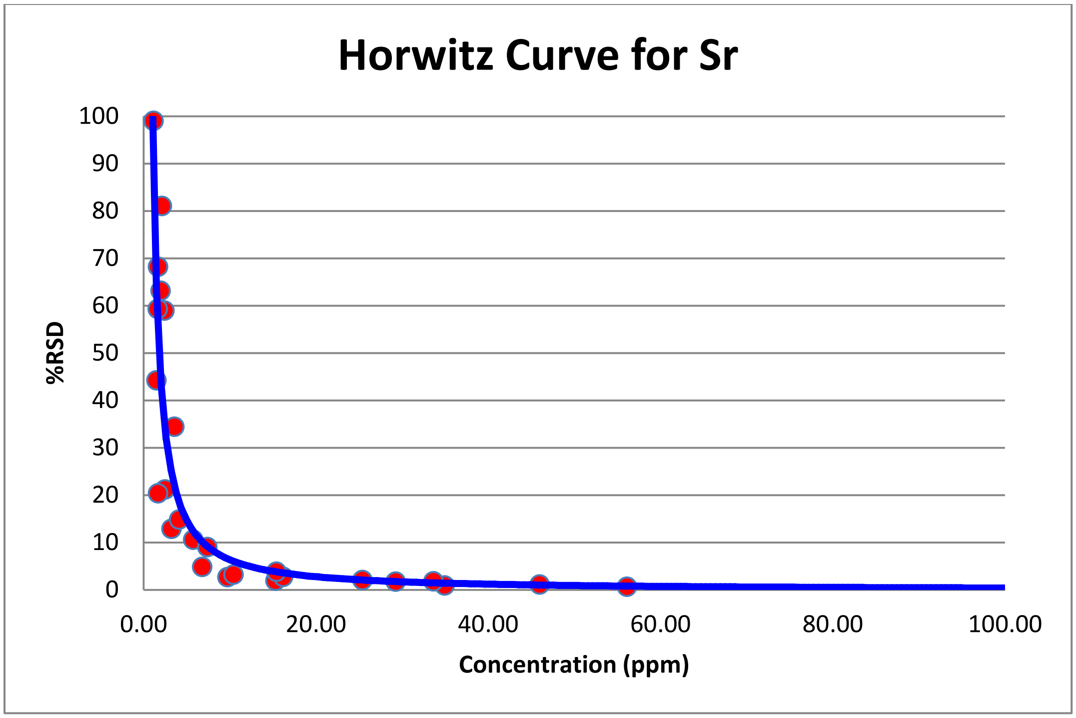

Figure 6. Horwitz Curve for the 40 obsidian calibration standards discussed above. Sr concentration (x-axis) is based on the average value of five measurements. Curve is fit to all data points, but the plot is constrained to samples with less than 100 ppm Sr to facilitate the evaluation of the low end of the curve. This plot shows that as concentration decreases (i.e., lower counting statistics), that %RSD increases thereby illustrating the point that measurement error is correlated with concentration. The lower one gets to detection instrument limits, the greater the analytical error. Again, this is not a reflection of Bruker's Tracer performance; similar results would be obtained with any properly calibrated EDXRF spectrometer.

Assessment of the XRF standards

A good calibration is critical to ensuring validity of results for XRF analyses. Without it, numbers generated are essentially useless—as is the case with some PXRF analyses. To assess the linearity of Bruker's obsidian calibration curve. Bruker's set of 40 obsidian standards (XRF13 inadvertently was not analyzed) were analyzed 5 times each, converted to ppm using the factory installed calibration, and averaged. Individual element plots are shown in Figures 9-17. Data for three samples are not included in these plots—samples 17, 18, and 20. Sample 20 is basalt not obsidian, and Samples 17 and 18 returned unusual values for some elements[2]. It is therefore recommended that samples 17, 18, and 20 not be included in future calibrations.

Plots of observed (averaged measured values, Appendix B) versus expected values (Glascock and Ferguson 2012) demonstrate the calibration is highly linear. Linearity is critical given that non-linear regions of a calibration will adversely affect the accuracy of samples falling within those regions.

Coefficient of determination values (also known as R^2 values) exceed 0.99 for all elements except Mn and Th which have known background-related issues from adjacent peaks (Fe and Rb respectively). Despites these issues, Mn performed extraordinarily well with R^2 value of ca. 0.985 and Zn likewise had a R^2 value of ca. 0.975.

Assessment of validity via analysis of Geologic Standards

Although the high R^2 values discussed above demonstrates that Bruker's obsidian calibration is linear and that the observed versus expected values are in agreement, it is not fair to assess accuracy using reference materials that are included in the calibration. All calibrations must be verified against independent quality control standards. As Shackley (2010) has stated previously, these standards must periodically be analyzed and publish the results to establish validity. The primary laboratory-based obsidian EDXRF laboratories run by Steve Shackley (Geoarchaeological XRF Lab), Craig Skinner (Northwest Research Obsidian Studies Laboratory, and Richard Hughes (Geochemical Research Laboratory) routinely publish values determined for the USGS RGM-1 obsidian standard as a means for establishing validity.

Tables 2 and 3 present data obtained from the analysis of pressed-powdered international obsidian standards (RGM-1 and NIST SRM-278) relative to their recommended values and published literature values. In all cases the Bruker data overlap with recommend values at 1 sigma thereby establishing the validity and reliability of the calibration.

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[2] Mike Glascock (personal correspondence to Speakman) has noted similar issues with these samples when they are analyzed by PXRF. This may be due to naturally occurring chemical variation in the sample matrix.

Table 2. *Replicate analyses of USGS RGM-1 and comparison to published values.*

	Mn	**Fe**	**Zn**	**Th**	**Rb**	**Sr**	**Y**	**Zr**	**Nb**
Bruker Tracer (n=5)	**321±28**	**13075±69**	**40±2**	**16±1**	**157±3**	**104±1**	**26±1**	**223±3**	**10±1**
USGS Recommended	279±50	13010±210	32	15±1.3	150±8	110±10	25	220±20	8.9±0.6
Shackley (2012)	302±14	13116±308	n.r.	16±3	151±3	106±3	25±2	219±5	9±2
Skinner (1996)	291±47	13480±745	37±7	n.r.	152±3	107±9	24±3	217±8	11±1
Hughes (2007)	278±10	13079±140	n.r.	n.r.	143±4	105±3	23±3	214±4	8±3

n.r.—not reported

Table 3. *Replicate analyses of NIST SRM-278 and comparison to published values.*

	Mn	**Fe**	**Zn**	**Th**	**Rb**	**Sr**	**Y**	**Zr**	**Nb**
Bruker Tracer (n=5)	**432±27**	**14521±100**	**55±4**	**13±2**	**133±2**	**62±1**	**41±1**	**281±2**	**18±1**
NIST Recommended	403±2	14269±140	n.r.	12.4±.3	127.5±.3	63.5±.1	n.r.	n.r.	n.r.
Glascock (2006)	397±23	14500±900	53±5	12.6±0.6	133±6	64±5	39±5	290±30	n.r.
Shackley (2012)	383±7	14329±37	n.r.	15±5	130±2	67±1	40±2	276±2	15±2

n.r.—not reported

CONCLUSIONS

Assessment of instrument stability, accuracy, precision, and validity described above demonstrate that the calibration developed by Bruker is appropriate for elemental analyses of obsidian. As of June 2012, there are at least 60 publications in which PXRF has been used for chemical characterization of obsidian. Data for many of these publications are problematic in that they oftentimes lack adequate calibration and/or failed to establish reliability and validity. Bruker's development of obsidian XRF standards in collaboration with MURR is a step in the right direction; this also makes Bruker the only PXRF instrument manufacturer that provides its customers with a high-quality obsidian calibration that produces valid and reliable results. Ultimately though, it is the responsibility of the PXRF user to evaluate and modify any factory calibrations as appropriate (or generate their own) to ensure that data are valid and reliable. Factory calibrations, while useful and informative, should never be accepted by the researcher as the final "solution" without first evaluating performance against known reference materials.

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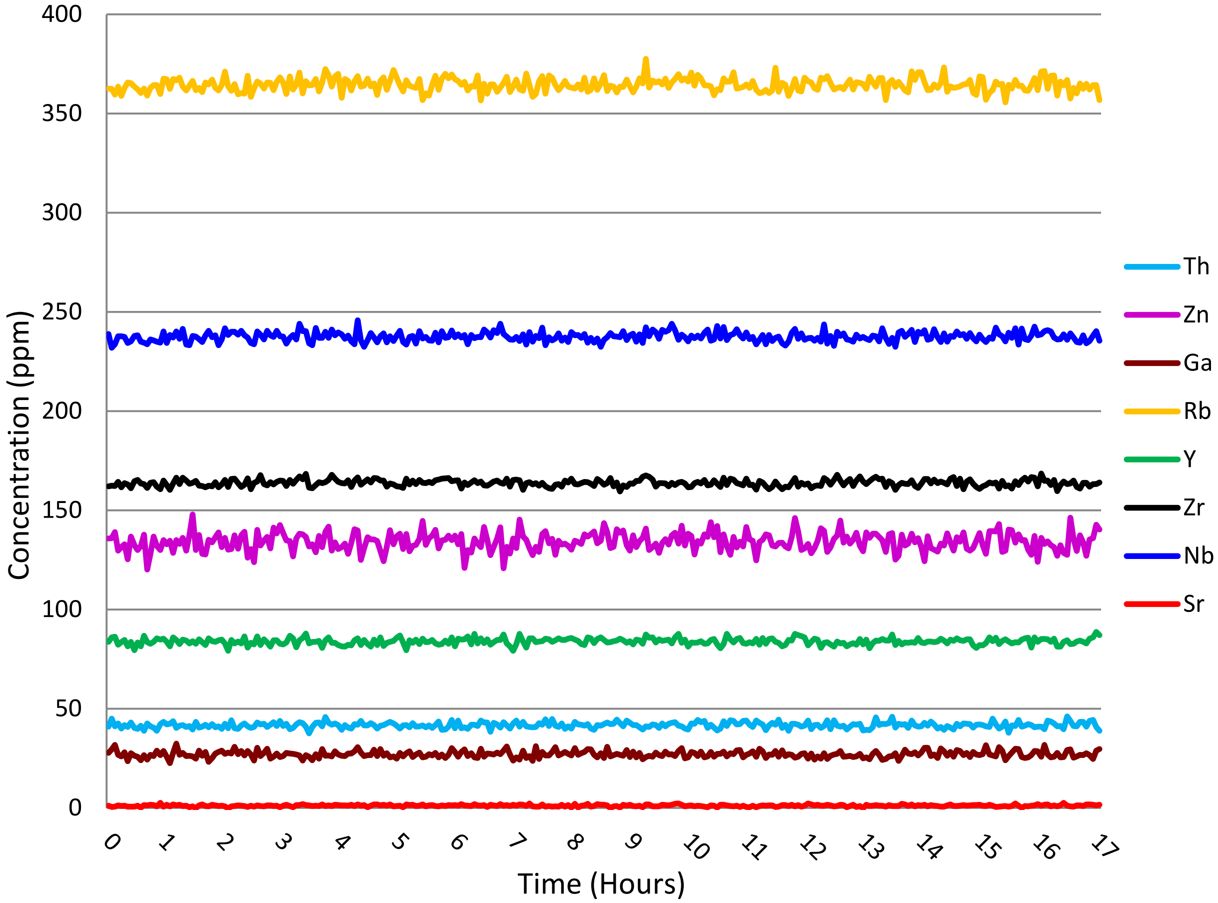

Figure 7. Results in ppm (y-axis) versus time (x-axis) for 307 consecutive 200-second counts of Bruker obsidian standard XRF08. Note that the overall trend for each element is “flat” indicating that instrumental drift is not an issue. Likewise note that the relative deviation between analyses is minimal and that no outliers are present. Refer to Table 1 for summary statistics for this analysis.

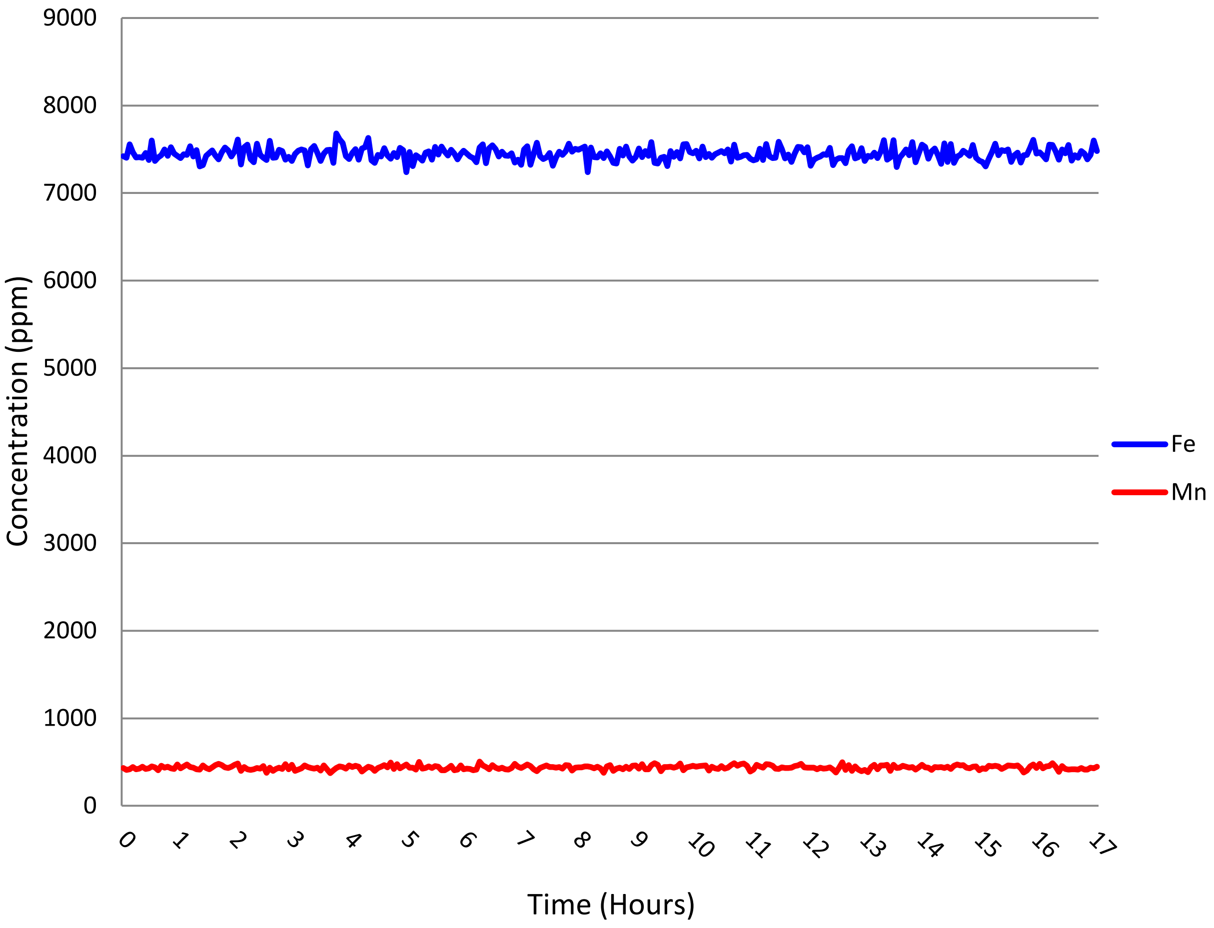

Figure 8. Results in ppm (y-axis) versus time (x-axis) for 307 consecutive 200-second counts of Bruker obsidian standard XRF08. Note that the overall trend for each element is "flat" indicating that instrumental drift is not an issue. Likewise note that the relative deviation between analyses is minimal and that no outliers are present. Refer to Table 1 for summary statistics for this analysis.

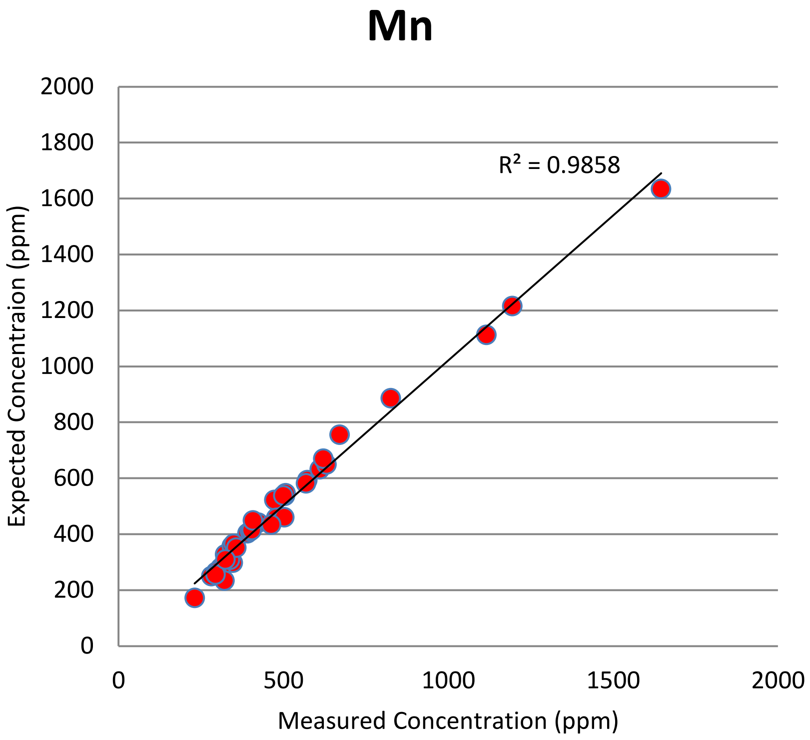

Figure 9. Measured (observed) versus expected concentrations for Mn in Bruker's obsidian XRF standards.

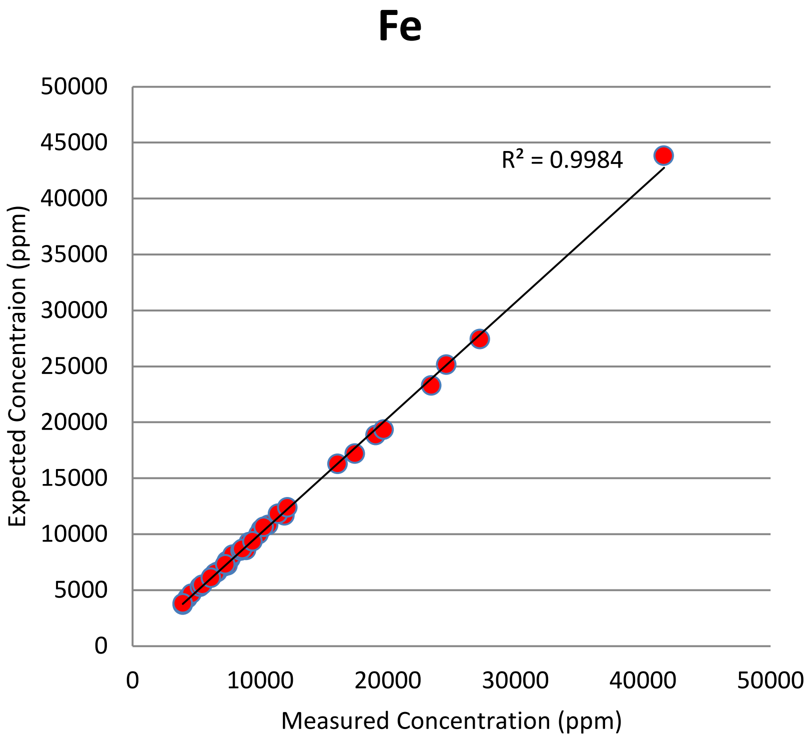

Figure 10. Measured (observed) versus expected concentrations for Fe in Bruker's obsidian XRF standards.

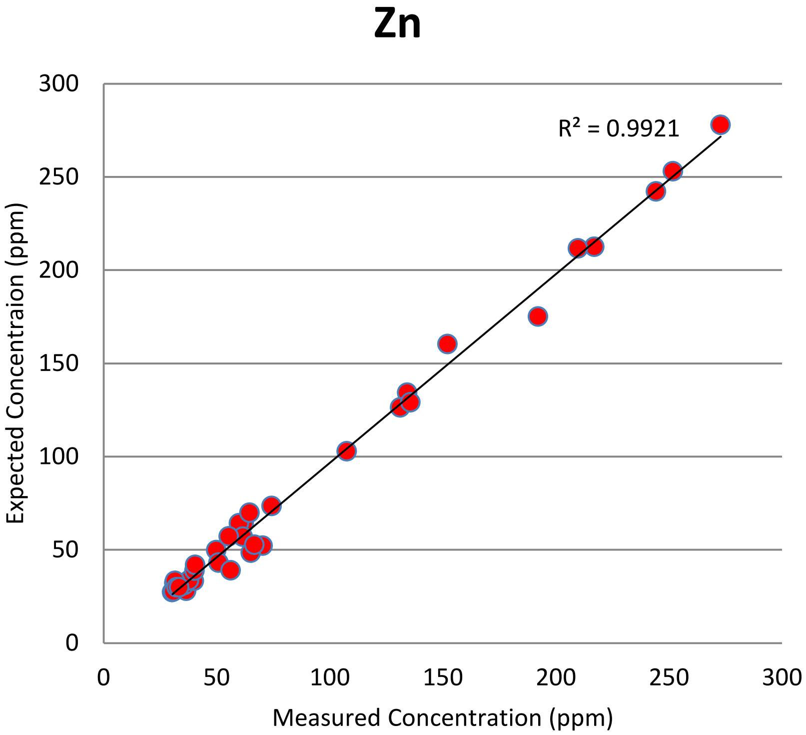

Figure 11. Measured (observed) versus expected concentrations for Zn in Bruker's obsidian XRF standards.

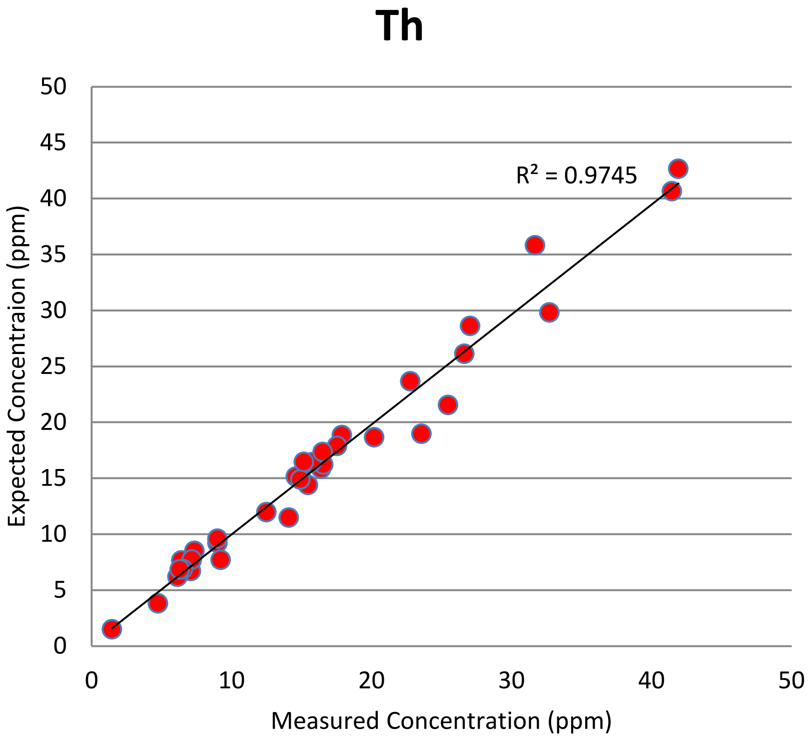

Figure 12. Measured (observed) versus expected concentrations for Th in Bruker's obsidian XRF standards.

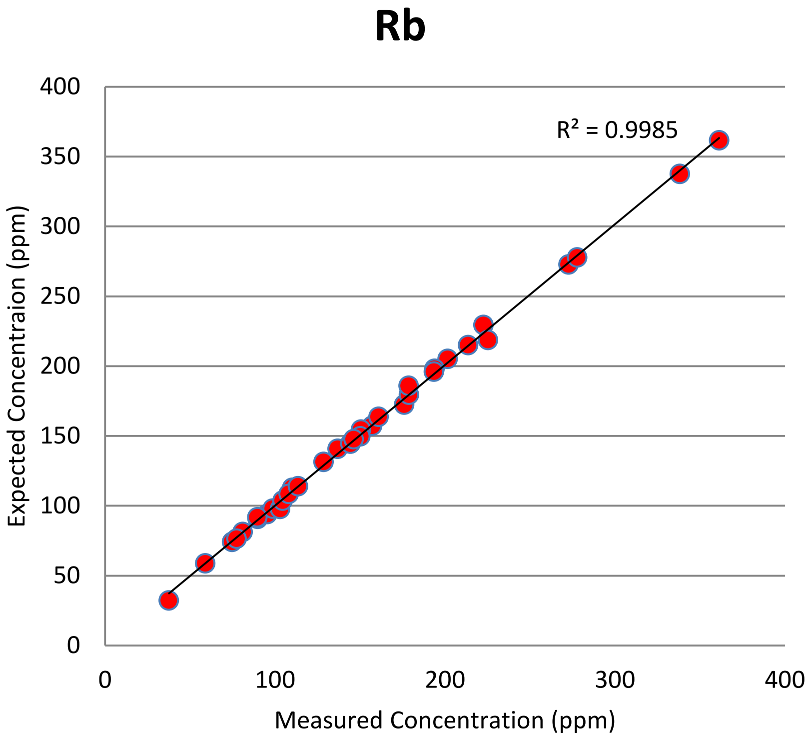

Figure 13. Measured (observed) versus expected concentrations for Rb in Bruker's obsidian XRF standards.

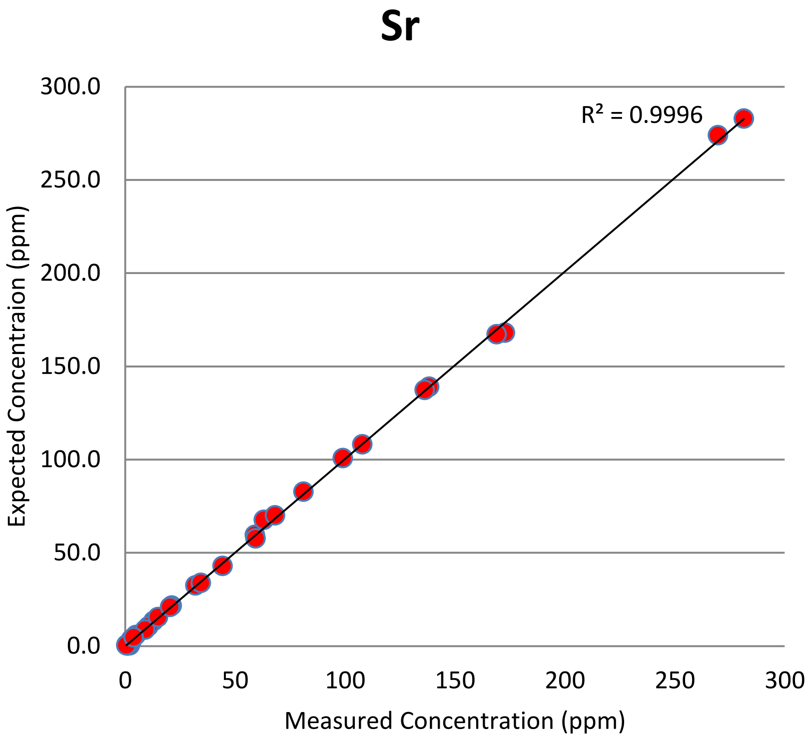

Figure 14. Measured (observed) versus expected concentrations for Sr in Bruker's obsidian XRF standards.

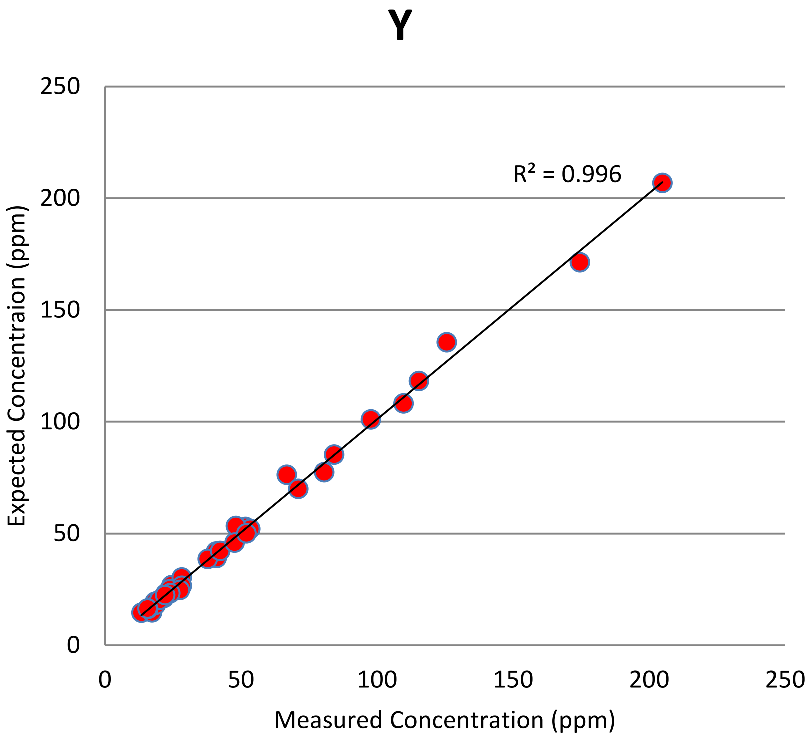

Figure 15. Measured (observed) versus expected concentrations for Y in Bruker's obsidian XRF standards.

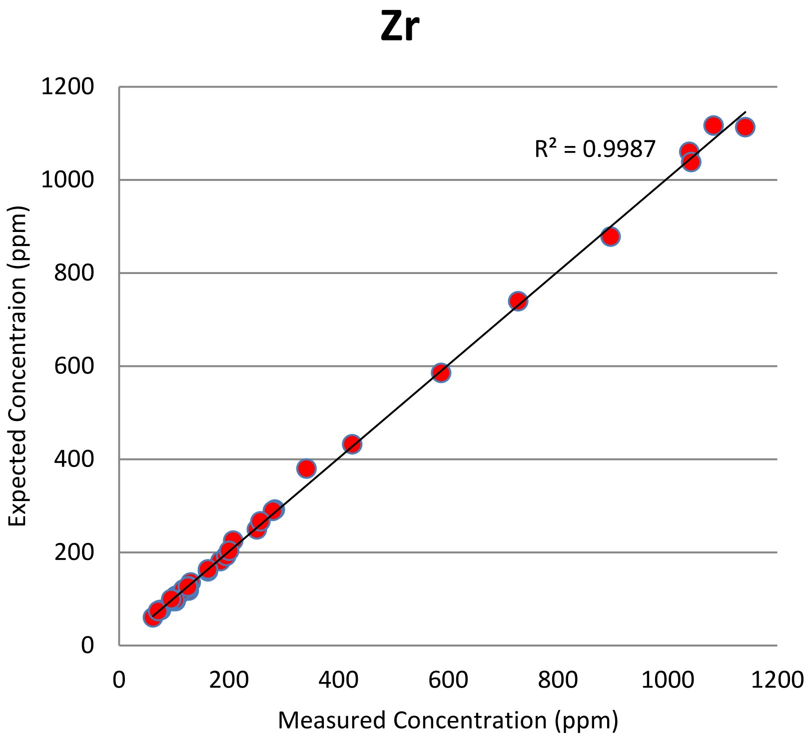

Figure 16. Measured (observed) versus expected concentrations for Zr in Bruker's obsidian XRF standards.

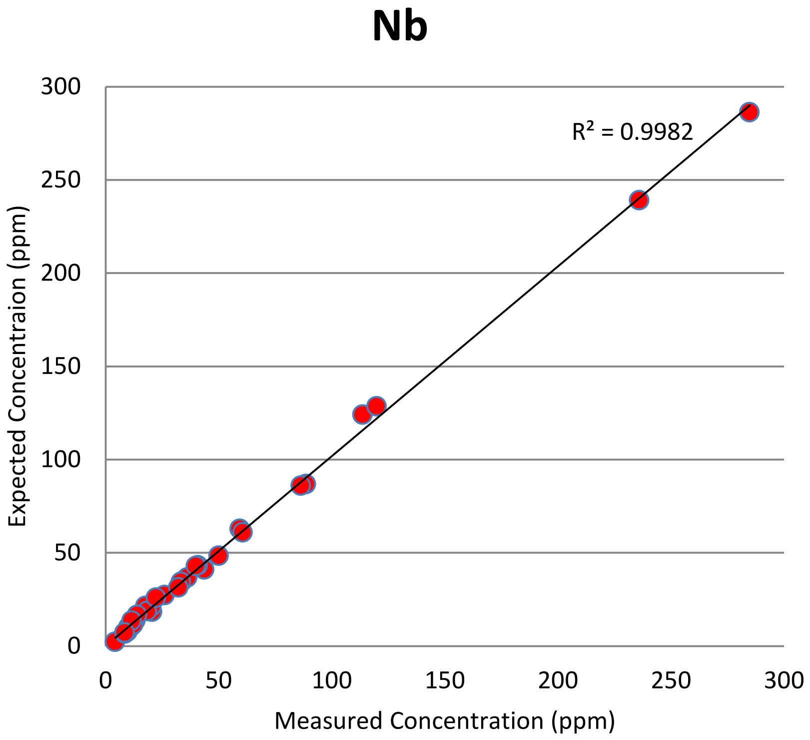

Figure 17. Measured (observed) versus expected concentrations for Nb in Bruker's obsidian XRF standards.

Appendix A. XRF data (in parts per million) generated for the 40 obsidian reference samples (measured values). Data are the average of five 200-second analyses.

ID	Mn	Fe	Zn	Ga	Th	Rb	Sr	Y	Zr	Nb
XRF01	670	3931	60	19	12	176	13	41	62	34
XRF02	476	4323	30	18	6	90	59	13	72	10
XRF03	323	6200	37	18	7	96	63	25	104	8
XRF04	1646	27221	152	19	6	59	1	67	342	18
XRF05	572	8912	50	18	1	38	173	28	131	4
XRF06	347	11905	252	30	24	273	1	205	284	285
XRF07	344	7676	51	18	18	179	5	28	127	21
XRF08	424	7451	134	28	42	361	1	84	162	236
XRF09	281	7387	31	18	9	110	81	22	126	9
XRF10	310	9136	40	18	15	145	108	17	185	13
XRF11	473	4603	36	18	7	99	44	24	76	11
XRF12	297	10076	38	18	15	137	68	28	195	10
XRF13					*Not Measured*					
XRF14	504	10628	70	18	7	81	138	18	103	9
XRF15	479	17426	131	19	9	103	2	81	587	44
XRF16	568	19061	136	20	16	157	1	71	728	59
XRF17	1932	50362	611	53	82	454	7	420	3236	632
XRF18	1107	22749	145	24	36	208	46	89	1021	265
XRF19	391	6642	56	18	27	223	11	41	110	26
XRF20	645	52685	107	18	1	14	257	18	79	4
XRF21	610	9873	62	18	18	151	169	38	251	36
XRF22	503	23421	217	26	41	338	2	115	1040	114
XRF23	630	24596	192	24	27	202	2	98	1043	89
XRF24	321	19689	244	29	33	225	2	175	1142	61
XRF25	1194	41641	273	25	25	179	9	126	1084	120
XRF26	463	11394	60	18	7	104	21	52	281	20
XRF27	399	5302	31	18	9	108	59	19	98	11
XRF28	403	7196	62	18	17	150	3	42	162	50
XRF29	338	7840	65	19	7	90	32	51	127	12
XRF30	1115	16061	210	25	20	194	3	110	896	86
XRF31	408	3925	32	18	16	144	3	22	74	41
XRF32	294	12131	108	19	15	146	1	53	425	33
XRF33	231	10277	40	18	32	278	34	48	208	18
XRF34	349	8481	55	19	17	161	4	48	200	40
XRF35	507	8609	65	19	15	114	281	20	117	18
XRF36	500	9388	74	18	23	194	15	52	258	32
XRF37	357	5459	32	18	15	129	20	24	102	14
XRF38	621	6481	41	18	5	75	136	22	71	11
XRF39	324	7265	33	18	6	77	99	16	95	8
XRF40	825	6131	67	19	14	214	270	16	126	22

Appendix B. XRF data (in parts per million) generated for the 17-hour stability test. Refer to Figures 6-7 and Table 1 of report.

ID	Mn	Fe	Zn	Ga	Th	Rb	Sr	Y	Zr	Nb	Time
8-001	431	7421	136	28	41	363	1	84	162	239	0.1
8-002	410	7404	136	30	45	362	0	86	162	232	0.1
8-003	418	7555	139	32	41	360	1	86	162	234	0.2
8-004	442	7465	130	27	43	363	1	82	164	238	0.2
8-005	419	7408	131	26	40	359	1	84	162	238	0.3
8-006	425	7410	133	28	42	363	1	85	164	237	0.3
8-007	448	7404	125	24	41	366	1	81	163	234	0.4
8-008	423	7459	137	28	43	365	1	84	161	235	0.4
8-009	428	7378	132	26	40	364	1	80	165	238	0.5
8-010	451	7601	130	26	40	362	1	83	165	238	0.6
8-011	439	7368	132	24	41	360	0	81	163	235	0.6
8-012	409	7408	138	27	39	362	1	87	163	234	0.7
8-013	458	7433	120	24	43	359	1	84	161	234	0.7
8-014	438	7498	128	27	41	363	2	83	164	236	0.8
8-015	448	7423	137	26	41	364	1	84	164	236	0.8
8-016	428	7522	132	29	39	364	1	85	162	235	0.9
8-017	421	7451	130	27	42	360	3	85	161	234	0.9
8-018	474	7425	135	29	43	367	1	85	165	240	1.0
8-019	430	7398	133	26	42	367	2	84	163	234	1.1
8-020	452	7445	135	23	42	362	1	81	160	238	1.1
8-021	473	7438	128	28	44	367	2	86	164	237	1.2
8-022	444	7535	135	32	40	367	1	85	166	240	1.2
8-023	435	7417	133	27	41	368	2	83	163	236	1.3
8-024	418	7489	136	28	42	363	1	85	166	241	1.3
8-025	414	7306	130	26	41	362	1	84	165	233	1.4
8-026	462	7317	138	26	41	364	0	83	163	233	1.4
8-027	434	7426	148	26	39	366	1	84	164	238	1.5
8-028	418	7457	130	25	43	362	0	83	165	238	1.6
8-029	441	7489	138	29	41	363	1	85	162	236	1.6
8-030	467	7429	128	26	41	361	2	84	162	235	1.7
8-031	481	7385	128	28	42	366	1	82	162	238	1.7
8-032	466	7465	135	23	41	365	1	85	162	241	1.8
8-033	441	7520	134	25	42	367	2	84	162	237	1.8
8-034	433	7488	136	27	41	363	1	84	164	238	1.9
8-035	448	7416	139	28	41	362	1	84	162	233	1.9
8-036	468	7476	131	29	40	364	1	85	163	236	2.0
8-037	485	7613	136	27	42	371	1	83	165	242	2.1
8-038	398	7327	130	28	40	364	0	79	162	238	2.1
8-039	444	7522	130	27	44	361	1	85	166	240	2.2
8-040	418	7552	137	31	40	365	1	83	166	240	2.2

8-041	409	7389	131	27	40	360	1	84	164	239	2.3
8-042	418	7353	137	29	42	360	1	83	162	240	2.3
8-043	431	7565	139	26	43	360	1	86	163	238	2.4
8-044	426	7437	126	29	41	369	1	81	166	237	2.4
8-045	455	7404	130	27	40	358	1	83	161	234	2.5
8-046	379	7378	124	24	41	363	1	82	164	234	2.6
8-047	438	7598	140	30	43	366	1	86	165	240	2.6
8-048	400	7401	132	26	42	365	1	82	168	238	2.7
8-049	421	7407	135	28	42	363	1	85	163	236	2.7
8-050	438	7493	137	30	41	366	1	83	163	240	2.8
8-051	421	7478	131	25	42	365	1	81	164	238	2.8
8-052	476	7379	141	26	43	362	1	84	163	237	2.9
8-053	417	7415	138	27	41	366	1	84	164	240	2.9
8-054	469	7368	143	26	44	368	0	83	165	238	3.0
8-055	398	7448	139	26	41	366	1	82	165	238	3.1
8-056	413	7484	135	28	42	360	2	83	162	234	3.1
8-057	427	7499	134	27	40	369	1	87	165	237	3.2
8-058	462	7488	127	27	40	362	0	85	163	238	3.2
8-059	444	7316	136	27	42	364	2	81	165	236	3.3
8-060	434	7503	138	26	43	371	1	85	167	244	3.3
8-061	424	7538	138	24	43	360	2	86	166	240	3.4
8-062	436	7459	137	27	41	366	1	88	168	240	3.4
8-063	403	7368	132	26	38	364	1	83	161	234	3.5
8-064	461	7450	133	24	41	364	1	84	161	233	3.6
8-065	417	7490	129	27	43	367	1	84	163	242	3.6
8-066	372	7494	137	25	43	361	1	84	164	237	3.7
8-067	406	7343	131	30	41	366	2	81	164	237	3.7
8-068	433	7679	139	26	46	372	1	84	164	240	3.8
8-069	453	7615	142	26	43	369	1	86	165	237	3.8
8-070	442	7570	130	26	42	364	1	83	168	241	3.9
8-071	425	7423	134	29	43	369	2	83	166	238	3.9
8-072	462	7387	130	27	42	370	1	82	164	240	4.0
8-073	444	7457	131	26	39	358	1	81	164	239	4.1
8-074	458	7504	133	26	42	367	1	81	163	236	4.1
8-075	447	7382	128	27	40	366	1	82	165	238	4.2
8-076	394	7509	134	27	40	361	2	82	162	235	4.2
8-077	421	7524	140	29	42	366	1	85	165	234	4.3
8-078	446	7631	140	31	42	369	2	85	167	246	4.3
8-079	437	7374	125	28	44	364	1	82	163	236	4.4
8-080	400	7346	131	26	42	364	2	85	164	232	4.4
8-081	433	7436	136	27	42	368	0	83	166	236	4.5
8-082	447	7418	135	27	43	364	1	81	164	239	4.6
8-083	464	7512	135	29	42	365	2	85	166	237	4.6

8-084	440	7428	134	26	40	359	2	82	166	235	4.7
8-085	494	7392	130	30	41	366	1	86	165	238	4.7
8-086	422	7458	124	26	42	368	2	82	165	239	4.8
8-087	475	7409	132	28	43	362	1	83	162	235	4.8
8-088	430	7515	140	25	43	366	2	84	164	238	4.9
8-089	451	7489	133	26	43	372	1	84	163	235	4.9
8-090	471	7237	137	25	41	368	1	86	162	238	5.0
8-091	437	7468	138	28	40	364	1	87	162	241	5.1
8-092	437	7309	130	26	42	361	0	83	161	235	5.1
8-093	416	7432	138	28	42	367	2	80	166	233	5.2
8-094	504	7407	129	29	41	364	1	84	163	237	5.2
8-095	426	7369	132	26	43	363	2	83	165	238	5.3
8-096	432	7460	132	27	41	363	1	85	163	234	5.3
8-097	450	7476	136	28	41	367	1	83	165	240	5.4
8-098	433	7383	145	25	42	357	2	85	164	237	5.4
8-099	456	7528	133	26	41	360	1	83	164	237	5.5
8-100	449	7438	136	27	42	359	1	84	164	236	5.6
8-101	407	7530	137	26	40	365	1	85	164	235	5.6
8-102	408	7474	140	28	42	369	1	83	165	239	5.7
8-103	431	7427	131	25	44	362	1	82	165	235	5.7
8-104	457	7495	135	27	39	368	1	83	166	240	5.8
8-105	405	7449	135	25	39	370	1	84	166	237	5.8
8-106	415	7386	137	27	41	368	1	83	166	237	5.9
8-107	463	7446	135	30	44	370	1	86	165	241	5.9
8-108	417	7484	137	28	40	367	1	81	165	237	6.0
8-109	425	7449	133	26	44	366	1	85	165	239	6.1
8-110	422	7417	138	28	40	364	2	85	161	237	6.1
8-111	409	7400	121	29	41	366	1	85	164	238	6.2
8-112	413	7352	130	26	40	362	1	86	163	234	6.2
8-113	507	7521	129	28	42	364	1	82	164	238	6.3
8-114	462	7557	136	25	42	364	2	88	165	237	6.3
8-115	445	7342	133	25	41	369	1	83	164	237	6.4
8-116	417	7514	131	30	44	357	1	85	165	237	6.4
8-117	466	7545	142	26	43	365	1	83	163	241	6.5
8-118	435	7501	135	27	43	360	1	85	162	240	6.6
8-119	422	7418	127	27	38	365	2	82	163	237	6.6
8-120	438	7473	131	27	43	365	1	83	164	241	6.7
8-121	419	7429	136	28	42	361	1	85	165	239	6.7
8-122	413	7426	141	27	40	363	2	85	164	244	6.8
8-123	433	7454	121	29	43	365	1	87	163	239	6.8
8-124	481	7348	132	31	42	368	2	83	166	237	6.9
8-125	448	7382	128	27	40	361	1	81	162	236	6.9
8-126	433	7324	136	24	43	364	2	79	165	236	7.0

8-127	449	7498	131	25	44	367	1	82	165	237	7.1
8-128	472	7534	145	24	41	362	2	88	165	235	7.1
8-129	454	7323	137	29	43	361	2	84	160	239	7.2
8-130	420	7448	135	25	41	370	1	81	164	233	7.2
8-131	398	7574	131	26	41	364	2	86	164	240	7.3
8-132	432	7421	127	24	41	358	1	86	163	235	7.3
8-133	448	7389	132	31	41	360	1	83	164	238	7.4
8-134	461	7408	129	25	43	366	1	84	162	237	7.4
8-135	444	7458	138	28	42	369	2	84	164	242	7.5
8-136	442	7313	140	26	45	360	1	85	162	233	7.6
8-137	435	7407	133	26	41	369	1	85	161	237	7.6
8-138	443	7474	136	28	45	368	1	84	161	236	7.7
8-139	426	7437	128	31	41	364	1	84	163	237	7.7
8-140	464	7475	135	26	41	362	1	85	163	239	7.8
8-141	462	7563	133	27	43	364	2	85	162	235	7.8
8-142	402	7472	133	28	40	366	1	85	165	237	7.9
8-143	435	7507	132	27	41	364	2	85	164	235	7.9
8-144	439	7495	130	26	40	363	0	86	166	240	8.0
8-145	439	7514	135	30	43	363	2	85	163	238	8.1
8-146	452	7529	134	27	42	365	0	84	163	238	8.1
8-147	453	7238	133	28	42	362	1	83	164	237	8.2
8-148	444	7522	138	28	41	368	1	82	164	239	8.2
8-149	428	7412	137	30	42	361	2	86	164	235	8.3
8-150	448	7408	138	29	40	362	1	86	163	237	8.3
8-151	431	7453	139	27	39	368	1	83	162	234	8.4
8-152	378	7400	133	26	42	362	2	85	166	237	8.4
8-153	451	7476	135	28	41	365	2	86	164	232	8.5
8-154	467	7418	144	25	42	369	2	85	163	236	8.6
8-155	401	7344	139	31	43	361	1	83	164	237	8.6
8-156	424	7338	131	26	42	364	0	84	166	239	8.7
8-157	436	7506	132	27	42	364	1	84	162	238	8.7
8-158	418	7429	141	27	44	361	1	84	164	237	8.8
8-159	447	7530	139	27	43	364	0	85	159	237	8.8
8-160	422	7417	140	26	41	363	2	85	163	240	8.9
8-161	459	7369	132	29	44	367	1	83	162	236	8.9
8-162	463	7412	130	26	43	364	2	84	164	238	9.0
8-163	424	7510	137	28	42	361	1	82	163	239	9.1
8-164	476	7410	131	25	42	364	1	85	165	235	9.1
8-165	417	7479	135	28	41	368	1	84	165	239	9.2
8-166	420	7424	136	24	40	365	0	83	167	234	9.2
8-167	464	7582	141	26	41	378	2	87	168	242	9.3
8-168	488	7345	130	26	41	363	2	86	167	238	9.3
8-169	470	7336	131	26	42	366	1	86	166	241	9.4

8-170	394	7404	133	28	42	366	1	83	162	240	9.4
8-171	442	7414	129	27	40	366	1	85	164	236	9.5
8-172	442	7310	133	26	43	365	2	84	164	241	9.6
8-173	447	7481	135	28	41	367	1	85	164	240	9.6
8-174	435	7413	133	27	42	363	1	85	162	241	9.7
8-175	448	7467	137	27	43	366	2	83	164	244	9.7
8-176	483	7396	139	26	43	367	2	86	163	241	9.8
8-177	407	7558	133	29	41	370	2	88	164	236	9.8
8-178	441	7562	142	30	41	367	2	83	164	238	9.9
8-179	446	7471	132	25	40	368	1	85	164	237	9.9
8-180	459	7454	138	25	40	366	1	81	162	235	10.0
8-181	446	7483	137	28	43	371	1	83	162	238	10.1
8-182	453	7397	128	28	42	364	1	83	164	237	10.1
8-183	460	7533	135	26	44	369	1	83	164	238	10.2
8-184	462	7410	133	28	43	368	1	84	163	237	10.2
8-185	402	7445	138	25	44	364	1	83	165	239	10.3
8-186	447	7404	137	26	40	364	0	83	163	241	10.3
8-187	431	7442	144	28	42	364	1	85	163	235	10.4
8-188	422	7463	136	26	41	359	1	85	165	236	10.4
8-189	454	7481	142	27	39	362	0	82	163	243	10.5
8-190	425	7454	129	27	40	362	2	80	162	237	10.6
8-191	435	7499	138	28	44	368	2	83	166	242	10.6
8-192	467	7361	132	26	41	366	1	88	163	236	10.7
8-193	487	7553	128	28	44	366	1	85	166	238	10.7
8-194	459	7404	137	27	44	371	1	83	165	239	10.8
8-195	475	7415	131	29	42	363	1	85	164	241	10.8
8-196	483	7431	134	29	42	363	0	86	163	238	10.9
8-197	460	7436	132	25	44	363	1	83	163	237	10.9
8-198	392	7393	142	27	44	365	0	83	166	240	11.0
8-199	416	7372	135	27	42	363	0	83	163	236	11.1
8-200	467	7384	135	29	41	366	1	83	163	237	11.1
8-201	452	7506	125	26	44	362	0	85	160	234	11.2
8-202	437	7377	134	30	43	360	1	82	165	236	11.2
8-203	475	7559	135	28	42	361	1	86	164	238	11.3
8-204	472	7421	138	25	39	362	1	83	162	234	11.3
8-205	459	7399	137	27	42	360	1	85	161	238	11.4
8-206	426	7405	132	27	43	362	1	85	162	235	11.4
8-207	422	7586	132	29	42	373	0	84	165	237	11.5
8-208	442	7501	134	26	44	361	1	83	162	238	11.6
8-209	433	7396	134	29	40	365	1	81	161	234	11.6
8-210	434	7441	132	26	42	364	1	82	162	233	11.7
8-211	437	7356	131	27	39	359	1	85	162	235	11.7
8-212	454	7449	137	27	42	362	2	84	164	240	11.8

8-213	460	7528	146	25	42	367	1	88	166	241	11.8
8-214	481	7524	139	26	42	361	1	87	162	236	11.9
8-215	441	7465	130	27	41	361	1	87	164	239	11.9
8-216	437	7522	131	28	41	368	1	86	163	236	12.0
8-217	436	7313	133	25	44	366	2	82	164	237	12.1
8-218	437	7382	128	27	40	366	2	84	161	237	12.1
8-219	417	7402	131	24	42	363	1	85	162	235	12.2
8-220	435	7419	135	26	42	362	2	85	162	237	12.2
8-221	424	7442	141	25	40	368	1	81	162	235	12.3
8-222	427	7435	140	28	41	367	1	83	166	244	12.3
8-223	440	7516	129	25	44	369	2	84	165	234	12.4
8-224	415	7319	131	26	40	365	1	82	163	238	12.4
8-225	381	7381	136	27	44	362	1	81	165	233	12.5
8-226	438	7398	137	27	41	363	1	84	168	240	12.6
8-227	497	7399	145	29	41	363	2	83	165	238	12.6
8-228	412	7342	134	26	41	362	1	83	163	239	12.7
8-229	465	7486	137	26	40	365	0	81	164	236	12.7
8-230	398	7535	133	26	41	367	1	82	166	236	12.8
8-231	450	7396	135	26	42	362	2	83	162	235	12.8
8-232	414	7409	139	26	42	366	0	82	165	238	12.9
8-233	396	7511	132	27	42	365	1	85	167	237	12.9
8-234	411	7365	129	25	39	365	0	82	165	237	13.0
8-235	385	7426	139	26	39	362	2	85	163	236	13.1
8-236	445	7413	136	25	39	369	1	80	165	236	13.1
8-237	469	7463	138	27	41	366	1	83	166	238	13.2
8-238	418	7400	138	29	46	363	1	84	167	238	13.2
8-239	462	7473	137	27	42	368	1	84	166	235	13.3
8-240	460	7605	135	24	42	368	1	85	166	242	13.3
8-241	467	7379	129	25	42	357	1	84	162	237	13.4
8-242	401	7407	138	26	43	365	1	84	165	234	13.4
8-243	468	7602	139	26	46	367	1	87	164	237	13.5
8-244	434	7298	125	28	40	363	1	82	160	232	13.6
8-245	436	7401	127	24	42	366	1	84	163	240	13.6
8-246	459	7448	138	26	42	364	2	82	164	240	13.7
8-247	447	7497	132	29	42	361	2	83	163	237	13.7
8-248	437	7432	133	27	40	361	1	83	163	239	13.8
8-249	443	7584	138	27	44	371	2	83	165	241	13.8
8-250	413	7353	134	28	42	367	1	83	162	235	13.9
8-251	441	7453	136	26	41	371	1	86	161	240	13.9
8-252	470	7553	131	28	41	371	1	83	163	239	14.0
8-253	440	7529	124	30	43	366	2	83	166	241	14.1
8-254	436	7391	137	30	41	362	1	84	166	236	14.1
8-255	412	7477	131	26	44	362	1	84	164	236	14.2

8-256	444	7508	130	27	42	365	1	83	165	241	14.2
8-257	442	7432	129	25	40	363	1	84	164	237	14.3
8-258	445	7333	133	30	41	365	1	85	164	235	14.3
8-259	431	7566	132	29	39	373	1	84	164	239	14.4
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8-261	423	7560	134	28	40	364	2	85	166	238	14.5
8-262	456	7343	130	26	40	363	1	84	167	237	14.6
8-263	472	7417	136	29	42	363	1	86	162	240	14.6
8-264	463	7437	134	29	41	364	1	84	166	238	14.7
8-265	465	7485	139	27	43	365	1	84	161	239	14.7
8-266	437	7457	131	28	42	365	1	85	165	236	14.8
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8-268	448	7548	131	28	41	360	2	82	163	237	14.9
8-269	450	7405	135	27	42	359	1	81	162	235	14.9
8-270	406	7369	139	27	42	369	2	82	161	239	15.0
8-271	428	7354	132	27	42	368	1	82	162	236	15.1
8-272	421	7303	128	32	41	357	1	83	163	235	15.1
8-273	458	7393	140	27	41	360	2	86	164	237	15.2
8-274	452	7470	139	26	45	362	1	84	164	236	15.2
8-275	459	7564	139	26	42	366	1	86	164	242	15.3
8-276	450	7432	143	31	40	364	1	83	161	239	15.3
8-277	422	7489	129	29	41	365	1	84	165	238	15.4
8-278	440	7481	130	24	44	356	1	85	162	235	15.4
8-279	462	7497	140	26	38	364	1	84	163	239	15.5
8-280	457	7356	140	28	42	362	1	83	161	237	15.6
8-281	454	7433	134	30	41	367	2	83	165	242	15.6
8-282	463	7461	138	30	44	364	1	83	163	234	15.7
8-283	427	7348	135	26	41	364	0	85	165	242	15.7
8-284	381	7432	135	25	41	361	1	85	166	236	15.8
8-285	403	7434	130	25	42	361	1	86	164	236	15.8
8-286	449	7516	128	27	42	364	1	81	167	238	15.9
8-287	474	7606	137	29	41	368	1	86	166	242	15.9
8-288	433	7452	124	28	41	362	2	84	162	238	16.0
8-289	480	7467	136	26	41	371	1	85	169	239	16.1
8-290	431	7430	133	32	40	371	2	85	165	240	16.1
8-291	451	7386	134	27	44	362	2	85	165	241	16.2
8-292	454	7554	132	25	43	369	1	84	163	240	16.2
8-293	487	7550	131	26	43	369	1	85	165	237	16.3
8-294	446	7475	127	28	41	359	1	81	160	236	16.3
8-295	388	7382	132	25	41	366	1	81	163	236	16.4
8-296	455	7497	128	26	40	364	2	84	165	239	16.4
8-297	421	7453	128	29	46	367	1	84	163	236	16.5
8-298	415	7549	146	29	44	358	1	83	163	239	16.6

8-299	419	7370	136	25	41	363	1	83	165	237	16.6
8-300	419	7434	129	26	41	360	1	84	162	235	16.7
8-301	414	7402	137	27	43	365	1	84	161	234	16.7
8-302	431	7478	134	27	43	362	1	84	164	238	16.8
8-303	415	7450	127	28	41	365	2	83	164	234	16.8
8-304	415	7385	135	27	44	362	2	85	162	235	16.9
8-305	437	7437	136	25	44	364	2	86	163	238	16.9
8-306	428	7601	143	29	41	364	1	89	163	240	17.0
8-307	449	7478	140	30	39	357	2	87	164	235	17.1