10. DATA REPORT: CHEMICAL ANALYSES OF BASALTIC ROCKS: AN INTERLABORATORY COMPARISON¹

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ABSTRACT

Samples of MORB basalts obtained during Ocean Drilling Program Leg 142 were supplied as unknown materials to four different land-based laboratories and analyzed by inductively coupled plasma-optical emission spectrometry (ICP-AES) and by X-ray fluorescence (XRF), partly to test the quality of the ship's XRF facility and partly to compare data by ICP-AES and a shore-based XRF laboratory.

The comparisons show that contamination of samples on the ship due to grinding in alumina mills is negligible, and that the ship's XRF laboratory produces good data for all major elements except phosphorus and for several trace components. However, some trace elements such as Ba are difficult to determine well by XRF at concentrations frequently found in MORB basalts.

INTRODUCTION

A major purpose of Leg 142 of the Ocean Drilling Program (ODP) was to study alteration processes in mid-oceanic ridge basalts (MORBs) and other rocks that could explain the genesis of hydrothermal solutions and the subsequent deposition of metal-rich active ridge sediments, which have been known since 1963 (Skornyakova, 1964; Arrhenius and Bonatti, 1965; Boström and Peterson, 1966, 1969). These sediments are rich in Fe, Mn, Ba, Cu, and Ni, so it is critical to understand the geochemical pathways of these elements (Boström et al., 1973). However, successful studies of hydrothermal leaching processes require high-quality analyses (Rona et al., 1980; Arvanitides et al., 1990).

No altered rocks were discovered during Leg 142, but a fair quantity of homogenous MORB material was obtained, making it possible to conduct an interlaboratory comparison of various analytical methods and to test the quality level of the analyses produced in the ship's X-ray fluorescence spectrometry (XRF) laboratory. XRF is the mostused method for geochemical studies aboard *JOIDES Resolution*, whereas inductively coupled plasma-optical emission spectrometry (ICP-AES) was the method used by most of the land-based laboratories.

We will report on comparisons of shipboard XRF data with results from four laboratories, involving (1) shore-based XRF studies, (2) studies using sequentially reading ICP-AES instruments, and (3) studies using multichannel (simultaneously reading) ICP-AES instruments. A comparative study involving the use of inductively coupled plasma-mass spectrometry for the determination of many trace components and rare earths will be reported elsewhere.

SAMPLE DESCRIPTIONS AND PREPARATIONS

The samples consist of typical MORB rocks collected during Leg 142; for descriptions, see Storms, Batiza, et al. (1993). In the following we will use standard ODP sample notations.

Most samples had been dried, crushed, and ground aboard ship and were therefore not further treated, except for drying at 100°C as required. However, samples received as rock pieces had to be crushed. This was done in a plattner mortar made of hard steel to lessen the impact from contaminants. This steel consists of about 99% Fe, 0.5% Mn, and 0.5% C, whereas Ni, Co, Cr, Zr, W, and Mo contents are low. The samples were kept in a heavy plastic bag to further lessen the contamination risk during this crushing, as was done aboard ship. Subsequent grinding was done in a Retch Mikroschnellmühle, which has a cylindrical grinding well and pestle of agate.

One sample from Section 142-846A-1M, about 400 g, consisted of sand- and pebble-sized basalt pieces heavily contaminated by drilling oils, fragments of drill bits, and other metallic matter. Repeated washings in an ultrasonic bath with organic solvents (methanol, acetone, and xylole), and the removal of magnetic particles using a hand magnet produced a cleaner fraction. This material was then wet sieved, producing a fraction larger than 2 mm in diameter. This +2mm fraction was handpicked under a binocular microscope to delete contaminants not removed by the previous treatment. Simultaneously, the +2-mm material was divided into a very clean-looking, largely glassy fraction, and a fraction less glassy and fine grained. The latter fraction contained a few thin specks (about 1 mm in diameter or less) of reddish brown and white matter, possibly representing ferric hydroxide and opaline silica.

These +2-mm fractions were subsequently rinsed for 15 minutes at 50°C in dilute hydrochloric acid (1 part concentrated HCl + 3 parts distilled water), to which reducing hydroxylamoniumchloride had been added. This treatment did not etch the uncontaminated rock and glass surfaces, but removed all reddish brown specks. The samples were then rinsed with distilled and deionized water, dried, and further ground for chemical analysis. The resulting very glassy fraction was labelled 1M-6 very clean rock, and the less glassy material 1M-6 clean rock. Representative subsamples of these fractions were sent to Wolfgang Bach, Justus-Liebig University, Giessen (JLUG). The remaining fraction was kept at Stockholm University (SU).

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One sample presented a special sampling and preparation problem, namely an alumina grinding puck that was broken aboard ship and contaminated Sample 142-846A-1M-2, 0–35cm. This puck was therefore analyzed to study the possible effects of this contamination. All loose dirt was removed from the puck, after which a 5-mm-thick wafer was cut from the puck, using a petrographic saw. The edges of the wafer, which were stained gray, were then removed with a carbide-tipped chisel. The wafer was easily crushed in a plattner mortar and subdivided in two samples, one for SU and one for JLUG. The SU sample was further ground in the Mikroschnellmühle. Because of the exceptional hardness of alumina, all agate surfaces were somewhat scratched, which caused some contamination of the alumina samples (see below).

ANALYTICAL PROCEDURES AND RESULTS

XRF Studies

The samples at JLUG were treated in the same way as those studied by Bach (1991) and those studies in the ship's laboratory (see "Explanatory Notes" in Storms, Batiza, et al., 1993). These analyses are labeled as JLUG in the tables.

ICP-AES Studies

Samples sent to SU were treated by two methods: (1) a metaborate digestion technique for the determination of major and some trace components (Sr, Zr, Cr) and (2) an HF-HClO₄-digestion method for the determination of most trace elements (Burman et al., 1977, 1978; Burman and Boström, 1979). The latter method fumes off SiO₂ and results in a solution 10 times richer in trace element than by the metaborate digestion. The instrument at SU was a 10-year-old ARL 3520 sequentially reading ICP-AES unit, which has since been replaced. These analyses are labeled SU in the tables.

Subsamples were also sent to SGAB in Luleå, northern Sweden (LU), an analytical company that specializes in the determination of elemental compositions of natural materials. The metaborate digestion method used at LU is identical to that at SU. However, at LU the obtained solutions are used for all elemental determinations; that is, no HF-HClO₄ digestion is used for the trace element determinations. Analytical results are labeled as LU in the tables.

Special aliquots of the metaborate-digested solutions at SU were sent to the company Höganäs Eldfast in southern Sweden and analyzed in an ICP-AES unit (model SPECTRO) with 40 fixed channels. The solutions were 10 times more diluted than all other solutions used for ICP-AES at SU and LU to avoid clogging of nebulizer and torch systems in the Höganäs spectrometer. These analyses are labeled SU-H in the tables.

The results of all analyses are given in Tables 1-8.

Accuracy and Precision

To test the performance of our methods we used the geostandard BHVO-1 for tests of accuracy and a MORB sample (G-224) from the East Pacific Rise at 23°S for reproducibility tests (Table 1); the recommended data for BHVO-1 derive from Govindaraju (1989). The accuracy test using BHVO-1 indicated quite satisfactory results for both SU and LU data; the standard was supplied as an unknown sample. Furthermore, the reproducibility of the G-224 rock data is very satisfactory. It should be noted that the XRF values in Table 1 are based on six separately produced glass discs that were analyzed repeatedly. This avoids the common but erroneous procedure of using the same disc repeatedly over the years, which ignores the errors due to variations in mounting method, etc.; that is, the procedure only shows variations in instrument performance. It is well known that many or perhaps most errors during analysis are caused by the non-instrumental steps (Flanagan, 1986; Hunt and Wilson, 1986).

Fable 1. Comparison of ana	yses of standard basalts	BHVO-1 an	d G-224.
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	BHVO-1 SU		BHVO-1	G-224		
		BHVO-1 LU	Rec value	Mean	SD	
SiO ₂	49.88	49.00	49.94	50.36	0.17	
TiO ₂	2.73	2.81	2.71	1.19	0.01	
AloÕi	13.88	13.90	13.80	14.92	0.09	
Fe ₂ O ₂	12.44	12.20	12.23	10.74	0.07	
MnO	0.173	0.173	0.168	0.178	0.004	
MgO	7.35	7.39	7.23	8.31	0.08	
CaO	11.41	11.40	11.40	12.74	0.06	
Na ₂ O	2.25	2.35	2.26	2.29	0.02	
K ₂ Ô	0.49	0.42	0.52	0.042	0.005	
P.O.	0.27	0.31	0.27	0.089	0.003	
Total	100.87	99.95	100.53	100.85	0.41	
Cr	308	302	289	373.4	6.7	
Zr	165	161	179	71.9	2.8	
Sr	396	392	403	74.4	1.3	
Ba	135	136	139			
Co	43	45	45	44.9	1.9	
Cu	136	117	136	77.3	5.7	
Ni	124	117	121	82.0	1.3	
Sc	33	29	32		0.02	
V	317	311	317			
Y	29	27	28	29.3	0.8	
Yb	1.9	2	2.0			
Zn	115	94	105	78.0	3.2	
La	17	18	16			
Ga	_		-	15.6	1.2	
Rb	-	-		1.7	0.6	

Notes: All major elements (SiO₂-Total) in wt%; all trace elements (Cr-Rb) in ppm. — = not determined, SU = analyses made at Stockholm University, LU = analyses made at SGAB, Luleå. Rec value = recommended values from literature (see text). G-224 represents a fresh MORB basalt from EPR at 23°S and is used as a lab standard at Justus-Liebig University for continuous tests of drift and other instrument performances. Major components in G-224 have been determined in 83 cases; traces in 36 cases.

This long-term test of the MORB G-224 involved 83 complete determinations of the major components and 36 of the trace elements (Bach, 1991) and revealed a drift in the XRF instrument of both a long-term and a short-term nature, which can be described as a longwave sinus curve overprinted by a short-wave one. The short-term drift (expressed as one standard deviation, SD) is fairly constant over extended periods of time, about 0.10% for SiO₂, 0.05% for Fe₂O₃, and 0.01% for TiO₂. This short-term noise scatters about another undulating mean value, which is offset by as much as 0.2% (SiO₂), 0.1% (Fe₂O₃), or 0.02 % (TiO₂) after prolonged analytical activity.

At SU several geostandards are routinely used during all analytical work in order to monitor drift, disturbances, and other uncertainties, a procedure we have used since 1967. For these reasons we also participate in collaborative interlaboratory studies to determine the best data for new geostandards, the last of which involved the Ailsa Craig granite and SY-4 (Boström, 1987; Boström, unpubl. data). Our data in Table 1 represents the test-run results during the period when the analyses reported in Tables 2-8 were performed. We have also noted that there may be a long-term drift in the obtained values in addition to the short-term noise. Such long-term noise is particularly easy to recognize during determination of SiO₂, for which deviations of 0.2%-0.3% may occur. At SU these problems are partly caused by the lack of thermal isolation around the spray chamber (sample introduction unit), but also can be attributed in part to the curvature in the calibration curve for SiO₂. Curved calibration curves such as the one for SiO₂ for Leg 142 are common for major components (see Storms, Batiza, et al., 1993, "Explanatory Notes" chapter, tables 2 and 3). As an additional test, some samples were analyzed 3 or 4 times (see Tables 3, 4, 6, and 7); these tests involved repeated metaborate and HF-HClO4 digestions on fresh aliquots of the rocks in order to incorporate the errors involved in the digestion steps. The resulting analyses showed standard deviations that were similar to or less than the values reported for the SU data in Table 5. The reproducibility and the accuracy of the SU analyses are therefore quite good.

A little-considered complication in most analyses of rocks is that many results are dependent on the selected recommended values for Table 2. Compositions of fresh and contaminated basalts from Hole 142-864A and contaminant (alumina grinding puck).

Sample:	142-864A-1M-2, 0-35 cm fresh		142-864 0–35 cm c	A-1M-2, ontaminated	AP	
Laboratory:	SU	LU	SU	LU	SU	JLUG
SiO ₂	49.07	49.30	44.70	45.00	2.9(?)	0.3
TiO ₂	1.65	1.70	1.41	1.49	0.01	_
Al ₂ Õ ₃	14.70	14.50	21.37	21.80	=97	≈99
Fe ₂ O ₃	11.61	11.60	10.16	10.80	0.11	
MnO	0.190	0.195	0.170	0.175	0.002	_
MgO	7.51	7.61	6.84	7.17	0.20	0.15
CaO	11.60	11.60	10.65	10.80	0.17	0.15
Na ₂ O	2.72	2.82	2.40	2.54	0.10	_
K ₂ Õ	0.12	BC	0.13	BC		-
P ₂ O ₅	0.16	0.17	0.15	0.15	0.04	-
Total	99.33	99.52	97.98	99.94		_
S	1140		1013		-	
Cr	244	237	242	252	7	=22
Zr	113	100	102	91	57	≈65
Sr	128	127	116	113	7	
Ba	14	14	19	18	82	
Cd	65		58			_
Co	35	45	27	38		
Cu	72	67	65	58		_
Ni	75	75	72	71	1	
Sc	47	41	42	37	-	-
V	337	323	297	289		
Y	34	38	30	34		
Yb	3.2	4.5	2.7	4.1		_
Zn	96	88	84	73		
La	3.7	4.5	3.4	4.0		
Ga				_		50
n	1	1	1	1	1	1

Notes: All major elements (SiO₂-Total) in wt%; all trace elements (S-Ga) in ppm. — = not determined. SU = analyses made at Stockholm University, LU = analyses made at SGAB, Luleå, JLUG = analysis made at Justus-Liebig University, Giessen. The approximative value of Al₂O₃ for the alumina puck (AP) is derived by difference (100% - other constituents); for details, see text. BC = determinations beyond the calibration curve; *n* = the number of analyses.

geostandards. Thus, for instance, collaborative studies of the granite Ailsa Craig reveal that the mean SiO_2 data obtained by ICP-AES, XRF, and by atomic absorption spectrometry (AA) may differ significantly. A student t-test of the standard errors (that is, the standard deviation divided by the square root of the number of determinations;

see Crow et al., 1960) suggests that these differences are significant. The mean for the SiO₂ data by AA is distinctly smaller than that by ICP-AES (-0.45%) and by XRF (Govindaraju, 1987). These poorly understood problems are not exclusively occurring for silica, but do obviously cause a problem in the selection of the proper recommended values (Abbey, 1991); all users of analytical data should be aware of these uncertainties.

Contamination Resulting from Grinding

Table 2 shows the compositions of the alumina puck and uncontaminated and contaminated rock (Section 142-846A-1M-2). The SU values for the contaminant show slightly higher values for SiO_2 than the JLUG data. This difference is probably caused by contamination of the SU sample during grinding in an agate mill, but this error is of little consequence for the following discussion.

The contaminated rock shows a considerable increase in alumina and barium, and significant drops in silica, iron, calcium, magnesium, vanadium, yttrium, ytterbium, zinc, and lanthanum concentrations. A simple conservative mixing model shows that the contaminated rock consists of some 8%-9% of material from the puck, with 91%-92% fresh rock as the balancing fraction; that is, the concentrations of the elements silica to lanthanum listed above are lowered because of the admixed alumina.

These contamination effects are easy to spot, particularly for Al and Ba. All basalts from Section 142-846A-1M-2, 0–85 cm, form a homogeneous group (see Tables 3, 4, and particularly 5); even an admixture of a few percent from the puck would cause a significant increase in the Al_2O_3 and Ba values. A comparison of mean data from Tables 4 and 5 (Table 4 for materials not processed in alumina grinders) clearly indicates that no contamination of significance took place during grinding of the rocks during Leg 142, except for Sample 142-846A-1M-2, 0–35 cm.

Variations in Data Between Different Laboratories

The overall agreement between most data in Tables 3-8 ranges from satisfactory to excellent. Seven different 142-846A-1M sam-

Sample:	IM-3, 0-35	1M-3, 0-35	1M-5, 118–135	1M-5, 118–135	1M-6, 0–75	1M-6, 0–75	1M-6, 75–142	1M-6, 75–142
Laboratory:	SU	LU	SU	LU	SU	LU	SU	LU
SiO ₂	49.92	49.70	49.72	49.20	49.85	49.30	49.36	49.70
TiO ₂	1.67	1.71	1.66	1.68	1.66	1.68	1.67	1.70
Al ₂ Õ ₃	14.38	14.50	14.20	14.40	14.25	14.40	14.41	14.50
Fe ₂ O ₃	11.79	11.70	11.78	11.50	11.83	11.50	11.86	11.60
MnO	0.194	0.197	0.193	0.194	0.195	0.193	0.196	0.196
MgO	7.53	7.66	7.44	7.57	7.49	7.56	7.55	7.64
CaO	11.61	11.80	11.58	11.50	11.63	11.60	11.71	11.70
Na ₂ O	2.72	2.81	2.71	2.83	2.70	2.81	2.74	2.86
K ₂ Ö	0.147	BC	0.157	BC	0.147	BC	0.145	BC
P205	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16
Total	100.12	100.29	99.6	99.07	99.91	99.22	99.80	100.09
S	1140		1120		1115		1116	
Cr	261	225	261	226	280	248	264	225
Zr	108	101	108	100	109	100	110	101
Sr	135	125	134	122	134	122	136	124
Ba	15	13	14	13	15	14	14	15
Cd	64		65	(<u></u>)	64	1000	65	
Co	32	39	33	43	33	43	33	42
Cu	69	97	69	78	69	64	70	64
Ni	75	64	74	72	73	76	75	74
Sc	50	41	50	41	50	41	51	42
V	329	326	333	321	333	322	337	325
Y	35	37	35	36	34	37	35	38
Yb	3	4	3	4	3	4	3	4
Zn	92	92	94	89	92	85	93	80
La	3	4	4	4	3	4	3	4
п	4	1	4	1	4	1	4	1

Table 3. Compositions of bulk samples of Core 142-864A-1M basalts.

Notes: All major elements (SiO₂-Total) in wt%; all trace elements (S-La) in ppm, based on number of analyses (n). — = not determined. BC = determinations beyond the calibration curve. SU = analyses made at Stockholm University, LU = analyses made at SGAB, Luleå.

Sample:		1M-6, 0-150, very clean rock				1M-6, 0-150, clean rock			
Laboratory:	SU	LU	JLUG	SD	SU	LU	JLUG	SD	SL
SiO2	49.83	49.20	49.97	0.27	49.31	49.20	50.17	0.06	49.97
TiO	1.70	1.68	1.61	0.01	1.68	1.67	1.62	0.01	1.64
AlaÕa	14.99	14.50	14.41	0.07	15.00	14.50	14.47	0.03	14.29
Fe ₂ O ₂	12.18	11.60	11.66	0.06	12.17	11.60	11.67	0.03	11.62
MnO	0.197	0.195	0.19	0.00	0.197	0.194	0.19	0.00	0.20
MgO	7.78	7.70	7.54	0.04	7.83	7.70	7.56	0.03	7.27
CaO	12.17	11.70	11.69	0.05	12.15	11.70	11.75	0.04	11.73
Na ₂ O	2.81	2.81	2.68	0.02	2.77	2.80	2.67	0.02	2.58
KaŌ	0.117	BC	0.12	0.01	0.137	BC	0.12	0.00	0.13
PaOr	0.17	0.17	0.15	0.00	0.17	0.17	0.15	0.00	0.12
Total	101.94	99.59	100.02	0.48	101.41	99.56	100.35	0.10	99.55
S	1210		100102	0.10	1230			0110	
Cr	263	259	257	3	274	241	260	3	236
Zr	113	100	108	1	115	100	107	ĩ	111
Sr	135	123	124	i	133	124	124	1	122
Ba	13	14	1		16	16	1		(8)
Cd	94				10	103			(0)
Co	36	48			30	51	1000		
Cu	69	61	60	1	68	66	71	2	75
Ni	75	75	60	1	74	77	60	1	73
Sc	50	41	09	543	52	41	02	1	15
v	331	324			337	321			357
v	35	37	35.6	0.3	36	36	35 1	07	37
Yh	33	4	55.0	0.5	30	30	33.1	0.7	51
70	05	77	0.4	1	07	67	05	1	90
La	35	4	94		7	1	95	1	90
Ga			174	0.6	1		16.0	0.6	
Nh			2.5	0.5		100	2.6	0.8	31
Rb			2.5	0.5			2.0	0.0	5.1
RU	3	1	1.0	0.4	2	1	1.0	0.7	2
n	3	1	0		3	1	0		2

Table 4. Mean data for specially treated large samples of basalts from Section 142-864A-1M-6.

Notes: All major elements (SiO₂-Total) in wt%; all trace elements (S-Rb) in ppm, based on the number of analyses (*n*). — = not determined. BC = beyond calibration curve. SU = analyses made at Stockholm University, LU = analyses made at SGAB, Luleå, JLUG = analyses made at Justus-Liebig University. The triplicate SU analyses represent three separate digestions of the rocks; the six JLUG analyses represent three separate sample mounts, each analyzed in duplicate. All standard deviations (SD) refer to JLUG data. SL = Data obtained in ship's laboratory during Leg 142 and represents the mean of two determinations. BC = determination beyond the calibration curve.

Table 5. Mean composition of all basalts from Core 142-864A-1M.

	SU	SU		U	SL	
	Mean	SD	Mean	SD	Mean	SD
SiO ₂	49.65	0.27	49.44	0.23	49.91	0.12
TiO ₂	1.67	0.03	1.69	0.02	1.64	0.01
Al_2O_3	14.51	0.36	14.47	0.05	14.31	0.07
Fe ₂ O ₃	11.90	0.23	11.59	0.07	11.62	0.05
MnO	0.195	0.004	0.195	0.001	0.20	0.01
MgO	7.58	0.17	7.63	0.06	7.32	0.11
CaO	11.77	0.27	11.66	0.10	11.71	0.05
Na ₂ O	2.74	0.06	2.82	0.02	2.55	0.03
K ₂ Ô	0.142	0.017	BC		0.14	0.02
PoOs	0.162	0.006	0.164	0.005	0.105	0.011
Total	98.64	0.99	99.62	0.44	99.50	0.25
S	1153	48				
Cr	266	16	237	13	237	5
Zr	110	3	100.2	0.6	111	1
Sr	134	4	123	1	122	1
Ba	14.4	2.2	14.1	1.3		
Cd	74	17	_			
Co	33	3	44	4		
Cu	72	2	71	13	75*	2
Ni	74	1	73	4	74*	2
Sc	44.6	0.5	41.1	0.3		
V	335	6	323	2	355	9
Y	35.6	0.5	36.9	0.8	36.3	0.6
Yb	2.79	0.04	4.3	0.2		
Zn	95	2	83	9	91*	4
La	4.6	1.7	4.4	0.1		
Nb					2.9	0.2
n	23		7		12	

Notes: All major elements (SiO₂-Total) in wt%; all trace elements (S-Nb) in ppm, based on number of analyses (n). — = not determined. SU = analyses made at Stockholm University, LU = analyses made at SGAB, Luleå. SD = standard deviation, BC = determinations beyond the calibration curve. * = mean data obtained in the ship's laboratory (SL) based on 11 determinations (one outlier deleted in each case). ples were analyzed by three participating laboratories, of which 23 determinations were made at SU, 7 at JLUG, and 12 at LU. The results show that these basalts form a very homogeneous group, as is also shown by the ship's laboratory (SL) data.

Some trends in the data should be pointed out, however, so that analytical procedures can be improved. Several SU analyses show somewhat high oxide sums, exceeding 100%. This is not necessarily wrong because the recommended value for BHVO-1 is 100.30%. Indeed, oxide sums exceeding 100% should be expected for some basalts when total iron is reported in three-valent form, because about 90% of all iron generally is present in divalent form in basalts. However, there is probably some source of error when these oxide sums exceed 101.00%. This problem may be related to difficulties in getting stable silica determinations, as discussed above, and also to the fact that the SU data for Fe2O3, MgO, CaO and Cr seem to be systematically somewhat larger than corresponding data from LU, JLUG, or SL. These problems are caused partly by the lack of thermal stabilization of the spectrometer's nebulizer unit, and partly by the fact that the sequential read-out system in the SU monochromator ARL 3520 prevents the use of internal standards to correct for short-term noise. However, in some cases monochromators are useful, because they permit fast selections of alternative spectral lines if a preferred analytical line has an interference. For many trace elements this unit has therefore proved excellent. This old instrument has recently been replaced with a new one, which unfortunately prohibits further tests.

Major elements and most traces for SU-H samples (Tables 7 and 8) show good agreement with many other determinations, except for Ba, which could not be measured with confidence. The reason for this is that no HF-HClO₄ dissolved solutions could be used owing to the corrosion risk for the plasma torch.

The same analyses also report some rather high Ni values, which probably represent real variations and not errors. Thus, sporadic determinations in the ship's laboratory also yielded high values for the elements Cu, Ni, and Zn (see Table 5). Studies of the basalt pebbles before analysis showed that some of them had tiny pores containing

Table 6. Composition of bulk samples of major aliquots of basalts from Section 142-846A-4Z-1.

Laboratory:	SU	LU	SU	LU	SL
Sample					
depth (cm):	0-35	0-35	Piece 2	Piece 2	Piece 1
SiO ₂	49.35	49.70	49.73	49.50	49.78
TiO ₂	1.78	1.81	1.73	1.80	1.75
Al ₂ Ô ₃	14.47	14.40	14.33	14.40	14.10
Fe ₂ O ₃	12.35	12.00	12.09	12.10	11.96
MnO	0.203	0.202	0.200	0.203	0.21
MgO	7.49	7.51	7.30	7.50	7.27
CaO	11.65	11.60	11.46	11.50	11.50
Na ₂ O	2.79	2.88	2.76	2.87	2.65
K ₂ Õ	0.125	BC	0.160	BC	0.15
PoOs	0.17	0.17	0.18	0.19	0.11
Total	100.38	100.29	99.94	100.11	99.46
S	1200	_	1210		
Cr	244	208	227	192	201
Zr	117	107	117	108	121
Sr	131	121	125	120	120
Ba	15	13	14	12	
Cd	67		66		
Co	34	43	35	44	
Cu	65	55	64	57	71
Ni	73	71	72	71	73
Sc	50	42	48	41	_
V	347	337	342	336	371
Y	37	34	35	40	40
Yb	3	5	3	4	
Zn	97	87	96	44	92
La	5	4	7	4	
Nb					3.1
n	4	1	1	1	1

Notes: All major elements (SiO₂-Total) in wt%; all trace elements (S-Nb) in ppm, based on number of analyses (n). — = not determined. SU = analyses made at Stockholm University, LU = analyses made at SGAB, Luleå. SL = data obtained in the ship's laboratory during Leg 142. BC indicates determinations beyond the calibration curve. minerals that looked like sulfides. Because these sulfides occur very irregularly, there is also reason to expect sporadic jumps in the data for Cu, Ni, and Zn. These conclusions are corroborated by two special analyses (SU-Spec) in Tables 7 and 8, which were done to show that the variations are real and not the result of freak events during the analytical process.

The LU data are generally very good for major components, judging from the agreement with other analyses. These results are expected in view of the fact that this laboratory consistently uses internal standards in the samples to correct for both short-term and long-term drift. However, the data for K are far too low, obviously because of a poor calibration curve, which has not worked well at low concentrations; in the tables this is marked BC, indicating that the values fall beyond the lower end of the calibration curve. Some trace elements are likewise remarkably variable; data for Cu and Zn can be surprisingly low compared with those from other laboratories, and the SD data for Co, Cu, Ni, and Zn show more scatter than the corresponding SU data: these analytical problems are also revealed by the compilation in Table 1. These problems at LU probably resulted from too intensive processing of samples during the metaborate fusing step; studies at SU suggest an almost systematic loss of Zn and possibly also disturbances in the Cu analyses as a consequence of faulty metaborate fusions.

The JLUG data are too few to justify more sweeping generalizations, but agreement with the other determinations is good. The data for Zn and Cr agree well with those from SU.

The SL data (Storms, Batiza, et al., 1993) show very good agreement with most other results for the major elements, except phosphorus, which is consistently low compared with data from SU, LU, and JLUG, and the MgO data, which appear to be too low. Furthermore, many trace component determinations appear quite good; data for Cu, Zn, and Ni, for instance, agree with those from SU, but data for Cr are consistently low and values for V are commonly high. Nevertheless, our overall impression is that the ship's XRF facility is excellent for the determination of most major components in rocks, as well as for the determination of some trace elements. Also, the quality of

Laboratory:	SU	LU	SU	LU	SU-H	SUSpec	SL
Sample depth (cm):	0–5	0–5	24-30	24-30	24-30	24-30	24-30
SiO ₂	49.88	49.10	49.44	49.80	49.93	49.61	49.64
TiO ₂	1.83	1.85	1.85	1.86	1.78	1.85	1.80
Al_2O_3	14.25	14.10	14.74	14.40	14.02	14.74	13.97
Fe ₂ O ₃	12.59	12.30	12.74	12.30	12.20	12.74	12.22
MnO	0.207	0.204	0.200	0.207	0.200	0.200	0.21
MgO	7.22	7.21	7.33	7.34	7.02	7.33	7.02
CaO	11.54	11.40	11.66	11.50	11.34	11.66	11.41
Na ₂ O	2.80	2.88	2.89	2.93	2.74	2.89	2.62
K ₂ Õ	0.123	BC	0.130	BC	0.137	0.130	0.14
P205	0.18	0.18	0.18	0.19	0.18	0.18	0.12
Total	100.62	99.24	101.16	100.60	99.55	101.33	99.14
S	1190		1210				_
Cr	226	176	210	153	185	211	176
Zr	120	110	122	113	108	125	123
Sr	129	119	125	120	ND	144	118
Ba	14	13	12	12	8*	13	-
Cd	70		66				_
Co	36	45	34	41	52	31	-
Cu	67	54	64	58	69	64	70
Ni	69	69	65	63	166	211	65
Sc	50	41	45	41	48	43	
v	354	343	349	344	287	347	366
Y	37	41	34	42	39	37	41
Yb	3	5	3	4			
Zn	98	85	97	77	81	83	95
La	4	4	7	5	<u> 60</u>		
Nb							2.3
n	4	1	1	1	1	1	1

Notes: All major elements (SiO₂-Total) in wt%; all trace elements (S-Nb) in ppm, based on number of analyses (*n*). — = not determined. SU = analyses made at Stockholm University; SU-H = data from Höganäs Eldfast; LU = analyses made at SGAB, Luleå; SL = data obtained in ship's laboratory during Leg 142. BC indicates determinations beyond the calibration curve. * = All SU-H data were determined in a major element program only, to avoid HF corrosion on the plasma torch in the spectrometer used in this case. All Ba data in these determinations are too close to the detection limit to be valid, because of the strong dilution of these samples.

Table 8. Compositional variations of bulk samples of major aliquots of basalts from Section 142-864B-2W-1.

Laboratory:	SU	LU	SU-H	SU-Spec	SL
Sample depth (cm):	16-18	16-18	16-18	16-18	16-18
SiO ₂	49.84	49.40	50.28		49,90
TiO ₂	1.75	1.70	1.64	1993	1.65
Al ₂ Õ ₃	14.98	14.50	14.38		14.19
Fe ₂ O ₃	12.13	11.70	11.69		11.57
MnO	0.200	0.199	0.190		0.20
MgO	7.49	7.52	7.26		7.20
CaO	12.10	11.80	11.77		11.76
Na ₂ O	2.78	2.79	2.65		2.57
K ₂ Õ	0.160	BC	0.140		0.17
P ₂ O ₅	0.18	0.18	0.19		0.12
Total	101.61	99.87	100.19		99.33
S	1200				—
Cr	249	241	236	253	226
Zr	114	101	96	114	113
Sr	127	122	-	122	124
Ba	13	12	7*	17	-
Cd	63	-	-	7555	_
Co	31	44	39	28	_
Cu	67	54	70	67	73
Ni	69	68	236	257	66
Sc	50	41	44	43	
V	329	327	290	324	342
Y	34	36		33	37
Yb	3	4			_
Zn	91	44	80	90	86
La	7	4	-	<u></u>	_
Nb					2.9
n	1	1	1	1	1

Notes: All major elements (SiO₂-Total) in wt%; all trace elements (S-Nb) in ppm. SU = analyses made at Stockholm University; SU-H = data from Höganäs Eldfast; LU = analyses made at SGAB, Luleå; SL = data obtained in the ship's laboratory during Leg 142. BC = determinations beyond the calibration curve; *n* = number of analyses. — = not determined. * = All SU-H data were determined in a major element program only, to avoid HF corrosion on the plasma torch in the spectrometer used in this case. All Ba data in these determinations are too close to the detection limit to be valid, because of the strong dilution of these samples.

the data produced in the ship's XRF facility is the same as that from many shore-based laboratories. Similar conclusions were reached by Hergt and Sims (1994), and appear reasonable in view of recent studies by Normand et al. (1989).

A further reassuring fact derives from the comparison of these SL results with data from the shore-based studies; the differences in data, for instance for silica or alumina, rarely amount to more than 0.5% and 0.2%, respectively. Many other interlaboratory studies, on the other hand, reveal numerous cases where corresponding differences may reach several percent, and for many trace elements it is not unusual for the highest value reported to be several times larger than the smallest value (Gladney et al., 1990; Gladney and Roelandts, 1988a, 1988b, 1990).

One weakness of XRF is the restricted capacity to determine many trace components at low concentrations, which are of interest for the study of many alteration processes as discussed above. This was demonstrated in a study of 1580 XRF-determinations of 13 trace elements in 20 geostandards (Boström and Bach, this volume). Determinations of Ba were therefore aborted during an early phase of Leg 142.

RECOMMENDATIONS

Statistical tests should be used more widely in the ship's XRF laboratory. The uncertainties in the calibration curves (e.g., as $Sy \cdot x$) should be explicitly studied before other final results are evaluated, as pointed out above and in Flanagan (1986). Such routines are generally followed in many chemical laboratories for all sets of data. Similar conclusions were reached by Dick, Erzinger, Stokking, et al. (1992). They pointed out that the interlaboratory variability for samples from ODP/DSDP Hole 504B is surprisingly high, even when only XRF analyses are considered. For instance, Ti/Zr ratios seemingly differ significantly with depth in the lower part of the hole, a variability that is caused by systematic differences in the determination of Ti and Zr in different laboratories. Although all of the data are precise, the accuracies obviously vary considerably. However, accuracies are rarely reported in geoscientific papers. This makes combining different data sets difficult, because these data sets must have the same precision and accuracy. This also applies to DSDP/ODP holes, which are revisited over a considerable time span. Consequently, when rock analyses are made at sea, it is critical to (1) carefully document the analytical precision and (2) perform analyses of widely used reference rocks, such as BHVO-1 and BCR-1, and report these findings in the *Initial Reports* volume, as was done during Leg 136 (Shipboard Scientific Party, 1992) and Leg 142 (Storms, Batiza, et al., 1993).

The advantages and drawbacks of introducing a faster and more versatile analytical system (e.g., an ICP-AES unit) has been discussed elsewhere in this volume.

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^{*}Abbreviations for names of organizations and publications in ODP reference lists follow the style given in *Chemical Abstracts Service Source Index* (published by American Chemical Society).

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