Quantitative SIMS analysis of GSJ rock reference samples

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Quantitative micro-analysis of silicate glasses has been developed using secondary ion mass spectrometry (SIMS). The standard rock references, issued by the Geological Survey of Japan (GSJ), were fused into glass beads and used as standards for SIMS analysis. Thirty eight elements at major, minor and trace concentration levels, were analyzed simultaneously on the standard glasses using an energy-filtering technique. In the concentration range of the glass standards, linear relationships were established for the following elements: Li, Be, B, Na, Mg, Al, P, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Cu, Rb, Sr, Y, Zr, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Hf. The typical accuracy of the analyses are within 10% of recommended values of GSJ standards for the elements over 1 ppm.

INTRODUCTION

Secondary ion mass spectrometry (SIMS) has attracted the interest of geochemists for over a decade because it offers the potential of complete *in situ* chemical and isotopic analyses of solid materials with ppm to ppb sensitivity and micron-scale spatial resolution. Several investigators have applied SIMS to the quantitative elemental analysis of minerals. However, progress of quantitative SIMS has been limited and not widely accepted by earth scientists.

The presence of molecular and multiply charged ions in the secondary ion mass spectrum of geological samples is a serious source of major complications, which is inherent in SIMS. Molecular interferences can be minimized by high mass resolution (Steele *et al.*, 1981; Yurimoto and Sueno, 1984; Reed, 1984) or energy filtering (Shimizu *et al.*, 1978; Ray and Hart, 1982; Metson *et al.*, 1983; Nesbitt *et al.*, 1986; Zinner and Crozaz, 1986). Both methods

have distinct advantages. For example, energy filtering is efficient in eliminating molecular ion interferences for masses greater than ~60 (Shimizu and Hart, 1982) and SIMS adjustment and peak jumping among masses are easier, while the high mass resolution mode is effective for resolving isobars, multiply charged ions and certain types of molecular ions (e.g. hydride).

The existence of matrix effects is another serious source of major complications in SIMS. SIMS quantification can be pursued using either theoretical or empirical approaches. Theoretical approaches, however, are currently impractical due to the uncertainties of compositional matrix effects on secondary-ion yields (Williams, 1985). The most successful method involves the use of standards to obtain relative sensitivity factors of the measured elements (Shimizu *et al.*, 1978; Steele *et al.*, 1981; Ray and Hart, 1982; Reed, 1984, 1986; Yurimoto and Sueno, 1985; Zinner and Crozaz, 1986). Major problems with this technique are the difficulty of obtaining suitable

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standards and the large numbers of standards required.

We have developed analytical methods for quantitative SIMS (Yurimoto and Sueno, 1984, 1985 and 1987; Yurimoto *et al.*, 1989). In this paper, we provide instrumental and standardization details for trace element analysis of silicates by SIMS. We also examine systematically the contribution of molecular-ion interferences and matrix effects to the secondary ion mass spectra of ten silicate-glass standards. An empirical approach based on energy filtering was used to establish calibration curves for 38 elements in glasses prepared from rock reference standards.

ANALYTICAL METHODS

Powdered standard rock samples (about 1g each of JA-1, JA-2, JA-3, JB-1, JB-1a, JB-2, JB-3, JF-1, JF-2, JG-1, JG-1a, JG-2, JG-3, JGb-1, JP-1, JR-1 and JR-2), issued by the Geological Survey of Japan (GSJ), were loaded into Pt capsules and fused at 1340°C for 5 minutes under atmospheric condition. The melt was quenched in water to produce glass. For JR-1 and JR-2, which are clear natural rhyolite glasses, the original rock specimen was also prepared. The samples were sliced by diamond saw and mounted in an epoxy pellet with final polishing by 0.3 μm alumina paste.

Data were obtained on a Cameca IMS-3F secondary ion microscope at the University of Tsukuba. The primary ion beam was mass filtered $^{16}\text{O}^-$ -accelerated to 14.5 keV and adjusted for a beam current of about 60 nA and a spot size of about 80 μm . The primary beam was rastered over 100 $\times$ 100 μm area during irradiation. Secondary ions sputtered were collected from the central area of 60 μm in diameter using a mechanical aperture. Kinetic energy filtering was achieved by offsetting the sample accelerating voltage (-100 V) while keeping the setting of the electrostatic analyzer voltage and the width and position of the energy slit constant. The energy band-pass was set to accept a 20 eV window. The exit slit was at its maximum opening resulting in a mass resolving power of ~ 500 .

Positive secondary ion intensities were measured, typically for 10 seconds, in order of mass number using peak jumping. The sequence was repeated from 10 to 20 times depending on the count rates of each mass.

Problems caused by electrostatic charging of the sample surface under sputtering by the primary ion beam were virtually eliminated by ~ 20 nm of gold film evaporated to the surface and by monitoring the kinetic energy distribution maximum of Si^+ .

Other analytical and instrumental conditions were similar to those employed by Yurimoto and Sueno (1984) and Yurimoto *et al.* (1989).

GLASS STANDARDS

Clear glass under optical microscopy has been prepared for ten kinds of the rock references (JA-1, JA-2, JA-3, JB-1, JB-1a, JB-2, JB-3, JGb-1, JR-1 and JR-2). Homogeneity of these glasses was evaluated by independent SIMS runs at more than ten different points of each glass. Results are shown in Table 1.

Coefficients for variation (CV%), which is relative standard deviation for reproduction at different points, are $<10\%$ for major elements and $\sim 10\%$ for trace elements (>10 ppm). This indicates that chemical heterogeneity of the samples does not exceed 10%. Since the CV% include fluctuations of intensity ratios depending on the daily changes of instrumental conditions of SIMS as well as chemical heterogeneity in the sample, chemical heterogeneity of the standards must be much smaller, possibly less than 5% at the analyzing volume, i.e. 60 μm in diameter and less than 1 μm depth (<10 ng).

There were no obvious differences in intensity ratios determined for the fused glasses and the original rock specimens of JR-series standards. Therefore, it can be concluded that compositional changes during the melting process are negligible, at least for the elements observed in this study.

For JF-1, JG-1, JG-1a, JG-2 and JP-1, some unmelted crystals were observed in the fused glass with the optical microscope. Although the

Fig. 1. Relationships between the secondary ion intensity ratio (against Si) and concentration (weight) ratio (against Si) of GSI rock references. The recommended values by Ando *et al.* (1989) are used as concentration of each elements. The error bars represent one sigma given in Table 1. For REE's monoxide interferences are already subtracted (see text). Special treatments are needed for regressions of Na, P, Sc and REE's (see text).

results of SIMS measurements for most major elements show no large discrepancies from the correlation curve of the homogeneous glass standards (Fig. 1), micro-scale compositional heterogeneity, greater than 50%, was found for some trace elements (e.g. REE) in these glasses, and also in JF-2 and JG-3 glasses. As a consequence, these heterogeneous glasses were not used as standards for the empirical approach to quantitative SIMS.

QUANTIFICATION

General

Isotopes used for quantification are listed in Table 2. Secondary ion intensities, corrected for natural isotopic abundances, were normalized to the intensity of Si. Relationships between the intensity ratio and concentration ratio (on the weight-for-weight basis) of recommended values (Ando *et al.*, 1989) against Si are presented in Fig. 1.

The results were fitted by a simple linear regression and a logarithmic regression. The correlation coefficients for both regressions have similar values. However, the logarithmic regression minimizes the relative errors, and is therefore much more effective for elements whose concentration distributes over a range of several magnitudes. Only logarithmic regression lines are shown in Fig. 1.

All of the values of secondary ion intensity ratios produce linear relationships when plotted against concentration ratios within uncertainties of measurement. Moreover it seems that possible interferences are negligible over the concentration range of the glass standards for all elements except P, Sc, heavy rare earth elements (REE's) and Hf. Therefore, within the analytical uncertainties, the correlation of a given element M can be simplified as:

$$[M] = F_M \frac{M^+}{Si^+} [Si]$$

where $[M]$ and $[Si]$ are concentrations of M and Si , respectively, M^+ and Si^+ , secondary ion intensity ratios of individual element, and F_M , rela-

tive sensitivity factor of M to Si . Since this simple relationship was well demonstrated for the individual element, the number of standards needed can be considerably reduced for practical purposes.

Comparisons of the SIMS measurements with the recommended values of Ando *et al.* (1989) are shown in Table 1. The agreement between SIMS and the recommended values are typically better than 10% accuracy level (see R.E. % of Table 1).

Na

Sodium ion intensities of Si-rich glass standards (JF- JG- and JR-series) have large discrepancies from a regression curve by the other glass standards (Fig. 1). The fact that the data points are on the right of the curve shows that there are more Na ions in these standards than expected (i.e., enhanced ionization). The matrix effects on Na ion intensities may be caused by the Si-induced enhancement (Shimizu, 1986).

Good correlations were obtained except for the Si-rich standards (Fig. 1). The relation is useful for quantification of the silica-poor materials (within 5% systematic error), and for semi-quantification of the silica-rich material (within 30% systematic error) (Table 1).

P and Sc

Nonzero intercepts on Fig. 1 indicate that interferences still remained on the masses of P and Sc after energy filtering. Since these are mono-isotopic elements, only the high mass resolution technique can produce an interference-free peak (Yurimoto and Sueno, 1984). According to the high mass resolution study, SiO^+ , AlO^+ and CaH^+ ions overlap with the Sc^+ peak, and SiH^+ ion with the P^+ peak. The CaH^+ interference is negligible (less than 10% of Sc^+ peak under no energy filtering) in this study.

Since these interferences seem to be contributing constantly to all standards under this SIMS condition, simple linear regressions were applied to these elements (Fig. 1). We obtained good correlation coefficients $R^2=0.974$ and

Table 1. Results of SIMS analysis of the glass standards

	JA-1					JA-2				
	GSJ88		SIMS			GSJ88		SIMS		
	ppmw	ppmw	sigma	CV%	R.E. %	ppmw	ppmw	sigma	CV%	R.E. %
Li	10.5	11.7	0.8	7%	-11%	28.7	23.1	0.3	1%	19%
Be	0.5	0.49	0.03	6%	1%	2.2	2.1	0.3	14%	4%
B	16	23	1	3%	-44%		17	0	2%	
Na	28606	30563	1242	4%	-7%	22825	21251	916	4%	7%
Mg	9705	10687	1743	16%	-10%	46295	46141	8026	17%	0%
Al	79298	82417	2307	3%	-4%	81098	79459	2359	3%	2%
Si	299560	299560				262711	262711			
P	698	741	25	3%	-6%	654	545	4	1%	17%
K	6475	6486	451	7%	0%	14942	12755	1450	11%	15%
Ca	40593	40251	3080	8%	1%	46310	45382	2676	6%	2%
Sc	28.4	21.9	3.3	15%	23%	19	19.1	0.4	2%	-1%
Ti	5213	5175	524	10%	1%	4015	4172	182	4%	-4%
V	105	91	8	9%	14%	130	146	3	2%	-12%
Cr	7.3	5.6	2.3	40%	23%	465	388	5	1%	17%
Mn	1162	1078	276	26%	7%	852	895	103	12%	-5%
Fe	48645	48551	4172	9%	0%	42885	45392	7597	17%	-6%
Co	11.8	11.4	2.6	23%	4%	30	29	2	6%	3%
Cu	42.2	33.0	12.5	38%	22%	28.6	26.5	1.0	4%	7%
Rb	11.8	12.3	1.5	12%	-4%	68	61	7	11%	10%
Sr	266	258	31	12%	3%	252	242	7	3%	4%
Y	31.4	27.6	3.2	12%	12%	18	18	2	11%	1%
Zr	87	97	10	10%	-12%	119	105	3	3%	12%
Cs	0.64	0.62	0.00	1%	3%	4.2	4.1	1.0	25%	3%
Ba	307	306	47	15%	0%	317	285	17	6%	10%
La	5.5	5.3	0.2	4%	5%	16	15.5	0.8	5%	3%
Ce	13.2	12.6	1.0	8%	5%	33	30.8	2.0	6%	7%
Pr	1.5	2.0	0.1	6%	-33%	5.9	3.4	0.2	5%	42%
Nd	11	10.4	0.4	4%	5%	14	13.8	0.1	1%	2%
Sm	3.6	3.1	0.3	11%	14%	3.1	2.8	0.3	11%	9%
Eu	1.2	1.2	0.1	10%	2%	0.91	1.16	0.31	27%	-28%
Gd	4.6	3.8	1.4	37%	17%	3.9	3.1	3.0	99%	21%
Tb	0.77	0.57	0.25	44%	26%	0.48	0.49	0.34	69%	-2%
Dy	4.9	4.5	0.6	14%	9%	1	2.9	0.3	9%	-192%
Ho	0.89	1.08	0.17	16%	-21%		0.64	0.10	15%	
Er	3.2	3.2	0.0	1%	0%		1.6	0.4	26%	
Tm	0.51	0.55	0.43	79%	-8%		0.32	0.13	42%	
Yb	2.9	2.8	0.1	2%	3%	1.6	1.7	0.0	2%	-5%
Lu	0.46	0.40	0.14	35%	14%	0.27	0.31	0.07	23%	-13%
Hf	2.4	3.0	0.6	20%	-25%	2.8	2.6	0.9	33%	9%

Table 1. (continued)

	JA-3					JB-1				
	GSJ88		SIMS			GSJ88		SIMS		
	ppmw	ppmw	sigma	CV%	R.E.%	ppmw	ppmw	sigma	CV%	R.E.%
Li	14	13.2	0.0	0%	6%	11.5	10.3	0.4	4%	10%
Be	0.7	0.77	0.12	16%	-10%	1.5	1.37	0.04	3%	9%
B		23	1	2%		12.4	9.1	0.6	7%	27%
Na	23492	23367	2392	10%	1%	20676	20558	1223	6%	1%
Mg	22002	24203	9448	39%	-10%	46597	42313	4394	10%	9%
Al	82422	80250	5020	6%	3%	76916	78346	3189	4%	-2%
Si	291143	291143				243959	243959			
P	480	532	70	13%	-11%	1134	1109	66	6%	2%
K	11705	10967	1634	15%	6%	11871	11407	806	7%	4%
Ca	44880	43663	4496	10%	3%	66392	63891	4184	7%	4%
Sc	21	26	4	14%	-25%	27.4	28.9	1.6	5%	-6%
Ti	4075	3866	383	10%	5%	8030	7403	596	8%	8%
V	172	177	1	1%	-3%	212	251	16	6%	-18%
Cr	67.5	78	13	17%	-16%	469	419	26	6%	11%
Mn	821	871	203	23%	-6%	1239	1004	228	23%	19%
Fe	46089	45392	13458	30%	2%	62591	55263	8735	16%	12%
Co	21	26	5	21%	-26%	38.7	36.4	0.8	2%	6%
Cu	45.3	30.2	8.6	29%	33%	56.3	63.2	12.8	20%	-12%
Rb	36	31	1	3%	14%	41.2	40.8	4.2	10%	1%
Sr	294	287	5	2%	2%	435	439	9	2%	-1%
Y	19	20	1	5%	-7%	24	28	1	5%	-15%
Zr	123	110	11	10%	11%	143	154	7	5%	-7%
Cs	2.2	1.4	0.4	29%	36%	1.19	1.29	0.59	46%	-9%
Ba	318	303	7	2%	5%	490	516	18	3%	-5%
La	9.7	8.7	0.6	7%	10%	38	40.4	9.8	24%	-6%
Ce	23	19.8	1.2	6%	14%	67	70.0	17.1	24%	-5%
Pr	2.9	2.4	0.2	10%	16%	7.5	7.9	2.5	31%	-5%
Nd	12	10.7	1.1	10%	11%	27	27.7	0.2	1%	-2%
Sm	3.3	3.1	0.2	8%	6%	5	5.1	0.3	5%	-2%
Eu	0.9	0.72	0.03	4%	20%	1.52	1.79	0.30	17%	-18%
Gd	2	2.9	1.3	47%	-43%	4.7	4.7	1.0	20%	0%
Tb		0.80	0.39	49%		0.76	0.79	0.28	36%	-4%
Dy	3.2	3.1	0.6	19%	4%	4	4.0	0.6	16%	0%
Ho		0.66	0.28	42%		0.7	0.77	0.30	38%	-10%
Er		1.7	0.3	20%		2.2	2.1	0.5	24%	4%
Tm		0.53	0.33	62%		0.35	0.26	0.03	13%	27%
Yb	2.2	2.1	0.3	15%	3%	2.1	2.4	0.2	7%	-13%
Lu	0.4	0.30	0.06	22%	25%	0.31	0.31	0.21	66%	-1%
Hf	3.8	2.9	1.2	42%	23%	3.4	2.9	1.1	37%	16%

Table 1. (continued)

	JB-1a					JB-2				
	GSJ88		SIMS			GSJ88		SIMS		
	ppmw	ppmw	sigma	CV%	R.E.%	ppmw	ppmw	sigma	CV%	R.E.%
Li	11.5	10.3	0.2	2%	11%	8.0	8.3	0.7	8%	-4%
Be	1.4	1.3	0.2	15%	7%	0.27	0.30	0.01	5%	-10%
B		7.3	0.3	4%		30	26.9	1.4	5%	10%
Na	20306	19554	932	5%	4%	15044	15345	778	5%	-2%
Mg	46717	46743	2743	6%	0%	28091	28615	1972	7%	-2%
Al	76810	76558	2791	4%	0%	77657	80145	3833	5%	-3%
Si	243913	243913				248776	248776			
P	1134	1010	9	1%	11%	436	410	45	11%	6%
K	11788	10618	391	4%	10%	3486	3648	292	8%	-5%
Ca	65963	67608	3479	5%	-2%	70680	71809	3556	5%	-2%
Sc	29	26.5	2.6	10%	8%	54	52.5	2.7	5%	3%
Ti	7790	7990	766	10%	-3%	7131	7484	670	9%	-5%
V	220	208	24	12%	6%	578	545	23	4%	6%
Cr	415	387	104	27%	7%	27.4	31	5	17%	-14%
Mn	1162	1111	30	3%	4%	1549	1508	339	22%	3%
Fe	63648	62896	3257	5%	1%	100332	101507	18983	19%	-1%
Co	39.5	32.5	3.7	11%	18%	39.8	39.7	3.5	9%	0%
Cu	55.5	57.6	6.5	11%	-4%	227	214	42	19%	6%
Rb	41	35	2	6%	16%	6.2	12.6	2.2	18%	-103%
Sr	443	446	1	0%	-1%	178	189	13	7%	-6%
Y	25	26	2	9%	-5%	26	27	1	2%	-6%
Zr	144	152	21	14%	-6%	52	55	3	5%	-6%
Cs	1.2	1.46	0.07	5%	-21%	0.90	1.05	0.10	10%	-16%
Ba	497	528	6	1%	-6%	208	216	6	3%	-4%
La	38	38.7	2.7	7%	-2%	2.4	2.7	0.2	6%	-13%
Ce	67	67.1	4.8	7%	0%	6.5	6.8	1.6	24%	-4%
Pr		7.3	0.9	12%		1.2	1.4	0.2	12%	-16%
Nd		27.4	0.7	2%		6.5	7.0	1.2	17%	-8%
Sm	5.2	4.8	0.0	1%	8%	2.3	2.7	0.3	12%	-17%
Eu	1.5	1.45	0.11	7%	3%	0.85	0.74	0.36	49%	13%
Gd		4.6	1.9	41%		3.3	4.1	0.5	12%	-25%
Tb	0.70	0.62	0.11	18%	11%	0.62	0.90	0.10	11%	-45%
Dy		3.6	0.6	16%		3.85	4.0	0.6	15%	-4%
Ho		0.66	0.17	26%		0.83	1.00	0.15	15%	-20%
Er		2.3	0.1	5%		2.4	2.9	1.0	34%	-22%
Tm	0.34	0.38	0.20	51%	-12%	0.50	0.55	0.39	70%	-11%
Yb	2.0	2.0	0.1	5%	2%	2.5	2.4	0.0	2%	4%
Lu	0.33	0.35	0.10	30%	-5%	0.40	0.41	0.07	18%	-3%
Hf	3.4	3.5	1.0	29%	-2%	1.4	1.9	0.7	40%	-34%

Table 1. (continued)

	JB-3					JGb-1				
	GSJ88	SIMS				GSJ88	SIMS			
	ppmw	ppmw	sigma	CV%	R.E.%	ppmw	ppmw	sigma	CV%	R.E.%
Li	7.2	7.6	0.4	6%	-6%	4.3	4.9	0.2	5%	-14%
Be	0.74	0.70	0.02	3%	6%	0.36	0.33	0.05	16%	7%
B	15	17.9	1.3	7%	-20%	2.4	4.8	0.6	12%	
Na	20898	21244	1284	6%	-2%	9115	9296	489	5%	-2%
Mg	31346	29270	1923	7%	7%	47199	46741	3150	7%	1%
Al	89409	87942	2387	3%	2%	93485	92533	4003	4%	1%
Si	238675	238675				203136	203136			
P	1265	1379	74	5%	-9%	218	223	20	9%	-2%
K	6475	6642	405	6%	-3%	1992	2173	146	7%	-9%
Ca	70465	69153	4245	6%	2%	85616	90504	4383	5%	-6%
Sc	35	35.3	4.7	13%	-1%	35	36.5	1.8	5%	-4%
Ti	8689	7729	827	11%	11%	9708	9917	582	6%	-2%
V	383	392	64	16%	-2%	640	597	7	1%	7%
Cr	60.4	75	5	7%	-25%	59.3	67	3	5%	-13%
Mn	1239	1178	255	22%	5%	1317	1400	56	4%	-6%
Fe	83097	72598	12092	17%	13%	106035	112612	3375	3%	-6%
Co	36.3	38.5	2.9	7%	-6%	61.6	64.0	1.7	3%	-4%
Cu	198	214	47	22%	-8%	86.8	118	9	8%	-36%
Rb	13	17	3	16%	-31%	4	12	0	3%	-200%
Sr	395	409	21	5%	-4%	321	330	30	9%	-3%
Y	28	29	2	6%	-2%	11	11	0	0%	2%
Zr	99.4	102	11	11%	-2%	33	39	7	17%	-17%
Cs	1.10	0.85	0.13	15%	22%	0.27	0.36	0.12	34%	-32%
Ba	251	243	11	5%	3%	63	64	0	0%	-1%
La	9.1	8.8	1.1	12%	4%	3.95	4.0	0.5	12%	-2%
Ce	20.5	22.4	2.3	10%	-9%	8	8.8	0.7	8%	-10%
Pr	3.2	3.7	0.4	10%	-16%	1.1	1.2	0.1	13%	-6%
Nd	16.6	16.4	0.5	3%	1%	5.7	6.2	0.2	3%	-9%
Sm	4.3	4.8	0.3	7%	-11%	1.5	1.7	0.3	19%	-11%
Eu	1.3	1.17	0.70	60%	10%	0.61	0.63	0.06	10%	-4%
Gd	4.6	4.2	2.2	51%	8%	1.5	2.0	0.3	17%	-33%
Tb	0.82	0.69	0.22	32%	16%	0.30	0.41	0.04	9%	-37%
Dy	4.4	5.0	1.0	20%	-14%	1.4	1.6	0.6	39%	-15%
Ho	0.84	0.91	0.19	21%	-8%	0.32	0.36	0.09	25%	-14%
Er	2.5	2.4	1.0	40%	4%	0.91	1.3	0.0	2%	-44%
Tm	0.50	0.39	0.08	20%	23%	0.17	0.17	0.10	59%	-1%
Yb	2.4	2.3	0.3	15%	3%	1	1.0	0.0	4%	1%
Lu	0.38	0.38	0.10	25%	-1%	0.16	0.20	0.08	41%	-25%
Hf	2.7	2.9	1.3	44%	-8%	0.84	0.77	0.2	30%	8%

Table 1. (continued)

	JR-1					JR-2				
	GSJ88		SIMS			GSJ88		SIMS		
	ppmw	ppmw	sigma	CV%	R.E.%	ppmw	ppmw	sigma	CV%	R.E.%
Li	62.3	69	5	8%	-11%	83	88	10	11%	-6%
Be	3.1	3.4	0.3	7%	-9%	3.4	3.6	0.4	10%	-7%
B	133	115	2	1%	14%	135	137	1	1%	-2%
Na	30384	38133	2987	8%	-26%	29866	37861	2429	6%	-27%
Mg	543	558	241	43%	-3%	301	282	60	21%	6%
Al	68234.7	68041	3391	5%	0%	67864	67213	2801	4%	1%
Si	352635	352635				353758	353758			
P	87	175	36	20%	-101%	44	63	37	59%	-43%
K	36608	40662	1517	4%	-11%	36940	40741	1653	4%	-10%
Ca	4502	4177	543	13%	7%	3216	3538	348	10%	-10%
Sc	5.2	5.7	0.7	13%	-10%	5.4	6.5	0.7	11%	-20%
Ti	599	779	445	57%	-30%	539	431	27	6%	20%
V		2.2	0.4	19%	73%		1.3	0.1	7%	84%
Cr	2.3	0.28	0.08	27%	88%	2.6	0.09	0.02	20%	97%
Mn	775	755	182	24%	3%	852	851	63	7%	0%
Fe	6685	7772	4273	55%	-16%	6001	5927	444	7%	1%
Co	0.65	2.1	0.7	33%	-225%	0.4	1.7	0.2	10%	-323%
Cu	1.4	2.0	0.4	20%	-40%	1.4	1.3	1.1	84%	9%
Rb	257	265	3	1%	-3%	297	328	12	4%	-11%
Sr	30	25	2	7%	18%	8	9.4	0.1	1%	-17%
Y	46	41	1	3%	11%	51	48	3	6%	6%
Zr	102	88	2	2%	13%	98.5	89.7	2.3	3%	9%
Cs	20.2	20.4	2.4	12%	-1%	26	27.5	1.9	7%	-6%
Ba	40	41.1	0.2	1%	-3%	39	11.5	1.9	17%	71%
La	21	17.2	2.9	17%	18%	17.5	12.2	1.3	11%	30%
Ce	49	36.8	6.7	18%	25%	38	29.1	2.6	9%	23%
Pr	6.1	5.0	1.1	22%	19%	5.5	3.9	0.5	12%	29%
Nd	25.5	19.8	1.7	9%	22%	24.8	16.1	1.1	7%	35%
Sm	6.2	5.6	0.1	2%	9%	6.2	4.9	0.2	4%	20%
Eu	0.31	0.29	0.02	6%	7%	0.13	0.15	0.12	82%	-17%
Gd	4.8	2.6	0.7	26%	46%	7.8	6.3	1.3	20%	20%
Tb	1.10	0.74	0.56	76%	33%	1.20	1.19	0.35	29%	1%
Dy	6.2	5.5	1.9	34%	11%	7.7	6.2	0.6	10%	19%
Ho	1.1	1.05	0.23	22%	4%	1.7	1.15	0.12	10%	32%
Er	3.9	3.1	0.2	6%	20%	5.2	4.4	0.0	1%	15%
Tm	0.73	0.76	0.26	34%	-4%	0.86	0.69	0.19	27%	20%
Yb	4.6	3.5	0.1	3%	25%	5.4	4.5	0.2	4%	16%
Lu	0.68	0.67	0.15	22%	2%	0.92	0.68	0.18	26%	26%
Hf	4.7	3.8	1.4	38%	19%	5.2	3.4	1.0	28%	34%

GSJ88: recommended value of Ando *et al.* (1989). Concentrations for major elements are calculated from the oxide forms. SIMS: quantitative SIMS value determined by empirical relationships shown in Fig. 1. Si concentration is internal standard. sigma, CV%: standard deviation and relative error for reproduction on several independent runs, respectively. SIMS, sigma and CV% were calculated from the mean secondary ion intensity ratios of each runs. R.E.%: relative error between GSJ88 and SIMS values. The errors over 20% are shown in bold face.

Fig. 2. Positive secondary ion mass spectra of JB-1a glass standards. The spectra are deconvoluted into contributions from REE and their monoxide.

0.972 for P and Sc, respectively.

Rare Earth Elements and Hf

Energy filtering effectively removed all complex molecular ions interfering with the elements measured here. The only serious interferences on REE's were monoxide ions and other interferences were negligible as described by Zinner and Crozaz (1986). The contribution of oxide interferences under the energy filtering are shown in Fig. 2. The mass spectra were decon-

volved by the similar procedure reported by Zinner and Crozaz (1986).

For the quantitative analysis of REE's, we selected 22 masses only slightly affected by interferences. The masses are listed in Table 2. Using information on natural isotopic abundances, the contributions of interference were deconvoluted by the solution of simultaneous linear equations on these masses. It is difficult to calculate the contributions of GdO and TbO because of the low intensity of REE and the reason reported by Zinner and Crozaz (1986). Since the empirical relationship of the yields of REE monoxide ions (Reed, 1983) were also observed for the glass standards, the contributions of GdO and TbO on ^{172}Yb , ^{174}Yb and ^{175}Lu , respectively, were subtracted by using the NdO^+/Nd^+ ratio at the same measurement point. Similarly the intensity of Hf is obtained by subtracting the DyO contribution which is derived from the SmO^+/Sm^+ ratio.

The results are plotted against the recommended values in Fig. 1. Since the JR-series data systematically deviate from the other glass standard trends, the plots except for JR-series were used for least-squares regression. All calibration curves are well defined linearly and pass through the origin within the random error of analysis.

Chondrite-normalized REE abundances determined by SIMS are compared with recommended values in Fig. 3. It can be seen that the match of both patterns is excellent for all glass standards, especially for light REE's. The error bars are dependent on the degrees of interference contributed and ion intensities of the masses (cf. Table 2 and Fig. 2).

Systematic shifts are clearly observed on the JR-series pattern (Fig. 3). The shifting may represent reduced REE ion yields caused by the SiO_2 contents in the sample.

Mass 64

Of the five Zn isotopes, ^{64}Zn is the most abundant isotope (48.6%). However, the secondary ion intensities of mass 64 show excellent correlation with Ti concentration (Fig. 1). The results show that the greatest species of mass 64 is TiO^+

Fig. 3. Chondrite-normalized REE abundances in GSJ rock references against atomic number. The error bars represent the sigma column given in Table 1. REE values by Anders and Ebihara (1982) are used for chondrite-normalization.

and the energy filtering is powerless in this case. This interference can be removed by the high mass resolution technique (Yurimoto and Sueno, 1984).

For Zn analysis using energy filtering, it is necessary to use the other isotope such as ^{66}Zn (27.9%) or ^{68}Zn (18.8%). The isotopes, ^{67}Zn and ^{70}Zn , may not be acceptable due to low abun-

dances.

SUMMARY

Glasses prepared from JA-1, JA-2, JA-3, JB-1, JB-1a, JB-2, JB-3, JGb-1, JR-1 and JR-2 rock standards were found to be homogeneous standards appropriate for SIMS micro-analysis.

Table 2. Elemental and interference species and the mass numbers

Species	Masss Number	Species	Mass Number
Li	7	Y	89
Be	9	Zr	90
B	11	Cs	133
Na	23	Ba	138
Mg	24, 26	La	139
Al	27	Ce	140
Si	28, 30	Pr	141
P, SiH	31	Nd	143, 146
K	39	Sm	147, 149
Ca	40	Eu, BaO	151, 153
Sc, SiO, AlO	45	Gd, Dy, NdO, SmO	160
Ti	47	Tb, NdO	159
V	51	Dy, NdO	161, 162
Cr	52	Dy, SmO	163
Mn	55	Ho, SmO	165
Fe	56	Er, NdO, SmO	166, 168
Co	59	Er, EuO	167
Cu	63	Tm, EuO	169
TiO	64	Yb, GdO	172, 174
Rb	85	Lu, TbO	175
Sr	88	Hf, DyO	177, 178, 179, 180

Simultaneous micro-analysis of major, minor and trace elements in ng samples is made possible by use of the glass standards. This method uses energy filtering and, for REE's and Hf, the contribution of simple oxide ions were corrected. Using specific SIMS operating conditions, linear calibration curves have been established for 38 elements (Li, Be, B, Na, Mg, Al, P, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Cu, Rb, Sr, Y, Zr, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Hf). The typical accuracy of the analyses are within 10% of the recommended values for the elements over 1 ppm.

Complications were encountered as described below:

(1) Secondary ion yield for Na was enhanced in JF-, JG- and JR-series glasses which have relatively higher Si concentrations than the other standard glasses, whereas the yield of REE was reduced on JR-series glasses. The results demonstrate that systematic errors occur among silicates with different Si abundances for these elements.

(2) Energy filtering was ineffective in removing interferences on the P and Sc peaks. The

detection limits of these elements are controlled by the background level of the masses.

Despite these problems, the empirical relationships obtained in this study are still useful for the application of quantitative SIMS to geological samples.

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