

Determination of Thallium in the USGS Glass Reference Materials BIR-1G, BHVO-2G and BCR-2G and Application to Quantitative Tl Concentrations by LA-ICP-MS

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Here, we present determinations of thallium (Tl) concentrations in the USGS reference materials BIR-1G, BHVO-2G and BCR-2G measured by solution ICP-MS. The Tl content in these three glasses spans a range of about 2–230 ng g⁻¹, which is similar to the values published for the respective powder materials. The determined range of Tl concentrations in these three glass reference materials makes them ideal for investigating Tl concentrations in basaltic and andesitic volcanic glasses. We also performed a series of laser ablation ICP-MS measurements on the three samples, which show that this technique is able to determine Tl concentrations in glass samples with concentrations as low as 2 ng g⁻¹.

Keywords: thallium, USGS glass reference materials, laser ablation, ICP-MS.

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Nous présentons ici des déterminations de concentrations en thallium (Tl) dans les matériaux de référence USGS BIR-1G, BHVO-2G et BCR-2G mesurée par solution ICP-MS. Les teneurs en Tl dans ces trois verres couvrent une gamme d'environ 2 à 230 ng g⁻¹, ce qui est similaire aux valeurs publiées pour les poudres de ces matériaux. La gamme de concentration en Tl déterminée dans ces trois verres de référence montre qu'ils sont idéals pour l'analyse des concentrations en Tl des verres volcaniques basaltiques et andésitiques. Nous avons également effectué une série de mesure par laser ablation ICP-MS sur les trois échantillons qui montre que cette technique permet de déterminer les concentrations en Tl dans des échantillons de verre à des niveaux concentrations aussi faibles que 2 ng g⁻¹.

Mots-clés : thallium, verres de référence USGS, ablation laser, ICPMS.

Thallium is one of the heaviest naturally occurring elements in the periodic table (isotopes ²⁰³Tl and ²⁰⁵Tl). In igneous systems, thallium is univalent and has a large ionic radius similar to the alkali metals K, Rb and Cs (Shannon 1976). These properties make it very incompatible in mantle minerals and lead to its enrichment in mantle melts and the continental crust (Heinrichs *et al.* 1980, Nielsen *et al.* 2005). In recent years, there has been an increased interest in Tl due to the discovery of significant variations in the stable isotope composition in various natural samples (Rehkämper and Halliday 1999, Rehkämper *et al.* 2002, Nielsen *et al.* 2006a, Nielsen and Rehkämper 2011). For example, studies have suggested that Tl isotopes in ocean island basalts (OIB) can trace the presence of recycled marine ferromanganese sediments in the mantle source (Nielsen *et al.* 2006a, 2007). Additionally, Tl isotopes may prove to be

an excellent tracer of inputs from the subducted slab to the mantle wedge (Prytulak *et al.* 2013).

One of the main difficulties when undertaking any geochemical study of Tl is the scarcity of knowledge about the general behaviour of this element in various environments. This problem stems from the fact that, historically, Earth scientists have rarely determined Tl. Although a few studies exist that reported Tl concentration data for relatively primitive igneous rocks (Jochum and Verma 1996, Noll *et al.* 1996, Nielsen *et al.* 2006a, 2007), most investigations of Tl behaviour in igneous systems determined Tl concentrations for more evolved igneous rocks, such as granites and pegmatites, which contain comparatively high Tl abundances in the µg g⁻¹ range (Shaw 1952, Heinrichs *et al.* 1980). However, due to the strongly incompatible nature of Tl, abundances in more primitive igneous rocks

such as andesites, basalts and peridotites were much more difficult to determine, because the detection limit was often higher than the amount of Tl contained in each rock sample.

Modern measurement techniques such as ICP-MS have the ability to detect very small amounts of Tl, and hence, there is no analytical reason to omit Tl from measurement protocols. Unfortunately, widely used reference materials including USGS basalts BIR-1, BHVO-1, BHVO-2 and BCR-2 do not have certified Tl concentrations and only recently have reliable data for these reference materials become available (Nielsen *et al.* 2007, Babechuk *et al.* 2010, Prytulak *et al.* 2013). These concentration data should enable more directly comparable data for rocks with Tl abundances in the range of 1–200 ng g⁻¹, which covers most primitive igneous rocks. An additional complication with Tl is that aqueous alteration and authigenic ferromanganese marine precipitates contain very large amounts of Tl (Rehkämper *et al.* 2002, Nielsen *et al.* 2006b). Thus, some samples, like mid-ocean ridge basalt (MORB) glasses, submarine OIB and arc lavas, may register very high Tl concentrations if care is not taken to remove the alteration and/or surface contamination. A simple method to circumvent this problem is to perform *in situ* laser ablation (LA) ICP-MS analyses of polished MORB, OIB and arc basalt glasses, where it can be directly observed that these foreign phases are not present. In order to obtain reliable LA-ICP-MS data, it is required that glass reference materials with Tl concentrations, chemical matrix and ablation behaviour similar to the investigated samples are available. Unfortunately, only little Tl data have been published for glass reference materials with concentrations below 10 µg g⁻¹ (Jochum *et al.* 2005, 2011b, Gagnon *et al.* 2008, Shaheen *et al.* 2008, Hu *et al.* 2009). In addition, the accuracy of some of this data could be questionable as all these studies used LA-ICP-MS with single-point calibration curves extrapolated over several orders of magnitude to measure Tl concentrations in low-Tl USGS reference materials.

Therefore, we conducted the first study aimed at providing the most precise Tl concentrations in the USGS glass reference materials BIR-1G, BHVO-2G and BCR-2G by solution ICP-MS. Based on the concentrations observed in the reference materials BIR-1, BHVO-2 and BCR-2 that are rock powders, we believe that it is likely that these silicate glasses span a range of Tl concentrations that encompass most primitive mantle melts. We also performed a test to verify that the Tl concentrations obtained for the glass materials yielded detectable Tl ion beams when determined using LA-ICP-MS. These reference materials should therefore

represent an excellent suite of glass reference materials to be used in studies of volcanic glasses with low Tl abundances.

Experimental

Chemicals and sample preparation

Acids (HF, HCl and HNO₃) used in this study were Baseline quality reagents purchased from Seastar Chemicals. Acid dilutions were performed with 18 MΩ cm grade water from a Millipore system.

All samples (USGS BIR-1, BCR-2, BHVO-2, BIR-1G, BCR-2G and BHVO-2G) were weighed out in duplicate and digested in 1:1 mixture of concentrated HF and HNO₃ on a hot plate overnight. Powder materials (BIR-1, BCR-2 and BHVO-2) were weighed as powders, whereas glass materials (BIR-1G, BCR-2G and BHVO-2G) were weighed out as small mm-sized chips. After digestion in HF, samples were evaporated to dryness followed by repeated cycles of re-dissolution in concentrated HNO₃ and evaporation in order to destroy fluoride residues. After complete digestion was attained, samples were diluted with 2% HNO₃ to a total volume of between 50 and 120 ml and an appropriate amount of indium was added to obtain a final indium concentration of ~ 1 ng g⁻¹.

Data acquisition and reduction

The solution portion of this study was conducted over three different analytical sessions. In each session, four USGS reference materials (Table 1) were utilised to construct a calibration curve, which, together with normalisation to indium, was used to calculate concentrations for the USGS glasses. All calibration curves had $r^2 > 0.96$ with the majority between $r^2 = 0.99$ –1. For each sample, at least one of the two splits weighed out was analysed on two separate occasions.

Measurements were taken with a single-collector inductively coupled plasma-sector field mass spectrometer (Thermo Finnigan Element 2, Bremen, Germany). For solution mode, samples were free-aspirated into the ICP-MS using a ~ 100 µl min⁻¹ Teflon™ nebuliser (Elemental Scientific, Omaha, Nebraska, USA), coupled with a cyclonic spray chamber. For *in situ* measurements, a New Wave 213 nm laser ablation system was used for sample introduction. The laser was operated with a fluence of 15 J cm⁻², a pulse frequency of 10 Hz and a spot size of 110 µm, which was utilised in order to maximise Tl ion beam and thus lower detection limit.

Table 1.
Reference materials used for calibration curves

Split	Sample mass (mg)	Dilution (g)	Session		
			A	B	C
BIR-1_1	53.8	54.71		X	X
BIR-1_2	50.3	100.01	X	X	
BHVO-2_1	19.5	92.55	X	X	
BHVO-2_2	36.2	51.87	X		X
BCR-2_1	58.5	121.63	X	X	X
BCR-2_2	26.6	113.2			X

Determinations were performed at both low ($M/\Delta M \sim 300$) and medium mass resolution ($M/\Delta M \sim 3000$), the former for Li, Be, Ni, Ga, Rb, Sr, Cs, Ba, Tl, Pb, Th and U and the latter for K, Cr, Mn, Co, Cu and Zn. In solution mode, In was measured in both mass resolutions. For K, mass 39 in medium resolution was measured; this catches the tail of the $^{38}\text{Ar}^1\text{H}$ mass, but the ratio of ^{39}K to $^{38}\text{Ar}^1\text{H}$ mass was always much greater than 100, making any ArH background correction negligible. In medium mass resolution, the $^{40}\text{Ar}^{40}\text{Ar}$ dimer was monitored and used to correct for overall drift of the magnet with time. Small magnetic offsets with respect to the medium resolution mass calibration were preset manually. For medium mass resolution, a 100% mass window was scanned, providing enough of a peak shape for fine-scale centring. Drift and offsets to the low mass resolution calibration were negligible, so a 30% mass window was scanned.

Data in solution mode were reduced by first correcting all analyses for instrumental drift. This was done by normalising intensities to the initial run (typically a procedural blank) by multiplying signal intensity by the sensitivity of In (number of counts per concentration unit in the solution) in the initial run and dividing by the sensitivity of In in the run of interest. Once drift-corrected, the signal intensities in the procedural blank were subtracted from all samples including those samples being used as calibration materials. An external calibration curve based on our recently published Tl concentrations (Prytulak *et al.* 2013) or accepted concentrations (in case of elements other than Tl) for the USGS powders was then generated, allowing intensities in unknowns (glasses) to be converted to concentration.

In laser ablation mode, the average gas background was first subtracted from the ablation signal. Instrumental drift and ablation efficiency were then accounted for by normalising to an initial measurement using an internal standard. In this case, we used the known concentration of an element for normalisation (^{25}Mg).

Results and discussion

Thallium

The Tl solution concentrations recorded for BIR-1G, BHVO-2G and BCR-2G (Tables 2–4) were all within uncertainty (1s) of the LA-ICP-MS studies that have reported Tl concentrations for all three glass reference materials (Gagnon *et al.* 2008, Hu *et al.* 2009), and our value for BHVO-2G is identical to the only other solution ICP-MS study to report Tl concentrations for a USGS glass reference material (Babechuk *et al.* 2010) (Table 5). The values obtained for the glass reference materials are furthermore relatively close to those of their corresponding rock powders (Table 5). Thallium is a volatile element with a melting temperature of 577 K. It is therefore possible that the high temperatures of ~ 1800 K (Wilson and Taggart, unpublished) employed to produce the glasses from the original powder may have caused some loss of Tl. This process is probably the reason for the $\sim 10\%$ lower Tl concentrations determined in BHVO-2G and BCR-2G. Even though the very low Tl concentrations in BIR-1 and BIR-1G are associated with significant uncertainties of $\sim 20\%$, BIR-1G clearly has a significantly higher Tl concentration than BIR-1. Due to the very low amounts of Tl present in the original sample, it is possible that the higher concentration in BIR-1G may have resulted from slight contamination during the powder melting process. This type of contamination has previously been observed for U and Pb in BIR-1G (Willbold and Jochum 2005).

It has been documented that Tl in NIST SRM glass reference materials 610–617 is heterogeneously distributed. This phenomenon is particularly evident at the rims of these glasses, whereas the cores yield no discernible Tl concentration variation as long as relatively large laser spot sizes are utilised (Eggins and Shelley 2002, Jochum *et al.* 2011a). It is not clear whether this is a problem, which also exists for the USGS glass reference materials studied here. No systematic investigation of Tl heterogeneity in the three

Table 2.
Results for BIR-1G

	Isotope	Split 1			Split 2			Avg	1 s	GeoReM	1 s
		A	B	C	A	B	C				
Li (LR)	7	3.11	3.25	3.35	3.19		3.44	3.27	0.13	3	0.7
Be (LR)	9	0.0959	0.12	0.096	0.083		0.087	0.096	0.015	0.1	
Ni (LR)	60	170	178	168	158		156	166	9	178	18
Ga (LR)	71	15.9	16.6	16.7	15.2		15.3	15.9	0.7	15	2
Rb (LR)	85	0.198	0.206	0.208	0.201		0.191	0.201	0.007	0.197	0.007
Sr (LR)	88	113	117	115	111		109	113	3	109	2
Cs (LR)	133	0.0054	0.0055	0.0054	0.0072		0.0069	0.0061	0.0009	0.007	0.002
Ba (LR)	138	6.64	6.82	6.61	14		13.6	9.5	3.9	6.5	0.07
Tl (LR)	205	0.0029	0.0028	0.0024	0.0023		0.0021	0.0025	0.0003		
Pb (LR)	208	3.41	3.55	3.42	3.08		3.03	3.30	0.23	3.7	0.3
Th (LR)	232	0.031	0.044	0.030	0.032		0.037	0.035	0.006	0.030	0.002
U (LR)	238	0.020	0.029	0.019	0.018		0.021	0.021	0.004	0.023	0.006
K (MR)	39	118	170	142			140	143	21	183	2*
Cr (MR)	53	371	373	372			344	365	14	392	24
Mn (MR)	55	1357	1406	1309			1190	1316	93	1470	80
Co (MR)	59	52.8	54.2	49.4			45.3	50	4	52	5
Cu (MR)	65	120	115	119			106	115	6	119	12
Zn (MR)	66	71.1	71.9	70.8			61.3	69	5	78	17

All concentrations in $\mu\text{g g}^{-1}$. A, B and C refer to the three different analytical sessions. LR, low-resolution mode; MR, medium-resolution mode. * Uncertainty estimated by the GeoReM database, not a standard deviation.

Table 3.
Results for BHVO-2G

	Isotope	Split 1			Split 2			Avg	1 s	GeoReM	1 s
		A	B	C	A	B	C				
Li (LR)	7		5.33		4.74	4.68		4.9	0.4	4.4	0.8
Be (LR)	9		1.03		1.03	0.983		1.01	0.03	1.3	0.2
Ni (LR)	60		118		121	115		118	3	116	7
Ga (LR)	71		22		22.1	22.3		22.1	0.2	22	3
Rb (LR)	85		9.38		9	8.84		9.07	0.28	9.20	0.04
Sr (LR)	88		408		399	393		400	8	396	1
Cs (LR)	133		0.096		0.098	0.094		0.096	0.002	0.10	0.02
Ba (LR)	138		136		134	133		134	2	131	2*
Tl (LR)	205		0.0148		0.0168	0.0154		0.016	0.001		
Pb (LR)	208		1.64		1.86	1.87		1.79	0.13	1.7	0.2
Th (LR)	232		1.25		1.15	1.2		1.20	0.05	1.22	0.05
U (LR)	238		0.468		0.42	0.434		0.441	0.025	0.403	0.003
K (MR)	39		4517		4569	4245		4444	174	4270	50*
Cr (MR)	53		254		278	248		260	16	293	12
Mn (MR)	55		1217		1287	1243		1249	35	1320	30
Co (MR)	59		39.1		43.5	39.2		41	3	44	2
Cu (MR)	65		105		129	113		116	12	127	11
Zn (MR)	66		92.6		106	86.2		95	10	102	6

All concentrations in $\mu\text{g g}^{-1}$. A, B and C refer to the three different analytical sessions. LR, low-resolution mode; MR, medium-resolution mode. * Uncertainty estimated by the GeoReM database, not a standard deviation.

USGS reference glasses currently exists. However, based on multiple laser spot analyses, Hu *et al.* (2009) concluded that Tl was not heterogeneously distributed in these glasses when spot sizes of 160 μm were employed. We did not observe any noticeable Tl concentration difference between the two splits investigated here (Tables 2–4), in agreement with the previous findings. However, because the Tl depletion of the

NIST SRM glasses is confined to the outermost 1–2 mm (Eggins and Shelley 2002, Jochum *et al.* 2011a) and we here studied chips several mm in diameter, it is most likely that we either did not sample any potential heterogeneity or that only an insignificant fraction of the glass chips were depleted such that any heterogeneity was within the precision of our measurement results. Hence, it remains likely

Table 4.
Results for BCR-2G

	Isotope	Split 1			Split 2			Avg	1 s	GeoReM	1 s
		A	B	C	A	B	C				
Li (LR)	7	9.79	9.4		8.96	8.57		9.2	0.5	9	1
Be (LR)	9	2.1	2.29		2.07	2.25		2.18	0.11	2.3	0.4
Ni (LR)	60	26.3	28.8		23.1	25.9		26	2	13	2
Ga (LR)	71	23.2	23.5		24.2	24.6		23.9	0.6	23	1
Rb (LR)	85	46.8	45.8		46.2	45.7		46.1	0.5	47	0.5*
Sr (LR)	88	333	339		329	336		334	4	342	4*
Cs (LR)	133	1.12	1.11		1.11	1.11		1.11	0.01	1.16	0.07
Ba (LR)	138	679	678		668	676		675	5	683	7*
Tl (LR)	205	0.231	0.233		0.232	0.239		0.234	0.004		
Pb (LR)	208	10.9	10.9		11.2	11.3		11.1	0.2	11	1
Th (LR)	232	5.1	5.4		5.0	5.2		5.2	0.2	5.9	0.3
U (LR)	238	1.49	1.58		1.45	1.57		1.52	0.06	1.69	0.12
K (MR)	39	14900	14340		13780	13260		14070	708	14900	150*
Cr (MR)	53	27	21.7		14.7	12.2		18.9	6.7	17	2
Mn (MR)	55	1387	1308		1413	1305		1353	55	1550	70
Co (MR)	59	34.2	29.6		34.9	29.9		32	3	38	2
Cu (MR)	65	18.1	16		18.4	16.7		17.3	1.1	21	5
Zn (MR)	66	134	122		131	120		127	7	125	5

All concentrations in $\mu\text{g g}^{-1}$. A, B and C refer to three different analytical sessions. LR, low resolution mode; MR, medium resolution mode. * Uncertainty estimated by the GeoReM database, not a standard deviation.

Table 5.
Thallium concentrations in ng g^{-1} for USGS reference materials

	Gagnon <i>et al.</i> (2008) ^a	Hu <i>et al.</i> (2009) ^a	Prytulak <i>et al.</i> (2013) ^b	Babechuk <i>et al.</i> (2010) ^b	This study ^b	1 s
BIR-1			1.3	1.3		
BHVO-2			18	19		
BCR-2			257	ND		
BIR-1G	5	4.4			2.5	0.3
BHVO-2G	30	18		16	16	1
BCR-2G	300	250			234	4

ND, not determined.

^a Analyses by LA-ICP-MS.

^b Analyses by solution ICP-MS.

that Tl is not homogeneously distributed in USGS reference glasses BCR-2G, BHVO-2G and BIR-1G and care must be taken to avoid analysis of the outermost 1–2 mm of these glass beads when conducting quantitative Tl determination by LA-ICP-MS.

Other elements

In general, our data for the remaining seventeen elements (Li, Be, K, Cr, Mn, Co, Ni, Cu, Zn, Ga, Rb, Sr, Cs, Ba, Pb, Th and U) agree very well with the values recommended by the GeoReM database (Tables 2–4), which compiles the most reliable data available for these reference materials. Notable exceptions were Ba in BIR-1G, for which the second split appears to be either contaminated or Ba is somehow heterogeneously distributed in this glass.

Potassium in BIR-1G and Ni in BCR-2G were also slightly different to the recommended values. These anomalous abundances are most likely related to the combination of low concentrations and using the medium resolution mode that diminishes the transmission of ions. Thus, we do not think that our values are more reliable than those recommended by GeoReM.

Test of new Tl values with LA-ICP-MS

In order to utilise the three glass reference materials for actual Tl concentration measurements by LA-ICP-MS, it is essential that the concentrations are high enough to yield a detectable signal. We tested this by analysing the three reference materials with a New Wave 213 nm laser coupled to a Thermo Element 2 ICP-MS. BIR-1G

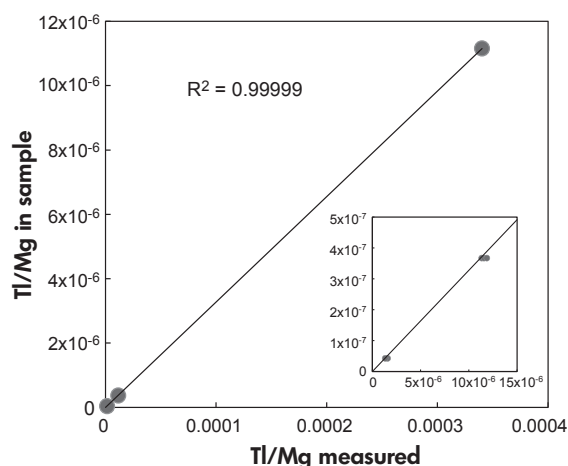


Figure 1. LA-ICP-MS calibration curve constructed using the Tl concentrations obtained for BCR-2G (highest Tl/Mg), BHVO-2G (intermediate Tl/Mg) and BIR-1G (lowest Tl/Mg) in this study. The x-axis represents ratios of the counts measured by LA-ICP-MS, while the y-axis denotes the ratio between certified Mg concentrations and the Tl concentrations determined here by solution ICP-MS. It can be seen that there was excellent correspondence between the two measurement techniques with a correlation coefficient very close to 1. Also shown is a magnified view of the low Tl/Mg area occupied by BHVO-2G and BIR-1G. It is evident that the laser measurements agreed very well with the solution measurements even at concentrations of a few ng g⁻¹ (the concentration of BIR-1G).

and BHVO-2G were analysed in triplicate and BCR-2G once. The results are shown in Figure 1 where it is evident that the technique is able to generate highly precise Tl concentrations even at glass concentrations of only a few ng g⁻¹. The excellent correspondence between the Tl intensities obtained by laser and concentrations measured by solution also gives us additional confidence in the accuracy of our solution measurements.

Conclusions

We have conducted measurements by solution ICP-MS of Tl concentrations in the three USGS glass reference materials BIR-1G, BHVO-2G and BCR-2G. Their concentrations are 2.5, 16 and 234 ng g⁻¹, respectively. The values for BHVO-2G and BCR-2G are ~ 10% lower than the respective powder reference materials, which can be explained by volatile loss of Tl during the glass fusion

process. BIR-1G has a slightly higher Tl concentration than BIR-1, which is most likely due to minor contamination during the melting process. This phenomenon has previously also been observed for U and Pb in the same reference glass (Willbold and Jochum 2005).

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