Synthesis and Preliminary Characterisation of New Silicate, Phosphate and Titanite Reference Glasses

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Eleven synthetic silicate and phosphate glasses were prepared to serve as reference materials for *in situ* microanalysis of clinopyroxenes, apatite and titanite, and other phosphate and titanite phases.

Analytical results using different micro-analytical techniques showed that the glass fragments were homogeneous in major and trace elements down to the micrometre scale. Trace element determinations using inductively coupled plasma-mass spectrometry (ICP-MS), multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS), laser-ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) and secondary ionisation mass spectrometry (SIMS) showed good agreement for most elements (Li, Be, B, Cs, Rb, Ba, Sr, Ga, Pb, U, Th, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Er, Tm, Yb, Lu, Zr, Hf, Ta, Nb) studied and provide provisional recommended values.

Keywords: glass, reference material, *in situ* analysis, trace elements, titanite, sphene, apatite, dacite, clinopyroxene, geochemistry.

Onze verres synthétiques de compositions silicatée et phosphatée ont été préparés afin de servir de matériaux de référence pour la micro-analyse in situ de clinopyroxènes, d'apatites et de titanites et d'autres phases phosphatées et titanifères. Les résultats analytiques obtenus à partir de différentes techniques de micro-analyse ont montré que les fragments de verre étaient homogènes en éléments majeurs et en trace, ceci jusqu'à l'échelle du micromètre. Les déterminations des concentrations en éléments en trace, faites par spectrométrie de masse à plasma inductif (ICP-MS), spectrométrie de masse à plasma inductif et multi-collecteur (MC-ICP-MS), spectrométrie de masse à plasma inductif et ablation laser (LA-ICP-MS) et spectrométrie de masse à ionisation secondaire (SIMS) ont montré un bon accord entre elles, pour la plupart des éléments étudiés (Li, Be, B, Cs, Rb, Ba, Sr, Ga, Pb, U, Th, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Er, Tm, Yb, Lu, Zr, Hf, Ta, Nb) et permettent de proposer des valeurs recommandées provisoires.

Mots-clés : verres, matériaux de référence, analyse in situ, éléments en trace, titanite, sphène, apatite, dacite, clinopyroxène, géochimie.

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The geochemical analysis of minerals and geological glasses relies on well characterised reference materials. In an ideal world, homogeneous reference materials should match the chemical compositions of the unknown phase as closely as possible.

However, most geochemical laboratories use National Institute of Standards and Technology certified reference materials (NIST SRM 610 or NIST SRM 612) for the determination of trace elements in minerals and glasses. This could pose a problem as the

NIST materials are often far removed from the chemical composition of the mineral or glass of interest. Recent advances in *in situ* determination of trace elements and their isotopes has sparked a particular interest in more appropriate reference materials for the analysis of accessory minerals such as titanites and phosphates. Whilst progress in methods of preparation (Jochum *et al.* 2000, 2005, 2006) has improved the analysis of natural glasses, homogeneous reference materials for the analysis of minerals are still scarce (Wiedenbeck *et al.* 1995, Sylvester and Ghaderi 1997, Black *et al.* 2003, 2004, McDowell *et al.* 2005, Ødegaard *et al.* 2005). This is especially true for accessory minerals such as zircon (ZrSiO_4), apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$), monazite (CePO_4) and titanite (CaTiSiO_5), whose compositions are very different from glassy reference materials such as the family of geologically relevant NIST glasses.

To partially address these matters, we have synthesised several novel silicate and phosphate glasses to approximately match the compositions of apatite, clinopyroxene and titanite. The aim of this paper is to describe the synthesis of eleven new reference material glasses together with homogeneity tests and some selected analytical results that may serve as preliminary reference values. We plan to distribute our glasses to interested laboratories over the next few years to collect more analytical data.

Experimental and analytical techniques

Synthesis

About 15 grams of each glass were prepared in conventional muffle furnaces in air using large platinum crucibles. Starting materials consisted of oxides, carbonates and phosphates (Table 1) and appropriate amounts were mixed in an agate mortar by hand for at least two hours. Trace elements (see Table 1 for details) were then added to the starting materials using ICP-MS standard solutions or as carbonates or oxides. The phosphate glasses (STDP3 and STDP5) were fused at 1600 °C for one hour whereas the silicate glasses were fused at 1500 °C for 3 hours. If necessary, the resulting glasses were re-ground and re-fused. Major element compositions of all eleven glasses are given in Table 2.

Silicate and phosphate melts were quenched by placing the platinum crucible in distilled water. Fragments of the glass were either drilled out of the crucible or carefully broken off. Potential sources of contamination by Zr or Mo could be due to ZrO_2 insulation boards in the muffle furnaces used, as well as from the MoSi_2 heating elements of the furnaces. Further sources of contamination were trace impurities in the starting materials. However, the determination of

Table 1.
Starting materials and experimental procedures

Glass	Starting materials	Trace elements added	Temperature of fusion (°C)	Duration (hr)
TNT666	CaCO_3 , TiO_2 , Al_2O_3 , SiO_2	Li, Be, B, Sc, Sr, Zr, Cs, La, Ce, Gd, Hf, Pb	1500	3
TNT777	CaCO_3 , TiO_2 , Al_2O_3 , SiO_2	Ga, Rb, Y, Nb, Ba, Pr, Sm, Lu, Ta, Th, U	1500	3
TNT150	CaCO_3 , TiO_2 , Al_2O_3 , SiO_2	Li, Be, B, Sc, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Sm, Gd, Lu, Hf, Ta, Pb, Th, U	1500	3
TNT1500	CaO , TiO_2 , Al_2O_3 , SiO_2	Li, Be, B, Sc, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Sm, Gd, Lu, Hf, Ta, Pb, Th, U	1500	3
CPX666	Al_2O_3 , SiO_2 , K_2CO_3 , CaCO_3	Li, Be, B, Sc, Sr, Zr, Cs, La, Ce, Gd, Hf, Pb	1500	3
CPX777	Al_2O_3 , SiO_2 , K_2CO_3 , CaCO_3	Ga, Rb, Y, Nb, Ba, Pr, Sm, Lu, Ta, Th, U	1500	3
DAC666	Na_2CO_3 , Al_2O_3 , SiO_2 , K_2CO_3 , CaCO_3 , TiO_2	Li, Be, B, Sc, Sr, Zr, Cs, La, Ce, Gd, Hf, Pb	1500	1
DAC777	Na_2CO_3 , Al_2O_3 , SiO_2 , K_2CO_3 , CaCO_3 , TiO_2	Ga, Rb, Y, Nb, Ba, Pr, Sm, Lu, Ta, Th, U	1500	1
STDP5	CaCO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$	Li, Be, B, Sc, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Sm, Gd, Lu, Hf, Ta, Pb, Th, U	1600	1
STDP3-150	CaCO_3 , Al_2O_3 , MgO , SiO_2 , $\text{NH}_4\text{H}_2\text{PO}_4$	Li, Be, B, Sc, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Sm, Gd, Lu, Hf, Ta, Pb, Th, U	1600	1
STDP3-1500	CaCO_3 , Al_2O_3 , MgO , SiO_2 , $\text{NH}_4\text{H}_2\text{PO}_4$	Li, Be, B, Sc, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Sm, Gd, Lu, Hf, Ta, Pb, Th, U	1600	1

Starting materials used were: CaCO_3 (Merck 99.99%), SiO_2 (Alfa 99.99%), TiO_2 (Alfa 99.99%), Na_2CO_3 (Merck 99.99%), K_2CO_3 (Merck 99.99%), MgO (Alfa 99.99%), $\text{NH}_4\text{H}_2\text{PO}_4$ (Alfa 99.9%), Al_2O_3 (Merck 99.99%). Note that MgO , TiO_2 , SiO_2 and Al_2O_3 were fired at 1000 °C for five hours to release any adsorbed water, hydroxides and other volatile impurities. The fired oxides were then kept in a laboratory dry furnace at 110 °C.

Table 2.
Major element composition of glasses

	Na ₂ O	K ₂ O	CaO	MgO	TiO ₂	Al ₂ O ₃	SiO ₂	P ₂ O ₅	Total
TNT666	0.016 (15)	0.08 (3)	28.04 (25)	b.d.	39.65 (41)	b.d.	30.14 (28)	n.a.	97.9
TNT777	b.d.	0.06 (2)	27.91 (24)	b.d.	39.55 (39)	b.d.	29.96 (22)	n.a.	97.5
TNT150	0.013 (10)	0.084 (14)	28.16 (14)	b.d.	39.86 (20)	0.11 (1)	29.97 (13)	n.a.	98.2
TNT1500	0.024 (16)	0.10 (14)	27.30 (14)	b.d.	38.86 (18)	0.12 (1)	28.86 (13)	n.a.	95.3
CPX666	0.04 (2)	0.024 (19)	25.21 (260)	14.09 (15)	6.91 (16)	8.72 (13)	42.9 (3)	n.a.	97.9
CPX777	0.029 (24)	0.018 (17)	25.02 (27)	14.06 (15)	6.92 (17)	8.72 (12)	42.9 (2)	n.a.	97.7
DAC666	4.37 (13)	3.19 (11)	8.08 (17)	b.d.	2.76 (7)	15.33 (19)	64.32 (28)	n.a.	98.1
DAC777	4.2 (1)	3.2 (1)	7.97 (15)	b.d.	2.73 (12)	15.32 (17)	64.04 (29)	n.a.	97.6
STDP5	-	-	31.81 (12)	-	-	-	-	65.91 (13)	97.7
STDP3-150	-	-	21.1 (1)	10.7 (2)	-	13.5 (1)	46.51 (15)	7.8 (5)	99.7
STDP3-1500	-	-	20.4 (2)	10.4 (1)	-	13.1 (2)	45.1 (2)	7.6 (3)	96.6

Results from electron probe microanalysis from several fragments of each glass (% m/m). Uncertainties (2RSD) from multiple analyses (>100) are given in brackets as last significant digits; e.g., 3.19 (11) should be read as 3.19 ± 0.11 or 3.1 (12) should be read as 3.1 ± 1.2.

b.d. = below limit of detection, n.a. = not analysed. TNT glasses represent glasses of titanite composition, the CPX glasses approximate Ti-rich clinopyroxene compositions, the DAC compositions are to represent dacitic compositions, and the STDP glasses are phosphate-glasses of varying compositions.

elements such as Tm, which was not added to the starting material, yielded values of only a few µg g⁻¹.

Synthesis of Ti-rich silicate glasses (TNT) was straightforward. However, the preparation of phosphate-bearing glasses (STDP) was much more complicated than was anticipated. The preparation of silicate glass with significant amounts of phosphorus was straightforward, but exsolution of immiscible phosphate liquids was encountered in some cases. In these cases, compositions were altered to prevent exsolution of immiscible phases. However, the synthesis of glasses which only contained calcium and phosphorus, and which would be ideal as reference materials for the analysis of whitlockite or apatite, turned out to be much more complicated. Glasses with high Ca/P (Ca/P > 65 molar) could not be synthesised in our laboratories as melting points commonly exceeded 1600 °C. In systems with Ca/P = 50 only very small amounts of glass could be synthesised as quench crystallisation of phosphate minerals often occurred. These materials are not presented here. However, we succeeded in preparing large quantities of phosphate glasses with Ca/P < 45 (Sinha *et al.* 2001).

Analytical methods

Electron probe microanalysis (EPMA)

A Cameca SX51 wavelength dispersive 5 spectrometer electron microprobe was used at Heidelberg University to determine major element compositions

and test homogeneity of several chips of each silicate and phosphate glass. We used an acceleration voltage of 15 kV which resulted in a probe current of 20 nA and each element was counted for 10 seconds (Prowatke and Klemme 2006). To minimise possible loss of alkali metals such as Na or K, these elements were measured first and the beam diameter was enlarged to 10 µm. Profile lengths of up to 2000 µm (up to 100 points) were measured across small fragments of the glasses. The overall analytical uncertainty of the method was typically smaller than 2% (2s) for all major elements studied.

Secondary ion mass spectrometry (SIMS)

A Cameca ims 3f ion probe at Heidelberg University was used to investigate trace element homogeneity in the glasses, using a nominal 10 kV primary beam of ¹⁶O⁻ ions. Positive secondary ions were accelerated to 4.5 keV. The energy window was set at 40 eV. We employed the energy filtering technique with an offset of 90 eV at a mass resolution M/ΔM (10%) of ≈ 400 to suppress interfering molecules and to minimise matrix effects. The primary current was 20 nA, resulting in a spatial resolution of ca. 20-25 µm diameter at the sample surface. Details of the analytical procedures are given by Prowatke and Klemme (2005). Profiles of SIMS analyses were done across all glass fragments and profile lengths varied between 200 and 2000 µm with distances between individual spots ranging between 50 and 100 µm.

Inductively coupled plasma-mass spectrometry (ICP-MS)

The analyses using inductively coupled plasma-mass spectrometry were performed at the ACME laboratories in Vancouver, Canada. An Elan inductively coupled plasma-mass spectrometer (Perkin Elmer) was used. The powdered sample (0.25 g) was decomposed by a mixed acid digestion (HClO_4 - HNO_3 - HCl) procedure under pressure. Rhenium served as the internal standard to correct for drift. The precision was generally better than 5% (2s) and total analytical uncertainties were estimated to be better than 10%.

Multi collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS)

Measurements were performed at the Zentrallabor für Geochronologie (ZLG) at the University of Münster, Germany. During the course of the measurements, two 1.3 and 3.6 mg fragments of TNT 150 and one 0.86 mg fragment of TNT 1500 were analysed by MC-ICP-MS. Contents of some HFSE (Zr, Hf, Nb, Ta) and Lu together with the $^{176}\text{Hf}/^{177}\text{Hf}$ isotope compositions were measured using an Isoprobe MC-ICP-MS. Operating conditions and analytical techniques are summarised in Münker *et al.* (2001) and Weyer *et al.* (2002). Hafnium isotope results are given relative to a value of 0.282160 for JMC 475, the typical external reproducibility was ± 0.5 ϵ -units (2s). Concentrations of the HFSE (except for Nb) were measured by isotope dilution using a mixed ^{94}Zr - ^{180}Hf - ^{180}Ta - ^{176}Lu isotope tracer which was calibrated against > 99.9% pure AMES metals. Niobium concentrations were measured as Zr/Nb against a Zr-Nb reference sample prepared by AMES metals and using the Zr concentrations determined from the isotope dilution measurements. Typical accuracies and 2s external reproducibilities were $\pm 1\%$ for Zr, Hf and Ta and $\pm 4\%$ for Nb concentrations. Typical external reproducibilities for Nb/Ta, Zr/Hf and Lu/Hf are $\pm 4\%$, $\pm 0.6\%$, and $\pm 1\%$, respectively. Errors as quoted in Table 6 also include propagated errors originating from blank measurements, assuming a $\pm 50\%$ blank uncertainty. Results between the two replicates of TNT 150 agree within the external reproducibilities quoted above (Table 6). Measured blanks were 550 ng for Zr, 39 pg for Hf, 9 pg for Nb, and 17 pg for Ta.

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS)

Laser ICP-MS analysis at the Australian National University were performed using an Agilent 7500 series mass spectrometer. The Resonetics 193 nm excimer laser was attenuated using a 25% reflectance mirror on the final bend of the custom-built laser flight tube. Laser optics, ablation cell geometry, and signal smoothing devices are described in Eggins *et al.* (2003). Ablation took place at 5 Hz, using a 60 μm spot. Analysis time was 60 seconds, with 45 seconds of background collection before ablation commenced. The following masses were measured: ^7Li , ^9Be , ^{11}B , ^{23}Na , ^{24}Mg , ^{29}Si , ^{31}P , ^{33}S , ^{43}Ca , ^{55}Mn , ^{67}Zn , ^{68}Zn , ^{71}Ga , ^{84}Sr , ^{85}Rb , ^{88}Sr , ^{89}Y , ^{90}Zr , ^{91}Zr , ^{93}Nb , ^{111}Cd , ^{133}Cs , ^{137}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{166}Er , ^{172}Tb , ^{175}Lu , ^{178}Hf , ^{181}Ta , ^{208}Pb , ^{232}Th , ^{238}U . All isotopes were counted for 10 ms. Including switching time, this cycle was repeated every 0.4502 seconds.

The laser ablation ICP-MS system at the Universität Frankfurt, Germany consisted of a New Wave 213 nm Nd:YAG laser (LUV-213) and a ThermoFinnigan Element 2 mass spectrometer. The laser was run at a pulse frequency of 10 Hz and a pulse energy of 0.8 mJ for a 75 μm spot size. For each sample, five consecutive measurements were performed. An Ar-He sample gas mixture served as carrier gas. ^{44}Ca was used as an internal standard and NIST SRM 612 (Pearce *et al.* 1997) was used for calibration.

Results and discussion

Homogeneity of the glasses

Homogeneity in terms of major and trace elements of any reference material is of fundamental importance. We, therefore, tested both major and trace element homogeneity of several fragments of each glass using electron microprobe, SIMS and laser ablation ICP-MS techniques. As a measure of variation across samples, we selected the two times relative standard deviation (2 RSD) of multiple analyses across several glass fragments in percent or, in case of the SIMS homogeneity tests, the relative variation of count rates of elements relative to internal standard elements such as Si or Ca.

Major element homogeneity

We investigated homogeneity using several glass fragments of each of the eleven glasses. Electron

Table 3.
Reproducibility (%) of major element determination using electron probe microanalysis

	TNT 666	TNT 777	TNT 150	TNT 1500	CPX 666	CPX 777	DAC 666	DAC 777	STDP 5	STDP3-150	STDP3-1500
Na ₂ O	93.8	-	76.9	66.7	50	82.8	3.0	2.4	-	-	-
K ₂ O	37.5	33.33	16.67	140.0	79.2	94.4	3.4	3.1	-	-	-
CaO	0.9	0.9	0.5	0.5	1	1.1	2.1	1.9	0.4	0.5	0.8
MgO	-	-	-	-	1.1	1.1	-	-	-	1.9	0.1
TiO ₂	-	-	-	-	2.3	2.5	2.5	4.4	-	-	-
Al ₂ O ₃	-	-	9.1	8.3	1.5	1.4	1.2	1.1	-	0.7	1.1
SiO ₂	0.9	0.7	0.4	0.5	0.7	0.5	0.4	0.5	-	0.3	0.4
P ₂ O ₅	-	-	-	-	-	-	-	-	0.2	1.8	1.5

Given are relative standard deviations in percent (1 RSD) of multiple analyses (> 50) using the electron microprobe (mainly as line scans across glass fragments) of several fragments of the individual glasses. Note that some of the high errors (e.g., Na and K in the TNT and CPX glasses) are mainly due to low concentrations of the element of interest close to the limit of detection with consequently poor counting statistics.

Table 4.
Homogeneity tests of all glasses using laser ablation ICP-MS: standard deviations of multiple analyses

	STDP3-1500	STDP3-150	STDP 5	TNT 150	TNT 1500	TNT 666	TNT 777	Cpx 666	Cpx 777	DAC 777	DAC 666
Li	0.84	1.67	1.07	1.20	0.26	1.02	7.82	1.49	0.69	0.77	0.65
Be	0.45	0.64	0.45	1.28	0.55	0.39	10.04	0.87	5.86	5.94	0.61
B	0.91	0.28	0.43	1.65	0.66	1.40	2.51	1.30	1.88	8.93	1.04
Cs	0.79	1.07	0.74	0.30	0.99	0.67	0.65	0.57	0.85	0.89	1.71
Rb	0.75	0.93	0.63	0.25	0.60	0.37	0.46	1.13	0.79	0.62	1.20
Ba	0.30	0.45	0.72	0.68	0.32	1.54	0.13	1.94	0.63	0.32	3.69
Sr	0.42	0.28	0.29	0.24	0.57	0.16	1.04	0.24	0.81	1.14	0.86
Ga	0.45	0.53	0.67	0.30	0.97	0.34	0.13	0.57	0.66	0.26	0.80
Pb	0.81	0.37	1.16	0.40	0.99	1.46	1.12	1.50	1.32	21.04	3.23
U	0.45	0.72	1.48	0.12	0.66	0.95	0.06	0.92	0.55	5.75	3.63
Th	0.55	0.61	1.28	0.15	1.04	3.62	0.37	3.32	0.29	0.27	4.28
Y	0.52	0.62	0.22	0.04	0.67	0.48	0.14	0.62	0.26	0.29	1.79
La	0.59	0.37	0.87	0.14	0.71	0.38	0.84	0.30	0.79	1.02	1.32
Ce	0.41	0.60	0.79	0.42	0.62	0.29	2.73	0.30	0.83	0.80	1.84
Pr	0.41	0.45	0.88	0.15	0.61	3.17	0.31	7.40	2.13	0.23	1.77
Nd	8.79	8.90	4.24	3.74	2.27	19.55	6.15	15.15	10.66	2.33	10.31
Sm	0.27	0.51	0.90	0.09	0.58	1.90	0.30	2.10	0.37	0.20	3.33
Eu	7.64	14.55	2.16	8.40	2.98	7.68	3.86	13.59	4.13	8.84	28.70
Gd	0.37	0.40	1.12	0.56	0.39	0.59	2.29	0.60	1.82	0.71	1.78
Er	6.51	12.73	4.89	1.98	2.82	9.70	10.54	21.83	2.53	7.80	6.73
Yb	5.45	3.99	3.85	5.32	1.78	7.39	1.30	11.04	1.79	4.84	5.59
Lu	0.70	0.44	1.23	0.23	0.87	1.89	0.10	2.44	0.04	0.16	2.59
Zr	0.48	1.30	0.42	0.17	0.53	0.33	0.15	0.26	0.52	0.78	0.80
Hf	0.50	0.53	1.40	0.14	0.59	0.58	2.32	0.68	2.72	2.59	2.22
Ta	0.68	0.39	1.19	0.13	0.69	1.01	0.20	1.79	0.20	0.31	2.14
Nb	0.62	0.57	0.58	0.09	0.36	0.09	0.25	0.66	0.34	0.24	1.83

Given are relative standard deviations (2 RSD, percent) of multiple analyses (mainly as multiple spots in lines across glass fragments) of several fragments of the individual glasses. Note that some of the high errors (e.g., Eu or Er in all glasses) are mainly due low concentrations of the element of interest close to the limit of detection, hence with consequently poor counting statistics. In this context it should be noted that the glasses have not been doped with either Eu, Nd or Er.

probe microanalysis profiles were performed across these fragments with spots spaced between 10 and 20 µm apart. Profiles ranged from about 200 µm to more than 2000 µm. Results of these profiles are given in Table 2 and reproducibility of the analytical results are indicated in Table 3.

Trace element homogeneity

In situ analytical techniques such as laser ablation ICP-MS or SIMS are the methods of choice to investigate the trace element homogeneity of the glasses. Several fragments of all glasses (including the DAC and

Table 5.
Results from homogeneity tests of some selected glasses using SIMS

Isotope (X)	TNT150 X ⁺ / ³⁰ Si ⁺	1 RSD	TNT1500 X ⁺ / ³⁰ Si ⁺	1 RSD	STDP5 X ⁺ / ⁴⁴ Ca ⁺	1 RSD	STDP3-150 X ⁺ / ³⁰ Si ⁺	1 RSD
⁸⁵ Rb	6.38E-03	0.77%	5.93E-02	0.44%	2.16E-02	0.49%	2.85E-03	1.35%
⁸⁸ Sr	3.07E-02	0.73%	2.55E-01	0.41%	9.33E-02	0.25%	1.50E-02	0.70%
⁸⁹ Y	3.72E-02	0.25%	3.85E-01	0.27%	1.29E-01	0.33%	1.78E-02	0.83%
⁹⁰ Zr	2.09E-02	0.68%	1.49E-01	0.25%	4.25E-02	0.43%	7.26E-03	1.49%
⁹³ Nb	1.79E-02	0.53%	1.49E-01	0.42%	4.78E-02	0.38%	7.22E-03	1.21%
¹³³ Cs	4.03E-03	0.95%	3.07E-02	0.86%	1.70E-02	0.65%	2.13E-03	1.07%
¹³⁸ Ba	1.00E-02	0.56%	9.48E-02	0.49%	3.61E-02	0.48%	4.14E-03	1.18%
¹³⁹ La	1.43E-02	0.91%	1.51E-01	0.65%	5.64E-02	0.36%	6.96E-03	0.93%
¹⁴⁰ Ce	1.43E-02	0.80%	1.44E-01	0.30%	5.46E-02	0.32%	6.86E-03	0.76%
¹⁴¹ Pr	1.69E-02	0.47%	1.80E-01	0.47%	6.42E-02	0.56%	7.86E-03	0.15%
¹⁴⁷ Sm	2.77E-03	1.19%	2.76E-02	0.80%	1.06E-02	0.56%	1.34E-03	1.31%
¹⁶⁰ Gd	3.30E-03	1.42%	3.33E-02	0.69%	1.40E-02	0.61%	1.84E-03	0.50%
¹⁷⁵ Lu	1.10E-02	1.03%	1.17E-01	0.62%	3.96E-02	0.52%	5.95E-03	0.28%
¹⁷⁸ Hf	1.64E-03	1.58%	1.77E-02	0.75%	5.83E-03	1.52%	1.03E-03	1.46%
¹⁸¹ Ta	2.73E-03	0.90%	2.77E-02	1.08%	1.02E-02	0.88%	1.73E-03	1.40%
²⁰⁸ Pb	3.64E-04	1.87%	3.56E-03	1.16%	3.51E-04	3.05%	6.24E-05	2.88%
²³² Th	3.59E-03	1.76%	3.89E-02	1.14%	1.91E-02	0.88%	2.91E-03	0.66%
²³⁸ U	3.88E-03	1.56%	3.99E-02	1.13%	1.59E-02	0.96%	2.20E-03	1.33%

Average values of the X⁺/³⁰Si or X⁺/⁴⁴Ca and their variation in percent (1 RSD) of all SIMS measurements. X refers to the isotope of interest which is ratioed against reference isotopes ⁴⁴Ca and ³⁰Si, e.g., the ⁸⁵Rb/³⁰Si⁺ ratio in TNT150 was 0.00638 ± 0.00005.

the CPX glasses) were analysed with LA-ICP-MS (Figure 1, Table 4). We express the variation across samples in terms of the relative standard deviation (RSD) of multiple analyses across several glass fragments in percent. We also performed some homogeneity tests on glasses using SIMS techniques (Figure 2). Since relevant microanalytical reference materials for phosphates and titanites were not available, we used ratios of doped trace elements ³⁰Si or ⁴⁴Ca to investigate homogeneity of our glass samples. As an example, Table 5 lists results from SIMS analyses of several fragments of the TNT150, TNT1500, STDP5 and STD3-150 glasses. We used the relative standard deviation (1s) as a measure of reproducibility. In summary, we observed that variations for all trace elements of interest (i.e., the ones which we had doped) were often much lower than 2% relative for both glasses with the notable exception of Pb which suffered from low ion yields during SIMS determination and consequently poor counting statistics.

In summary, electron microprobe analysis and detailed studies using SIMS and laser ablation ICP-MS indicated that the individual glass fragments were homogenous with respect to both major and all studied trace elements at the µm to mm scale. Repetitive measurements of most trace elements varied within the analytical uncertainties, that is, within a few percent.

Analytical results

Table 6 lists analytical results from all measurements on our eight glasses. The results include measurements with solution ICP-MS, laser ablation ICP-MS, and isotope dilution multi-collector ICP-MS.

Provisional recommended values

Table 7 lists provisional recommended values and other analytical results classified as information values. As our glasses were analysed with several different analytical techniques with different inherent uncertainties, we used the following rationale to determine which values were suitable for recommendation and which analytical data were of information value only. Preferred were data from isotope dilution multi collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) because of the excellent accuracy and reproducibility of the measurements. Unfortunately, we can only present measurements for selected number elements such as Zr, Hf, Nb, Ta and Lu. The MC-ICP-MS data for these elements were selected as recommended values.

Further measurements on our glasses were performed using solution ICP-MS and laser ablation ICP-MS. We chose to recommend analytical results from these

Table 6.
All analytical data ($\mu\text{g g}^{-1}$) for all glasses studied, including the uncertainties of the techniques used

n	LAM ANU TNT 666 4	2 RSD	ICP ACME TNT 666 2	2 RSD	LAM ANU TNT 777 4	2 RSD	ICP ACME TNT 777 2	2 RSD	LAM FRA TNT 777 2	2 RSD	LAM ANU Cpx 666 5	2 RSD	ICP ACME Cpx 666 2	2 RSD	LAM FRA Cpx 666 2	2 RSD
Li	51	1	53	5	0.18	0.01	0.4	0.1	-	-	66.8	1	63.3	6.3	-	-
Be	68.6	0.3	-	-	0.02	0	-	-	-	-	82.7	0.7	-	-	-	-
B	46.9	0.7	-	-	3.4	0.1	-	-	-	97.8	1.3	-	-	-	-	-
Cs	521	3	535	54	3.8	0	3.8	0.4	2	0.2	1063	6	926	93	848	16
Rb	5.85	0.02	7	0.7	330.6	1.5	287	29	311	7	8.3	0.1	6.8	0.7	5	0.6
Ba	13.5	0.2	19	1.9	1031.3	1.3	963	96	936	33	8.6	0.2	11	1.1	10	0.8
Sr	662	1	591	59	11	0.1	9	0.9	6	0.5	1287	3	1123	112	1091	24
Ga	20.3	0.1	4.3	0.4	481.1	0.6	100	-	530	15	673	4	100	-	490	7
Pb	910	13	1038	104	3.4	0	5.3	0.5	1.6	0.5	1693	25	1485	148	1234	66
U	2.5	0.02	9.2	0.9	1779	1	1752	175	1361	64	5.7	0.1	5.5	0.6	4	0.4
Th	0.32	0.01	4.5	0.5	1782	7	985	98	1160	65	1.1	-	1.4	0.1	3	0.6
Y	0.71	0.003	2.2	0.2	716.5	1	453	45	521	16	2.1	0.01	2.2	0.2	2	1
La	1042	4	1023	102.3	0.458	0.004	1	0.1	-	-	1304	4	1209	121	995	18
Ce	1080	3	1035	103.5	0.327	0.009	0.44	0.04	-	-	1452	4	1439	144	1255	33
Pr	0.15	0.005	3.3	0.3	995	3	939	94	788	36	-	-	-	-	-	-
Nd	0.04	0.007	0.1	0	0.15	0.01	0.4	0.04	-	-	-	-	-	-	-	-
Sm	0.19	0.004	3.5	0.4	1030	3	1008	101	805	42	-	-	-	-	6	1.4
Eu	-	-	1.1	-	-	-	0.3	0.03	-	-	-	-	1.1	-	-	-
Gd	1069	6	924	92	5.7	0.1	106.2	10.6	-	-	1325	8	1175	117	1011	31
Er	0.07	0.01	0.1	0.01	0.08	0.01	1.2	0.12	-	-	0.05	0.01	0.1	0.01	-	-
Tm	-	-	1.1	-	-	-	1.1	-	-	-	-	-	1.1	-	-	-
Yb	0.19	0.01	-	-	0.98	0.01	0.7	0.1	-	-	0.25	0.03	16.3	1.6	-	-
Lu	0.208	0.004	-	-	1343	1	-	-	834	42	0.76	0.02	1.1	0.1	1	0.1
Zr	667	2	-	-	16.99	0.03	-	-	9	1.3	772	2	661	66	621	17
Hf	1262	7	-	-	2.5	0.1	-	-	3	1.2	1457	10	1000	-	1200	37
Ta	3.29	0.03	-	-	1470	3	-	-	949	51	2.3	0.04	1.1	-	2	0.6
Nb	44.96	0.04	-	-	790	2	-	-	711	20	77	0.1	2	0.2	5	0.5

Table 6 (continued).
All analytical data ($\mu\text{g g}^{-1}$) for all glasses studied, including the uncertainties of the techniques used

n	LAM ANU Cpx 777 5	2 RSD	ICP ACME Cpx 777 2	2 RSD	LAM FRA Cpx 777 2	2 RSD	LAM ANU DAC 666 5	2 RSD	ICP ACME DAC 666 2	2 RSD	LAM FRA DAC 666 2	2 RSD	LAM ANU DAC 777 5	2 RSD	ICPMS ACME DAC 777 2	2 RSD
Li	64.9	0.4	60.9	6.1	-	-	72.9	0.5	69.8	7	-	73.7	0.6	68.7	6.9	
Be	0.2	0	-	-	-	-	83.2	0.5	-	-	-	0.47	0.03	-	-	
B	6.3	0.1	-	-	-	-	86.6	0.9	-	-	-	3.1	0.3	-	-	
Cs	2.5	0	2.8	0.3	2	0.1	1186	20	1160	116	1071	11	0.1	10.5	1.1	
Rb	697	5	615	61	602	12	12.5	0.2	12	1.2	9	889	5	883	88	
Ba	1259	8	1156	116	1269	21	2.9	0.1	5	0.5	8	1289	4	1323	132	
Sr	9	0.1	9	0.9	6.1	0.9	767	7	757	76	777	4.6	0.1	5	0.5	
Ga	5.19	0.03	5.3	0.5	89	4	638	5	100	-	499	9.66	0.02	10.3	1	
Pb	4.96	0.07	5.8	0.6	-	-	1698	55	1170	117	1316	5.1	1.1	6.4	0.6	
U	2051	11	1915	191	1932	50	5.2	0.2	6.9	0.7	3	2167	124	1946	195	
Th	1952	6	1961	196	1710	23	1.39	0.06	4.9	0.5	7	2183	6	1625	163	
Y	766	2	725	73	652	9	1.76	0.03	2.3	0.2	2	814	2	829	83	
La	13.3	0.1	14	1.4	9	1	1206	16	1301	130	1143	3.47	0.04	4	0.4	
Ce	2.91	0.02	3.6	0.4	2.1	0.8	1244	23	1470	147	1183	2.7	0.02	3.3	0.3	
Pr	0.188	0.004	0.3	0.03	-	-	1.89	0.03	2.1	0.2	2	1269	3	1360	136	
Nd	0.24	0.03	0.3	0.03	-	-	0.09	0.01	0.2	0.02	-	0.29	0.01	0.3	0.03	
Sm	1139	4	1237	124	1166	12	2.4	0.1	3.1	0.3	14	1246	2	1465	146	
Eu	0.14	0.01	0.4	0.04	-	-	0.02	0.01	1	-	-	0.15	0.01	0.5	0.1	
Gd	0.62	0.01	1.1	0.1	-	-	1221	22	1249	125	1197	10.1	0.1	168	17	
Er	0.21	0.01	1.6	0.16	-	-	0.047	0.003	1	-	-	0.24	0.02	1.8	0.18	
Tm	-	-	0.1	0.01	-	-	-	-	1	-	-	-	-	0.1	0.01	
Yb	1.38	0.02	1.6	0.2	-	-	0.21	0.01	173	1.7	-	1.5	0.1	1.8	0.2	
Lu	1455	1	1437	144	1178	12	0.81	0.02	1.5	0.2	5	1592.6	2.6	1645	165	
Zr	12.5	0.1	-	-	9	1.5	706	6	786	79	756	7.6	0.1	8.3	0.8	
Hf	1.4	0.04	-	-	5.1	2.3	1374	31	1000	-	1464	2.1	0.1	4.2	0.4	
Ta	1613	3	-	-	1372	24	3	0.1	5.2	0.5	8	1854	6	2000	-	
Nb	838	3	-	-	844	11	3.3	0.1	3.8	0.4	6	993	2	726	73	

Table 6 (continued).
All analytical data ($\mu\text{g g}^{-1}$) for all glasses studied, including the uncertainties of the techniques used

n	LAM FRA DAC 777 2	2 RSD	LAM ANU TNT 150 3	2 RSD	MC MS TNT 150 1	2 RSD	MC MS TNT 150 1	2 RSD	ICP ACME TNT 150 2	2 RSD	LAM ANU TNT 1500 6	2 RSD	ICP ACME TNT 1500 2	2 RSD	MC MS TNT 1500 1	2 RSD
Li	-	-	91.1	1.1	-	-	-	-	95	10	175.2	0.5	190	19	-	-
Be	-	-	144	2	-	-	-	-	-	-	203	1	-	-	-	-
B	-	-	66	1	-	-	-	-	-	-	144	1	-	-	-	-
Cs	7	2	100.2	0.3	-	-	-	-	95	9	709	7	700	70	-	-
Rb	743	23	121.6	0.3	-	-	-	-	107	11	1058	6	1061	106	-	-
Ba	1192	43	156	1	-	-	-	-	154	15	1359	4	1335	134	-	-
Sr	3	2	149.5	0.4	-	-	-	-	131	13	1378	8	1264	126	-	-
Ga	76	3	2.97	0.01	-	-	-	-	1	0.1	25.9	0.3	3.3	0.3	-	-
Pb	5	1	82.8	0.3	-	-	-	-	96	10	799	8	903	90	-	-
U	1964	165	140	0.2	-	-	-	-	150	15	1336	9	1396	140	-	-
Th	1884	101	139	0.2	-	-	-	-	103	10	1413	15	1215	122	-	-
Y	698	21	144	0.1	-	-	-	-	94	9	1441	10	1097	110	-	-
La	5	1	119.2	0.2	-	-	-	-	113	11	1205	9	1141	114	-	-
Ce	3	2	139.2	0.6	-	-	-	-	110	11	1347	8	1291	129	-	-
Pr	1143	49	132.1	0.2	-	-	-	-	113	11	1335	8	1349	135	-	-
Nd	-	-	0.41	0.02	-	-	-	-	0.4	0.04	0.55	0.01	0.6	0.06	-	-
Sm	1173	39	135.8	0.1	-	-	-	-	117	12	1251	7	1304	130	-	-
Eu	-	-	0.028	0.002	-	-	-	-	1.1	-	0.18	0.01	0.5	0.1	-	-
Gd	6	5	138.1	0.8	-	-	-	-	114	11	1285	5	1273	127	-	-
Er	-	-	0.059	0.001	-	-	-	-	0.2	0.02	0.27	0.01	1.7	0.17	-	-
Tm	-	-	-	-	-	-	-	-	1.1	-	-	-	0.1	0	-	-
Yb	-	-	0.21	0.01	-	-	-	-	1.9	0.2	1.62	0.03	179	1.8	-	-
Lu	1313	65	138.1	0.3	143.4	1.4	142.9	1.4	-	-	1373	12	-	110	1469	15
Zr	10	5	198.7	0.3	224.6	2.2	226.1	2.3	-	-	1396	7	-	103	1622	16
Hf	15	11	129.6	0.2	149	1	151	2	-	-	1299	8	-	-	1611	16
Ta	1634	79	146.3	0.2	149.9	1.5	150.8	1.5	-	-	1447	10	-	112	1489	15
Nb	1044	30	185.3	0.2	174	7	164	7	-	-	1463	5	-	85	1357	54
¹⁷⁶ Hf/	-	-	-	-	0.282292	-	-	-	-	-	-	-	-	-	-	-
¹⁷⁷ Hf	-	-	-	-	0.000006	0.000008	0.282318	0.000008	-	-	-	-	-	-	0.282326	0.000007
¹⁷⁶ Lu/	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
¹⁷⁷ Hf	-	-	-	-	0.136	0.001	0.134	0.001	-	-	-	-	-	-	0.129	0.001

Table 6 (continued).

All analytical data ($\mu\text{g g}^{-1}$) for all glasses studied, including the uncertainties of the techniques used

n	LAM ANU STDP3 150 4	2 RSD	ICP ACME STDP3 150 2	2 RSD	LAM ANU STDP3 1500 5	2 RSD	LAM ANU STDP 5 5	2 RSD	ICP ACME STDP 5 2	2 RSD
Li	12.8	0.2	11.8	1.2	99	1	88	1	89	9
Be	10.7	0.1	-	-	99.5	0.4	88.3	0.4	-	-
B	65.6	0.2	-	-	159	1	59.1	0.3	-	-
Cs	148	1.6	136	14	1495	12	1268	9	1441	144
Rb	153	1.4	136	14	1545	12	1310	8	1585	158
Ba	153	0.7	157	16	1520	5	1396	10	1481	148
Sr	200	0.6	193	19	1474	6	1420	4	1448	145
Ga	17	0.1	13	1	42.9	0.2	37.4	0.3	5	0.5
Pb	158	0.6	145	14	1584	13	1327	15	1501	150
U	145	1	143	14	1446	7	1385	21	1371	137
Th	142	0.9	156	16	1434	8	1423	18	1046	105
Y	134	0.8	142	14	1426	7	1475	3	1470	147
La	118	0.4	119	12	1241	7	1214	11	1219	122
Ce	148	0.9	145	15	1522	6	1468	12	1533	153
Pr	136	0.6	127	13	1425	6	1390	12	1496	150
Nd	0.19	0.02	0.3	0.03	0.4	0.04	0.25	0.01	0.55	0.06
Sm	127	1	127	13	1282	4	1224	11	1467	147
Eu	-	-	0.1	0.01	0.16	0.01	0.147	0.003	0.5	0.1
Gd	125	1	123	12	1281	5	1315	15	1434	143
Er	0.05	0.01	0.2	0.02	0.23	0.02	0.21	0.01	1.7	0.2
Tm	-	-	0.1	-	-	-	-	-	0.1	0.01
Yb	0.2	0.01	1.9	0.2	1.5	0.1	1.5	0.1	19	2
Lu	136	1	138	14	1407	10	1439	18	1419	142
Zr	133	2	151	15	1301	6	1335	6	-	-
Hf	129	1	161	16	1306	7	1344	19	-	-
Ta	148	1	193	19	1518	10	1463	17	-	-
Nb	149	1	143	14	1521	9	1285	8	-	-

ICP: results from solution ICP-MS measurements, LAM: results from laser ablation ICP-MS measurements, MC: results from isotope dilution multi-collector ICP-MS measurements. Given are average values from numerous individual measurements (n = number of analyses) with associated RSDs of the analytical techniques. Two analyses from isotope dilution multi-collector ICP-MS of the TNT150 samples are given as individual results. FRA: University of Frankfurt Germany; MS: University of Münster, Germany; ACME: ACME Laboratories, Vancouver, Canada; ANU: Australian National University, Canberra, Australia.

Table 7.

Selected provisional recommended values ($\mu\text{g g}^{-1}$) and some other analytical results ($\mu\text{g g}^{-1}$) with information value only for the glasses

	TNT 666 Recommended value	2 RSD	Information value	2s	TNT 777 Recommended value	2 RSD	Information value	2 RSD	CPX 666 Recommended value	2 RSD	Information value	2 RSD
Li	52	1.7	-	-	-	-	-	-	65	2.5	-	-
Be	-	-	69	0.3	-	-	-	-	-	-	82.7	0.7
B	-	-	47	0.7	-	-	-	-	-	-	97.8	1.3
Cs	528	10.2	-	-	-	-	3	1	946	109	-	-
Rb	6.4	0.8	-	-	309	22	-	-	7	1.6	-	-
Ba	16.2	3.9	-	-	977	49	-	-	10	1.2	-	-
Sr	626	50	-	-	-	-	8.7	2.5	-	-	1167	105
Ga	-	-	12	11	506	35	-	-	-	-	581	129
Pb	974	90	-	-	-	-	3.4	1.8	-	-	1470	230
U	-	-	5.8	4.7	1630	234	-	-	-	-	5	0.9
Th	-	-	0.32	0.01	-	-	1309	419	-	-	2	1
Y	-	-	1.5	1.1	-	-	564	137	2	0.1	-	-
La	1032	13	-	-	-	-	0.73	0.38	-	-	1169	158
Ce	1058	32	-	-	-	-	0.38	0.08	-	-	1382	110
Pr	-	-	-	-	967	40	-	-	-	-	0.21	0.13

Table 7 (continued).

Selected provisional recommended values ($\mu\text{g g}^{-1}$) and some other analytical results ($\mu\text{g g}^{-1}$) with information value only for the glasses

	TNT 666 Recommended value	2 RSD	Information value	2s	TNT 777 Recommended value	2 RSD	Information value	2 RSD	CPX 666 Recommended value	2 RSD	Information value	2 RSD
Nd	-	-	0.07	0.04	-	-	0.27	0.18	-	-	0.08	0.03
Sm	-	-	-	-	1019	16	-	-	-	-	-	-
Eu	-	-	-	-	-	-	0.15	0.21	-	-	-	-
Gd	996	103	-	-	-	-	-	-	1170	157	-	-
Tb	-	-	-	-	-	-	-	-	-	-	-	-
Dy	-	-	-	-	-	-	-	-	-	-	-	-
Ho	-	-	-	-	-	-	-	-	-	-	-	-
Er	-	-	-	-	-	-	-	-	-	-	0.07	0.04
Tm	-	-	-	-	-	-	-	-	-	-	-	-
Yb	-	-	0.19	0.01	-	-	1	0.2	-	-	-	-
Lu	-	-	0.21	0	1343	1	-	-	-	-	1	0.2
Zr	667	2	-	-	16.99	0.03	-	-	685	78	-	-
Hf	1262	7	-	-	-	-	2.5	0.1	1329	182	-	-
Ta	3.29	0.03	-	-	1470	3	-	-	-	-	2.1	0.2
Nb	44.96	0.04	-	-	790	2	-	-	-	-	4.9	2.9
	CPX 777 Recommended value	2 RSD	Information value	2 RSD	DAC 666 Recommended value	2 RSD	Information value	2 RSD	DAC 777 Recommended value	2 RSD	Information value	2 RSD
Li	63	2.9	-	-	71	2	-	-	71	3.5	-	-
Be	-	-	-	-	-	-	83.2	0.5	-	-	0.5	0.03
B	-	-	6.3	0.1	-	-	86.6	0.9	-	-	3.1	0.3
Cs	-	-	2.4	0.4	1139	60	-	-	-	-	10	2.2
Rb	638	52	-	-	-	-	11.2	1.9	838	83	-	-
Ba	1228	63	-	-	-	-	5.3	2.6	1268	68	-	-
Sr	-	-	8	1.7	767	10	-	-	-	-	4	1.1
Ga	-	-	5	0.1	568	98	-	-	-	-	10	0.5
Pb	-	-	5	0.6	1394	273	-	-	-	-	5	0.8
U	1966	74	-	-	-	-	5	2	2025	123	-	-
Th	1874	142	-	-	-	-	4	2.8	1898	279	-	-
Y	714	58	-	-	2	0.3	-	-	780	72	-	-
La	-	-	12	2.7	1217	80	-	-	-	-	4	0.8
Ce	-	-	2.9	0.8	1299	151	-	-	-	-	3	0.3
Pr	-	-	0.2	0.1	-	-	2	0.1	1258	109	-	-
Nd	-	-	0.27	0.04	-	-	-	-	-	-	0.29	0.01
Sm	1181	50.8	-	-	-	-	3	0.5	1294	152	-	-
Eu	-	-	-	-	-	-	-	-	-	-	-	-
Gd	-	-	1	0.3	1222	26	-	-	-	-	-	-
Tb	-	-	-	-	-	-	-	-	-	-	-	-
Dy	-	-	-	-	-	-	-	-	-	-	-	-
Ho	-	-	-	-	-	-	-	-	-	-	-	-
Er	-	-	-	-	-	-	-	-	-	-	-	-
Tm	-	-	-	-	-	-	-	-	-	-	-	-
Yb	-	-	1.5	0.2	-	-	-	-	-	-	1.6	0.2
Lu	1357	155	-	-	-	-	-	-	1517	179	-	-
Zr	-	-	11	2.5	749	41	-	-	-	-	9	1.2
Hf	-	-	3	2.6	1419	63	-	-	-	-	3	1.5
Ta	-	-	1613	3	-	-	5	2.5	1744	156	-	-
Nb	841	4.2	-	-	-	-	4	1.4	921	171	-	-

Table 7 (continued).

Selected provisional recommended values ($\mu\text{g g}^{-1}$) and some other analytical results ($\mu\text{g g}^{-1}$) with information value only for the glasses

	TNT 150	2 RSD	Information value	2 RSD	TNT 1500	2 RSD	Information value	2 RSD	STDP3 150	2 RSD	Information value	2 RSD
	Recommended value				Recommended value				Recommended value			
Li	93	3.1	-	-	-	-	183	11	12	1	-	-
Be	-	-	144	2	-	-	203	1	-	-	10.7	0.1
B	-	-	66	1	-	-	144	1	-	-	65.6	0.2
Cs	97	3.9	-	-	705	6	-	-	142	9	-	-
Rb	114	10	-	-	1059	3	-	-	145	12	-	-
Ba	155	2	-	-	1347	17	-	-	155	3	-	-
Sr	140	13	-	-	1321	80	-	-	196	5	-	-
Ga	-	-	2	1.4	-	-	-	-	15	3	-	-
Pb	89	9	-	-	851	73	-	-	151	9	-	-
U	145	7	-	-	1366	42	-	-	144	1	-	-
Th	121	26	-	-	1314	140	-	-	149	10	-	-
Y	119	35	-	-	-	-	1269	243	138	6	-	-
La	116	4	-	-	1173	45	-	-	118.7	0.4	-	-
Ce	125	21	-	-	1319	40	-	-	147	2	-	-
Pr	123	13	-	-	1342	10	-	-	132	6	-	-
Nd	-	-	0.403	0.004	-	-	0.58	0.03	-	-	0.2	0.1
Sm	126	13	-	-	1278	37	-	-	127.4	0.03	-	-
Eu	-	-	-	-	-	-	-	-	-	-	-	-
Gd	126	17	-	-	1279	9	-	-	124	2	-	-
Tb	-	-	-	-	-	-	-	-	-	-	-	-
Dy	-	-	-	-	-	-	-	-	-	-	-	-
Ho	-	-	-	-	-	-	-	-	-	-	-	-
Er	-	-	-	-	-	-	-	-	-	-	-	-
Tm	-	-	-	-	-	-	-	-	-	-	-	-
Yb	-	-	-	-	1.62	0.03	-	-	-	-	-	-
Lu	143.2*	1.4	-	-	1469*	15	-	-	137	1	-	-
Zr	225.4*	2.2	-	-	1622*	16	-	-	142	12	-	-
Hf	150*	2	-	-	1611*	16	-	-	145	23	-	-
Ta	150.4*	1.5	-	-	1489*	15	-	-	170	32	-	-
Nb	169*	7	-	-	1357*	54	-	-	146	4	-	-

	STDP3 1500	2 RSD	Information value	2 RSD	STDP 5	2 RSD	Information value	2 RSD
	Recommended value				Recommended value			
Li	-	-	99	1	89	1	-	-
Be	-	-	99.5	0.4	-	-	88.3	0.4
B	-	-	158.6	1.4	-	-	59.1	0.3
Cs	-	-	1495	12	1355	122	-	-
Rb	-	-	1545	12	1447	194	-	-
Ba	-	-	1520	5	1438	60	-	-
Sr	-	-	1474	6	1434	20	-	-
Ga	-	-	42.9	0.2	-	-	-	-
Pb	-	-	1584	13	1414	123	-	-
U	-	-	1446	7	1378	10	-	-
Th	-	-	1434	8	1235	266	-	-
Y	-	-	1426	7	1473	4	-	-
La	-	-	1241	7	1216	4	-	-
Ce	-	-	1522	6	1501	46	-	-
Pr	-	-	1425	6	1443	75	-	-
Nd	-	-	0.4	0.04	-	-	-	-
Sm	-	-	1282	4	1346	172	-	-
Eu	-	-	0.16	0.01	-	-	-	-
Gd	-	-	1281	5	1375	84	-	-
Tb	-	-	-	-	-	-	-	-
Dy	-	-	-	-	-	-	-	-
Ho	-	-	-	-	-	-	-	-
Er	-	-	0.23	0.02	-	-	-	-
Tm	-	-	-	-	-	-	-	-
Yb	-	-	1.5	0.1	-	-	-	-
Lu	-	-	1407	10	1429	14	-	-
Zr	-	-	1301	6	1335	6	1335	6
Hf	-	-	1306	7	1344	19	1344	19
Ta	-	-	1518	10	1463	17	1463	17
Nb	-	-	1521	9	1285	8	1285	8

A selection of preliminary recommended values for the silicate, phosphate and titanite glasses studied. Other values with information value (italics) only are also given. Recommended values were only assigned to glasses when results from several analytical techniques agreed with each other to a variance of less than 15%. *: recommended values based on isotope dilution MC-ICP-MS measurements only.

Figure 1. Homogeneity tests of all glasses using laser ablation ICP-MS.
Standard deviation is 2 RSD (percent) of multiple analyses.

Figure 2. Homogeneity tests of some selected glasses using SIMS.
Standard deviation is 1 RSD (percent) of multiple analyses.

measurements if results from several analytical techniques (mainly solution ICP-MS and LA-ICP-MS) agreed within 15%. In this case, the recommended values consist of weighted averages with the associated standard deviations. Also, in cases where we have only measurements using one analytical technique, i.e., in the case of Be and B, or the STDP3-1500 glass, these data were regarded as information values only.

Possible applications

Our new glasses may be used as reference samples for the trace element analysis of accessory minerals such as apatite, titanite or other phosphates or titanites. This may be of interest to those who study the behaviour of trace elements in igneous and metamorphic rocks or those who aim to date the crystallisation of accessory minerals. Recent advances in *in situ* dating techniques with ion probe or laser ablation ICP-MS has renewed the interest in accessory minerals especially titanite and apatite. Our new reference materials may prove helpful during the characterisation of these minerals. Further, as our TNT glasses have been characterised for trace element concentrations as well as in $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ isotopic data, they may also be of interest to those who intend to measure the Hf isotopic composition of titanites.

Furthermore, apatite and titanite are important minerals used in fission-track dating (e.g., Hasebe *et al.* 2004). As there is no accepted apatite reference material which could be used to calibrate U or Th contents, our STDP glasses may be of use for the measurement of U and Th. During the course of this study it became apparent that U concentrations measured by SIMS gave highly consistent results. For example, U/Ti SIMS sensitivity factors for TNT150 and TNT1500 agreed within 12% (2s) with those derived from measurements of USGS and MPI-DING glasses (Luvizotto *et al.* in prep). This may be taken as evidence for only weak, if any, matrix dependency of U concentration measured with SIMS, using the conditions employed in this study. We believe that this should encourage more advanced fission-track dating studies where U concentrations in apatite are determined *in situ* close to the area of fission track counting rather than from conventional bulk neutron activation analysis (Cox *et al.* 2000, Hasebe *et al.* 2004). Both the titanite glasses (TNT150 and TNT1500) and the apatite glasses (STDP5 and STDP3-150) are homogeneous within 3% for all measured trace elements (Tables 4 and 5). These glasses are therefore ideal candidates for reference materials for apatite and titanite fission track dating (Hasebe *et al.* 2004). We are willing to share small amounts of the presented reference materials to the scientific community on request (stephan.klemme@ed.ac.uk or stefan.prowatke@swarovski.com), reserving the right to charge a fee to cover costs.

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