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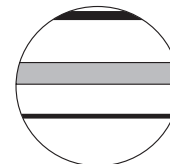
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High spatial resolution electron probe microanalysis of tephra and melt inclusions without beam-induced chemical modification

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Abstract

Wavelength dispersive analysis of tephra grains and melt inclusions by EPMA has been carried out using a focused beam of 3 μm diameter without detected loss of sodium or potassium in standard glasses, including anhydrous basalts, a slightly hydrated rhyolite and a sodium-rich intermediate composition. The ability to make analyses without chemical modification is strongly dependent upon current density at the analysis site. Analysis with narrow beams requires extremely low beam currents that are normally associated with energy dispersive analysis. Experiments indicate that a value of 0.1 nA/ μm^2 must not be exceeded, at least for moderately hydrated samples, if sodium loss is to be avoided. High resolution analysis without beam-induced analytical artefacts enables fully quantitative analysis of very distal and/or highly vesicular tephra and very small melt inclusions without the need to use post-analysis corrections. This development has enabled high quality analyses from crypto-tephra layers that were previously impossible to analyse, and has removed the potential for sampling bias within mixed tephra layers by making (in most cases) tephra grains accessible for analysis. The use of focused beams also increases the level of automation, and hence the cost-effectiveness of data collection. The current data suggest limits to the applicability of the beam conditions reported, and that they may lead to alkali loss in compositions most prone to beam-induced modification such as significantly hydrated and/or sodic tephra.

Keywords

crypto-tephra, current density, EPMA, high spatial resolution, Na-loss

Introduction

Chemical analysis of tephra layers and melt inclusions is a vital component of a wide range of research including investigations of palaeoclimate, the environmental impact of eruptions, archaeological studies, and volcanological research into eruption causes, conduit and eruption processes. Recognition of products from individual eruptions over the widest geographic areas enables better modelling of atmospheric dispersal of tephra and understanding of environmental impacts, through improved accuracy in tephra volume estimates and from measurement of volatile contents, the atmospheric loading of sulphur, halogens (by EPMA) and H_2O and CO_2 (by SIMS). Identification of tephra within their entire preserved fallout areas maximises the resolution of tephrostratigraphies and permits tephrochronological correlations across the widest possible areas. This requires analysis of proximal tephra and lavas, and of distal tephra from diverse depositional environments, including peat bogs, marine and lacustrine sediments, and glacial ice.

Distal tephra present special challenges, principally because of small grain sizes, which together with sometimes high degrees of vesicularity and crystallisation limit the size of target areas for analysis, commonly to less than 10 μm across. This paper reports analytical protocols developed for the analysis of very small tephra grains and melt inclusions without incurring beam-induced chemical modification.

Tephra analysis by EPMA

Electron probe microanalysis (EPMA) remains at the forefront of tephra analysis because of the technique's high spatial resolution, good analytical sensitivity, precision and accuracy, the ability to discriminate between source volcanoes and between tephra from single volcanoes via analysis of ten elements, the rapidity and cost-effectiveness of data collection, and the wide availability published analytical data, and of data bases of tephra analyses that assist with the identification of individual layers (e.g. Edingburgh's TephraBase, Newton, 1996; Newton et al., 2007). Associated with the technique however, is the well-documented problem of chemical modification during analysis if the analytical conditions are not chosen with care, a problem especially affecting hydrous and alkali-rich samples (e.g. Hunt and Hill, 1993, 2001; Morgan and London, 1996, 2005; Nielsen and Sigurdsson, 1981; Spray and Rae, 1995; Vassamillet and Caldwell, 1969). Beam damage

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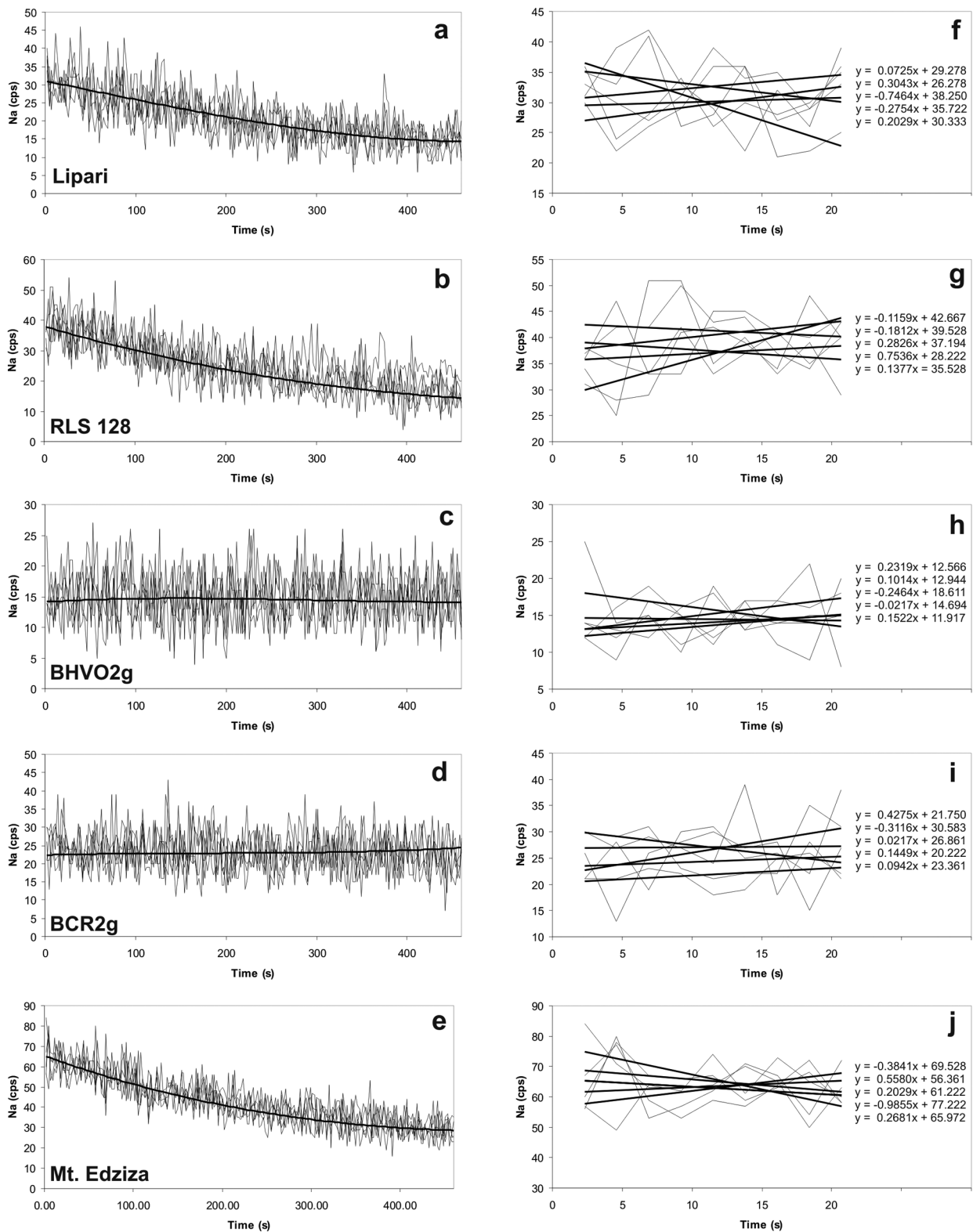


Figure 1. Count rates for Na over periods of 460 s and 20 s measured with beam diameter of 3 μm and current of 0.5 nA

occurs through a combination of charging and heating within the sample caused by the incident electrons. This causes depletion of alkalis, especially Na, within the upper 0.5–>1 μm of the sample and higher concentrations in a layer immediately below this (e.g. Goodhew and Gulley, 1974; Humphreys et al., 2006). The effect is critically dependent on the beam conditions used and also on the composition of the sample. Migration of the alkalis away from

the volume from which x-rays are produced during electron probe microanalysis also causes, in addition to deficits in measured Na and K, erroneously high apparent concentrations of other elements, most notably Si and Al (e.g. Morgan and London, 1996).

Of the various strategies that have been successfully employed in previous research to prevent or correct for Na loss during EPMA analysis, the most common has been the use of diffuse

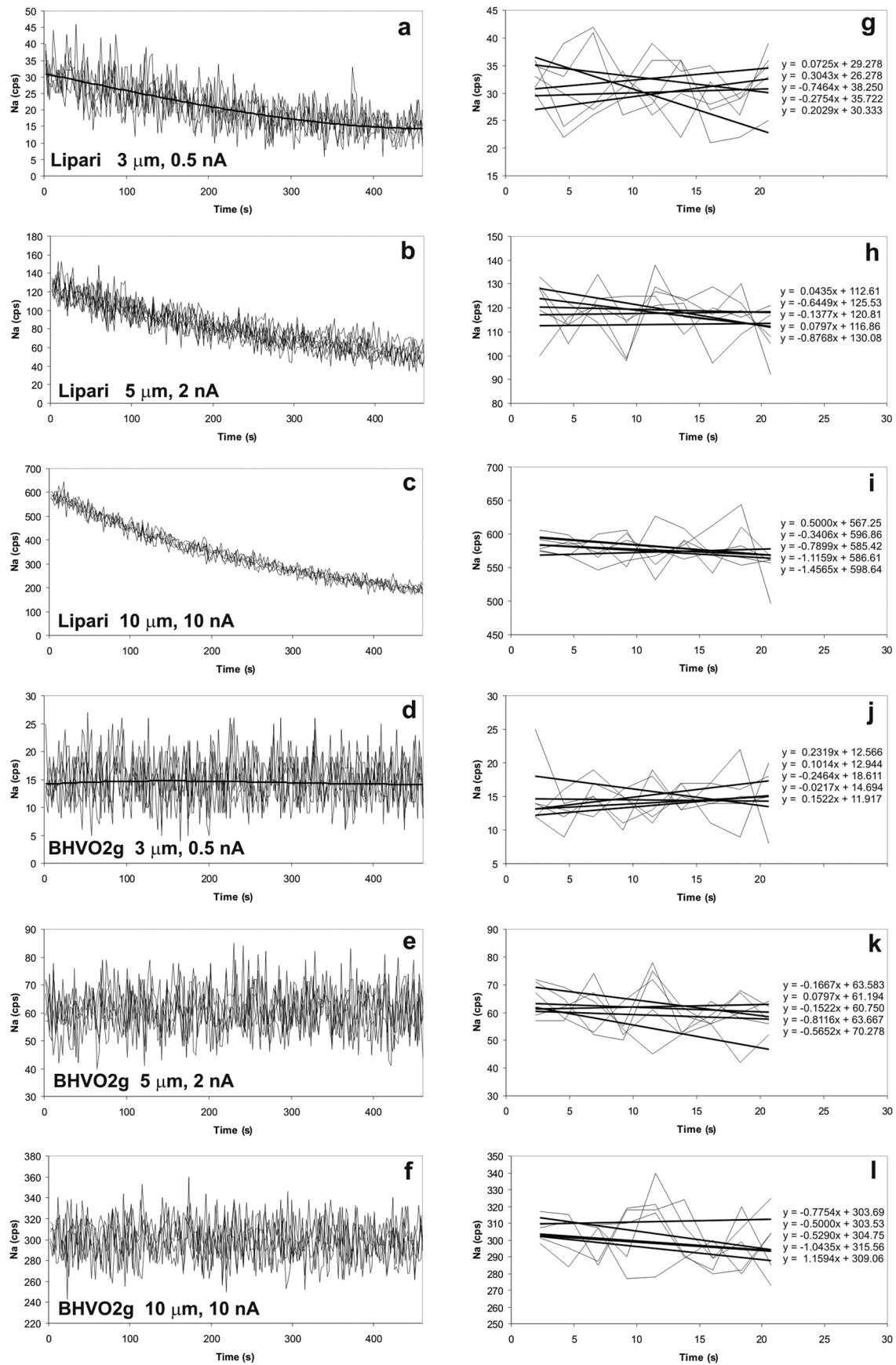


Figure 2. Count rates for Na for the Lipari and BHVO2g standard glasses over periods of 460 s and 20 s measured with beam conditions of 3 μm diameter and current of 0.5 nA; 5 μm and current of 2 nA, and 10 μm and current of 10 nA

and/or rastered electron beams covering areas of at least 10–20 μm across (Hunt and Hill, 2001; Morgan and London, 2005). This prevents Na-loss, but limits the types of samples that can be

analysed. Empirical measurement of Na losses with continuous exposure to electron beams have been used to calculate ‘zero time’ Na contents in samples susceptible to beam damage (Jbara

Table 1. Beam and spectrometer settings and other set-up parameters

Beam diameter	Beam current (nA) (Current density (nA/μm ²))		Spectrometer settings and order of analysis				
3 μm	0.5	(0.071)	Sp1 TAP Al	Sp2 LLIF	Sp3 LPET	Sp4 PET	Sp5 LTAP Na
	2	(0.283)	Si	Fe	K Ca	K Ca	Mg
	80	(4.074)	F	Mn	Cl P S Ti	Cl P S Ti	F
5 μm	2	(0.102)	Sp1 TAP Al Si	Sp2 LLIF Fe	Sp3 LPET K Ca	Sp4 PET K Ca	Sp5 LTAP Na Mg
	80	(4.074)	F	Mn	Cl P S Ti	Cl P S Ti	F
5 μm, High Na	0.7	(0.036)	Sp1 TAP Al	Sp2 LLIF	Sp3 LPET	Sp4 PET	Sp5 LTAP Na
	2	(0.102)	Si	Fe	K Ca	K Ca	Mg
	80	(4.074)	F	Mn	Cl P S Ti	Cl P S Ti	F
Calibration Standards	F (MgF ₂), Na (jadeite), Mg (MgAl spinel), Al (BIR-1g glass), Si (wollastonite), P (apatite), S (pyrite; baryte), Cl (NaCl), K (orthoclase), Ca (wollastonite), Ti (rutile), Mn (Mn metal), Fe (synthetic fayalite).						

et al., 1995; Nielsen and Sigurdsson, 1981). Software to calculate zero time values is available for Cameca instruments. The compositional dependence on rates of Na loss (Figures 1 and 2; Morgan and London, 2005) requires recalibration of these loss parameters for new samples. A less commonly applied method is cooling the sample (Jbara et al., 1995; Kearns et al., 2002; Nielsen and Sigurdsson, 1981). A cold stage is not a standard feature on current electron probe microanalysers, requiring customisation using components available from additional manufacturers.

The approach taken by the author has been to avoid Na loss whilst utilising the standard capabilities of the Cameca SX100 instrument, without resorting to custom-made hardware or software, in order to produce analytical protocols that can be implemented as widely as possible among the research community.

The key parameter in the avoidance of beam-induced chemical modification is the current density within the sample at the analysis location. Current density is optimised by adopting the best combination of beam current and diameter (Morgan and London, 2005). Previous work by these authors and others (e.g. Hunt and Hill, 2001) recommended the use of current densities of <0.01 nA/μm² for anhydrous glasses and <0.006 nA/μm² for more beam-sensitive materials, using beam diameters of 10 μm or greater.

Analytical conditions

Experiments were carried out using the Cameca SX100 electron probe microanalyser at the School of Geosciences, University of Edinburgh. This instrument is equipped with five WD spectrometers, and operates via Cameca's Windows-based PeakSight software (Version 4.2). Beam diameter was measured using a secondary electron image of the contamination spot deposited on a Lipari glass standard at 2 nA during a 20 s period. All analyses

were carried out at 15 kV. Data reduction used the X-Phi method within Cameca's PeakSight software. Optimised experimental conditions for a beam diameter 3 μm and for analysis of the high Na Edziza tephra using a 5 μm diameter beam are listed in Table 1. Cameca's PeakSight software provides the ability to apply up to four separate beam conditions during the course of a single analysis. This is an important attribute for high resolution analysis of Na-rich samples as Na and Si or Al can be measured simultaneously at a very low current, with the usual two currents applied in addition for the remaining elements. For the 5 μm diameter setup, counting times on peak were 20 s and on background 10 s except for fluorine, (50 s + 40 s), titanium (30 s + 15 s), manganese (50 s + 40 s) and iron (40 s + 20 s). For the 3 μm diameter setup, all counting times were as for the 5 μm setup except Al and Mg (30 s + 15 s). The counting times used for the 3 μm diameter setup were used for the high Na 5 μm diameter setup. For all elements, the K α line was measured. Analytical sensitivity was increased and counting times and measurement errors reduced at the low beam currents used by making simultaneous measurement of F, P, S, Cl, K, Ca and Ti on two spectrometers.

Analyses of well-characterised, internationally used glass secondary standards of rhyolitic (Lipari, RLS128) and basaltic (BHVO2g, BCR2g) compositions were carried out under a range of beam conditions. Analyses were made from the large pieces used as secondary standards during analytical runs, and on the same glasses crushed to small grain sizes that mimic those of fine-grained distal tephra layers (except BHVO2g, for which surplus for crushing was not available). Grains with maximum dimensions of 10–40 μm were selected within the crushed samples for analysis. Analyses of an intermediate composition tephra containing 8.2 wt.% Na₂O (Mt Edziza Sheep Track, supplied for the INTAV inter-lab tephra analysis study (Kuehn et al., forthcoming), and

Table 2a. Data for Lipari. Standard block $n=50$; crushed standard $n=26$

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
Av.	74.24	0.08	12.92	1.50	0.07	0.04	0.74	4.01	5.13	0.01	99.09
St.Dev.	0.71	0.02	0.57	0.19	0.02	0.02	0.08	0.37	0.21	0.01	
Det. Lim.		135			274	279				110	
Crushed	73.90	0.08	13.07	1.53	0.07	0.04	0.75	4.18	5.16	0.00	99.35
St.Dev.	0.71	0.01	0.53	0.17	0.01	0.02	0.07	0.41	0.23	0.00	
XRF ^a	74.03	0.08	12.72	1.73	0.08	0.00	0.72	4.06	5.18	0.00	98.96

Table 2b. Data for RLS-128. Standard block $n=30$; crushed standard $n=12$

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
Av.	76.10	0.21	11.42	2.18	0.16	0.06	0.10	5.20	4.54	0.00	100.1
St.Dev.	0.74	0.01	0.53	0.22	0.02	0.02	0.05	0.40	0.21	0.01	
Det. Lim.		135			450	320				180	
Crushed	75.74	0.21	11.21	2.05	0.16	0.06	0.12	5.24	4.48	0.00	99.80
St.Dev.	0.72	0.01	0.47	0.20	0.02	0.02	0.05	0.45	0.21	0.01	
USGS ^b	76.12	0.17	11.28	2.23	0.16	0.06	0.11	5.35	4.58	0.00	100.5

Table 2c. Data for BHVO2g. Standard block $n=40$

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
Av.	49.98	2.85	13.65	10.99	0.17	7.24	11.39	2.29	0.51	0.26	99.38
St.Dev.	0.61	0.03	0.69	0.46	0.04	0.17	0.28	0.33	0.08	0.03	
Det. Lim.					490				550	185	
USGS ^c	49.90	2.73	13.50	11.07	0.17	7.23	11.40	2.22	0.52	0.27	99.15

Table 2d. Data for BCR2g. Standard block $n=25$; crushed standard $n=11$

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
Av.	54.95	2.36	13.79	11.77	0.20	3.61	7.02	3.29	1.80	0.36	99.11
St.Dev.	0.64	0.02	0.60	0.48	0.02	0.10	0.22	0.35	0.13	0.01	
Det. Lim.					490				550	185	
Crushed	54.59	2.32	13.68	12.27	0.20	3.67	7.28	3.28	1.80	0.34	99.50
St.Dev.	0.62	0.02	0.54	0.44	0.02	0.10	0.23	0.38	0.13	0.02	
USGS ^c	54.10	2.26	13.50	12.41	0.20	3.59	7.12	3.16	1.79	0.35	98.64

Table 2e. Data for Mt Edziza sheep track tephra with 5 μ m beam. $n=40$

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
Av.	61.84	0.25	17.89	4.50	0.14	0.12	1.05	8.24	5.35	0.03	99.88
St.Dev.	1.14	0.02	0.39	0.44	0.02	0.03	0.10	0.48	0.23	0.01	
Det. Lim.		174			231	324	532			69	
INTAV ^d	61.50	0.24	17.80	4.60	0.13	0.12	1.08	8.20	5.30	0.05	99.02

Table 2f. Data for Mt Edziza sheep track tephra with 3 μ m beam. $n=27$

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
Av.	62.06	0.25	18.11	4.49	0.14	0.12	1.07	8.34	5.41	0.03	100.04
St.Dev.	0.81	0.01	0.62	0.30	0.02	0.03	0.09	0.72	0.22	0.01	
Det. Lim.		100			238	261	532			88	

^aXRF analysis by Prof. S. Sparks.

^bCumulative average of analyses made at Edinburgh using beam diameter of 10 μ m.

^cData from USGS (Jochum et al., 2005).

^dData from INTAV interlaboratory comparison (Kuehn et al., personal communication, 2010).

included with permission of Dr Duane Froese and Dr Steve Kuehn) were also carried out. Analysis times for Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe normally used in tephrochronology were 4.5 min, and 7 min with the addition of F, S and Cl. Fluorine K α was

measured using the TAP rather than the more sensitive PC1 (Si/W) crystal to avoid occupying one spectrometer for this element alone, and to avoid the need to correct for the significant overlap of the iron L α_1 line (Witter and Kuehner, 2004).

Results

Analytical data, measurement standard deviations in wt.% element and detection limits in ppm for elements at concentrations lower than 1 oxide wt.% from the standard materials measured are presented in Table 2. The present data are in very good agreement with the accepted ranges of values for all elements measured. The notable discrepancy between the bulk and microbeam data for FeO in the Lipari glass is caused by the presence of iron oxide grains, which cause higher values of iron in bulk analyses. No detectable loss of sodium or potassium, or corresponding increase in Al or Si concentrations were observed from these or other standard glasses with each of these elements measured at current densities on $0.102 \text{ nA}/\mu\text{m}^2$. This is 17 times higher than the $0.006 \text{ nA}/\mu\text{m}^2$ using a 2 nA beam current suggested by Morgan and London (2005) and approximately equivalent to the current density at which 7–9% Na loss was reported from synthetic hydrous haplogranite glass samples in the same study. The hydrous component in Morgan and London's study was determined by difference from EPMA analyses as 6.6 wt.%. This unusually high hydrous component explains the greater sensitivity to beam damage of their sample. For a virtually anhydrous tephra of intermediate composition from Mt Edziza containing 8.2 wt.% Na_2O , no Na loss was caused using a 5 μm diameter beam and 0.7 nA current – a current density of $0.036 \text{ nA}/\mu\text{m}^2$. Analysis of the Mt Edziza tephra with the 3 μm diameter beam caused no apparent Na loss when Na and Al were measured with a beam current of 0.5 nA (Table 1). The slightly elevated Si for this beam condition is within error equivalent to the concentration measured with the 5 μm beam. However, in detail, there is a slight but consistent negative gradient in Na counts from this sample over periods of 50–70 s over which Na + Si x-ray measurement occurred. The slight elevation in Si concentration measured is thus due to the loss of Na during the later 2 nA current at which Si was measured and although the analyses are close to the reported 'ideal' value (Kuehn et al., forthcoming) (Table 2e), suggest that some beam damage occurs at these settings for Na-rich compositions with only minor hydrous component. The setup was modified to avoid this problem by employing three TAP crystals to measure Na, Al and Si simultaneously (TAP instead of PET on spectrometer 4, with measurement of K, Ca, Cl, P, S and Ti on one spectrometer only). However, contrary to expectation, this resulted in SiO_2 concentrations of >62–63 wt.%. This occurs no matter which TAP crystal is used for Si measurement and at counting times on peak of between 6 and 20 s. The reason for the effect is as yet unclear.

Standard deviations of measurements made using the 3 μm beam on large areas and for the crushed standards (Table 2a–d and f) are mostly identical, and all are closely similar to each other and also to those using the standard 5 μm diameter beam (Table 2e). Detection limits for elements present at low concentrations are also closely comparable. The use of the very low beam currents for WDS measurements thus causes neither increases in analytical error nor significant loss of analytical sensitivity for the compositions analysed.

Analysis at 2 nA with beam diameters less than 5 μm produced measurable Na loss in the Lipari standard (0.1–0.15 wt.% Na_2O for 2 nA and a 4 μm diameter) but no detectable loss in the BHVO2g glass. There is considerable experimental evidence for the relative resilience of basaltic glasses, especially

when anhydrous or slightly hydrated, under electron bombardment. Data from the current study indicate that for the materials studied significantly higher current densities, and thus smaller beam diameters than previously suggested can be used. It is suggested that on the basis of the present data, current densities of up to $0.1 \text{ nA}/\mu\text{m}^2$ can be attempted even for rhyolitic glasses containing 1 wt.% of hydrous component such as the Lipari standard.

Counts per second (cps) on the Na $K\alpha$ peak maximum for a 3 μm diameter beam using the LTAP analysing crystal are shown in Figure 1. These measurements were made using the Chart Recorder utility within Cameca's PeakSight software. The greater stability of Na within basaltic glasses relative to rhyolitic glasses is clearly shown. Average third-order polynomial best fit lines are shown for Figure 1a–e. Count rates over short intervals may be modelled using linear best fits. Count rates for the first 20 s of each measurement are shown in Figure 1f–j, together with linear best fit lines for each measurement and the line equations. For comparison, in Figure 2 equivalent data are presented for standards Lipari and BHVO2g using the standard Edinburgh 5 μm diameter 2 nA beam and for the 10 μm diameter 10 nA beam tested by Morgan and London (2005) and commonly used for tephra analysis (Hunt and Hill, 1996; Kuehn et al., forthcoming). The small gradients in Figures 1f–i and 2g–l are similar and show that no loss of sodium is occurring during the 20 s measurement of Na $K\alpha$ x-rays under any of the beam conditions applied.

Discussion

The results show that WDS analysis can produce high quality data using beam currents more normally employed by EDS analysis, without the loss of sodium during analysis from areas only 3 μm in diameter. Spectrometer configuration is of critical importance for the analysis of beam-sensitive materials such as tephra. Suitably configured five spectrometer instruments offer significant benefits for analysis of sensitive materials through their ability to analyse all of the most beam-sensitive elements Na and K, plus Al and Si very early during an analysis. The large analysing crystals are at least three times more sensitive than standard sized crystals and enable more rapid and/or more sensitive analysis whilst maintaining good analytical precision. Instruments equipped with large TAP analysing crystals have special advantages with respect to avoidance of sodium loss, enabling high-precision measurement of sodium in short counting times.

Current density increases more rapidly with increasing beam current for narrower beams relative to more diffuse beams. Attempts to use highly focused beams (1–2 μm diameters) therefore suffer far more from beam-induced effects at currents suitable for WDS analysis (> 1 nA). If, as current data suggest, a current density of 0.1 is the upper limit before Na loss becomes detectable, then for beams of 4 μm and 3 μm in diameter, it is predicted that Na, K, Al and Si could be measured at currents of 1.3 nA and 0.7 nA, respectively, without beam-induced effects. For a 2 μm diameter beam, a current of 0.3 nA would be required. For Cameca instruments, automatic regulation of beam currents is not possible below 0.5 nA, requiring independent monitoring of currents during analysis. The use of low beam currents in order to avoid Na-loss would therefore appear to be limited to beam diameters of 3 μm with current instrument specifications.

The current densities during the current analyses are significantly greater than those recommended by Morgan and London (1996, 2005) or Hunt and Hill (1993, 2001). These conditions are, however, not universally applicable. Morgan and London (2005) reported a 7.4% relative Na loss using a 2 nA, 5 µm diameter beam. This emphasises the variable, composition-dependent beam sensitivity of glasses, the need to analyse a wide range of secondary standard materials when evaluating the suitability of experimental settings, and of critical evaluation of data produced from new samples. However, the extremely hydrous 6.60 wt.% H₂O synthetic haplogranite melt used by Morgan and London (2005) represents a composition of unusually high sensitivity to beam damage, and one rarely encountered within the majority of tephra studies. The current study, and reproduction at Edinburgh of established compositions of many tephra layers analysed elsewhere with less focused beams, show that for many glass compositions, especially basaltic materials and less hydrated rhyolitic and intermediate tephtras, higher current densities may be applied without the risk of chemical modification. This enables high quality data collection from a greater range of fine grained and/or highly vesicular material with small areas of glass available for analysis. An indication of the limits of applicability of the 3 µm beam conditions listed in Table 1 is provided by the data for the highly sodic Mt Edziza (Table 2f), for which although Na-loss appears not to have occurred, no analytical conditions at this beam diameter were able to prevent at least very slight apparent increases in the Si content (although as noted this is within errors an identical concentration as that produced by the 5 µm beam). From this it is predicted that for tephtras that are sodic and hydrous, such focused beams should produce a degree of Na loss, and that the analytical conditions reported here will be less applicable or potentially inapplicable to such compositions.

There is great variability in the analytical conditions used for tephra analysis by various laboratories, which can affect data quality (Hunt and Hill, 1996; Kuehn et al., forthcoming). This has the potential to cause a serious impact on the ability to make reliable correlations between tephra layers that are chemically similar, to hamper the identification of previously unknown layers and to reduce temporal resolutions available from tephrochronological sequences. It is important to report analytical conditions as fully as possible, including x-ray lines, calibration standards, peak and background counting times, beam voltage, current(s) and diameter(s), instrument model, software version and raw x-ray processing algorithm. This will provide greater security in the use of published data, especially from older literature, and of online data bases of tephra analyses.

High resolution analysis without beam-induced analytical artefacts enables fully quantitative analysis of very distal and/or highly vesicular tephtras and very small melt inclusions without the need to use post-analysis corrections. This development has enabled high quality analyses from crypto-tephra layers that were previously impossible to analyse, and has removed the potential for sampling bias within mixed tephra layers by making (in most cases) all tephra grains accessible for analysis. The use of focused beams also increases the level of automation, and hence the cost-effectiveness of data collection.

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