

## Quantitative methods for electron microprobe analysis of sodium in natural and synthetic glasses

CHARLES H. NIELSEN<sup>1</sup> AND HARALDUR SIGURDSSON

Graduate School of Oceanography  
University of Rhode Island  
Narragansett, R.I. 02882

### Abstract

Two methods have been developed for the microprobe analysis of sodium in natural and synthetic glasses that exhibit time-dependent element migration during electron bombardment. A cryogenic method is based on the cooling of the sample to  $-90^{\circ}\text{C}$  at which temperature sodium diffusion rate from the excitation volume is reduced to zero. An empirical correction method determines the shape of the sodium decay curve as a function of time during electron bombardment, which under normal operating conditions, gives initial sodium concentration by extrapolation.

### Introduction

The precise determination of sodium concentration in hydrous and rhyolitic synthetic and natural glasses is one of the principal problems in quantitative electron microprobe analysis due to the time-dependent loss in intensity of the Na K line during continuous electron bombardment. Concurrent with the alkali loss one may observe a corresponding increase in counts and, hence, apparent concentrations of the non-mobile elements in the phase. This phenomenon has particularly presented problems in experimental petrology in the analysis of hydrous glassy charges (Helz, 1976; Kushiro, 1972). A loss of over 50% of the sodium counts and some loss in potassium was observed, for example, during the analysis of glassy basaltic quench products with a beam current of as low as  $0.01\ \mu\text{A}$  at 15kV and a  $5\ \mu\text{m}$  spot size (Mysen and Kushiro, 1975). The increased application of the electron probe microanalyzer (EPMA) to the study of terrestrial and deep-sea tephra deposits has further emphasized the problem of sodium loss. For example, the sodium loss during analysis of the Minoan tephra from Santorini volcano was measured as 50% of the original concentration during 30 seconds analysis time at a beam current of  $0.0125\ \mu\text{A}$  at 15kV and a beam diameter of 5 to  $10\ \mu\text{m}$  (Watkins

*et al.*, 1978). We describe here two analytical methods that address this problem. One approach eliminates the loss of sodium and potassium during analysis by a cryogenic technique, while the other more practical approach provides a quantitative correction procedure.

### Previous work

Typically  $0.02\ \mu\text{A}$  at 15kV represents reasonable working conditions for quantitative analysis of geologic materials. For many natural and synthetic glasses considerable structural damage is incurred even at these levels due to localized heating from the focused beam after the first few seconds of exposure. The most notable of the beam-induced compositional changes is a reduction in concentration of mobile alkali metal ions. The effect is most prominent for sodium and to a lesser extent for potassium, calcium and barium (Borom and Hanneman, 1967). Reports of alkali loss can be found extensively throughout the literature, for example, see Varshneya *et al.* (1966), Vassamillet and Caldwell, (1969), Goodhew and Gulley, (1974), and Watkins *et al.* (1978).

Depletion of alkali ions from glass during microprobe analysis is most likely due to the process first described by Lineweaver (1962). A fraction of incident electrons separates the alkali atoms from the bridging oxygen atoms forming two ions. The oxygen ions migrate to the surface and may appear as a gas bubble trapped under the carbon coating. The alkali

<sup>1</sup> Present address: JEOL (USA) INC., 11 Dearborn Road, Peabody, Massachusetts 01960.

ions remain in place until a particular temperature is reached at which time they begin to diffuse through the sample. A space charge layer, formed several microns beneath the surface where the incident electrons come to rest within the sample acts as a sink for these mobile alkali ions. The mobile ions diffuse out of the excited volume toward the space charge layer, resulting in a decreased alkali X-ray production. The thermal character of the process accounts for the existence of what Vassamillet and Caldwell (1969) have termed the incubation period, *i.e.*, a nearly flat region in the beginning of the decay curve where little, if any, depletion takes place. The incubation period, therefore, represents the time required for the sample to attain the temperature necessary for noticeable alkali diffusion.

Several attempts have been made to eliminate alkali loss by altering the analytical conditions. Moving the sample during the analysis allows collection of X-rays before the material has a chance to heat up. Rastering or defocusing the beam over a large area also has the effect of reducing the heating rate. These methods are effective only when large ( $\sim 100 \mu\text{m}$ ) homogeneous samples are available which is generally not the case for silicic glassy tephra or experimental charges. Goodhew (1975) has shown that by increasing the accelerating voltage the space charge layer is formed at a greater depth in the sample. This reduces the electric field to which the alkali ions in the excited volume are subjected and hence slows the decay rate. The combination of increased accelerating voltage, reduced beam current and energy dispersive spectrometers provides reasonable quantitative results (Goodhew, 1975). Unfortunately, this method requires accelerating voltages much higher than those compatible with the Bence-Albee correction scheme and relies on energy-dispersive detectors which limit the accuracy of the analysis.

In order to utilize wavelength dispersive spectrometers (WDS) for quantitative analysis of sodium and potassium in natural and synthetic glasses, we have found it necessary to develop a sample condition that eliminates or at least minimizes alkali mobility during exposure to the beam. Vassamillet and Caldwell (1969) have shown that for potassium the diffusion rate increases with increasing initial specimen temperature. It should follow, therefore, that by *reducing* the specimen temperature sufficiently the diffusion process should cease. If so, the initial concentration can then be measured at a temperature where diffusion is negligible.

## Methods

Rhyolitic glass fragments (KN-18) containing 5.68%  $\text{Na}_2\text{O}$  and 4.39%  $\text{K}_2\text{O}$  and ranging in size from 20 to 200  $\mu\text{m}$  in diameter were mounted in a small brass disc with epoxy. The mount was polished and coated with approximately 200 angstroms of carbon. The loss of sodium from the rhyolitic glass during electron bombardment was monitored both at 25°C under vacuum, and under cryogenic conditions. A cryogenic cold-finger cooled the sample through a copper braid to a final temperature of  $-110^\circ\text{C}$  in a specimen chamber under vacuum of  $5 \times 10^{-6}$  Torr. During cooling the rate of sodium loss was monitored every 10°C for a 60 second period. Counts were automatically accumulated in 2 second intervals from samples exposed to a focused, 0.02  $\mu\text{A}$ , 15 kV electron beam. The EPMA (JEOL JXA-50A) was standardized using basaltic glass VG-2 and a synthetic mineral composition of 85% diopside—15% jadeite. The standards were mounted in a brass disc with the unknowns so that standardization could be checked without having to warm the sample. Quantitative EPMA analyses were performed on unexposed samples of known composition at a temperature of  $-110^\circ\text{C}$ , with counting times of 30 seconds per element. Corrections were made on-line with a Bence-Albee routine supplied by Krisel Control.

## Results

The decay curves of Na and K X-ray intensities at room temperature are presented in Figure 1. The error bars indicate plus or minus one standard deviation uncertainty in the peak rate from simple counting statistics. The dramatic slope of the Na curve illustrates the severity of the problem of alkali-loss which reduces the initial count rate by 50% within the first 10 seconds of exposure to the beam. The shape of the sodium curve is very nearly exponential and seems to reach a steady state condition after approximately 45 seconds. Observed loss of potassium counts is much less and nearly linear.

The decay rate, as measured by the steepness of the curve, varies as a function of several physical parameters. For instance, the sample size is important because the smaller the sample the faster the temperature will rise for similar materials. Other factors include the embedding material, the thickness of the conductive coating, the thermal conductivity of the sample and the alkali and water contents of the glass.

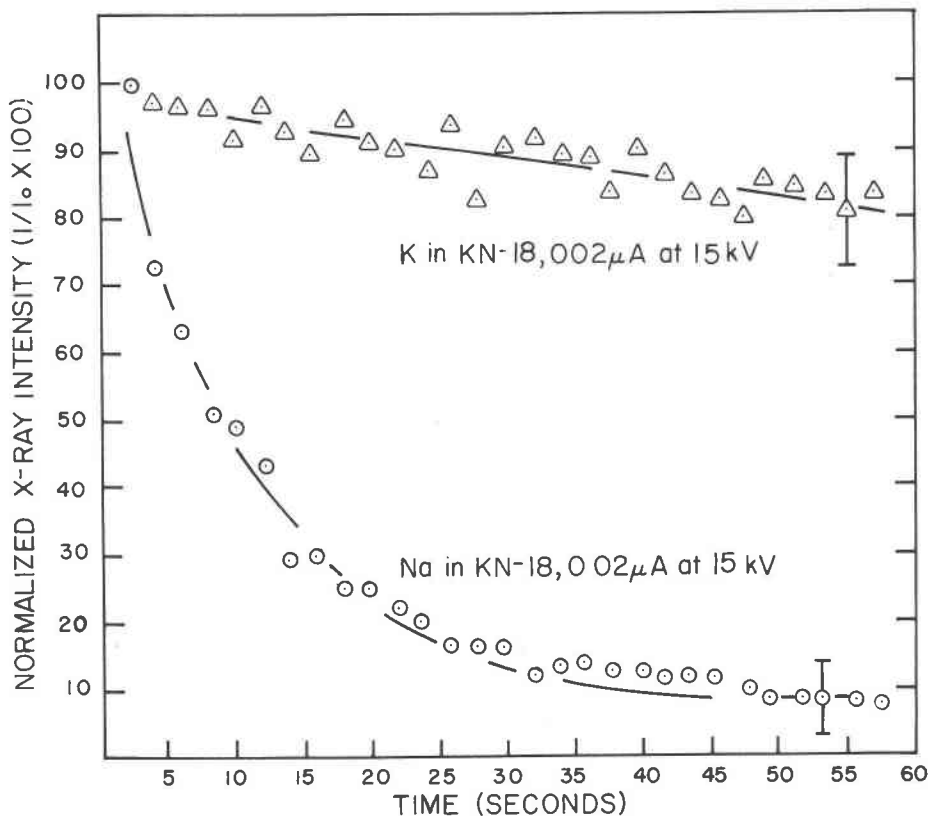


Fig. 1. Sodium and potassium loss from natural rhyolitic glass during electron microprobe analysis under normal operating conditions.

#### A. Empirical correction method

As noted above, the shape of the alkali metal decay curves appear to obey some functional relationship with time. The function which most closely fits the decline of sodium intensity with time was empirically determined to be a simple exponential. Hence, a straight-line relationship should be obtained by plotting the natural log of the intensity data versus time as illustrated in Figure 2 for several cases. This approximation can be utilized to estimate the initial alkali concentration from the decay curve by performing a least squares fit and then determining the intensity intercept on the semi-log plot and converting to concentration. It must be stressed here that it is assumed that the decay begins at  $t = 0$  and does not go through an incubation period or an initial increase in count rate. Also, this technique neglects the increase in apparent concentration of the non-mobile elements present in the phase.

A computer-based automation system was used to standardize the microprobe for sodium, collect sodium counts at two-second intervals, store the data

for the decay curve, plot the log of intensity versus time, and perform the statistical analysis. Sodium standards that are stable under the beam, such as a solid solution of 85% diopside—15% jadeite, were used to calibrate the system. To test the routine, several materials of known composition which experienced sodium depletion were analyzed. Table 1 lists the "true" sodium values together with those obtained by our empirical method. The values reported represent the averages and standard deviations of 25 measurements. The standard deviations of sodium concentration measured by the empirical decay curve method are in all cases well within experimental error of the accepted  $\text{Na}_2\text{O}$  concentration.

#### B. Cryogenic correction method

In the empirical method described above the sodium concentration is measured while the sample undergoes a dynamic compositional change. In order to determine the absolute alkali content, however, the sample must be analyzed under stable conditions. To this end cryogenic experiments were performed to

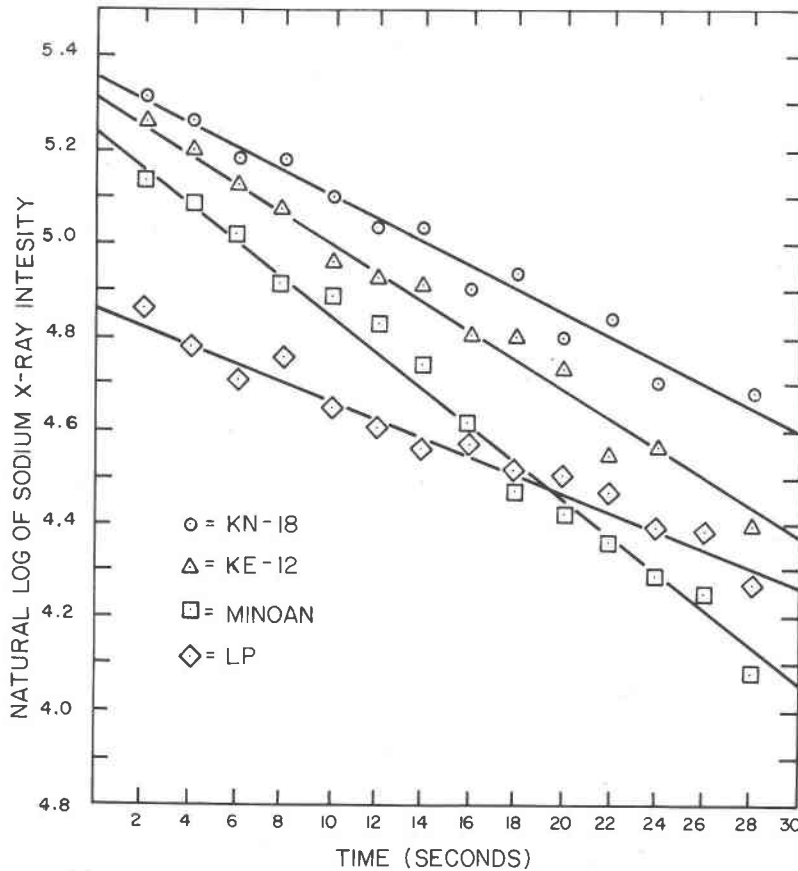


Fig. 2. Sodium decay plots for four natural rhyolitic glasses, plotted as the natural log of X-ray intensity versus time.

suppress the sodium depletion. A natural rhyolitic glass sample (KN-18) was cooled to a final temperature of  $-110^{\circ}\text{C}$  at a rate of 1 degree C/min. Sample temperature was monitored with a thermocouple embedded with the glasses in the epoxy mount. During the cooling period a series of 60-second decay curves were accumulated at  $10^{\circ}\text{C}$  intervals. Results of this experiment are presented as a series of decay curves in Figure 3. The lowest curve, determined at  $20^{\circ}\text{C}$ , has the highest slope and levels off within 40 seconds. The curve recorded at a temperature of  $-10^{\circ}\text{C}$  shows a marked reduction in the diffusion rate and does not level off within the 60 second observation. Other data collected at lower temperatures yielded decay curves with decreasing slopes. At approximately  $-90^{\circ}\text{C}$  the concentration remained stable, within experimental error, for the entire 60 second observation. Cooling to the lowest attainable temperatures of  $-110^{\circ}\text{C}$  produced results similar to those obtained at  $-90^{\circ}\text{C}$ .

The results indicate that at a sample temperature of  $-90^{\circ}\text{C}$  sodium is stable in the glass for at least 60 seconds and therefore quantitative determination

should be possible. Quantitative microprobe analyses were performed on several samples to test the method. Calibration of the system was made at  $-110^{\circ}\text{C}$  using known standards. Two samples of known composition (KN-18 and LP) were analyzed using the beam conditions stated above. The averages of 10 analyses of each sample are given in Table 2 along with the accepted values. The low standard deviations and percent errors demonstrate that the

Table 1. Empirical determination of sodium in rhyolitic glasses under normal operating conditions, *i.e.*,  $0.02\ \mu\text{A}$  beam current, 15kV accelerating voltage with a focused spot.

Sample	Accepted $\text{Na}_2\text{O}$ concentration	Measured $\text{Na}_2\text{O}$ concentration	Relative % error
KN-18	5.68*	5.53±0.25	2.68%
KE-12	5.40*	5.34±0.30	1.12%
LP	3.22*	3.32±0.18	3.06%
Minoan Tephra	5.11*	4.98±0.27	2.57%

\* X-ray fluorescence analysis; S. A. Malik, D. A. Bunsgaard and R. McDonald, pers. comm.

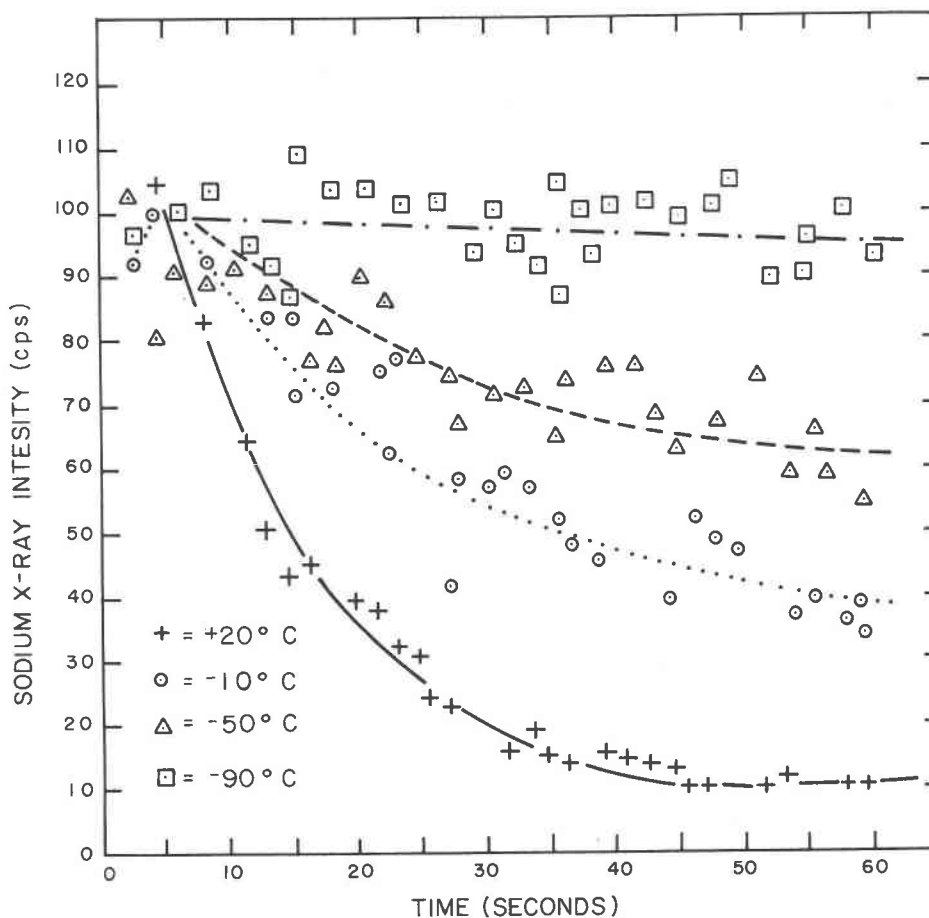


Fig. 3. The effect of sample temperature on sodium-loss from a rhyolitic glass (KN-18) during electron bombardment. Cryogenic cooling of the sample mount to  $-90$  degrees C suppresses alkali diffusion in the glass and enables direct quantitative analysis.

Table 2. Microprobe analyses of rhyolitic glasses under normal beam conditions at  $-110^{\circ}\text{C}$  sample temperature.

Oxide	KN-18			LP		
	Accepted Composition*	This work	Relative % error	Accepted Composition*	This work	Relative % error
SiO <sub>2</sub>	74.6	75.0 (.25)**	0.5	76.49	76.9 (.30)**	0.66
Al <sub>2</sub> O <sub>3</sub>	10.53	10.67 (.06)	1.3	12.59	12.50 (.10)	0.71
FeO*	3.54	3.52 (.08)	2.3	1.05	1.09 (.05)	3.8
MgO	0.01	0.02 (.01)	-	0.06	0.05 (.01)	-
CaO	0.015	0.17 (.01)	4.0	0.31	0.33 (.03)	6.5
Na <sub>2</sub> O	5.68	5.47 (.09)	3.7	4.34	4.28 (.10)	1.4
K <sub>2</sub> O	4.39	4.25 (.06)	3.2	4.59	4.50 (.10)	2.0
TiO <sub>2</sub>	0.18	0.20 (.02)	11.1	0.10	0.10 (.01)	-
P <sub>2</sub> O <sub>5</sub>	0.01	-	-	0.01	-	-
MnO	0.06	0.05 (.01)	-	0.06	0.06 (.01)	-
Total	99.06	99.35		99.60	99.81	

\*X-ray fluorescence analysis; S.A. Malik, D.A. Bunsgaard and R. McDonald, pers. comm.

\*\*One standard deviation, based on ten measurements.

precision and accuracy of these analyses are as good as those of glass samples which do not experience alkali depletion.

The two major problems encountered with the cryogenic technique are specimen contamination and the additional time required to prepare and change samples. Hydrocarbon contamination on the cryogenically cooled sample was experienced but could be reduced by increasing the surface area of the cold-finger and by taking steps to keep the instrument clean. The time required to cool the sample to the working temperature results in increased analysis time but this can be reduced by mounting several samples together.

### Conclusions

The severe loss of sodium counts during microprobe analysis of silicate glasses can be corrected for or avoided. The migration of sodium due to heating under the electron beam can be arrested by cooling the sample to  $-90^{\circ}\text{C}$  during analysis. This cryogenic method involves, however, longer analysis time and special preparation techniques. A more rapid routine of estimating the sodium concentration has therefore been developed. This empirical technique estimates the initial sodium concentration from the rate of decay in sodium counts during continuous electron bombardment of the sample and routinely gives accurate data.

### Acknowledgment

The authors would like to thank Dr. L. Finger for a preliminary review of this work.

### References

- Borom, M. P. and Hannerman, R. E. (1967). Local compositional changes in alkali silicate glasses during electron microprobe analysis. *Journal of Applied Physics* 38, 2406-2410.
- Goodhew, P. J. and Gulley, J. E. C. (1974). The determination of alkali metals in glasses by electron probe microanalysis. *Glass Technology*, 15, 123-126.
- Goodhew, P. J. (1975). Electron probe microanalysis of glasses containing alkali metals. *Microstructural Science*, 3, 631-641.
- Helz, R. T. (1976). Phase relations of basalts in their melting ranges at  $\text{PCH}_2\text{O} = 5\text{kb}$ . Part II. Melt compositions. *Journal of Petrology* 17, 139-193.
- Kushiro, I. (1972). Effect of water on the composition of magmas formed at high pressures. *Journal of Petrology*, 13, 311-334.
- Lineweaver, J. L. (1962). Oxygen outgassing caused by electron bombardment of glass. *Journal of Applied Physics*, 34, 1786-1791.
- Mysen, B. O. and Kishiro, I. (1977). Compositional variations of coexisting phases with degree of melting of periodate in the upper mantle. *American Mineralogist*, 62, 843-856.
- Varshneya, A. K., Cooper, A. R., and Cable, M. (1966). Changes in composition during electron microprobe analysis of  $\text{K}_2\text{O}-\text{SrO}-\text{SiO}_2$  glass. *Journal of Applied Physics*, 37, 2199-2202.
- Vassamillet, L. F. and Caldwell, V. E. (1969). Electron-probe microanalysis of alkali metals in glasses. *Journal of Applied Physics*, 40, 1637-1640.
- Watkins, N.D., Sparks R. S. J., Sigurdsson, H., Huang, T. C., Federman, A., Carey, S. and Ninkovich, D. (1978). Volume and extent of the Minoan Tephra from Santorini volcano: New evidence from deep-sea sediment cores. *Nature*, 271, 122-126.

*Manuscript received, May 12, 1980;*  
*accepted for publication, December 29, 1980.*