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QUANTITATIVE ELECTRON-MICROPROBE ANALYSIS OF ALKALI SILICATE GLASSES: A REVIEW AND USER GUIDE

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ABSTRACT

The mobilization of alkali metals in alkali silicate glasses and certain minerals during electron-microprobe analysis is a result of beam-induced heating and charging effects within the sample. The following procedures are recommended in order to minimize these effects. (1) Total beam-power should be less than 100 μW to reduce heating within the irradiated volume; this is best achieved by decreasing the beam current and by using a cryogenic stage, though the latter may be impractical for routine analysis. (2) Sample charging can be minimized by using lower beam-power, but higher voltages may be required to displace accumulating electrons to deeper levels within the sample. (3) Heating and charging effects can be reduced significantly if defocused beam or raster scan-modes are used. (4) Sample conductivity can be improved by applying double carbon coats, by coating both sides of the sample, and by using conductive slide-mounts (*i.e.*, copper instead of glass). (5) Count-times should be shortened to minimize the rate and extent of alkali migration, while maintaining the statistical validity of the data. (6) Corrections for alkali migration should be done prior to ZAF corrections. The low power requirements and high efficiency of the Si(Li) detector clearly favor energy-dispersion (EDS) over wavelength-dispersion spectrometry (WDS) for the quantitative analysis of alkali silicate glasses.

Keywords: alkali silicate glass, electron-microprobe analysis, energy-dispersion spectrometry, wavelength-dispersion spectrometry, alkali-metal mobility, space-charge layer, electromigration.

SOMMAIRE

La mobilisation des alcalins dans les verres silicatés à alcalins et dans certains minéraux pendant une analyse à la microsonde électronique est le résultat du réchauffement d'un échantillon par le faisceau et de l'accumulation des charges internes. Le protocole suivant sert à minimiser ces effets. (1) La puissance totale du faisceau devrait être inférieure à 100 μW afin de réduire la chaleur du volume irradié; on doit donc diminuer le courant du faisceau et utiliser un porte-échantillon cryogénique, quoique cette dernière mesure pourrait s'avérer incommode dans le contexte d'analyses routinières. (2) L'accumulation des charges est minimisée en réduisant la puissance du faisceau, quoiqu'un potentiel plus élevé pourrait s'avérer nécessaire pour déplacer les électrons accumulés vers un niveau plus profond dans l'échantillon. (3) Les effets dus au chauffement et à l'accumulation des charges sont sensiblement réduits en utilisant un faisceau défocalisé ou un mode de prélèvement des données par balayage. (4) La conductivité de l'échantillon peut être améliorée en appliquant une double couche de carbone ou une couche des deux côtés de l'échantillon, et en adoptant une lame à conductivité plus élevée, faite par exemple de cuivre au lieu de verre. (5) Le temps de comptage devrait être raccourci afin de minimiser le taux et la portée de la migration des alcalins, tout en maintenant la validité statistique des données. (6) Les corrections visant à compenser pour la migration des alcalins devrait être effectuées avant la correction pour le nombre atomique, l'absorption et la fluorescence. Il est évident que les faibles exigeances en puissance et l'efficacité élevée d'un détecteur Si(Li) favorisent une analyse quantitative de verres siliceux riches en alcalins par dispersion d'énergie plutôt que par dispersion de longueurs d'onde.

(Traduit par la Rédaction)

Mots-clés: verre siliceux à alcalins, analyse par microsonde électronique, dispersion d'énergie, dispersion de longueurs d'onde, mobilité des alcalins, couche surchargée, électromigration.

INTRODUCTION

Silicate glasses are an important group of materials, of interest to both the Earth scientist and industry. For naturally occurring aluminosilicate glasses, much can be learned about the geological conditions of their formation if accurate and precise compositional data can be obtained. In commercial applications, it may be necessary to analyze synthetic glasses on a routine basis for purposes of quality control. Much of the work on natural glasses requires the analysis of microscopic volumes: zones of intercumulus material in igneous rocks, thin rinds of glass on pillow lavas, and veins of friction-generated "melt" (pseudotachylyte) generated along slip surfaces. Many run products of the experimental petrologist comprise small volumes of synthesized glass (*e.g.*, Beard & Lofgren 1991). The electron microprobe (Castaing 1951) is an ideal tool with which to analyze these materials, but it is widely recognized that the alkali metals (particularly Na) can diffuse out of or into the analyzed volume (*e.g.*, Sweatman & Long 1969, Goldstein *et al.* 1992, Reed 1993). This effect is dependent on a number of factors, including the SiO_2 and H_2O contents of the analyzed material, and the dissipation of power around the excitation volume. As a consequence, it is easy to collect incorrect analytical data, and accurate analysis can be difficult. This work reviews the situation regarding the electron-microprobe analysis of silicate glasses, presents models for the cause of ionic mobility, and suggests procedures for the minimization of beam-induced losses and gains in alkali metals.

NATURAL GLASSES

Many natural glasses are of volcanic origin (Table 1). The composition of a quenched igneous product can be informative; basic glasses can be less fractionated than associated crystalline rocks, and so indicate more about source magmas (*e.g.*, Natland 1991). Glasses can also be diagnostic of deformation processes at high and ultrahigh strain-rates, such as seismic slip (*e.g.*, with the formation of pseudotachylyte: Spray 1987, 1993) and meteorite impact (*e.g.*, with the generation of tektites: Koeberl 1986). The high-speed atmospheric entry of meteors can also induce glassy fusion-induced crusts on their surfaces due to air–projectile frictional heating (McSween 1987). Diaplectic glass is produced by the passage of a shock wave through a rock (*e.g.*, Bischoff & Stöffler 1992), with the transformation occurring in the solid state without melting. Certain metamict minerals (Table 1) are rendered glassy by α-particle-induced structural damage during the decay of unstable isotopes (*e.g.*, of U, Th). However, none of these minerals contain significant alkalis.

TABLE 1. SOME NATURALLY OCCURRING GLASSY MATERIALS

Materials	Origin
Obsidian Pitchstone Tachylyte Pele's hair/tears Glassy pyroclastic material	volcanic and supercooled
Planetary regoliths (e.g., moon) Meteorite shock veins Tektites Diaplectites (e.g., maskelynite) Lechatelierite*	impact-induced (supercooled or diaplectic)
Pseudotachylyte Fusion crusts on meteorites	friction-induced and supercooled
Metamict minerals (e.g., allanite, monazite, thorite, zircon)	irradiated

* also produced by lightning strikes in sand (fulgurite)

SYNTHETIC GLASSES

Synthetic inorganic glasses (Table 2) can be classified into four groups. Network-modified SiO_2 glasses are the most important in terms of commercial applications (Doremus 1973, Zarzycki 1991). Halide, chalcogenide and metallic glasses are relatively recent

TABLE 2. MAIN SYNTHETIC INORGANIC GLASSES

Type	Component(s)	Qualities
Oxide glasses	SiO_2 (usually with network-modifiers)	Chemical resistance, thermal shock resistance (e.g., borosilicates = pyrex)
	B_2O_3 P_2O_5 GeO_2	As single component oxides, these are currently of scientific interest
Halide glasses	BeF_2, ZrF_4, AlF_3, Ln(lanthanide)F_3, ZnF_2,PbF_2, BaF_2, $ZnCl_2$, etc. (i.e., potential optical fibres)	Excellent optical transmission properties
Chalcogenide glasses	Group VI elements combined with Groups IV and V elements	Infrared optical transmission and electrical switching
Metallic glasses	Metal-metalloid* Metal-metal	Very low magnetic losses, high mechanical strength and hardness, high chemical corrosion resistance and radiation resistance

* metalloid: e.g., B, C, Si, P, Ge

developments, and have various advanced-technology applications. Network modifiers in the SiO_2 glasses include Mg, Ba, Ca, Li, K and Na. Compositional determinations of manufactured silicate glass at the microscopic scale are not usually a routine requirement. This is because the amounts and types of ingredients are predetermined at the design stage, and so the composition is known and controlled. Furthermore, the product is normally homogeneous. However, electron-microprobe analysis can be used for rapid quality-control and for assessment of compositional homogeneity. In these instances, the importance of Na as a network-modifying cation can lead to problems with analytical accuracy.

EDS VERSUS WDS ANALYSIS

X-rays emitted from the sample surface can be collected by either an energy-dispersion spectrometer (EDS) or wavelength-dispersion spectrometers (WDS). The first commercial electron microprobe that appeared in 1958 deployed only WDS spectrometers, and it was not until the late 1960s that the solid-state lithium-drifted silicon [*i.e.*, Si(Li)] detector was developed to eventually facilitate quantitative EDS analysis (Fitzgerald *et al.* 1968, Reed 1993). The two types of spectrometer differ in a number of important respects (Table 3) that are pertinent to the analysis of alkali silicate glasses. The WDS spectrometer has higher resolution and better detection-limits (10 ppm for optimum operating conditions) than does the EDS spectrometer. However, the detector efficiency for WDS is significantly poorer than that of EDS. Consequently, whereas both types of spectrometer can be operated at comparable voltage, the WDS requires higher beam-currents to achieve an adequate X-ray count-rate (Table 3). The higher power required for WDS results in higher temperatures and greater charging within the sample, especially where a focused beam is used, and this promotes diffusion of the alkali metals within the silicate glass.

The advent of improved EDS systems means that fully quantitative major-element analysis is now routine (*e.g.*, Statham & Nashashibi 1988). Thus, the lower beam-current requirement of the ED spectrometer means that EDS is the better method for determining the major-element composition of glasses (bearing in mind that EDS power requirements are largely dependent on the distance of the detector from the area analyzed and the geometry of the collimator and silicon detector).

TABLE 3. CHARACTERISTICS OF EDS VERSUS WDS ANALYTICAL TECHNIQUES

	EDS	WDS
Typical voltage range (kV)	15 - 30	15 - 30
Viable current range (nA)	0.25 - 5	5 - 50
Power range (μW)	3.75 - 100	75 - 1000
Resolution (eV)	<150	<10
Optimum detection limits	0.1 wt%	<100 ppm
Detector	solid state	gas phase
Detector efficiency (%)	≈100	≈25

THE EFFECT OF ELECTRON BOMBARDMENT ON ALKALI SILICATE GLASSES

How can mobilization of alkali metals be recognized? (1) Alkali-metal count-rate may shift at constant voltage and current. (2) Loss may be indicated by low analytical totals; however, if the glass contains H or halogens, low overall totals can be due to H_2O content (*e.g.*, Stolper 1982) or halogen loss (*e.g.*, Stormer *et al.* 1993). Gains are more difficult to detect because the analytical total may not be noticeably high. Gains can occur where extended count-times, higher beam-currents, or thinner conductive coatings are used, especially if the glass has a low thermal conductivity (Borom & Hanneman 1967). However, alkali-metal gains occur less commonly than alkali-metal losses.

If loss has occurred, a map of Na distribution will show a sodium "hole" that approximates the excitation diameter of the electron beam (Fig. 1a). A line scan across such a hole has a pit-like shape (Fig. 1b). The rate of Na loss varies with time. An initially steep decline in count rate is typically followed by a reduced but relatively steady-state count-rate. With loss of Na from the excitation volume, the count rates of the remaining elements increase. This occurs because the electron microprobe measures the mass fraction of elements present in the interaction volume, so that a loss of one or more elements is compensated by an apparent gain in those remaining. This is illustrated in Figure 1c, where the relative decrease in Na counts over time is mirrored by a relative increase in Si counts. Varshneya *et al.* (1966) documented a similar effect in a K_2O–SrO–SiO_2 glass owing to K loss. If a gain has occurred, a map of Na distribution will show a Na build-up (Fig. 1d). A line scan across such a build-up has a mound-like shape (Fig. 1e). If Na increases within the analyzed volume, the count rates of the remaining elements decrease, such that there is an apparent reduction in their content (Fig. 1f). Borom & Hanneman (1967) showed that this occurs for K_2O–SiO_2 and Na_2O–FeO–SiO_2 glasses under certain operating conditions.

Steady-state conditions eventually tend to prevail for alkali-metal loss, although for long-duration count-times (several minutes), initial losses may be superseded by gains. If alkali-metal gains occur on initial bombardment, they can persist or become highly erratic with time. The time-dependency of the mobility of alkali metals has important implications regarding the count-times that are used for analysis.

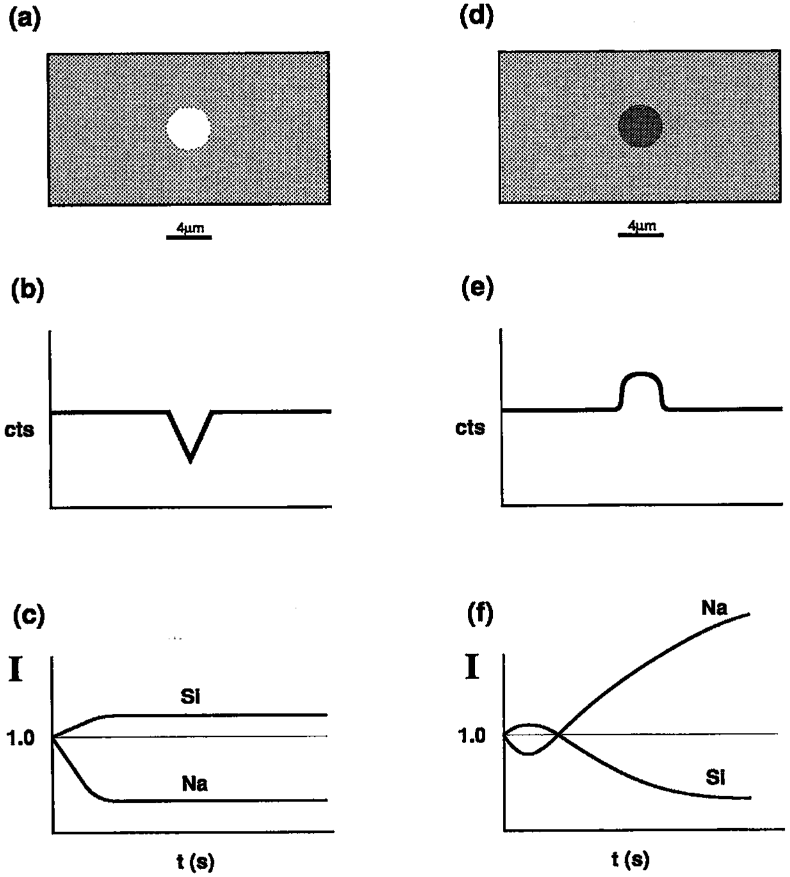

FIG. 1. (a) Part plan view of a polished thin section of an alkali silicate glass showing Na distribution. Note electron-beam-induced "hole" where Na is absent. (b) Section line-scan for Na for same sample as above (cts = counts). Note presence of Na "well". (c) Time-dependence (t) of X-ray intensities (I) normalized to zero time for Na and Si. Note Na loss and Si gain. (d) Plan view as for (a) above, but note zone of Na increase. (e) Section line-scan for Na for same sample (d) as above. Note Na "mound". (f) Time-dependence as for (c) opposite, but note overall Na gain and Si loss, as well as initial reversal in trends.

The degree of alkali-metal migration is also dependent on the mode of analysis. Point (focused-beam) analysis results in greater migration, whereas defocused beam and raster scanning have less extreme effects. Table 4 shows the results of analyzing the same point or area four times using point, defocused and raster scan-modes on basaltic glass VG2 (Jarosewich 1975). The mean Na_2O value from the point analysis is the lowest, and this method shows a more consistent depletion in Na for successive analysis of the same spot. Both defocused and raster-scan modes produce an acceptable mean result, which is higher than the average point analysis and closer to that of the quoted international standard value. Furthermore, there is no decrease in Na_2O content with successive analysis with defocused and raster scan-modes.

The next step is to try to understand how alkali-metal migration occurs, so that the problem can be avoided or minimized.

CAUSES OF MOBILITY OF ALKALI METALS DURING ELECTRON BOMBARDMENT

A number of mechanisms have been proposed to account for alkali-metal loss and gain during electron bombardment of alkali silicate glasses. These include sample volatilization (Baird & Zenger 1966) and electromigration (*e.g.*, Graham *et al.* 1984, Cazaux

TABLE 4. EDS ANALYSES* OF BASALTIC GLASS STANDARD VG2 FOR Na USING DIFFERENT BEAM-MODES

	beam mode		
	focused (D ≈ 1 μm)	defocused (D ≈ 20 μm)	raster (≈ 1,000 μm^2)
1	2.70	2.74	2.71
2	2.47	2.80	2.53
3	2.28	2.73	2.69
4	2.36	2.60	2.82
Mean	2.45	2.72	2.69
Standard value	2.62		

*Operating conditions: 15 kV, 2.5 nA.

1986). Autefage & Couderc (1980) suggested that alkali-metal mobilization occurs in two stages: (1) thermally activated breaking of Na–O bonds and initial ionic diffusion, and (2) electromigration of free Na$^+$ ions to the zone of electron build-up (space-charge layer).

Beam-induced thermal effects

Castaing (1951) and Friskney & Haworth (1967) have calculated that for operating conditions of 25–30 kV and 100 nA, temperature increases in the order of 1000°C or more may arise for focused beams (1 μm in diameter) in uncoated samples. Analyzing a sample of low thermal conductivity (*i.e.*, a glass) in an uncoated state can lead to beam-induced surface damage, manifest as pits and craters, some of which develop elevated rims (Borom & Hanneman 1967). If a coating medium is used (usually carbon for geological materials), the temperature rise can be reduced by as much as an order of magnitude (*i.e.*, down to approximately 100°C). Vassamillet & Caldwell (1969) equated the energy dissipation of the beam to an equilibrium temperature for the periphery of the irradiated volume given by

$$T - T_0 \approx (W/2\pi kr) \qquad (1)$$

where T is the rise in temperature at the periphery of the irradiated volume, T_0 is the ambient temperature of the sample, W is power in watts, k is the thermal conductivity of the sample (W m^{-1} °C^{-1}), and r is the radius of irradiated area in meters. For a K_2O–SiO_2 glass, Vassamillet & Caldwell (1969) found that T_c (the critical temperature for K mobilization) is approximately equal to 85°C, and is likely to be less than this for Na because of its greater ionic mobility.

Figure 2 shows temperature increase as a function of power and beam radius using a thermal conductivity (k) value of 1 W m^{-1} °C^{-1} appropriate for silicate glasses (Ashby & Jones 1986, p. 151). Position z indicates a value for focused-beam operation suitable for WDS analysis (1 μm at 300 μW). Position z also corresponds to the proposed T_c of Vassamillet &

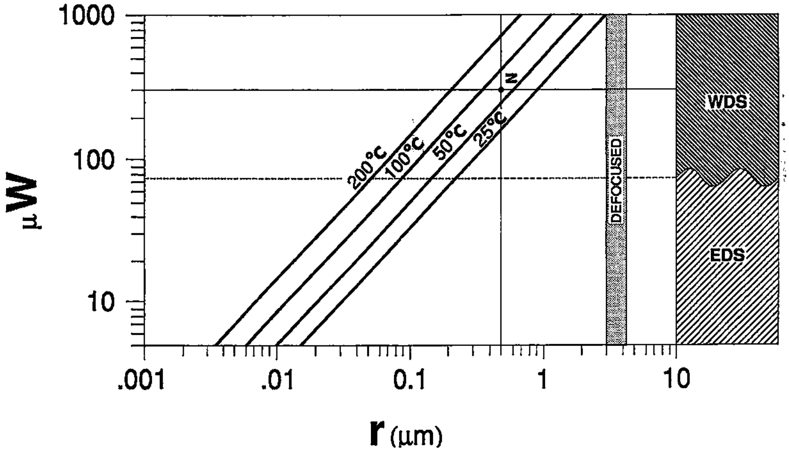

FIG. 2. Electron-beam power *versus* beam radius and resultant temperature increases at the periphery of the irradiated volume using the equation of Vassamillet & Caldwell (1969). Point z corresponds to typical WDS conditions of analysis (see Table 4), as well as the temperature of onset of diffusion of alkali metals in silicate glasses (T_c ≈ 85°C). Defocused beam radii shown shaded. Power requirements for WDS and EDS analysis are indicated on right.

Caldwell (1969), which shows that those values parallel to the isotherms and to the left of z would facilitate alkali-metal migration ($\geq$85°C). Note that typical values of r for a defocused beam (*i.e.*, yielding analyzed areas of 10–20 μm diameter) result in T being much less than T_c, such that bond disruption and diffusion are averted for both EDS and WDS operation.

Overall, it can be seen that the likelihood of mobilizing Na is significantly reduced with EDS compared to WDS. In fact, for WDS analysis, it seems difficult not to mobilize the alkali metals in silicate glasses if a focused beam is used. Use of low power with WDS necessitates long count-times, which are also counterproductive.

The space-charge layer

An important concept in our understanding of electromigration is that of the "space-charge layer", which is purported to develop where the electron gain of the sample exceeds the electron dissipation. Whether alkali-metal ions are lost from or gained in the irradiated volume depends on the size and location of the space-charge layer within the sample.

Lineweaver (1963), in his study of $Na_2O–SiO_2$ glass cathode-ray tubes, showed that oxygen is released from glass surfaces during electron rastering, and proposed that incident electrons accumulate at some finite depth within the sample to form a "negative-charge region" (Fig. 3). Owing to this electron build-up, Na ions decouple from their oxygen (unbridged) ions and migrate to the negative zone, to be either neutralized to elemental form (inducing a color change known as "electron browning"), or to bond to new oxygen ions. A concomitant decrease in Na X-ray intensities was noted, and the analyzed volume became depleted in this metal. Movement of Na ions down to the charge layer results in oxygen being released from the upper part of the sample where, on losing electrons to the electrode, it escapes from the surface as O_2 (Fig. 4).

The Lineweaver mechanism has been widely accepted, but it is not applicable in all situations. Borom & Hanneman (1967) found that under certain conditions, an increase in alkali-metal X-ray intensities can occur, with a corresponding decrease in the intensities for the remaining elements. This is characteristic of more intense beams and thinner conductive coatings, especially where less stable varieties of glass are being analyzed. They attributed this to increased thermal effects and to destruction (vaporization) of the conductive coating. This allows electrons to accumulate at the sample surface, such that the mobile Na ions are attracted toward the more negatively charged surface.

Both the Lineweaver (1963) and Borom & Hanneman (1967) models can be reconciled if the space-charge layer can move within the sample. Estour (1971) showed that the rate of decay in the X-ray counts for Na could be minimized if higher accelerating voltages are used (*i.e.*, >20 kV). This was attributed to the accumulation of electrons at deeper levels in the sample owing to their greater kinetic energy, such that the near-surface Na ions are effectively shielded from the relocated, more remote space-charge layer.

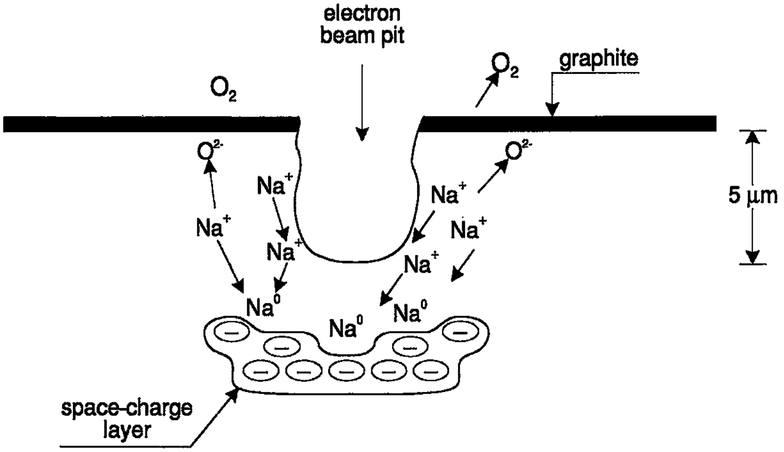

FIG. 3. Cross-section of polished thin section of an alkali silicate glass showing the formation of a "space-charge layer" comprising accumulated electrons within the sample. Na–O bonds are broken, then Na cations migrate to the negative charge layer, where they are neutralized.

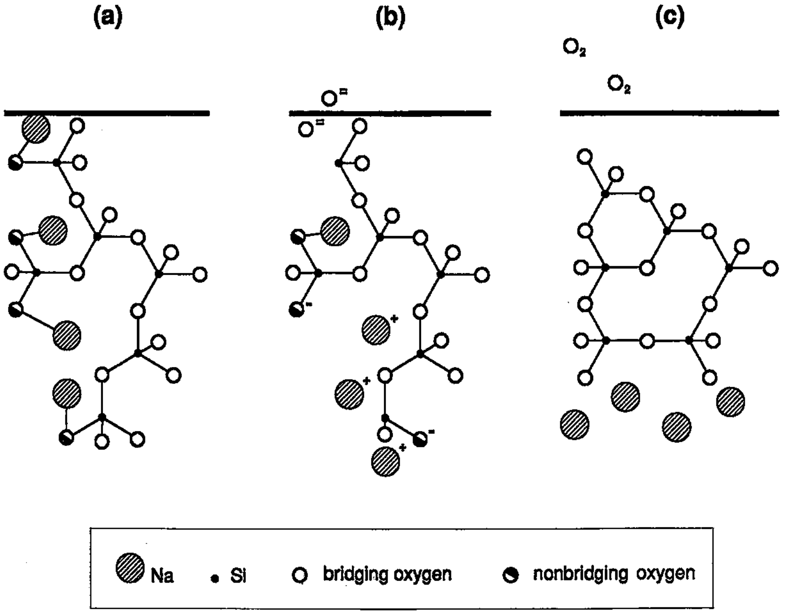

FIG. 4. Lineweaver's model for alkali-metal loss: (a) prebombardment structure of Na_2O–SiO_2 glass (simplified); (b) Na–O bond breaking, downward migration of Na^+ and upward movement of O^{2-} and (c) final (immediately postbombardment) modified structure, with neutralized Na atoms and O_2 evolving from the sample surface. Modified after Lineweaver (1963).

However, a higher voltage significantly reduces X-ray generation, such that Estour (1971) had to increase the probe current (to 20 nA) in order to generate sufficient X-rays for the less efficient crystal spectrometer (WDS). By doing so, he increased temperatures, and so Na loss recurred. Goodhew & Gulley (1974) confirmed Estour's findings and showed that probe currents two orders of magnitude smaller could be used with EDS, and Na mobility could be virtually eliminated. The best results were obtained at 30 kV and 0.2 nA (Fig. 5). Goodhew (1975) subsequently showed that if each analysis were carried out at a fresh point on the sample, the Na decay rate could be reduced below 0.5% of the count rate. This would constitute only 1–2% loss in a total count over a few hundred seconds.

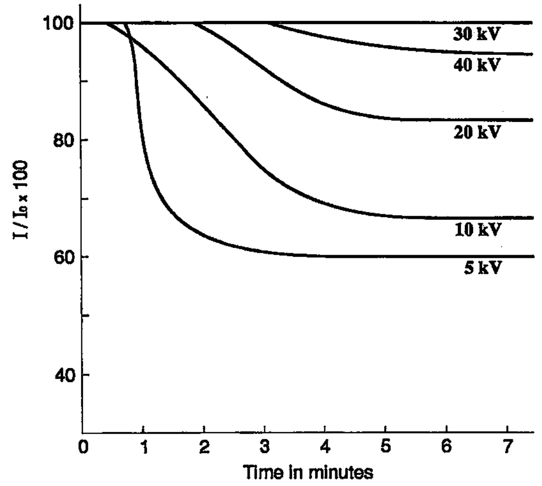

FIG. 5. Decay of Na$K\alpha$ count rate during EDS analysis for a variety of accelerating voltages at a beam current of 0.2 nA (after Goodhew & Gulley 1974). I and I_0 are the X-ray intensities (counts) normalized to 100 at times $t = 0 + t_n$ and $t = 0$, respectively.

Compositional dependence of alkali-metal migration

The susceptibility of glasses to beam-induced mobilization of alkali metals is also dependent on the chemical composition of the glass as well as on the analytical operating conditions. Highly siliceous glasses show high susceptibility to alkali mobility, whereas more basic (low-SiO_2) material does not. The former are designated the so-called unstable glasses (Zarzycki 1991) which, geologically, would include rhyolitic glass. The stable glasses include those of mafic composition. The reason for the variable alkali-metal response to electron bombardment remains unclear, but it may depend on the degree of polymerization of the SiO_4 and AlO_4 tetrahedra. A high degree of polymerization involves a more open network of tetrahedra that allows diffusion of alkali metal cations to occur with greater ease. Low polymerization results in a more densely packed structure of the glass, through which it is more difficult for the alkali metals to diffuse. Depolymerization is caused by, for example, the presence of Fe and Mg breaking the SiO_2 chains into shorter units. As well as effectively blocking the movement of alkali ions, these network-modifying elements increase electrical and thermal conductivities and hence reduce thermal and charging effects. Most geologically important glasses are aluminosilicates, where the presence of Al also acts to reduce alkali volatility. The compositional dependence of alkali mobility must be borne in mind when selecting operating conditions. High-SiO_2, high-alkali-metal, low-transition-metal glasses are particular difficult to analyze quantitatively.

MINIMIZING ALKALI MIGRATION IN GLASSES

In order to minimize alkali migration, it is necessary to minimize both thermal effects and the development of the space-charge layer. These two effects are related. The energy required to break the Na(K)–O bond is related to the temperature generated during power dissipation. Alkali migration is dependent on the size of the space-charge layer, which is controlled by beam power and by the conductivities of both coating and sample. The location of the space-charge layer can be controlled by varying the beam voltage and the total count-time.

Finally, it is noted that alkali migration is not restricted to glassy materials. Negative charging of the sample surface and concomitant Na and K fluctuations have been noted, amongst other minerals, in sepiolite (Butt & Vigers 1977), autunite (Graham *et al.* 1984), feldspars (Ribbe & Smith 1966), feldspathoids (Brousse *et al.* 1969), jadeite and scapolite (Autefage 1980). In all cases, the minerals were analyzed by WDS, and maximum mobility occurred when a focused beam (*i.e.*, approximately 1 μm in diameter) was used.

The following guidelines will help to optimize analytical conditions for the quantitative analysis of alkali silicate glasses:

(1) *Power*: the temperature rise in the irradiated volume within the sample is strongly controlled by beam power. Reduction in kV is limited by the requirement for 2–3 × overvoltage ratio (*e.g.*, Fe 6.4 keV × 2.5 = 16 kV). Reducing the current will reduce thermal effects, but this also lowers the intensity of X rays generated, such that WDS analysis becomes impractical. Reduction of the beam current is more feasible with EDS.

(2) *Relocation of the space-charge layer*: the space-charge layer may be moved deeper in the sample by higher accelerating voltages (*i.e.*, 30 kV). This minimizes attraction of alkalis from higher levels within the irradiated volume. If beam power is to be kept low, even lower currents will have to be used and, again, this favors EDS over WDS. It should be noted that ZAF corrections may be in error at high kV.

(3) *Initial temperature of the sample*: the beam-induced rise in temperature (T) within the irradiated volume may be greatly reduced by the ambient temperature (T_0) of the sample [see equation (1)]. If a cold stage cooled by a cryo-unit is used, about –140° can be attained at the stage. However, analysis would become extremely time-consuming. Using a conductive sample-mount (*i.e.*, copper) also helps to improve heat removal from the analyzed area.

(4) *Beam mode*: if point analysis is not required, use defocused (WDS or EDS) or raster scan-modes (EDS only). Such scan modes involve a larger beam-area, so that the power per unit area and hence temperature increase is reduced significantly. Rastering is difficult with WDS because of more precise geometrical requirements, but high-speed wide-area analysis techniques have been developed whereby the sample is moved physically beneath a static beam (*e.g.*, Ono *et al.* 1985).

(5) *Conductivity*: with insulating materials, problems of low thermal and electrical conductivities of samples can lead to adverse development of the space-charge layer. This situation can be improved by thicker (double) carbon coats and by coating both sides of the sample. Preparation of ultrathin samples glued onto conducting (*e.g.*, copper) mounts also may help to alleviate development of the space-charge layer. However, too thick a coating can cause more problems than it alleviates because it increases absorption of both incoming electrons and outgoing X-rays and so reduces the observed X-ray intensities. Furthermore, to obtain a consistent thickness of the coating, it is important to ensure that the standards are coated at the same time as the samples to be analyzed or, if coated separately, by use of thickness monitor (Greaves 1970).

(6) *Count-time*: because of the time-dependent nature of alkali mobility, reduction of the count-time can help to reduce migration. A careful balance must be struck between shorter count-times and accumulation of adequate counts. Reduced count-times are more feasible with EDS because of the greater efficiency of Si(Li) detectors. If only two WD (or even three) spectrometers are available, the sample must be irradiated for a long period to collect sufficient counts for 9–10 elements. Even if the sample is analyzed for Na first, the concomitant increase in other elements continues to occur through the remaining count-time.

(7) *For EDS analysis*: use a "thin window" if available, or operate in windowless mode. This allows more counts to enter the detector and so reduces count-time. However, windowless mode risks permanent damage to the detector if the probe vacuum fails.

(8) *For WDS analysis*: owing to the ease with which

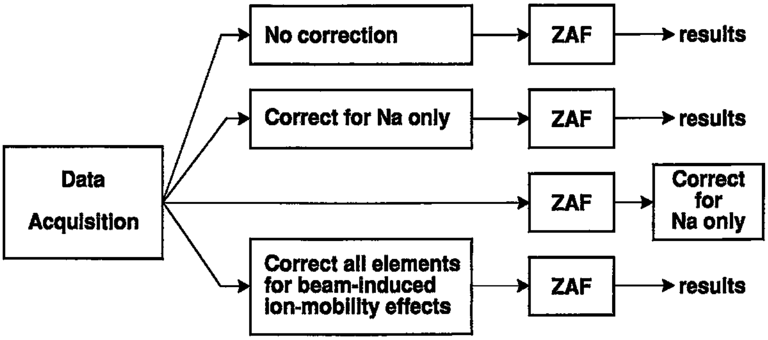

FIG. 6. Data-processing options to correct for migration of alkali metals. Performing pre-ZAF corrections for all elements in order to rectify beam-induced ion mobility effects is the only proper solution.

the alkali metals are mobilized in the WDS mode at routine operating conditions, analyze for Na and K first, so that their loss or gain is minimized. Note that this does not reduce the obverse effect (Figs. 1c, f) on other elements (*e.g.*, Roberts *et al.* 1990).

(9) *Data corrections*: Correct all elements for beam-induced ion-mobility effects prior to ZAF correction (Fig. 6). Collect decay or enrichment curves for all elements simultaneously. Na loss may be estimated by extrapolating the count-rate back to zero time (Nielsen & Sigurdsson 1981). Some workers correct for alkali loss or gain by adjusting the Na and K values *after* on-line ZAF processing, but such an approach fails to compensate for the apparent increase (or decrease) in the remaining (unmobilized) elements and leads to the compounding of analytical error.

(10) *International standards*: use international glass standards (*e.g.*, Myers *et al.* 1976, Abbey 1983, N.I.S.T. 1994) to calibrate and to test for alkali migration and check overall results.

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REFERENCES

ABBEY, S. (1983): Studies in "standard samples" of silicate rocks and minerals 1969–1982. *Geol. Surv. Can., Pap.* **83-15**.

ASHBY, M.F. & JONES, D.R.H. (1986): *Engineering Materials. 2. An Introduction to Microstructures, Processing and Design.* Pergamon Press, Oxford, U.K.

AUTEFAGE, F. (1980): Variations de la teneur en sodium et en potassium dans des minéraux au cours de leur analyse à la microsonde électronique. *Bull. Minéral.* **103**, 48-53.

________ & COUDERC, J.-J. (1980): Étude du mécanisme de la migration du sodium et du potassium au cours de leur analyse à la microsonde électronique. *Bull. Minéral.* **103**, 623-629.

BAIRD, A.K. & ZENGER, D.H. (1966): Use of the soft X-ray spectrograph and the electron-probe microanalyzer for determination of elements carbon through iron in minerals and rocks. *Adv. X-Ray Anal.* **9**, 487-503.

BEARD, J.S. & LOFGREN, G.E. (1991): Dehydration melting and water-saturated melting of basaltic and andesitic greenstones and amphibolites at 1, 3, and 6.9 kb. *J. Petrol.* **32**, 365-401.

BISCHOFF, A. & STÖFFLER, D. (1992): Shock metamorphism as a fundamental process in the evolution of planetary bodies: information from meteorites. *Eur. J. Mineral.* **4**, 707-755.

BOROM, M.P. & HANNEMAN, R.E. (1967): Local compositional changes in alkali-silicate glasses during electron microprobe analysis. *J. Appl. Phys.* **38**, 2406-2407.

BROUSSE, R., VARET, J. & BIZOUARD, H. (1969): Iron in the minerals of the sodalite group. *Contrib. Mineral. Petrol.* **22**, 169-184.

BUTT, C.R.M. & VIGERS, R.B.W. (1977): Rapid increase of sodium count rates during the electron microprobe analysis of sepiolite. The role of zeolitic water. *X-ray Spectrom.* **6**, 144-148.

CASTAING, R. (1951): *Application des sondes électroniques à une méthode d'analyse ponctuelle chimique et cristallographique.* Thèse, Université de Paris, Paris, France.

CAZAUX, J. (1986): Some considerations on the electric field induced in insulators by electron bombardment. *J. Appl. Phys.* **59**, 1418-1430.

Doremus, R.H. (1973): *Glass Science*. John Wiley and Sons, New York, N.Y.

Estour, H. (1971): Observation sur la modification de verres par le faisceau électronique d'une microsonde. *Verres réfract.* **25**, 11-17.

Fitzgerald, R., Keil, K. & Heinrich, K.F.J. (1968): Solid-state energy-dispersion spectrometer for electron microprobe X-ray analysis. *Science* **159**, 528-530.

Friskney, C.A. & Haworth, C.W. (1967): Heat-flow problems in electron-probe microanalysis. *J. Appl. Phys.* **38**, 3796-3798.

Goldstein, J.I., Newbury, D.E., Echlin, P., Joy, D.C., Romig, A.D., Lyman, C.E., Fiori, C. & Lifshin, E. (1992): *Scanning Electron Microscopy and X-Ray Microanalysis* (second edition). Plenum Press, New York, N.Y.

Goodhew, P.J. (1975): Electron probe microanalysis of glasses containing alkali metals. *Microstruct. Sci.* **3**, 631-641.

________ & Gulley, J.E.C. (1974): The determination of alkali metals in glasses by electron probe microanalysis. *Glass Tech.* **15**, 123-126.

Graham, J., Butt, C.R.M. & Vigers, R.B.W. (1984): Subsurface charging, a source of error in microprobe analysis. *X-Ray Spectrom.* **13**, 126-133.

Greaves, C. (1970): Film thickness measurement by monitoring methods. *Vacuum* **20**, 332-340.

Jarosewich, E. (1975): Chemical analysis of two microprobe standards. *In* Mineral Sciences Investigations 1972–73 (W.G. Melson, ed.). *Smithsonian Contrib. Earth Sci.* **14**, 85-86.

Koeberl, C. (1986): Geochemistry of tektites and impact glasses. *Annu. Rev. Earth Planet. Sci.* **14**, 323-350.

Lineweaver, J.L. (1963): Oxygen outgassing caused by electron bombardment of glass. *J. Appl. Phys.* **34**, 1786-1791.

McSween, H.Y. (1987): *Meteorites and their Parent Planets*. Cambridge University Press, Cambridge, U.K.

Myers, A.T., Havens, R.G., Connor, J.J., Conklin, N.M. & Rose, H.J., Jr. (1976): Glass reference standards for the trace element analysis of geologic materials – compilation of interlaboratory data. *U.S. Geol. Surv., Prof. Pap.* **1013**.

Natland, J. (1991): Mineralogy and crystallization of oceanic basalts. *In* Oceanic Basalts (P.F. Floyd, ed.). Blackie and Son, Glasgow, U.K. (63-93).

Nielsen, C.H. & Sigurdsson, H. (1981): Quantitative methods for electron microprobe analysis of sodium in natural and synthetic glasses. *Am. Mineral.* **66**, 547-552.

N.I.S.T. (1994): Standard Reference Materials. *Nat. Inst. Standards and Technology, Spec. Publ.* **260**. U.S. Department of Commerce, Gaithersburg, Maryland.

Ono, Y., Nielsen, C.H., Tagata, S. & Seo, Y. (1985): High speed wide area analysis by electron microprobe. *In* Microbeam Analysis, 20th Annual Conf. (J.T. Armstrong, ed.). San Francisco Press, San Francisco, California (421-423).

Reed, S.J.B. (1993): *Electron Microprobe Analysis* (second edition). Cambridge University Press, Cambridge, U.K.

Ribbe, P.H. & Smith, J.V. (1966): X-ray emission microanalysis of rock-forming minerals. IV. Plagioclase feldspars. *J. Geol.* **74**, 217-233.

Roberts, A.C., Sabina, A.P., Ercit, T.S., Grice, J.D., Szymański, J.T. & Ramik, R.A. (1990): Voggite, a new hydrated Na–Zr hydroxide–phosphate–carbonate from the Francon Quarry, Montreal, Quebec. *Can. Mineral.* **28**, 155-159.

Spray, J.G. (1987): Artificial generation of pseudotachylyte using friction welding apparatus: simulation of melting on a fault plane. *J. Struct. Geol.* **9**, 49-60.

________ (1993): Viscosity determinations of some frictionally generated silicate melts: implications for fault zone rheology at high strain rates. *J. Geophys. Res.* **98**, 8053-8068.

Statham, P.J. & Nashashibi, T. (1988): The impact of low-noise design on X-ray microanalytical performance. *In* Microbeam Analysis, 23rd Annual Conference (D.E. Newbury, ed.). San Francisco Press, San Francisco, California (50-54).

Stolper, E. (1982): Water in silicate glasses: an infrared spectroscopic study. *Contrib. Mineral. Petrol.* **81**, 1-17.

Stormer, J.C., Pierson, M.L. & Tacker, R.C. (1993): Variation of F and Cl X-ray intensity due to anisotropic diffusion in apatite during electron microprobe analysis. *Am. Mineral.* **78**, 641-648.

Sweatman, T.R. & Long, J.V.P. (1969): Quantitative electron-probe microanalysis of rock-forming minerals. *J. Petrol.* **10**, 332-379.

Varshneya, A.K., Cooper, A.R. & Cable, M. (1966): Changes in composition during electron microprobe analysis of K_2O–SrO–SiO_2 glass. *J. Appl. Phys.* **37**, 2199.

Vassamillet, L.F. & Caldwell, V.E. (1969): Electron-probe microanalysis of alkali metals in glasses. *J. Appl. Phys.* **40**, 1637-1643.

Zarzycki, J. (1991): *Glasses and the Vitreous State*. Cambridge University Press, New York, N.Y.

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