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# THE OPTICAL FUSION OF WHOLE-ROCK POWDERS AND THEIR ANALYSIS BY AN ELECTRON-MICROPROBE TECHNIQUE

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## ABSTRACT

An optical furnace has been designed and used successfully to produce direct-fusion glasses from a wide range of rock compositions. These glasses have been analyzed by a rapid energy-dispersive electron-microprobe technique to give results that compare very satisfactorily with quantitative analyses obtained by wet chemical and X-ray fluorescence methods.

*Keywords*: electron microprobe, energy-dispersive analysis, optical fusion, glasses, Ascension Is.

## SOMMAIRE

Au moyen d'un four optique construit par nous, nous avons pu vitrifier directement une série de roches préalablement pulvérisées couvrant un domaine étendu de composition. L'analyse de ces verres à la microsonde électronique (mode de dispersion d'énergie) donne des résultats tout-à-fait comparables à ceux qu'ont fournis des analyses quantitatives par voie humide et par fluorescence X.

(Traduit par la Rédaction)

*Mots clés*: microsonde électronique, analyses par dispersion d'énergie, fusion optique, verres, île de l'Ascension.

## INTRODUCTION

Several methods of sample preparation for whole-rock analysis with the electron microprobe have been suggested, *e.g.*, pressed powder, direct fusion and flux fusion. Either flux fusion is an adaptation of the method used by Norrish & Chappell (1977) for X-ray fluorescence analysis, or else it uses $Li_2B_4O_7$ alone in flux:sample proportions as low as 3:1 (Arrhenius *et al.* 1964, Gulson & Lovering 1968, Reed 1970, Mori *et al.* 1971, Inman 1972, Wittkopp & O'Day 1973). Direct fusion is carried out either in a quench furnace with graphite crucibles (Rucklidge *et al.* 1970) or with molybdenum or iridium strip heaters, either in air or in an inert atmosphere (Nicholls 1974, Brown 1977).

All these techniques suffer from particular disadvantages. Pressed powders are suitable only if the grain size can be kept much smaller than the analyzed volume and substantially less than the depth of electron penetration (1–5 $\mu$m). If this is not the case, the analyzed volume may not be representative of the bulk composition and, furthermore, normal ZAF corrections are not applicable. An added difficulty is encountered in rendering powders conductive. The carbon film normally deposited for this purpose commonly fails either because it breaks when the sample is transferred into and out of vacuum or else, perhaps, because there is inadequate electrical conductivity between individual particles.

The use of large amounts of flux to assist in fusion results in a deterioration in both accuracy and sensitivity. The reduction of the flux:sample ratio to, say, 3:1 reduces these problems, but then loss of Fe to the crucible increases with viscosity. All methods involving the addition of flux also have the disadvantage that both flux and sample must be weighed accurately. Flux melting has the advantage, however, of retaining P and S and of being able to accommodate all rock compositions.

Direct melting of samples also has disadvantages. If a muffle or a quench furnace is used, crucibles are required. Alumina crucibles are costly and cannot be reused. If graphite crucibles are used for such direct fusions, Fe and other transition metals are lost to the crucibles by reduction of oxides to metals. Some of these problems are avoided by using a strip furnace, but others are introduced: the 10–20 mg of powder that can be melted in such a furnace may not be representative of a sample unless it is ground to very much less than 100 $\mu$m; only iridium and rhenium can be used in air. Although molybdenum has several advantages, it must be used in an inert atmosphere; it contaminates the glasses significantly (0.3–0.8 wt. %) and absorbs Fe and Ti from the glass (Brown 1977, Cameron-Schimann 1978). Such effects are enhanced by the high surface-to-volume ratio of the glass in a strip furnace. Whereas this high ratio combined with high strip temperatures will tend to increase alkali volatilization, the rapidity of fusion will work in the opposite direction. However, the short run time may also lead to inhomogeneities in the glass (Brown 1977).

## DEFINITION OF THE PROBLEM

To be analyzable by the electron microprobe a prepared rock sample must be: (1) *Homogeneous* at the scale of the volume excited by the electron beam. It was found that a convenient method of analyzing as large a volume as possible was to use a rastered beam to sweep over four areas of about 600 x 500 μm, thus including a volume of $\sim 4 \times 10^{-6}$ cm$^3$ (average depth of penetration of the electron beam $\sim 3$ μm). The rock sample must, therefore, be homogeneous at the scale of about $10^{-5}$ g. (2) *Nonporous and polishable*: Using a porous sample and a nonporous standard, or sample and standard of different porosity, results in different conditions of X-ray production. Normal ZAF corrections will not be applicable. (3) *Undiluted:* Peak-to-background ratios of dilute samples are decreased relative to pure samples, and consequently detection limits are increased and accuracy is decreased.

Additionally, the prepared sample should be representative of the original sample, at least within the limits of precision of the analytical method. Preparation should be rapid and inexpensive to take advantage of the capabilities for rapid analysis of microprobes, particularly those equipped with energy-dispersive spectrometers.

## PRELIMINARY WORK

To find a satisfactory solution to these problems, one must consider certain physical dimensions and parameters, *e.g.*, sample size, evaporation losses from melts, diffusion rates in melts and limits of glass-forming compositions.

### *Homogeneity and representativity*

When a glass is produced from a powdered rock sample, the volume to be analyzed by the electron microprobe ($\sim 4 \times 10^{-6}$ cm$^3$) must be representative of the sample, *i.e.*, its composition must be indistinguishable from that of the sample (within the limits of precision of the analytical method used). Firstly, the scale of homogeneity of the rock powder must be determined, so that the size of the smallest volume to be melted that will be representative of the sample can be calculated. Secondly, it must be determined whether melting to form a glass will reduce this size relative to that of the analyzed volume.

The problem of sampling error was discussed by Wilson (1964) and Ingamells *et al.* (1972). From their work, sampling errors can be calculated for various cases. Thus, for a granite ground 100% to –100 μm, containing 1.5% FeO bound in biotite (6% of the rock and containing 25% FeO), sampling errors for various sampling sizes will be as follows:

| | | | |
|---|---|---|---|
| *relative error* (%) | 0.1 | 0.3 | 1.0 |
| *sample size* (mg) | 1000 | 100 | 10 |

For minor elements, especially those concentrated in single phases, sampling errors will be much larger. Considering the possible sensitivity and precision of the microprobe method, a sample size of 0.1–0.5 g will be adequate for major and minor elements.

Fusion of this 0.1–0.5 g of rock powder must result in a reduction of the sampling size to $10^{-5}$ g. Two mechanisms will tend to homogenize the melt: (i) self-diffusion of elements and (ii) convection or mixing due to movement of bubbles (or both). Data from Borom & Pask (1968), Eitel (1964), Sippel (1963), Towers & Chipman (1957), Towers *et al.* (1953) and Winchell (1971) show that in synthetic glasses at 1400°C, the mean displacement of ions over 300 s varies from 0.08 mm for Si to 1.73 mm for Na. Here, $X^2$ (mean displacement) $= 2DT$ (Ramberg 1952), in which $D$ is the diffusion coefficient and $T$, time. Comparison with the radius (2 mm) of a sphere of glass of 0.1 g shows that diffusion is barely sufficient even for Na. However, convection increases the mean displacement by a factor of 30 (Shimada 1954).

### *Glass making*

The most common method of making a glass from rock powder is to place a crucible containing the powder in a furnace and heat it to a temperature above the liquidus. Among commonly used crucibles, only recrystallized alumina and the platinum-group metals can be employed over the whole temperature range required for the melting of most rocks. However, recrystallized alumina contaminates the melts, and crucibles of platinum-group metals absorb transition elements from the melt. These effects are not too serious in brief runs (less than 15 min for amounts of 3–5 g). Graphite can be employed up to temperatures sufficiently high to melt all types of rocks, but a complicating factor is that it must be used in an oxygen-free enclosure; even then, it has a tendency to burn by reducing transition-element oxides to the metals. Of the above, only graphite can be reused and is sufficiently inexpensive to be considered for large numbers of analyses.

Homogeneous glasses can be produced rapidly and with a minimum of equipment by using a flux. The method used for X-ray-fluorescence analysis (Norrish & Chappell 1977) can be adapted. $La_2O_3$ is unnecessary as matrix corrections are made routinely and rather accurately

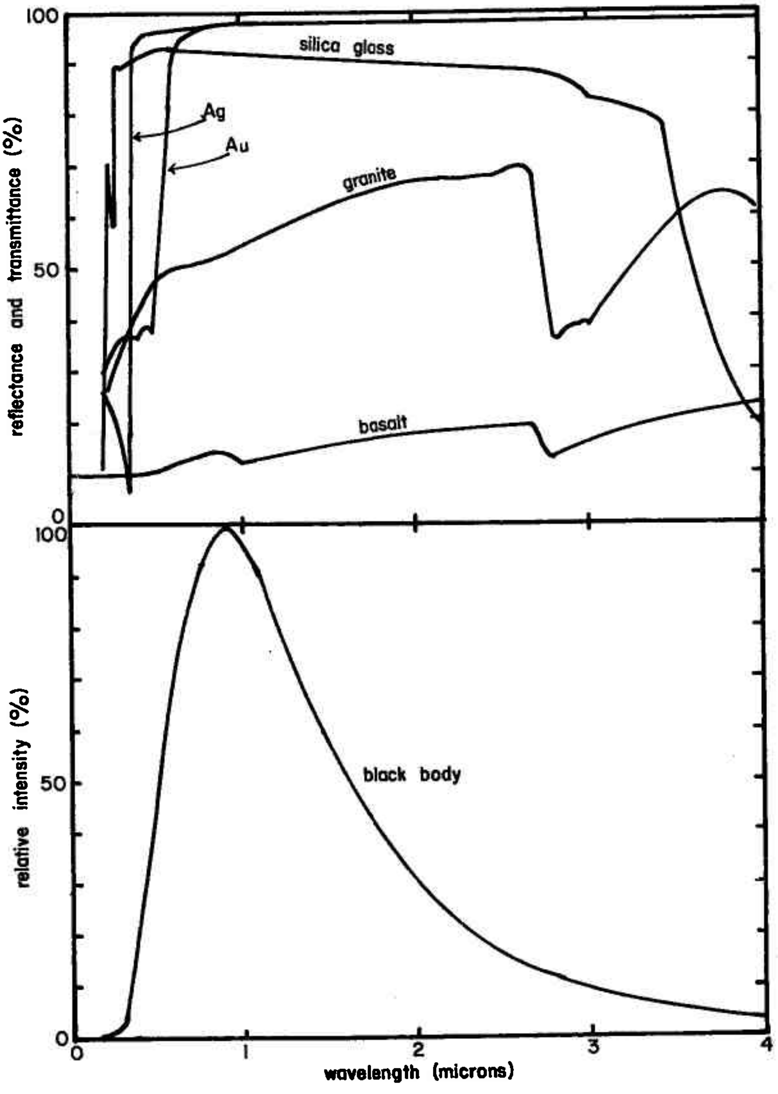

Fig. 1. Radiative properties of materials. Top: albedo of granite and basalt powders, reflectance of gold and silver, and transmittance of silica glass (less than 1 cm thick). Bottom: spectral distribution of energy emitted by a black body at 3200 K.

in microprobe analysis. The main drawback is the low sensitivity resulting from the seven-fold dilution. However, the dilution ratio can be reduced and our experiments show that glass can be produced in a Pt–Au crucible over a Meeker burner with a flux:rock (granite or basalt) ratio as low as 1:2. However, such low proportions of flux increase the time required for fusion, increase absorption of transition elements by the crucible and very significantly decrease the crucible life-span.

Thus, a method that requires no crucible and that is also rapid and inexpensive is needed. The technique developed for this purpose, which is described in the following section, uses an *image furnace*.

## THE IMAGE FURNACE

An image furnace is a device for projecting the image of a high-intensity radiation source onto the surface of the object to be heated. The source might be a carbon arc, a short-arc lamp, a filament lamp or the sun. The optical device may consist of (1) paraboloidal or ellipsoidal mirrors, or (2) lenses. The efficiency of an image furnace is proportional both to the fraction of the source energy that can actually be focused onto the subject to be heated and also, inversely, to the albedo of the object for the spectral range of radiation reaching it.

Several studies have been made of the radiative properties of geological materials (*e.g.*, Adams & Filice 1967, Hovis & Callahan 1966). They show (Fig. 1a) that in the spectral range 0.4–22 μm, (1) felsic igneous rocks have a Higher albedo than mafic rocks, as might be expected from their color; (2) albedo increases strongly as particle size decreases; the albedo of an unsorted powder is similar to that of the finest fraction; (3) albedo increases from 0.4 μm to the near-infrared but is low again above 5 μm, and (4) most rock types show strong absorption bands between 2 and 3 μm. From these considerations, one should choose as small a source as possible emitting in the ultraviolet or in the infrared range, either above 5 or between 2 and 3 μm. However, ultraviolet and far-infrared radiations require the use of special optical material.

Amongst the three compact light-sources that could be used, short-arc lamps emit most of their energy between 0.25 and 1.1 μm. Carbon arcs are of various types, but in general a large proportion of their emitted energy is in the ultraviolet and visible regions. Both of these sources require rather complex and expensive power supplies. However, as they are nearly point sources they have the advantage of possessing very high radiance (power/unit surface-area). The emission of the incandescent lamp is similar to that of a black body, with a maximum (at 3000 K) at 0.9 μm. Thus, a large part of their energy is in the infrared. The spectral efficiency for the present purpose is about equivalent to that of a carbon arc or a short-arc lamp. A disadvantage is a lower radiance (larger source at equal power), but there are advantages of low cost, simplicity and flexibility: the power output can be varied, according to the type of material to be melted, by means of a simple rheostat. In the prototype, a 120 V – 2000 W tungsten–halogen lamp with a silica glass envelope was used (type BWA of G.T.E. Sylvania). At 120 V, it approximates a black-body radiation source at 3200 K (Fig. 1b).

The optical components of the image furnace (Figs. 2, 3) consist of (1) an ellipsoidal main mirror: diameter 40.64 cm (16 in.), clearance (from apex to near focal point) 12.7 cm (5 in.), working distance (from apex to far focal point) 50.8 cm (20 in.), collecting efficiency 50% (catalogue number 3E–16–5–20, Special Optics, Cedar Grove, New Jersey, U.S.A.); (2) a hemispherical backup mirror: diameter 7.62 cm (3 in.), and (3) a conical collector mirror: height 12.7 cm (5 in.), diameter 17.78 cm (7 in.) and 4.57 cm (1.8 in.).

The fraction of emitted energy reaching the object to be heated depends on geometrical and optical characteristics of the furnace as well as on the materials used for mirrors and windows. In the prototype, first-surface gold-coated mirrors were used. Gold and silver have the highest reflectance within the spectral range considered. The reflectance of gold decreases sharply below 0.6 μm, but a lamp such as the one used emits little energy below that; gold also has the advantage of being chemically inert. Such mirrors should not be used above a few hundred degrees Celsius, so that cooling is necessary. Most of the image furnace's optical components are located outside a vacuum chamber containing the sample. The window of this chamber, made of silica glass (General Electric type 105), has nearly 100% transmittance from 0.3 to 2.7 μm and more than 70% from 0.25 to 3.5 μm (Fig. 1a). This interval contains over 95% of the energy radiated by the lamp.

The lamp is located at the near focal point of the main mirror, which collects directly 50% of the energy emitted and focuses it to the far focal point (sample position). The backup

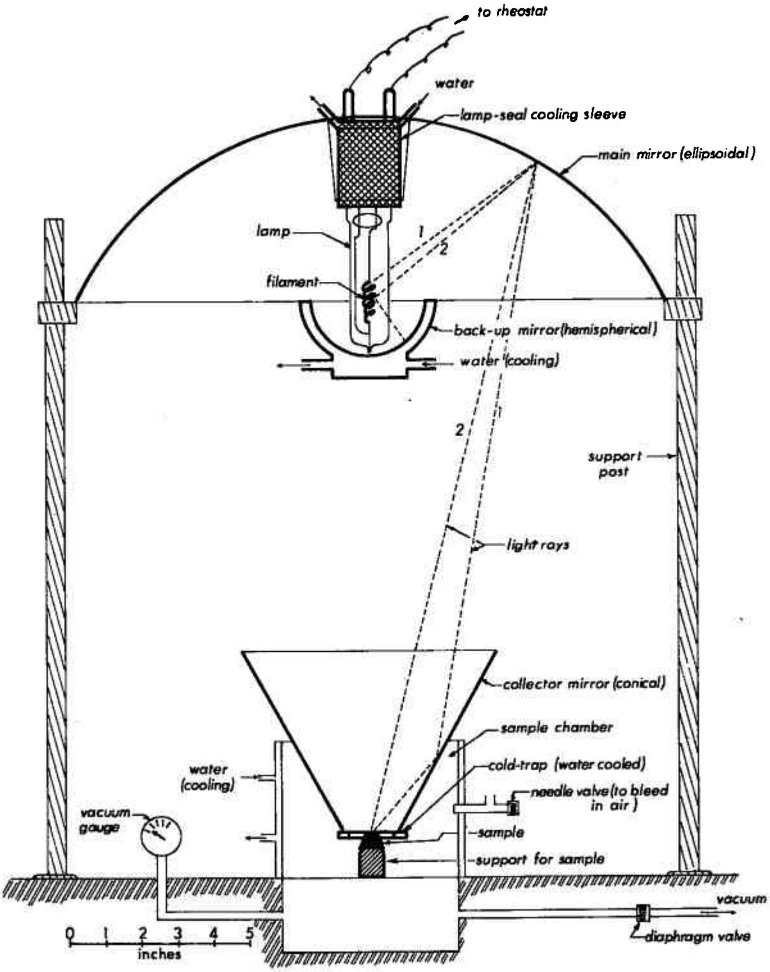

FIG. 2. Scale diagram of the optical furnace.

mirror collects the other 50% of the emitted energy, sending it back through the source to the main mirror. Because of the finite size of the source (9 x 35 mm), the image formed by the main mirror is large (90 mm diameter). The irradiance of this image is not homogeneous; the inner 25-mm-diameter circle, which is the surface to be heated, receives about 30% of the energy. The conical collector mirror concentrates a major portion of the outer 70% of the beamed energy onto this surface. Thus, the irradiance in the inner 25 mm circle is increased by 100–150%.

The main mirror and lamp are air-cooled, whereas the backup mirror and lamp-seal area are water-cooled. The sample sits in a vacuum chamber that is water-cooled as is also the ring supporting the small bell-jar, the latter being made from a 15 ml wide-form silica-glass crucible with the rim ground flat to hold vacuum.

The image furnace was built on a disused vacuum coating unit. The sample chamber is connected to the mechanical vacuum pump. The diffusion pump can also be connected if a hard vacuum is ever required. A needle valve is provided to bleed air or an inert gas into the chamber, whereas a diaphragm valve between the chamber and pump permits rapid and flexible vacuum control. In normal operation a pressure of between ¼ and ¾ atm is maintained and controlled using a Bourdon gauge; other gauges are available for hard vacuum. The upper part of the apparatus is enclosed in a thin aluminum casing to shield the operator from the ultraviolet radiation of the lamp and others from its glare.

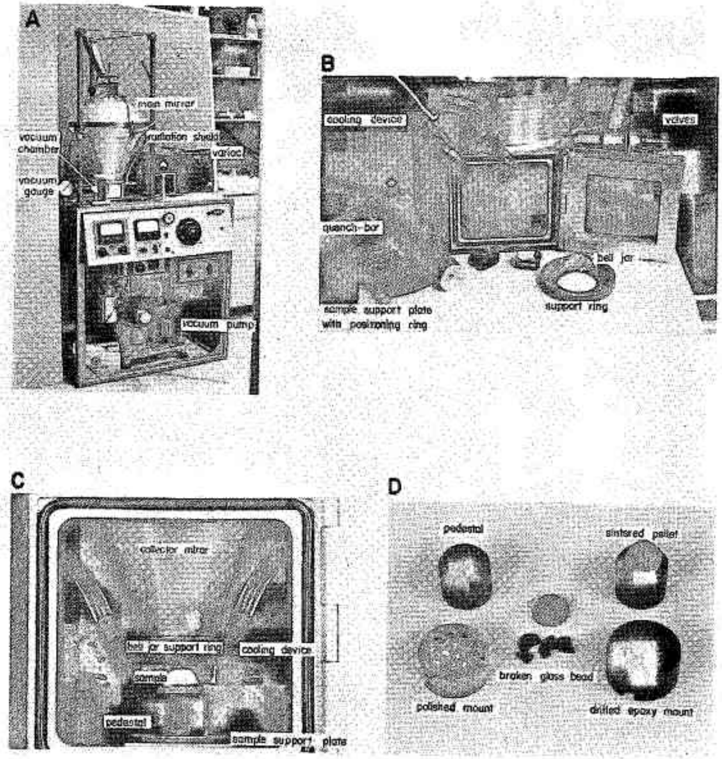

FIG. 3. The image furnace. A: general view of the instrument. B: the vacuum chamber with door open and components removed for viewing. C: the inside of the vacuum chamber with a sample in position for fusion. D: samples in various stages of preparation.

## FUSION PROCEDURE

### *Preparation*

The rock sample should be ground 100% to −100 μm to decrease sampling errors and aid in the melting, which will be more rapid with fine powder. A rough but useful test is that no grains will be detectable between the fingers if the powder is sufficiently fine.

During direct fusion some volatile components are lost: $H_2O$, $CO_2$, S, Cl and, in part, P. If such loss occurs during fusion in the image furnace, some of the evaporate is deposited onto the bell-jar, reducing its transmittance. This problem can be avoided by preheating about 0.5–2.0 g of sample powder in a 4 ml porcelain crucible for 12 hours at 1000°C in a muffle furnace. This eliminates most of the volatiles that otherwise would be lost during direct fusion, and produces a sintered pellet that can be tipped out of the crucible in one piece (Fig. 3). If a loss-on-ignition determination is required, it can be done at this stage. Preheating is most efficiently done in large batches (up to 40 crucibles) by using a tray made from refractory brick.

### *Fusion*

The sintered pellet is tipped from the crucible to sit inverted on the top of an Inconel® pedestal and is then introduced into the chamber of the image furnace. Inconel contains 72% Ni, 6–10% Fe and 14–17% Cr; this alloy has a good resistance to oxidation at high temperature. Ordinary steel would produce scales during fusion. The chamber is evacuated to ¾ – ¼ atm depending upon whether the composition of the sample is basic or acid. This partial vacuum is sufficient to extract bubbles that form in the melt, but soft enough to avoid loss of components by vapor transport. The voltage is then increased until fusion begins and then further increased by 10 to 20 volts (to a maximum of 120 volts) and held there for about 5 minutes for samples that melt readily, or 10 minutes for more refractory materials. After melting is complete, the sample is removed from the furnace and quenched with an aluminum bar.

The upper half or two-thirds of the pellet is melted, whereas the lower part acts as the hearth, thereby eliminating the problem of contamination by crucible walls. The elimination of bubbles not only makes an easily polished glass, but also aids homogenization. Mixing is enhanced in viscous melts by varying the pressure during melting.

### *Processing*

Glass chips of sufficient size to produce a polished surface of 3–4 mm² are mounted in epoxy resin, 12 or more groups *per* 2.5-cm-diameter mount. It is convenient to prepare epoxy-resin blanks, drill 12 holes a few mm deep, embed the glass chips in fresh epoxy resin, and then set the mount upside down on a glass plate (*e.g.*, a petrographic slide) for curing. Thus, all chips will be at the same level near the surface, ensuring easier grinding.

For best results, grinding prior to polishing should be on silicon carbide paper, not on a cast-iron wheel or glass plates with silicon carbide powder. Otherwise, procedures are the same as those for other polished mounts for microprobe work.

### *Analysis*

The procedure used for analysis is very similar to that outlined by Smith & Gold (1976). The energy-dispersive technique employed gives fully quantitative analyses for major and minor elements from Na to Zn, plus Zr and Ba. Thus, 22 elements are determined simultaneously and automatically. Analyses are made for 200 s using a rastered beam sweeping over an area of 300 x 250 or 600 x 500 $\mu$m. If the rock is acid and the melt from which the glass was formed is viscous, minor residual inhomogeneities can be averaged by selecting four such areas and sweeping each for 100 s. The data produced are processed through the FORTRAN IV program EDATA (Smith & Gold 1976), which applies all necessary corrections including those for background, overlap, escape peaks, drift and ZAF effects.

### *Vaporization losses*

Losses of $H_2O$, $CO_2$, S, Cl and P (in part) will occur in all direct-melting methods. Phosphorus losses can be minimized by using as short a melting time as possible. These losses detract little from the usefulness of the method, but other losses may be more significant, alkalis being of particular concern.

At temperatures above 1000°C, the partial pressure of vapor of some of the constituents of rocks is sufficiently high that losses may occur; this may be a potential source of error in the result. To a first approximation, a melt may be considered as a mixture of oxides. At the surface of the melt, an oxide $MO(1)$ is in equilibrium with its vapor constituted by $MO(g)$, $M(g)$, $O(g)$, *etc.* The surface of the enclosing chamber is at a much lower temperature and the vapor pressure of $MO$ is lower there than near the surface of the melt; a concentration gradient is established and mass transfer occurs. In soft vacuum or at $P = 1$ atm, the mass-loss rate is pressure dependent and a diffusion-controlled process. Experiments on synthetic glass at P = 1 atm show loss rates from 3 to 150 x $10^{-4}$ mg/cm² at 1400–1500°C (Dietzel & Merker 1957, Oldfield & Wright 1962). The losses involve Na, mainly.

Experiments on tektites and lunar rocks are more akin to the present problem as they deal with complex natural systems, one granitic and the other basaltic. Walter & Carron (1964) found weight losses at $10^{-6}$ atm of 3–7 x $10^{-2}$ mg/cm²min at 2000–2100°C and 1.4 x $10^{-3}$mg/cm²min at 1780°C. The vapor pressure at 1600°C was measured as 0.3 atm. Centolanzi & Chapman (1966) measured a vapor pressure of $10^{-5}$ atm at 1600°C and mass-loss rates that vary (at 1825°C) from 1 mg/cm²min at 0.1 atm to 0.1 mg/cm²min at 1 atm. These two sets of results on tektites are quite contradictory; the method used by Centolanzi & Chapman (1966), direct measurement of weight loss by evaporation, is more similar to the present situation.

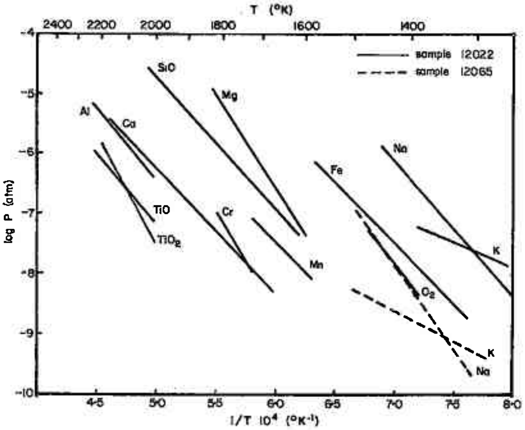

FIG. 4. Vaporization behavior of lunar basalts in vacuum; "log P (atm)" refers to partial pressure for each of the elements or oxides (after De Maria *et al.* 1971).

Biggar & O'Hara (1972) measured mass-loss rates for $Na_2O$ and $K_2O$ of 0.1 mg/cm$^2$min at 1175°C and $P = 10^{-7}$ to $10^{-8}$ atm from a tholeiite. De Maria *et al.* (1971) measured the vapor pressure of lunar basalts. Their findings are shown in Figure 4. The differences between the two samples may be related to differences in viscosity: sample 12022, 7 poises and sample 12065, 11 poises at 1400°C (Weill *et al.* 1970). Thus, vaporization losses may be significant for alkalis and iron if a hard vacuum is used during melting.

In conclusion, it appears that vaporization losses will be negligible provided that the pressure during melting is kept above 0.1 atm for low-viscosity melts (basalts, ultramafic rocks, peralkaline rocks) and 0.01 atm for high-viscosity melts (granites, granodiorites).

### *Limits of glass-forming compositions*

Limits of glass-forming compositions are set by the ability of the furnace to melt a given composition and by the ability of a melt to form a glass on cooling. Certain rock compositions cannot be melted in this image furnace because of their high liquidus-temperature (*e.g.*, ultramafic compositions with MgO $> 45\%$) or their high albedo (or both). Other compositions (*e.g.*, $Al_2O_3 + SiO_2 < 45\%$) form a melt that does not solidify as a glass but instead crystallizes even on rapid quenching. Yet other compositions produce immiscible liquids that quench to inhomogeneous glasses. A discussion of the formation of glasses can be found in Rawson (1967).

Most rocks can be considered as mixtures of silica, alumina, alkali and alkaline-earth oxides, and iron oxide. The lower limits of silica content (in mol %) for glass-formation in some synthetic systems, after Imaoka (1962), are: $SiO_2$–$K_2O$ 45.5%; $SiO_2$–$Na_2O$ 42.0%; $SiO_2$–BaO 60.0%; $SiO_2$–CaO 43.3% and $SiO_2$–MgO 57.5% $SiO_2$. Ternary systems of the same oxides show silica limits intermediate between the two binary systems, sometimes somewhat lower (Imaoka & Yamazaki 1968). In igneous rocks, compositions beyond the glass-forming domain are reached only in ultramafic rocks (high MgO) and in carbonatites (high CaO and $CO_2$). Fields of liquid immiscibility can be observed in several phase diagrams shown in Levin *et al.* (1964, 1969). Such fields, however, are temperature-dependent and, in most cases, beyond natural compositions.

Volatile-rich compositions present a problem. During the preheating stage, carbonates and sulfides are transformed into oxides, possibly producing non-glass-forming compositions; carbonaceous matter burns, and $CO_2$ and $SO_2$ are eliminated with $H_2O$. As a result, the proportion of glass-forming oxides ($SiO_2$, $Al_2O_3$) becomes too small and the liquid cannot be quenched to a glass. Phosphates and sulfates are not dissociated during preheating whereas they are in the image furnace, especially under vacuum. Samples containing more than 1–2% phosphate or sulfate should be melted at atmospheric pressure. If more than 4–5% phosphorus is present, another melting technique should be used.

## DISCUSSION

### *Advantages and disadvantages*

There are a number of significant advantages to the technique outlined:

(1) Because the sample forms its own hearth, there are no problems of contamination on the one hand, nor of loss of material to the crucible on the other. There seems to be no vertical compositional gradient paralleling the temperature gradient, probably because of the speed of the melting and the mixing effect of bubbles streaming from the melt. At the same time, diffusion in the melt is sufficiently rapid to homogenize it, and the volume of glass formed from a 0.5–2.0 g sample is statistically representative of the original rock if powdered to the dimensions suggested.

(2) Because dilution of the sample with flux is unnecessary in most cases, sensitivity and accuracy are high, and peak:background ratios are maintained at a maximum.

(3) Operation of the equipment is simple and flexible. Temperature, vacuum and atmosphere can all be easily controlled. The glasses can be produced by any careful person of normal technical ability after very brief training.

(4) The energy-dispersive analytical technique advocated (EDA) is rapid and permits the simultaneous analysis of up to 22 elements with an accuracy for major elements at least as good as wavelength-dispersive microprobe analysis (WDA) or XRF techniques. Because of the lack of focusing requirements in EDA, it is unnecessary to have the perfect surface-polish required with the fully focusing crystal spectrometers used in WDA; also, a broadly rastered beam can be used to analyze a much larger volume.

(5) Sample preparation is rapid, at least as rapid as the preparation of glass discs for XRF analysis. For samples processed in batches of, say, 30 to 40, it takes, about 20 minutes *per* sample to

carry out all phases of the preparation including sintering, fusion and making polished mounts. (6) Cost of sample preparation and analysis is low. The cost of obtaining a fully quantitative analysis (to us, for 22 elements) is estimated to be close to $20 *per* sample, including all materials, labor, microprobe time and data-reduction (computing) costs, provided again that samples are run in batches.

The technique also has some disadvantages, most of which are related to the direct-melting method rather than to the type of furnace used. Volatile elements including $H_2O$, $CO_2$, Cl, F, S, P (in part), probably Pb and possibly other elements in the Pb and S groups are lost. The method has certain limits in terms of the compositions that can be handled. The furnace can heat dark-colored powders to 1700–1800°C but light-colored samples can be raised to 1400–1500°C only. Temperatures could undoubtedly be increased somewhat by modifications to the optical design.

Glasses cannot be prepared from ultramafic compositions or from carbonate-rich sediments by the technique outlined. Also, if $SiO_2 + Al_2O_3 > 85\text{–}90\%$, the melt is very viscous and has a high liquidus temperature and a high albedo. Silicates with $Fe_2O_3 > 20\text{–}25\%$ commonly show immiscibility phenomena with the formation of silica-rich and oxide-rich liquids. If more than 4–5% phosphorus is present, it evaporates in the image furnace, coating the silica-glass isolation window and reducing furnace efficiency. A similar effect may be expected with sulfate-rich rocks.

Most of these problems associated with particular rock compositions can be avoided by using $Li_2B_4O_7$ flux in 1:1 to 2:1 ratio with sample, with subsequent melting being carried out in air. For the most accurate analysis, sample and flux should be weighed. However, in most cases, satisfactory accuracy is achieved by assuming that the difference between the oxide totals of the elements analyzed and 100% has the flux composition. Where the Fe content is high, it must be calculated partly as $Fe_2O_3$ and partly as FeO. Wet-chemical analyses of glasses with and without flux have shown that Fe is only partly oxidized; about 66% of the total Fe is present as $Fe_2O_3$.

### *Analytical results*

The reliability and accuracy of the method developed were tested by carrying out analyses of a collection of international rock standards and a few rocks analyzed locally by classical wet-chemical methods. The results are presented

TABLE 1. COMPARISON BETWEEN 'KNOWN COMPOSITION' AND ELECTRON-MICROPROBE ANALYSES OF GLASSES PRODUCED FROM A VARIETY OF ROCK TYPES

| | T-1 Tonalite | | | | | | AVG-1 Andesite[1] | | | | BCR-1 Basalt[1] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Glass A | | | Glass B | | | | | | | | | |
| | 'Best Values'[2] | A1[3] | A2 | A3 | B1 | B2 | 'Usable Values'[2] | Glass A | Glass B | Glass C | 'Usable Values' | Glass A | Glass B | Glass C |
| Si | 29.90 | 29.80 | 29.76 | 29.86 | 29.88 | 29.46 | 28.34 | 28.63 | 28.82 | 28.74 | 25.57 | 25.83 | 25.72 | 25.76 |
| Ti | 0.36 | 0.37 | 0.35 | 0.42 | 0.44 | 0.39 | 0.64 | 0.59 | 0.61 | 0.66 | 1.32 | 1.35 | 1.29 | 1.34 |
| Al | 8.86 | 9.01 | 9.01 | 8.94 | 8.92 | 9.21 | 9.26 | 9.36 | 9.37 | 9.35 | 7.23 | 7.28 | 7.23 | 7.20 |
| Fe | 4.24 | 4.49 | 4.43 | 4.39 | 4.31 | 4.52 | 4.86 | 4.96 | 4.79 | 4.84 | 10.48 | 10.47 | 10.54 | 10.47 |
| Mn | 0.09 | 0.08 | 0.06 | 0.07 | 0.06 | 0.07 | 0.08 | 0.04 | - | - | 0.15 | 0.05 | 0.09 | 0.09 |
| Mg | 1.15 | 0.91 | 0.91 | 0.88 | 0.86 | 0.93 | 0.95 | 0.59 | 0.59 | 0.59 | 2.10 | 1.60 | 1.70 | 1.61 |
| Ca | 3.72 | 3.79 | 3.79 | 3.79 | 3.71 | 3.89 | 3.63 | 3.57 | 3.53 | 3.54 | 4.98 | 4.89 | 4.99 | 4.91 |
| Na | 3.33 | 3.19 | 3.35 | 3.28 | 3.50 | 3.33 | 3.25 | 3.14 | 3.03 | 3.04 | 2.43 | 2.25 | 2.27 | 2.43 |
| K | 1.05 | 0.99 | 1.00 | 0.99 | 0.95 | 0.94 | 2.47 | 2.49 | 2.50 | 2.52 | 1.39 | 1.42 | 1.36 | 1.38 |
| O | 47.30 | 47.37 | 47.34 | 47.38 | 47.37 | 47.26 | 46.52 | 46.63 | 46.76 | 46.72 | 44.35 | 44.86 | 44.81 | 44.81 |

| | R145 Rhyolite | | | | | | H42 Metabentonite | | | | R184 Gneiss[7] | | | R182 Ultramafic Rock[8] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Glass A | | Glass B | | | Glass A | | | | | | | | |
| | Wet Chem.[4] | XRF[5] | A1 | A2 | B1 | B2 | Wet Chem.[6] | A1 | A2 | Glass B | Wet Chem.[6] | Glass A | Glass B | Wet Chem | Glass A | Glass B |
| Si | 32.10 | 33.92 | 32.14 | 32.12 | 32.12 | 32.08 | 28.34 | 28.80 | 28.68 | 28.78 | 29.85 | 29.94 | 29.69 | 20.40 | 20.00 | 20.40 |
| Ti | 0.24 | 0.20 | 0.21 | 0.23 | 0.23 | 0.25 | 0.19 | 0.14 | 0.21 | 0.23 | 0.45 | 0.34 | 0.42 | 0.36 | 0.46 | 0.43 |
| Al | 8.69 | 7.19 | 8.50 | 8.55 | 8.53 | 8.52 | 12.96 | 12.07 | 12.13 | 12.01 | 10.75 | 10.79 | 10.93 | 3.00 | 2.74 | 2.64 |
| Fe | 2.00 | 1.81 | 2.08 | 2.08 | 2.20 | 2.16 | 0.83 | 1.45 | 1.48 | 1.51 | 4.61 | 4.76 | 4.85 | 11.12 | 12.77 | 12.15 |
| Mn | 0.03 | 0.03 | - | - | - | - | - | - | - | - | 0.02 | - | - | 0.14 | 0.17 | 0.12 |
| Mg | 1.00 | 0.72 | 0.89 | 0.87 | 0.85 | 0.86 | 2.85 | 2.17 | 2.19 | 2.20 | 1.39 | 1.10 | 1.14 | 18.78 | 17.27 | 17.64 |
| Ca | 3.07 | 2.70 | 3.15 | 3.15 | 3.16 | 3.15 | 0.43 | 1.23 | 1.20 | 1.23 | 0.54 | 0.54 | 0.54 | 1.85 | 2.38 | 2.28 |
| Na | 3.04 | 3.03 | 3.24 | 3.22 | 3.15 | 3.21 | 0.09 | - | - | - | 1.39 | 1.22 | 1.21 | 0.44 | 0.23 | 0.10 |
| K | 1.31 | 1.53 | 1.42 | 1.42 | 1.40 | 1.42 | 6.59 | 6.68 | 6.68 | 6.56 | 3.38 | 3.49 | 3.45 | 0.43 | 0.39 | 0.39 |
| O | 48.52 | 48.87 | 48.37 | 48.36 | 48.36 | 48.35 | 47.72 | 47.46 | 47.43 | 47.48 | 47.62 | 47.82 | 47.77 | 43.48 | 43.08 | 43.37 |
| Cr | | | | | | | | | | | | | | - | 0.29 | 0.28 |
| Ni | | | | | | | | | | | | | | - | 0.22 | 0.20 |

All analyses are recalculated to 100%, volatile-free; oxygen is calculated by stoichiometry, using the known ratio of $Fe^{2+}/Fe^{(total)}$ or 0.66 for the glasses. Microprobe analyses were made using one 400s count, rastering an area 300 x 250 microns.
[1] Glasses A and B are made with the image furnace, glass C was made by P. Roedder. [2] As per Abbey 1972. [3] 1, 2, and 3 are analyses of different areas of the same glass. [4] Wet-chemical analysis at University of Alberta, A. Stelmach analyst. [5] X-ray fluorescence analysis at University of Durham. [6] Analysis from A.P.I. Research Project #49. [7] Garnet-cordierite-spinel gneiss.
[8] Wet-chemical analysis not of same sample as glasses.

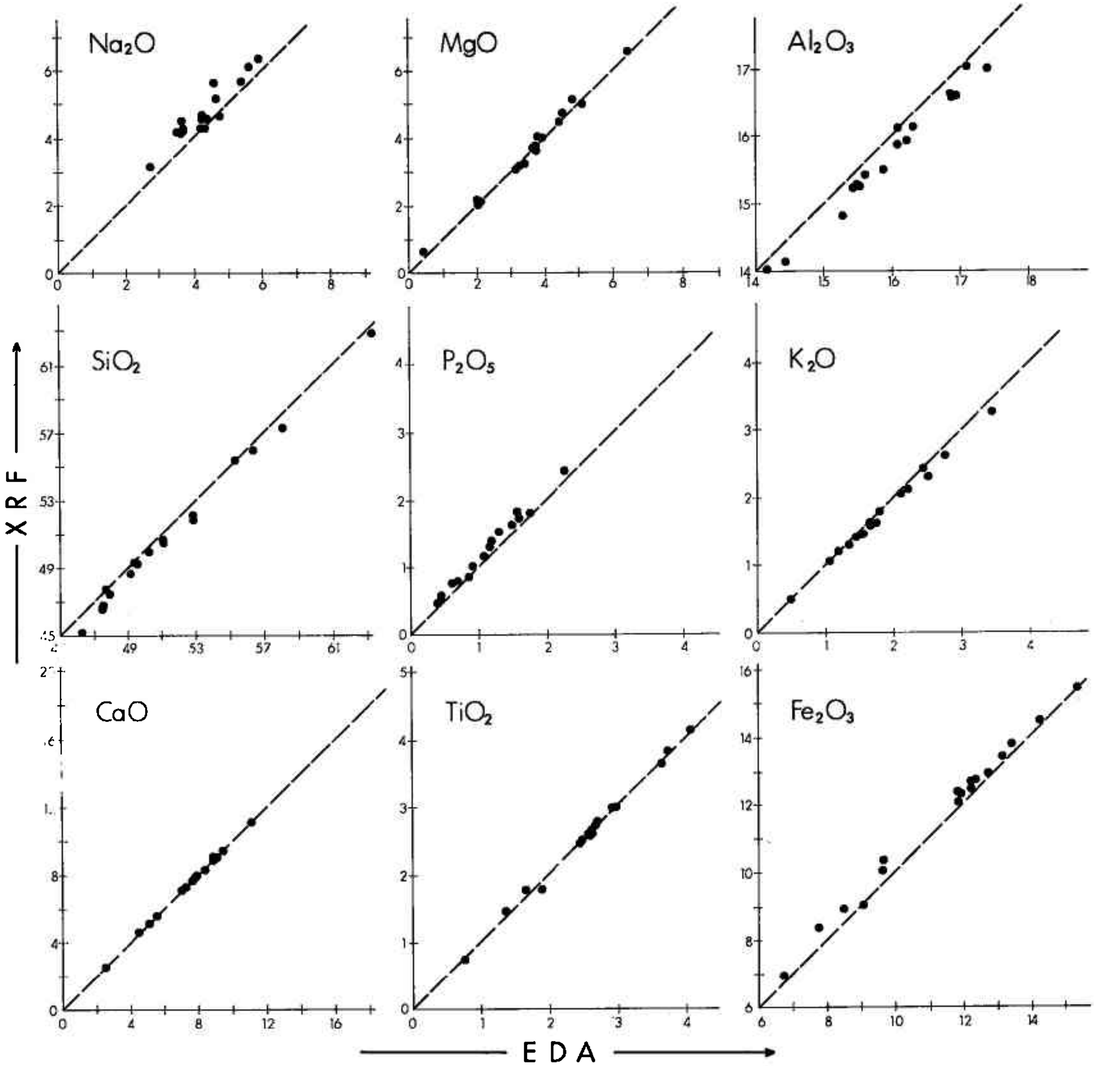

FIG. 5. A comparison of the results obtained using the microprobe method described in this paper and the fully quantitative X-ray-fluorescence method (Norrish & Chappell 1977), for a series of 17 basaltic to trachytic lavas from Ascension Island.

in Table 1, where it will be seen that, in general, correspondence is excellent. The systematically low values in the results for Na and Mg on these standards were traced to the buildup of an oil film on the Be window of the Si(Li) detector. The problem was subsequently cured and good results were obtained for these light elements.

The analyses of samples T-1, BCR-1 and AVG-1 show good agreement with the "best" or "usable" values, and there is no significant variation from glass to glass of the same sample or from one area to another on the same glass. As predicted in the discussion above, there is clearly no detectable loss of K. In the case of sample R145, it is difficult to decide which of the three analyses is best (wet chemical, X-ray fluorescence or microprobe). Samples H42 and R182 are examples of extreme compositions (aluminous and ultramafic, respectively). Again there is no significant difference between the two glasses of each sample. Sample R184 shows that rocks containing refractory minerals, such as spinel or garnet, can be melted completely to give a homogeneous glass.

To compare the technique described here with the fully quantitative X-ray technique described by Norrish & Chappell (1977), a suite of 17 basaltic to trachytic rocks from Ascension Island that had been analyzed particularly carefully by the XRF technique was reanalyzed by the microprobe method. The results are shown in Figure 5. In such diagrams, all points ideally should lie on a straight line with a slope of unity. Scatter of points reflects analytical errors from causes such as the fundamental statistical fluctuations that are associated with X-ray generation, as well as sampling errors and, in the case of the microprobe method, residual inhomogeneities in the glass. On the other hand, systematic departures from the ideal slope of unity, such as can be detected (*e.g.*, for Na, Al, Si and Fe), are likely to reflect errors in the accepted concentrations for the standards. Such departures are small in all instances seen here and may well be associated with the microprobe rather than the XRF analysis because "default" standard values were used for all elements in the microprobe work. Such "default" values are obtained on some previous occasion, when the instrument is calibrated, then stored for recall if no analytical standard is included in a run. The fact that this approach can be adopted so successfully is a reflection of the excellent long-term stability of an energy-dispersive system. In the case of Na and P it could be argued that the systematic departures reflect a loss of these elements from the sample during preparation in the optical furnace. Although this cannot be disproved from the data presented, large numbers of analyses that have now been carried out by the method described here give no indication that such is the case, at least so far as Na is concerned.

## CONCLUSION

Direct melting of powdered rock samples with an image furnace, using the procedures outlined above, is a rapid, low-cost method of preparing a broad spectrum of sample compositions for microprobe analysis. Aside from a few extreme compositions, the limitation of the method is only the glass-forming ability of the rocks themselves. Where this limit is reached, mixing at 1:1 by volume of $Li_2B_4O_7$ and the powdered sample enables melting (at atmospheric pressure). The analytical results agree well with known compositions and demonstrate the inter- and intra-glass homogeneity of a variety of compositions, including rocks bearing refractory minerals.

Combining direct melting of rock samples with the energy-dispersive capabilities of an electron microprobe and a suitable data-processing program results in a method of whole-rock analysis that compares favorably in speed, quality and cost with other modern methods, such as X-ray fluorescence.

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