The effect of crushing on the release of volatile components from heated obsidian

COLLECTION and analysis of gases from active volcanoes has often been used to provide data on the nature of the magmatic volatile phase (Shepherd, 1925; Jaggar, 1940; Huntingdon, 1973). Comparison of gas and magma can be obtained only by collections at active volcanoes, which imposes an enormous restriction on the range of available data. Ancient volcanic rocks represent a far wider spectrum of conditions, but to obtain data on the volatile phase coexisting with the magmas at the time of eruption, it is necessary to use the evidence preserved in the lavas.

Many workers have attempted to do this by heating lavas in a vacuum and analysing, by various methods, the resulting gases (Chamberlain, 1908; Shepherd, 1938; Muenow, 1973; Killingley and Muenow, 1975). It is the purpose of this note to indicate that whether the sample is powdered or not prior to heating exerts a considerable influence over the resulting gas composition. Data from experiments on the release of H_2O and CO_2 from an obsidian from Lipari (Eolian Islands) are presented.

The rock used in this study is a rhyolite obsidian, a dense, black, glassy rock with little or no evidence of devitrification (which Noble et al., 1967, consider to be a major cause of volatile loss). In our procedure, the sample is placed in a platinum boat within a silica glass (Vitreosil) tube, which is heated in a Nichrome-wound resistance furnace. The furnace temperature is controlled with a Eurotherm PID/SCR10 temperature controller connected to a calibrated Pt/Pt-10%Rh thermocouple placed adjacent to the sample tube, this system controls the temperature to within ± 5 °C at 1000 °C. The Vitreosil tube is connected through an adjustable leak valve to the stainless-steel inlet line of a VG Micromass 2 mass spectrometer (fig. 1). Prior to heating, the sample tube is evacuated to less than 10^{-3} torr. The mass spectrometer is calibrated with the appropriate pure gases, and a mixture of N_2, CO, CO_2, CH_4, A, and H_2 was analysed throughout the experimental programme to detect any variation of sensitivity.

The experiments reported in this note examine the pattern of release of gas species from the obsidian. Of particular interest was the effect, on the amount and composition of gas released, of powdering the sample before extraction. Shepherd (1925) had indicated that the grain size of the sample did affect the composition of the gases released, but subsequently this factor seems to have been largely ignored. Two forms of sample were used in our isothermal extraction experiments, uncrushed (5 mm) chips, or powder (produced in a Tema mill).

The isothermal pattern of release of volatiles was determined at 1000 °C. The sample was heated up to 1000 °C over 30 min (pumping away all the gases produced at lower temperatures) and the gas was then allowed into the mass spectrometer. Simultaneously, the scan motor was started and allowed to scan the mass spectrum continuously (from m/e 12 to m/e 60 and also m/e 2), or alternatively one particular m/e peak could be followed continuously. The resulting mass spectra were displayed on a chart recorder that provides a plot of species ion intensity against time, from which a similar plot for a blank run could be subtracted. The total run time was up to 8 hr, and the spectrum was scanned in 4 min. From the mass spectrum produced, the species were identified from their parent (or major) ion peaks, tabulations of which are given by Cornu and Massot (1966). The ion intensity, after correction for the relative sensitivity to a particular gas, is a function of the partial pressure of that gas. Earlier experiments had shown that this obsidian released nearly all of its gas above 1000 °C, confirming the results of

Harmand and Zimmermann (1976), therefore this seemed a logical temperature at which to examine the effects of crushing the sample.

Consideration of the results obtained reveals two major differences between crushed and uncrushed samples (fig. 2). Firstly, the powdered sample released considerably less H_2O at 1000 °C than the chips, although it released a comparable amount of CO_2, this depletion of powders in high-temperature water has previously been noted for Hawaiian basaltic glasses by Killingley and Muenow (1975). The second major difference is the release pattern itself. For the powdered sample both CO_2 and H_2O increase fairly rapidly, reach a stable level that is maintained for about 4 h before the amount of gas measured decreases as the rate of gas evolution drops below the rate of flow through the mass spectrometer. In contrast the uncrushed sample shows that both species show a delay of about 30 min before significant gas evolution begins. In the case of H_2O, the delay is followed by an extremely rapid increase in gas evolution and a slow decay without a long intervening period during which the gas emission remains constant. The curve for CO_2 is essentially similar to that for the powdered sample. This delayed sudden release of water from the chips can possibly be attributed to bubble burst after a delay in which the internal pressure increases to a level where the resistance of the viscous medium is overcome. Thus the result of crushing the sample is to decrease the amount of high-temperature water that is released; this is a serious modification probably brought about by the release of water contained in microvesicles that are ruptured during crushing.
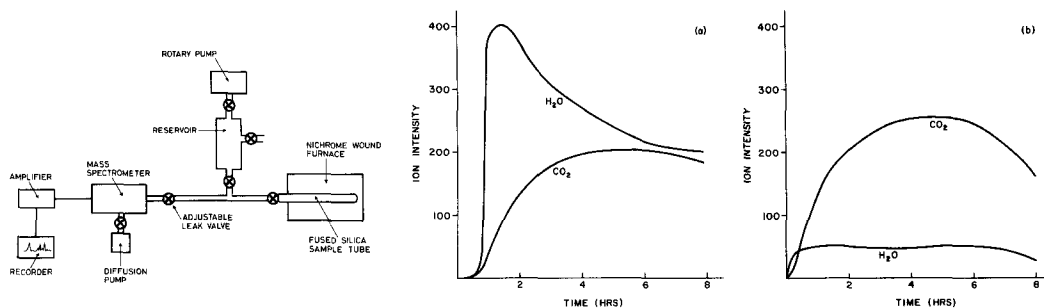
FIGS. 1 and 2: FIG. 1 (left). Block diagram showing the basic layout of the experimental system used for gas extraction from Lipari obsidian. FIG. 2 (right). Variation with time of volatiles released from a 1 g sample of Lipari obsidian at 1000 °C. Curve interpolated from data points every 4 min. Ion intensity in arbitrary units. (a, left) uncrushed sample, (b, right) crushed sample.

Additional experiments have been performed using a stepwise (200-1000 °C in 100 °C steps) heating programme. This provided further information on the differences shown above, in so far as the powdered sample released relatively greater amounts of gas at low temperatures than the uncrushed sample. The analytical results suggest that these low-temperature gases are a mixture of gases released from the sample during crushing (then adsorbed on the freshly created surfaces) and adsorbed extraneous gases (water, air). S.E.M. studies confirmed the presence of microvesicles in the uncrushed obsidian.

The modification of the released volatiles by crushing should be noted when considering the validity of analysing a rock powder for volatile constituents, as the sites in which certain volatiles are held may be destroyed during crushing, thus preferentially depleting the powder in certain constituents. Secondly, the period of time between achieving the selected temperature and analysis is critical, as totally different compositions would result from analyses conducted at $T < 30$ min, $T = 30$ min, and $T > 30$ min (fig. 2b). Time may be the most important factor to be taken into account when comparing results obtained by different techniques.

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Titanium in aegirines—a comment on: Crystallization trends of pyroxenes from the alkaline volcanic rocks of Tenerife, Canary Islands, by P. W. Scott

IN a study of the clinopyroxenes from the volcanic rocks of Tenerife, Scott (1976) describes the occurrence of aegirine in the groundmass of phonolites and nepheline-syenite inclusions. Scott (1976) has commented on the following five points:

Many aegirines show enrichment of Ti as Na increases; Na often exceeds Fe^{3+} (total) in the structural formula; Al is insufficient to account for all Ti as $CaTiAl_2O_6$ (Kushiro, 1962); many of the aegirines can be accounted for by the substitutions of the type: $Ti_y^{4+} + Fe_z^{3+} \rightleftharpoons Fe_y^{3+} + Si_z$ and $Ti_y^{4+} + Al_z^{3+} \rightleftharpoons Fe_y^{3+} + Si_z$ as proposed by Flower (1974) (however, the most Ti-rich aegirines still contain an excess of Ti); and substitution of Ti as Ti^{3+} can account for the excess Ti while maintaining charge balance.

Data collected by the author on titanian aegirines from a variety of alkaline rocks has been interpreted differently (Ferguson, 1977). The proposed neptunite end-component (Ferguson, 1977) also accounts for some unusual titanian sahlites in which $Al < 2Ti$ (Cundari, 1973). However, the occurrence of Ti^{3+} in the titanian aegirines, as proposed by Scott (1976), was not discussed and thus requires comment.

Ti^{3+} and Fe^{3+} are well known to be unstable together in aqueous solution, Ti^{3+} reducing the Fe^{3+} to Fe^{2+} (see Helsop and Robinson, 1967). Consideration of the redox cell $Ti^{3+} + Fe^{3+} \rightleftharpoons Ti^{4+} + Fe^{2+}$ with an E.M.F. of about 0.72 volt also indicates that the $Ti^{4+} + Fe^{2+}$ pair is strongly favoured. There is no evidence to suggest that this should not apply also to silicate melts.