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THE FOAMING OF LAVAS

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ABSTRACT

Foaming is of great practical and theoretical significance for volcanic processes on the earth, the moon, and perhaps the meteorite parent bodies. The theory of foams agrees with steelmaking experience to indicate that their presence depends on the existence of solutes in the lavas which reduce the surface tension, and are not saturated. These solutes concentrate at the surface, and are called surfactants. The surfactant responsible for the formation of volcanic ash has not been identified; it appears to be related to the oxygen partial pressure above the lava. This fact may explain why lunar and meteoritic melts are not observed to foam. Experimental studies are needed to clarify the process.

THE FOAMING OF LAVAS

Introduction

The contrast between the rather mild effects of Hawaiian volcanism and the catastrophic effects of Peleean and Plinian volcanism (Macdonald, 1972) is traceable, at least in part, to the production of volcanic ash by the explosive volcanoes. For this reason, it is of especial interest to try to understand the mechanism which leads to the formation of ash.

It is found that although lithic components (i.e. fragments of crystalline rock) form a part of the ash from many volcanoes, yet the majority of ash, including in particular that from the greatest terrestrial eruptions, consists principally of vitric tuff, i.e. glassy fragments of solidified rock foam (Heiken, 1972). The rock foam itself is often observed as pumice.

It follows that the process of foaming is of great importance for the understanding of the production of volcanic ash and the associated explosive volcanism. In the present paper, we discuss the formation of foams, with especial application to silicates.

Foams

If a bubble of gas rises to the top of a liquid, it will, at least momentarily, appear as a sort of blister on the surface of the liquid. In a pure liquid of low viscosity, the bubble promptly breaks (in 10^{-2} second in water, according to Kitchener and Cooper, 1959). Evidently the bubble will be retarded in a viscous liquid; and the final bursting of the bubble will be particularly slow because strong shearing action in the liquid is demanded. If a large number of bubbles are formed simultaneously in a viscous liquid, they can sometimes be observed to jostle together; they do not immediately coalesce, because of the intense shearing required. They slide past each other, retaining spherical, or nearly spherical form. Such a foam is called in German a "Kugelschaum"; in English it is an unstable foam. Such foams are generally shortlived and not very important.

There is a more important class of foams, called in German "Polyederschaum", and in English, metastable foams, in which the bubbles come close together, and the wall, or septum between the bubbles becomes flat or gently

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curved. When a lot of bubbles are involved, each becomes a polyhedron (often an irregular dodecahedron) whence the German name. Most of the liquid drains out from between the bubbles; but under some circumstances, the drainage stops, and the foam can survive for a long time.

We are thus led to ask: What stops the liquid from draining completely out of the septa in a metastable foam? It is not simply surface tension, because surface tension in a pure liquid acts with equal force upward and downward; it cannot counteract the downward force of gravity. What is required is a gradient of surface tension, such that the thinnest parts of the septum will have the strongest surface tension.

Bikerman (1958) states that C. Marangoni, about 100 years ago, found the explanation. A substance of low surface tension coats both sides of the septum. When the septum is stretched, and so thinned, the coatings are also stretched and hence diluted. Since the coatings reduced the surface tension, stretching them increases the surface tension, and so a gradient of surface tension is produced, which permits the septum to survive.

The formation of the coatings will occur naturally if there is some substance, dissolved in the liquid forming the septa, which has the following properties:

    a. It lowers the surface tension of the liquid.
    b. It is present in less than saturation amounts.

Such a solute is called a surface-active agent, or surfactant. The surfactant will migrate to the surface because surface tension represents potential energy — in fact the surface energy in joules per square meter has the same dimensions and the same numerical values as the surface tension in the usual units of newtons per meter. Since the state of equilibrium is (as usual) that of minimum potential energy, the surfactant tends to form a surface film reducing the surface energy. Gibbs derived, from thermodynamic considerations, the following expression for the extra concentration of the surfactant at the surface:

$$\Gamma = - \frac{c}{RT} \frac{d\gamma}{dc}$$

where Γ is the excess surface concentration in mol/m^2, c is the bulk concentration (mol/m^3), R is the gas constant, T the Kelvin temperature, and γ the surface tension (N/m). Intuitively, one can see that if a drop of a surfactant falls on a liquid, it will be promptly stretched out to cover the liquid surface just because the liquid outside the drop of surfactant will pull more strongly than the liquid inside the spot.

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Foaming of Silicates

In terrestrial volcanic pumice and ash, it is clear that we are dealing with polyederschaum, i.e. metastable foams consisting of polyhedra. This is explicitly observable in pumices; in volcanic ash, it is also clear that the vitric particles tend to be fragments of septa, or of the edges of polyhedra (called Plateau borders) or of the vertices where a number of Plateau borders meet).

It follows that we need to know what substances may be acting as surfactants. No experimental data are available to us at this point. On the other hand, it is known that lunar sample lavas rarely show foams, and that what foams do appear tend to be of the kugelschaum type, i.e. they have spherical bubbles. Foams are also rare in meteorites. It may thus be that foaming is connected with some parameter which has very different values on the earth and in extraterrestrial rocks.

In an earlier paper (O'Keefe, 1976) the idea of McBirney and Murase (1972) was supported, namely that the surfactant is water. Later is was realized that in most volcanic rocks, the water is exsolving during the eruption. It follows that water must be at or near saturation at this time, and therefore is not a suitable surfactant. Industrial studies of foaming do not, in general, mention water as a possible surfactant.

A series of important papers have been written on the subject of silicate foaming by metallurgists, especially those concerned with steelmaking. In the older basic openhearth process, the steel was produced in a furnace heated from above. Here a foam on the slag tended to reduce the transfer of heat from the flame to the metal. In the newer Linz-Donawitz or basic oxygen process, large amounts of pure oxygen are injected into the crucible. This produces intense foaming, which is desirable because it promotes oxidation of the carbon, silicon and phosphorus (Urquhart and Davenport, 1973). At the same time, controls are needed to prevent the foam from overflowing the crucible. Accordingly, the subject of foaming in slags, and the related subject of the surface tension of slags have considerable economic significance, and have been studied in some detail.

Boni and Derge (1956) reviewed the literature on silicate surface tension. Cooper and Kitchener (1959) attributed the foaming of silicates principally to the presence of surfactants; they noted that pure CaO - SiO_2 melts do not foam appreciably, even when the viscosity is high; they found that P_2O_5 is an important surfactant; they also found that Cr_2O_3 and B_2O_3 were effective. Cooper and McCabe (1960) studied the effects of varying SiO_2. They considered that

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the best surfactants are likely to be those with the maximum value of the <u>ionic</u> <u>potential</u>, defined as Z/r, where Z is the charge on the ion, and r its radius. Swisher and McCabe (1964) studied Cr_2O_3 as a foaming agent. Less effective foaming agents are, they found, P_2O_5, V_2O_5, Na_2O. They confirmed the Marangoni theory for silicates. In a useful review, Kozakevitch (1969) pointed out that the oxidizing power (p_{O_2}) of foaming slags was noticeably higher that that of non-foaming slags. In particular, his curves show that Fe_2O_3 is a moderately effective surfactant, at least in liquid FeO.

Sharma and Philbrook (1971) also consider that the oxidation state is an important factor in promoting foaming. They, however, consider that the p_{O_2} at the surface of a slag may be locally altered by contact with an atmosphere; they suggest that SiO_2 may be partly reduced to SiO in a reducing atmosphere, with a corresponding reduction in surface tension. Similarly one might expect that foamability might be affected by the replacement of Fe_2O_3 by FeO or the reduction of P_2O_5 in phosphates to P_4O_6, which is a strong reducing agent in its own right. Ultimate reduction could result in phosphide formation which would tend to stabilize the phosphorus in a bound compound which would effectively remove it from the system. The iron phosphides are resistant to oxidation and hence any surfactant contribution by phosphorus would be more or less removed. The final analysis of the significance of the p_{O_2} can only be accomplished by further studies. Since the conditions of formation of the moon and most meteorites strongly suggest low p_{O_2}, it would then follow that the formation of surfactants such as P_2O_5, Cr_2O_3, Fe_2O_3, etc., would be limited and these lavas should not and are observed not to have signficantly foamed.

Applications of Studies of Foaming

a. <u>Terrestrial</u>. Since the most dangerous volcanoes are those which emit ash, it follows that an understanding of the foaming of lavas (which produce ash) is of great significance for the study of volcanism. These studies are interesting in themselves; in addition, they may eventually offer a hope of predicting volcanic eruptions.

It is even conceivable that by the use of foaming agents or anti-foaming agents, it might be possible to alleviate the destructive effects of some volcanic eruptions. The mechanics of the eruption is certainly affected by foaming; and foaming is sometimes sensitive to small quantities of surfactant (a few parts per million in some cases); thus the notion of altering the behavior of a volcano by putting some surface-active material into it might not be out of the question.

A model of this problem is presented by geysers, which in some ways resemble low-temperature volcanoes. It is known that a geyser can be caused to

erupt by dropping soap into it; for this reason, Park Service regulations forbid visitors to "soap" the geysers. The mechanism by which geysers respond to soaping is not known; but it may be of practical as well as theoretical interest, because geothermal wells often become geysers.

Let us also note that although at present, the geophysicists must learn from the metallurgical engineers about silicate foams, yet the geophysicists and geochemists do possess very delicate tools which have not yet been applied to the problem; it might well turn out in the end that geophysical investigations would be useful in steelmaking.

b. <u>Lunar.</u> It is widely believed that the lunar soil is the product of re-peated meteorite impact, and is not the ejecta of lunar volcanoes. However, a number of studies by younger men (C. R. Chapman, P. Schultz, L. Sparks) suggest that the impact idea may have been carried too far. A critical question involves the absence of pyroclastic forms (i.e. volcanic ash, and especially pumice fragments) in the lunar surface materials. Since the p_{O_2} of lunar rocks is about 6 orders of magnitude below that of terrestrial rocks, it is clear that the question of the foamability of lunar lavas is open to question. If lunar lavas are incapable of foaming, or if they cannot foam in the kind of (very reducing) atmosphere which would be in equilibrium with lunar rocks, then the absence of pyroclastic forms from lunar soils does not say anything about the question of volcanism versus impact for the formation of the lunar soils.

Involved with the question of lunar soils is the larger question of the origin of lunar craters. Are they chiefly due to impact or to volcanism? If the soils are volcanic, then at least in certain size ranges, the craters are also volcanic. The basic assumption of contemporary planetology is that nearly all craters on the moon and the planets are due to impact; thus a finding that volcanism has played a major role or perhaps the predominant role in the formation of the lunar soil would constitute a major upheaval.

c. <u>Tektites.</u> Tektites never show foams, but do include some glass particles whose external appearance is much like that of lunar soil. If tektite glass is incapable of foaming when gases of the appropriate p_{O_2} are forced through it, then this is a major step in understanding of these glasses.

d. <u>Meteorites.</u> Among the most puzzling phenomena of meteorites are the chondrules. These are small (millimeter and sub-millimeter) objects, more or less spherical, found in the commonest kind of stony meteorites. Many chondrules clearly formed by crystallization from liquid drops. The overall resemblance of a chondritic meterorite to a terrestrial volcanic tuff

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was noticed from the earliest times. However, identification as a tuff has been obstructed by the fact that whereas terrestrial volcanic ash nearly always shows the shardy forms of crushed pumice, the chondritic meteorites never show these forms. Conversely, chondrules of the type of the congealed drop are common in meteorites, but are extremely rare in terrestrial volcanic tuffs. They are comparable in many ways to the above-mentioned lunar spherules.

These peculiarities would be understandable if it should turn out to be true that meteoritic lavas, particularly in the presence of gases of the appropriate very low oxygen partial pressure, cannot or do not form foams.

It may be useful to note that those chondrules which are _not_ formed by crystallization of liquid drops are stony fragments rounded by attrition. Similar fragments are ejected by terrestrial volcanoes (Heiken, 1972).

Conclusions and Recommendations

It seems likely that the foaming of terrestrial lavas is a consequence, not only of the presence of volcanic gas, but also of the presence of a surfactant at the lava surfaces. The surfactant may be related to the gases which are passing through the lavas, or it may be a substance dissolved in the lavas. In either case, it seems likely that foaming is promoted by high values of the oxygen partial pressures.

It is recommended that terrestrial lavas be compared with lunar lavas

    a. In a direct assessment of relative foamability
    b. In terms of surface tension, under atmospheres of varying p_{O_2}
    c. By direct measurement of surface chemistry.

Similar experiments with meteorites and tektites would be significant.

It is further recommended that experiments be tried with various amounts of surfactants such as Fe_2O_3, P_2O_5, to determine the surfactants responsible for the foaming of terrestrial lavas and, it is hoped, the non-foaming behavior of lunar samples and meteorites.

ACKNOWLEDGMENTS

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