LETTER

The structure and composition of microspheres from the Kilauea volcano, Hawaii

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ABSTRACT

Microspheres from the plume of the Kilauea volcano, Hawaii, display previously unrecognized structural and compositional features indicating that the spheres are concentrically differentiated and at least partially crystalline. The surfaces of some spheres display evenly spaced hexagonal, submicrometer grains whose compositions suggest that they may be spinels. Distinctive prismatic and dendritic structures on the surfaces of the microspheres are remarkably consistent through the population and indicate that the spheres have crystalline outer shells. Indications of chemical etching are present, probably from exposure to HF in the volcanic plume. The structures and compositions of the microspheres suggest that they differentiated and then solidifed during rapid cooling, as they passed through the gradients of temperature, chemical composition, and redox conditions established in the plume as air diluted the gaseous species evolved from magma.

INTRODUCTION

Many aspects of volcanic plumes and the gases and particles they contain have been described (Cadle et al., 1969; Chuan et al., 1986; Ivlev et al., 1989). These include the presence of silicate microspheres in the particulate fractions of volcanic plumes (Wohletz and McQueen, 1984; Lefevre et al., 1986, 1991; Heiken and Wohletz, 1985). The microspheres have been previously identified as glass, with bulk chemical compositions ranging from that of the magma to nearly pure SiO_2. We observed a suite of microspheres in filter samples from the plume emitted from the central Pu'u 'O'o crater of Kilauea volcano, island of Hawaii, January 28, 1987. Here we report that the textural features and chemical compositions of the Kilauea microspheres indicate that many are crystalline and chemically differentiated. Their distinct chemical variations and surface and interior textures are repeated throughout the population with striking similarity, and they appear to be related to processes of formation. The spherules appear to have formed rapidly in the cooling, air-diluted plume by a process of oxidation, differentiation leading to the formation of concentric shells with different chemical compositions, and crystallization.

SAMPLE COLLECTION

The samples were collected by drawing the air-diluted plume gas (from a point 3 m above the floor of the crater, at nearly ambient temperatures) through a cellulose acetate filter disk with an effective pore size of 0.4 mm, a method used for the collection of metal-bearing aerosols (Hinkley, 1991). At the time of collection, degassing in the Pu'u 'O'o crater was through chimneys that vented the rubble-filled crater floor; there was no lava lake. Cut portions of the filter disk were C-coated for scanning electron microscopy (SEM) and X-ray microanalysis. Hundreds of microspheres from a 6-mm^2 area of filter were surveyed using SEM. They ranged in size from <1 to approximately 20 μm in diameter. The average composition of a suite of a number of low-Si spherules approaches that of Kilauea melt of the same time period (Table 1). The MgO concentration of the melt (unpublished data of U.S. Geological Survey, Hawaiian Volcano Observatory) yields a temperature of approximately 1160 °C (Helz and Thornber, 1987).

DISCUSSION

One of the more striking of all of the textural and compositional features observed is the presence of iron titanium aluminum chromium oxide grains, possibly spinel, exposed as regular hexagonal outlines equidistantly spaced over the smooth surfaces of the outer shells of larger spherules (to 20 μm in diameter). Figure 1 shows a sphere with such grains whose Fe-Ti-Al-Cr compositions (Table 1) indicate that they may be spinel crystals. Grains on other microspheres also appear to be composed of iron titanium aluminum chromium (plus magnesium) oxides, although the elemental proportions vary widely. We propose that these grains crystallized in the microsphere surface layer in short time intervals, beginning when the still-liquid spherules in the plume first passed from the reducing conditions of the basalt magma and its undiluted gaseous emissions to the oxidizing conditions brought on
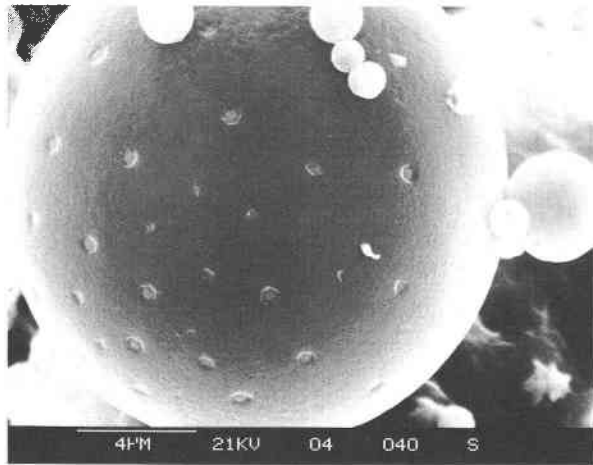
Fig. 1. Secondary electron image of a microsphere showing regularly spaced iron titanium aluminum chromium oxide crystals (possibly spinel). See Table 1 for approximate compositions.

TABLE 1. Chemical compositions for various regions on microspheres

	Spinel	Outer shell (Fig. 2)	Inner shell (Fig. 2)	Si-rich spherule	Av. low-Si spherules	1987 melt
SiO_2	nd	62	59	95	55	50.55
TiO_2	12	nd	nd	0.7	2.2	2.55
Al_2O_3	13	20	8.3	0.4	12	13.59
Cr_2O_3	9	nd	nd	nd	tr	0.03
MgO	9	1.2	6.6	0.1	7.2	7.11
CaO	nd	0.7	17	0.5	10	11.49
FeO	68	9.6	7.7	1.5	10	11.05
Na_2O	nd	5.9	0.5	0.1	3.2	2.54
K_2O	nd	0.2	nd	0	0.6	0.49
F	na	nd	nd	1.1	nd	na

Note: values are in weight percent oxide. X-ray analyses of representative features observed in the Kilauea aerosol sample. Most of the features analyzed are smaller than the diameter of the X-ray analytical volume ($\sim$2 μm) and therefore contain some contribution from either adjacent features or shells. Analytical errors are $\pm$10% (relative) concentration unless otherwise stated. Spinel: approximate representative composition of iron titanium aluminum chromium oxides determined by assuming 0% SiO_2 and subtracting proportional amounts of other elements present in adjacent outer shell. Analytical error $\pm$20% (relative) concentration. Outer shell: approximate representative composition of the felsic outer shell of a spherule similar to the one shown in Fig. 2. Inner shell: approximate representative mafic inner shell composition (dark area within prismatic feature at the center of Fig. 2). Si-rich spherule: approximate representative composition of surface of high silica spherule (Fig. 4). Av. low Si spherules: average composition of several low silica spherules. The 1987 melt: representative composition of 1987 Kilauea melt (unpublished data of U.S. Geological Survey, Hawaiian Volcano Observatory). (Abbreviations: tr = trace, nd = not detected, na = not analyzed for.)

by air dilution of the gas stream. The interval would end at the time that further air dilution caused a temperature decrease and rapid solidification. Very rapid growth of fine-grained spinel (magnetite) has been observed on lava tube surfaces near skylight openings, where the introduction of atmospheric gas changes the reducing conditions that dominated in the vapors degassed from the flowing basaltic lava (K. Hon, 1992 personal communication). The diffusion of spinel-compatible components toward each crystallization site of the microsphere in Figure 1 would have taken place over an area of about 1–4 μm^2 on the surface of the spherule and possibly from a considerably greater depth toward the center of the microsphere. From the apparent number and sizes of oxide grains present, and with the assumption that they are restricted to the surface of the microsphere, the total volume of oxide grains appears to be about 0.5% of the volume of the microsphere. If the sole source of Cr_2O_3 for the oxide grains were the Cr_2O_3 distributed through the undifferentiated microsphere, a minimum concentration of 0.05% Cr_2O_3 would be required in the microsphere before grain growth (assuming total partitioning of Cr to the grains). However, reported Cr_2O_3 concentrations in the melt are two to five times lower (see Table 1), and, in order to explain the growth of oxide grains of compositions similar to that shown in Table 1, it may be necessary to postulate the presence of preexisting Cr-rich nuclei within the oxide grains (viz., chromite, which would be formed under more strongly reducing conditions than those required for other spinels; such strongly reducing conditions would exist within the magma). In contrast, the other components of the oxide grains (Al, Fe, Ti) are present in sufficient concentrations in the undifferentiated spherules to present no restriction on the growth of the oxide grains. If the oxide grains are spinel, and if the spinel crystals are in the typical octahedral form, then the recurrent hexagonal outlines seen in Figure 1 would re-

quire specific crystallographic orientations of the grains with respect to the surface of the sphere. Such conditions may be controlled by processes of nucleation and grain growth at the surface of a small spherical object. The need for special conditions to explain the hexagonal forms that are observed requires acknowledgment of the possibility that the oxide grains are not crystallographically of the spinel group, but may be spinellids of the hexagonal or trigonal systems.

Other common textures include regular prismatic windows with consistent angular terminations, framing distinctive three-membered radial ridges. In Figure 2 the prismatic feature forms a window in the outer shell ($\sim$1 μm thick) of a spherule, revealing an inner shell. Such prismatic features show with remarkable consistency the same outline and angles, as well as the three radial ridges that are visible at the apex of the prism in Figure 2. The compositions (Table 1) of the two shells of the spherule are distinct, the inner sphere having concentrated the Mg and Ca, the outer shell having more Si, Al, and alkalis. The angles at the prism apices are similar to those in type I quartz and feldspar intergrowths that constitute graphic granite (Stel, 1992). However, the compositions of the outer shells appear too Fe-rich to be purely a quartz-feldspar intergrowth, and it is possible that other phases are present on a scale too fine to distinguish.

Many of the larger microspheres ($>$2 μm) show a variety of compositions and complicated surface textures not previously reported. These textures are similar to
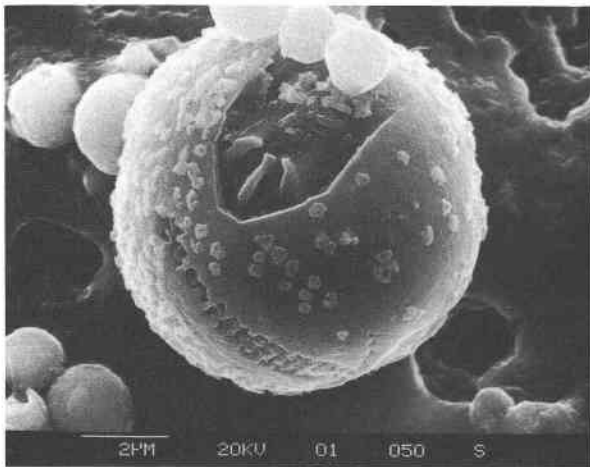
Fig. 2. Secondary electron image of a microsphere showing typical prismatic structure in the outer layer, with angular outline and three radial features. Representative compositions for the inner and outer shells are given in Table 1. Note band with graphic texture along lower left side of sphere.

Fig. 4. Secondary electron image of microsphere showing radiating growth feature with extraordinary bilateral symmetry, on either side of dashed line.

symplectic textures of igneous rocks, including graphic, prismatic, and dendritic forms. Their presence demonstrates that the spherules are at least partially crystalline, contrasting with earlier reports that such microspheres are glass (Lefevre et al., 1991). Figure 2 is an example of the graphic cuneiform texture seen on many spherules, and Figures 2–4 all show large microspheres that display these graphic surface textures, each of which is repeated with notable similarity in a large fraction of the population of spheres >2 μm. Dendritic growth is common and can be seen in Figures 3 and 4. Dendritic quartz typically forms in a cotectic system when there is undercooling (Trivedi and Somboonsuk, 1984) by a minimum of 55° (Swanson and Fenn, 1986), a condition that is geologically uncommon but well matched to the physical con-
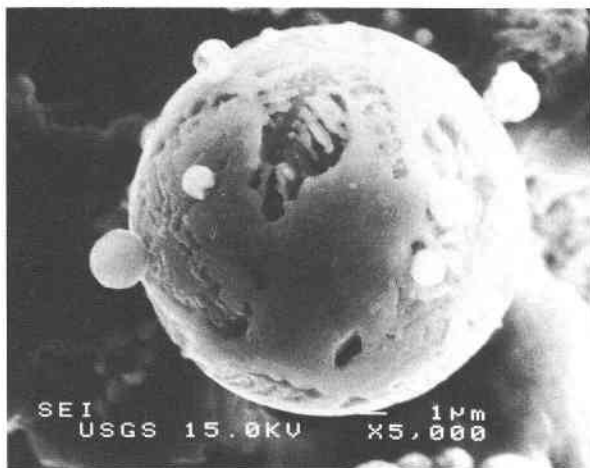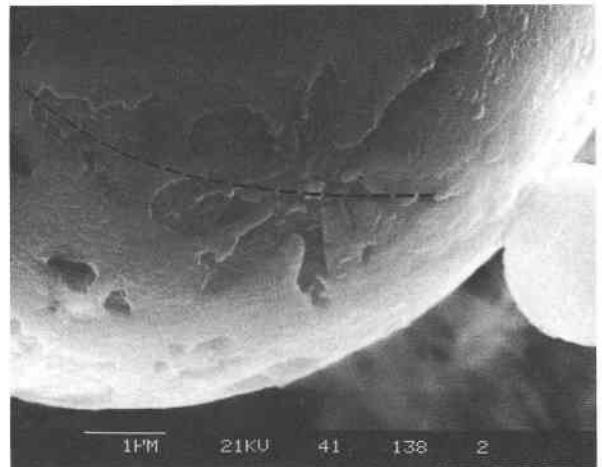
ditions expected for the rapid cooling of plume material rising from its interface with the melt. Surprisingly detailed bilateral symmetry can be seen in the patterned growth feature in Figure 4. A relatively uncommon but distinctive type of spherule is shown in Figure 5, with prominent cracks and a composition approaching pure SiO_2 (Table 1; also noted elsewhere, Lefevre et al., 1986). The cracks and accompanying deformation suggest that microspheres of this type are hollow. Generally, surfaces of the smaller microspheres (<2 μm) are featureless or show uncomplicated structures when imaged at magnification up to 20000×.

Chemical etching of several textural features may be present. Many of the spherules have an etched appearance, displaying deep cavities surrounding oxide grains and dendritic patterns in both positive and negative relief. The exposures of different shells and patterns on the

Fig. 3. Secondary electron image of microsphere showing typical dendritic features.
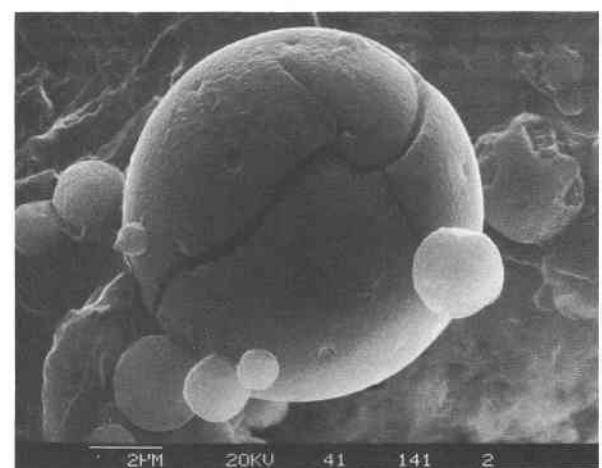

Fig. 5. Secondary electron image of high-silica microsphere with cracked shell and regularly spaced oxides on surface.

surfaces of different spherules suggest that they are seen in various stages of chemical erosion after having completed growth. Undiluted Kilauea plume gases typically contain about 0.25% HF (Greenland, 1984), an oxidized species that must form only after the first air dilution of the magmatic gases. Therefore, etching most likely begins about the time of full solidification of the microspheres but could continue even after sample collection by the action of HF dissolved in the viscous aqueous sulfate solutions that commonly condense onto the surfaces of particles and sampling apparatus from the cooling plume. Different degrees of etching may indicate different residence times in the gas plume.

ACKNOWLEDGMENTS

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