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## BLUE GLASS FROM CRATERS OF THE MOON

NATIONAL MONUMENT, IDAHO

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## Abstract

A unique, azure-blue lava surface occurs in Craters of the Moon National Monument, Idaho. The scoriaceous structure, glassy luster and sinuous pattern of this 2 mile flow support the local name Blue Dragon. The blue color exists in a 2-3 millimeter, frothy glass layer exposed on the weathered surface. The basalt is abnormally rich in  $\text{FeO}$  and  $\text{P}_2\text{O}_5$ . At the time of eruption the magma was probably confined at elevated temperature, in a reducing environment until sufficient lava accumulated to breach the subsurface tubes extending horizontally from a cinder core source. The highly fluid lava acquired an immediate surface skin in the form of a black complex ferric oxide-silicate (cronstedite) crust. The sub-crustal, rapidly cooling lava containing olivine, feldspar and magnetite in a siliceous matrix favored atomic grouping of the form  $\text{Fe}^{2+} - \text{O} - \text{Fe}^{3+}$  in the glassy structure. Such ferrous ferrite chromophores create blue color in iron bearing glass according to glass technologists.

## INTRODUCTION

A glassy, azure-blue lava surface occurring in Craters of the Moon National Monument, Idaho, was first noted by Russell (1902). A further description by Limbert (1924) and by Stearns (1924) established the local name Blue Dragon for this particular tongue of lava. Murtaugh (1961) mapped the Blue Dragon, approximately one-half mile wide and two miles long, as one of the latest, thin pahoehoe flows extending southwest from bulbous toes at the base of the major cinder cone, Big Cinder Butte. Buried lava tubes extending laterally south-west from the base of Big Cinder Butte breach the surface several hundred yards from the cone and the sinuous lava pattern, cascading down dip evidences high fluidity compared to the earlier molten lavas. The surface of the flow, now a pitted black film less than a millimeter thick, has eroded to expose the 2-3 millimeter blue layer which grades into ordinary basalt. In the strong desert sun the unique appearance of the flow cannot be ignored as the scoriaceous structure, glassy luster and azure blue color exposed by weathering combine to provide an iridescent, scaly effect reminiscent of reptilian skin.

## DISCUSSION

The blue glaze seen in hand specimen is created by granules of intensely blue glass observable on a surface inspected under low magnification. Thin sections prepared for both transmitted and reflected light fail to capture the blue color. The leached and oxidized topmost glass in thin section displays hematitic stain in flow bands with fine grains of magnetite in profusion. Progressing into the surface the minerals olivine, plagioclase and magnetite appear to be normally dispersed in a matrix of glass.

Submicroscopic spherules of deep brown glass are detected and the increasing optical density of the glass, coupled with the excess of magnetite, renders the section opaque at 2-3 millimeters depth.

Hydrofluoric acid dissolves the glass matrix, removing the blue color which does not appear in the resulting solution. Heating the surface under atmospheric conditions for 48 hours at 700°C alters the blue to a reddish brown. Wet chemical analyses<sup>1</sup> of the Blue Dragon lava appear in Table 1. The lava compares to the average continental basalt of Manson (1967) except for the unusually high FeO and P<sub>2</sub>O<sub>5</sub> content. Evidence of large quantities of P<sub>2</sub>O<sub>5</sub> in the Blue Dragon lava is supported by x-ray fluorescence spectra<sup>2</sup>. There appears to be no significant difference between the chemistry of the blue glaze and the lower parts of the flow. The large P<sub>2</sub>O<sub>5</sub> content does not appear to be related to the nearby Phosphoria Formation<sup>?</sup> but may be interpreted as resulting from a late stage magmatic differentiation (Henderson, 1968). Apatite was not observed existing as a mineral in the thin sections. Spectrographic examination<sup>3</sup> of the surface detected the usual minor quantities of Sr, Zr, Pb, and Cu; Co and Ni were not reported present.

X-ray scanning patterns<sup>4</sup> of the blue glass surface provide the principal lines of gamma-FeO(OH). The peaks at 7.23 Å, 3.22 Å, and 2.56 Å, with the proper intensity ratios are supported by

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a half dozen distinctive minor peaks at larger 2 $\theta$  angles. Surfaces on fragments from within the flow do not produce this pattern. Blue surfaces observed on steel plate treated to an iron phosphate coating resemble the surface reflections of the Blue Dragon. These hard surfaces with very fine amorphous texture are known to be iron oxides containing both  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions (Metals Handbook, II, 1964). X-ray spectra of such treated surfaces indicate the structure  $\gamma\text{-FeO(OH)}$ <sup>1</sup>. Azure blue glass surface reflections which are strikingly similar to that of the Blue Dragon lava are prepared from ceramic glazes<sup>2</sup>. Such glaze coloration may be created using Kona Spar (37 wt. %),  $\text{CaCO}_3$ (18), Ball clay(8),  $\text{SiO}_2$ (24),  $\text{Fe}_2\text{O}_3$ (13), and fired at 1300°C in a reducing atmosphere. Weyl and Kreidel (1941) produced blue glass by adding 2 mol % ferrophosphorous (approx. 75 Fe, 25 P) to their glass melt under atmospheric conditions. Weyl (1951) made extensive study of colored glasses and considered the blue color of the mineral vivianite  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  to be an interaction between an  $\text{Fe}^{2+}$  and an  $\text{Fe}^{3+}$  atom linked together by oxygen.

A general theory of optical and thermal electron transfer between two different ions in the same environment has recently been advanced by Hush (1967). Allen and Hush (1967) propose that light absorption resulting in an electron transfer from a lower to a higher oxidation state of the same element be termed homonuclear intervalence-transfer absorption. These authors point out good theoretical reasons for expecting intervalence-transfer absorption and indicate the probability of absorption will be smaller the larger the internuclear distance, giving rise to absorption in the visible region of the spectrum. The strong colors of the mixed-valence compounds are assumed to be usually due to transitions of this kind. It is recognized an absorption band for the  $\text{Fe}^{2+}$  ion exists in the infra-red with overlap into the visible region.

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Table 1. Chemical Analysis of Blue Dragon Basalt

|                                 | Surface <sup>a</sup> <i>blue glass zone</i> | Depth <sup>b</sup> |
|---------------------------------|---------------------------------------------|--------------------|
| SiO <sub>2</sub>                | 49.13                                       | 46.59              |
| Al <sub>2</sub> O <sub>3</sub>  | 14.79                                       | 12.77              |
| Fe <sub>2</sub> O <sub>3</sub>  | 2.82                                        | 2.20               |
| FeO ✓                           | 13.83                                       | 13.94              |
| CaO                             | 7.08                                        | 7.50               |
| MgO                             | 3.06                                        | 3.90               |
| MnO                             | 0.24                                        | 0.27               |
| TiO <sub>2</sub>                | 2.36                                        | 3.16               |
| P <sub>2</sub> O <sub>5</sub> ✓ | 0.90                                        | 2.52               |
| Na <sub>2</sub> O               | 3.74                                        | 3.85               |
| K <sub>2</sub> O                | 2.00                                        | 1.92               |
| H <sub>2</sub> O (-)            | 0.11                                        | 0.37               |
| H <sub>2</sub> O (+)            | 0.03                                        | 0.67               |
| CO <sub>2</sub>                 | 0.07                                        | ----               |
| Total                           | 100.03%                                     | 99.66%             |

Tadashi Asari, analyst

<sup>a</sup> blue glass zone

<sup>b</sup> 10 cm below blue glass zone

### CONCLUSION

At the time of eruption of the Blue Dragon magma was probably confined at elevated temperature; containing an abnormally high percentage of  $\text{Fe}^{2+}$  iron due to the presence of 2-3% phosphorus as a reducing agent in the magma. When sufficient lava accumulated to breach the bulbous toes, formed at the extremities of subsurface tubes, the gaseous, highly fluid lava spread rapidly and acquired an immediate surface barrier to the atmosphere in the form of a black complex ferric oxide-silicate (cronstedite) skin. The cooling glassy matrix below this thin barrier favored chromophore groupings of the form  $\text{Fe}^{3+}-\text{O}-\text{Fe}^{2+}$ . The ratio  $\text{Fe}^{3+}/\text{Fe}^{2+}$  is critical to the formation of blue color and the effect of the OH ion, if any, is unknown. The cause of the blue color appears to be homonuclear intervalence-transfer absorption.

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