preventing specimen oxidation. In addition, some of the liquid nitrogen can be poured off with the powder. On boiling, released nitrogen gas will purge the storage container of oxygen before it is sealed.

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THE STAINING MECHANISM OF POTASSIUM FELDSPAR AND THE ORIGIN OF HIERATITE[1]

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ABSTRACT

K-feldspar must be exposed to HF vapor or immersed in HF in order to stain it yellow with sodium cobaltinitrite. The white product from the reaction of HF vapor with K-feldspar and leucite is hieratite (cubic K_2SiF_6) and aluminum

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trifluoride trihydrate; only hieratite forms by immersion in HF. Reaction of sodium cobaltinitrite with hieratite is the mechanism by which K-feldspar and leucite are stained. These experiments confirm that hieratite may be formed in nature by reaction of HF vapor or HF-bearing solutions with pre-existing potassium-bearing silicate minerals as indicated by its field occurrence.

INTRODUCTION

Interest in the staining of feldspars continues unabated because of its utility in the modal analysis of rocks. All recent improvements on the staining of potassium feldspar are essentially modifications of the HF-sodium cobaltinitrite method proposed by Gabriel and Cox (1929). Despite its widespread use and the numerous papers dealing with the method of Gabriel and Cox, the mechanism of the staining reaction for potassium feldspars is not understood. It is known, however, that prior exposure of K-feldspar to HF fumes or prior immersion of K-feldspar in HF is necessary in order to form the yellow complex with sodium cobaltinitrite, and that only the HF reaction product on the feldspar surface and not the feldspar itself is stained.

EXPERIMENTAL RESULTS

Fahey (1964) developed a chemical procedure for separating coesite and stishovite from siliceous rocks based on the relative solubility in HF of the silica polymorphs. He pointed out that HF leach residues from rocks commonly contain persistent fluorides which must be destroyed with HNO_3, and Sclar *et al.* (1964), noted that HF treatment of a synthetic mixture of clinoenstatite, forsterite, and stishovite yielded a residue composed of sellaite (MgF_2) and stishovite. To determine whether Fahey's HF method for isolating the high-pressure polymorphs of silica could be applied to rocks containing abundant mica-group minerals and K-feldspar, finely ground samples (-325 mesh) of muscovite, illite (API No. 35), microcline, adularia, and sanidine were treated in a water solution of 5.5 percent HF and 10 percent HCl (by volume) for seven days at room temperature. A duplicate set of the K-feldspar samples was treated with a water solution of 5.5 percent HF (by volume) for the same period of time. All the residues except the muscovite residue consisted dominantly of colorless isotropic cubes, octahedra, and cubo-octahedra of hieratite (cubic K_2SiF_6). The hieratite was identified by its X-ray powder diffraction pattern (Swanson *et al.*, 1955) and its index of refraction of 1.34 (measured by immersion in water-acetone solutions) which is in agreement with artificial (Raiteri, 1922) and natural (Zambonini and Carobbi, 1926) hieratite. The illite residue also contained quartz, illite, rutile, zircon, and tourmaline. Emission spectographic analyses of the starting illite and the illite residue confirmed the concentration of potassium and the depletion of aluminum and magnesium in the residue. The muscovite residue consisted dominantly of muscovite and subordinately of cubo-octahedral crystals of hieratite, some of which may be epitaxially related to muscovite [(100) of hieratite parallel to (001) of muscovite].

Despite the large number of reports on the synthesis of hieratite (*e.g.*, Mellor, 1925; Ketelaar, 1935; Barrer *et al.*, 1953; Swanson *et al.*, 1955), this appears to be the first report of the synthesis of hieratite by direct HF attack on potassium-bearing minerals. It should be noted, however, that Denaeyer and Ledent (1952) described an occurrence of hieratite and camermanite (hexagonal K_2SiF_6) associated with gypsum and other potassium salts as incrustations on bricks of a smokestack used for venting industrial gases including HF, H_2SO_4, and SO_2. They concluded that K_2SiF_6 was formed by reaction of HF vapor with the small amounts of potassium in the siliceous bricks and mortar.

Cleavage pieces of microcline and orthoclase and crystals of leucite were exposed to HF fumes at room temperature for periods of 1 minute to 5 days. X-ray diffraction patterns of the white reaction products show that they all consist of hieratite and the tetragonal aluminum trifluoride trihydrate phase ($AlF_3 \cdot 3H_2O$) of Freeman (1956) (XPDF Card 9-108). It is evident that reaction of cubic K_2SiF_6 with an aqueous solution of sodium cobaltinitrite is the mechanism by which the yellow precipitate, reportedly $K_2Na[Co(NO_2)_6]$ (Feigl, 1958), is produced, and that the function of HF in the staining procedure is to form a reactive potassium compound from K-feldspar and leucite. Immersion of K-feldspar in concentrated HF results in a white reaction product which consists solely of hieratite; the aluminum trifluoride trihydrate phase is apparently soluble in aqueous solutions of HF.

STAINING OF VOLCANIC ROCKS

Although the K-feldspar of two-feldspar plutonic rocks stains readily with an exposure to HF fumes of 5 to 10 seconds followed by immersion in a saturated solution of sodium cobaltinitrate for 15 to 60 seconds, the alkali feldspar of one-feldspar volcanic rocks reportedly does not respond well to this staining method. Based on experiments with two alkali feldspars (orthoclase 40 percent by weight) from volcanic rocks, Chayes and Zies (1961) report that a 15-second etch with HF fumes followed by a 5-minute immersion in sodium cobaltinitrite is necessary to obtain even a pale patchy granular stain. Furthermore, they found that, for a given HF etching time, staining times of more than 5 minutes did not result in a better stain. Chayes and Zies point out that the insensitivity of many sanidines and anorthoclases is not likely to be due simply to their lower potassium content inasmuch as very small quantities of potassium can be detected by the cobaltinitrite test. Correspondingly, Ford and Boudette (1968) report that anorthoclase phenocrysts from trachytes ($Or_{17}Ab_{65}An_{18}$ and $Or_{16}Ab_{74}An_{10}$) could not be stained satisfactorily by the method of Gabriel and Cox and at best "took on a very faint and irregularly mottled yellow color". They report further that these anorthoclases reacted as sodic plagioclase with a modification of the amaranth stain procedure of Laniz *et al.* (1964). A possible explanation of the observations of Chayes and Zies and of Ford and Boudette based on the results of this study is that sodium- and potassium-bearing feldspars such as sanidine and anorthoclase react with HF fumes to yield an intimate mixture of two discrete silicofluoride phases, namely, potassium-free malladrite (rhombohedral Na_2SiF_6) and sodium-free hieratite. Only the hieratite would react with sodium cobaltinitrite to give the yellow stain, and, if the alkali feldspar is sodium-rich, the hieratite may be so diluted by the non-reactive malladrite that the yellow stain may appear faint and mottled. Experimental studies bearing on this possibility are in progress.

OCCURRENCE AND ORIGIN OF HIERATITE

Hieratite occurs as a product of volcanic exhalations around fumarolic vents on Vesuvius and on Vulcano in the Lipari Islands (Palache *et al.*, 1951). It was recently found on Tristan da Cunha in association with other fluorides as incrustations on the trachyandesite flow of the eruption of 1961 (Baker *et al.*, 1964). All of the known host rocks for hieratite are potassium-bearing igneous rocks, some of which contain abundant K-feldspar and/or leucite. Clearly, the field occurrence indicates that hieratite is formed under surface or near-surface conditions by the chemical reaction of HF vapor or HF-bearing solutions with K-feldspar, leucite, or cryptocrystalline potassium-bearing igneous rocks. The experimental results reported in this paper support this conclusion.

Hieratite-bearing volcanic rocks containing abundant K-feldspar and/or leucite should be examined for a possible natural occurrence of the aluminum trifluoride trihydrate phase.

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