

HYDRAULIC PROPERTIES CONTROL PHYLLOSILICATE AND ZEOLITE FORMATION IN BASALTIC TUFFS: IMPLICATIONS FOR DETECTION OF ALTERATION PROCESSES ON MARS.

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Introduction: The discovery of diverse phyllosilicates [1, 2] and potential zeolites [3, 4] on Mars has revolutionized our understanding of early Mars history when abundant water and relatively neutral conditions may have made past life possible. Characterization of alteration minerals, including phyllosilicates and sulfates in their geologic context will be crucial to assessing the past environment and habitability on Mars. These secondary minerals form by interaction of an aqueous fluid with basaltic protolith materials [1, 2, 5]. Frequent occurrence of phyllosilicates along stratigraphic horizons [e.g., 6, 7] may either reflect in-place alteration governed by hydrothermal fluid flow, or redeposition of previously altered materials.

Fluids preferentially flow through rocks where the hydraulic conductivity (permeability and porosity) is greatest, which is a function of rock textures such as grain size and sorting. To investigate the influence of primary rock textures on alteration assemblages in basaltic materials, we examine variably altered hydrovolcanic tuffs from Fort Rock Volcanic Field, Oregon as an analog for Mars. We present field and petrographic observations in combination with mineral assemblages determined by micro X-Ray Diffraction (μ XRD) [8], using Co $\kappa\alpha$ and a 300 μ m moncapillary. Of particular interest is the occurrence and make up of palagonite, a yellow, heterogeneous, poorly crystalline substance formed by concurrent dissolution of hydrated glass and precipitation of insoluble clay and zeolite minerals [9].

Hydrologic controls on alteration of basaltic tuffs: In hydrovolcanic tuffs, primary volcanic textures vary widely and reflect changing eruption dynamics and availability of external water [e.g. 10, 11]. Tuffs may be matrix- or clast-supported; grain sizes may vary from coarse scoria to laminated fine ash beds; beds may be normally or reversely graded, poorly to well-sorted, or finely laminated to massive; and clasts may be dominantly accidental to dominantly juvenile, or vesicular to avesicular. Each of these textures has implications for primary hydraulic conductivities; permeabilities and porosities are greater in coarser grained, clast-supported layers deposited during eruptive bursts than in layers of fine ash that represent either settling airfall after the bursts, or more efficient fragmentation processes.

The dependence of fluid flow and alteration on volcanic texture is illustrated by a section of tuff that has undergone overprinting hydrothermal alteration by circulating fluids (Fig 1).

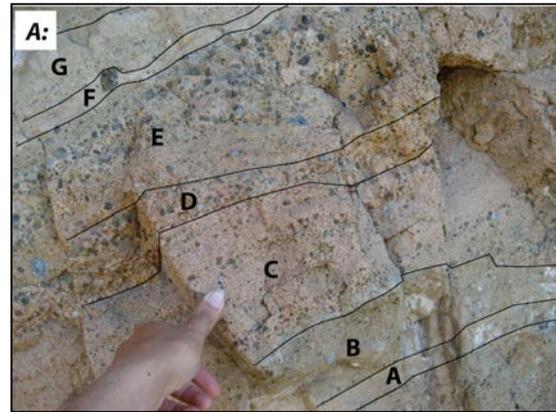
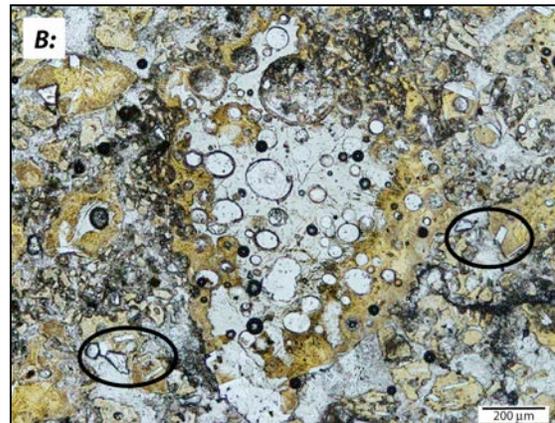


Fig 1A: A ~0.5 m section of hydrovolcanic tuff at Flat Top tuff cone in Fort Rock VF that has undergone hydrothermal alteration. The section is bounded by relatively impermeable fine ash layers A and F-G. Undulating beds and varying bed thicknesses may reflect volcanic deposition or soft sediment deformation.



1B: Plane polarized micrograph of altered coarse ash from Layer C. Small black circles are epoxy bubbles. Igneous minerals include olivine and plagioclase (examples circled in black in Fig. 1B) and appear relatively unaltered.

The transformation of basaltic glass (clear in plane polarized light) to yellow fibro-palagonite [9] is incomplete and occurs as rims around coarse ash shards (Fig. 1B) and in interiors of particularly vesicular clasts. The degree of palagonization is greater in matrix-supported layers, such as layer B (Fig. 1A), where

flow rates are lower and higher temperature fluids are retained in contact with clasts for longer periods of time.

Zeolites precipitate in primary pore spaces, including between scoria clasts and ash shards, in veins, and in vesicles within clasts and within the matrix. Coarse zeolites are found in the coarse-grained, clast supported layer D and the upper part of reversely graded E where there are larger pore spaces and greater permeability enhances fluid flow (Fig. 1A). Analysis of thin sections reveals that secondary mineral precipitation brings about a net change in rock porosity from ~10-25% to <5%. Occurrence of secondary minerals along layers of high initial permeability and porosity is strong indication that their formation postdated deposition.

Alteration mineralogy: Two thin sections were examined *in situ* using a Brüker D8 Discover μ XRD, representing less and more pervasively altered tuffs.

The less altered sample (FR-10-16) was sampled near the top of the lithified Fort Rock tuff ring. Little to no hydrothermal fluid circulation is indicated by pore spaces (~20% of the rock) that are free of secondary precipitates and no zeolites were identified. Amorphous to poorly crystalline yellow palagonite makes up <5% of the thin section (Fig. 2A). Saponite and nontronite were identified in yellow spots (Fig. 2B). These minerals form at relatively high temperatures (>120°C) [12], suggesting localized palagonitization by water-rich vapors when the pile was still hot.

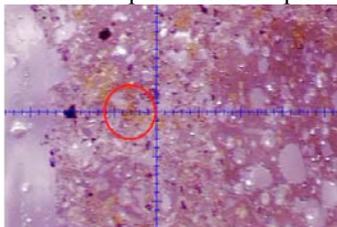


Fig 2A. Yellow-brown palagonite in matrix (FR-10-16). X-ray beam at examined spot (red circle) is nominally 300 μ m.

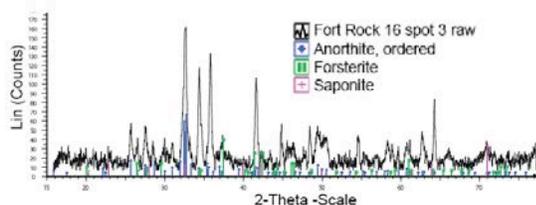


Fig 2B. μ XRD pattern of spot in Fig. 2A.

Examination of the more pervasively altered sample (layer B from Fig. 1A; FR-10-76B1) reveals a more diverse alteration mineral assemblage (Fig. 3), including the zeolites chabazite, analcime, and phillipsite. Phyllosilicates identified in yellow palagonite include nontronite, and saponite. Other alteration min-

erals, such as hematite, brucite, ankerite, and magnesioalcalite were also identified in the section. These minerals suggest hydrothermal alteration by relatively neutral solutions.

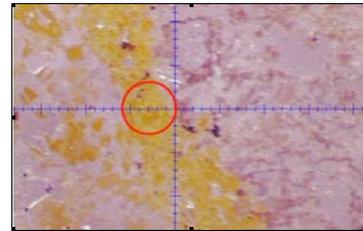


Fig 3A. Palagonitized rim of glassy clast (FR-10-76B). X-ray beam at examined spot (red circle) is nominally 300 μ m.

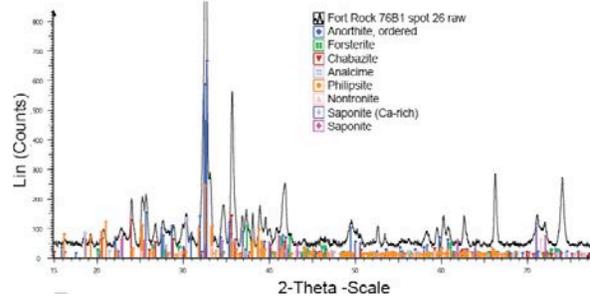


Fig 3B. μ XRD pattern of spot in Fig. 3A.

Implications for identifying alteration processes on Mars: (1) Overprinting hydrothermal alteration is controlled by the primary hydraulic properties of the rock. Occurrence along stratigraphic horizons may reflect post-depositional processes. (2) Hydrothermal alteration does not affect all phases or elements equally and the basaltic protolith may still be investigated. (3) The rate of formation and stability of phyllosilicate and zeolite minerals is linked to temperature, pH, water:rock ratios, and oxidation state. In particular, zeolites form only under low temperature, hydrous, neutral to alkaline conditions, such as by hydrothermal, diagenetic, or low temperature metamorphic processes [12] and *in situ* identification in a geologic context may be critical for interpreting habitability on Mars.

References: [1] Bibring, J.-P. et al. (2005) *Science*, 307, 1576-1581. [2] Mustard, J.F. et al. (2008) *Nature*, 454, 305-309. [3] Ruff, S.W. (2004) *Icarus*, 168, 131-143. [4] Ehlman, B.L. et al. (2009) *JGR*, 114, E00D08. [5] Murchie, S.L. (2009) *JGR*, 114, E00D06. [6] Milliken, R.E. et al. (2010) *GRL*, 37, L04201. [7] Wray, J.J. et al. (2008) *GRL*, 35, L12202. [8] Flemming, R.L. et al. (2007) *Can. J. Earth Sci.*, 44, 1333-1346. [9] Stronck, N.A. & Schmincke, H.-U. (2007) *Int. J. Earth Sci.*, 91, 680-697. [10] Brand, B.D. & Clarke, A.B. (2009) *J. Volc. Geotherm. Res.*, 180, 203-224. [11] Wohletz, K.H. & Sheridan, M.F. (1979) *GSA Spec. Paper 180*, 177-194. [12] Hay, R.L. (1986) *Pure Appl. Chem.*, 58, 1339-1342.