# OXIDATION OF BASALTIC TEPHRAS: INFLUENCE ON REFLECTANCE IN THE 1 $\mu$m REGION

William H. Farrand and Robert B. Singer, Planetary Image Research Laboratory, LPL, University of Arizona, Tucson, AZ 85721

Vitric basaltic glasses[*] are widespread on the Earth, Moon and Mars as well. On Earth, basaltic ashes resulting from Strombolian fire fountaining are prominent at such volcanic centers as Hawaii and Iceland. Basaltic tephras can also result from hydrovolcanic activity [1]. To distinguish these tephras from those formed in anhydrous eruptions they can be referred to as *hydroclastic* materials [2]. The dark mantling deposits of the Moon [3], presumed to be the product of Strombolian fire fountaining, are formed of basaltic glasses. Given the Moon's reduced state, these ashes never alter. However, on Mars, as on the Earth basaltic glasses are susceptible to alteration. Indeed, the alteration product of sideromelane, palagonite, is thought by many to be a major component in Martian dust [4,5]. Possible extensive deposits of unaltered basaltic ash, perhaps rich in tachylite, have also been identified in Valles Marineris on Mars [6].

Pristine basaltic hydroclasts are composed dominantly of sideromelane. Sideromelane alters via a process of hydration and oxidation to the mineraloid palagonite. In the current instance, we are concerned solely with the oxidation process. The best way to track the process of oxidation is in the transformation of iron from the ferrous to the ferric state, and an ideal tool for tracking that transformation is visible and near infrared (Vis/IR) spectrometry.

As part of an ongoing study into the products of hydrovolcanism, tuffs were examined from the Cerro Colorado and Pavant Butte tuff cones. The former resides in the northeastern corner of the Pinacate Volcanic Field in Sonora, Mexico and the latter is in the Black Rock Desert of southern Utah. Numerous samples were collected and many of these had their Vis/IR reflectance measured at Brown University's RELAB facility [7].

Figures 1a and 1b show spectra from Cerro Colorado and Pavant Butte respectively. The high reflectance spectra in each of the aforementioned figures are oxidized palagonite tuffs. The low reflectance spectra are unoxidized sideromelane tuffs. Evident in both sets of spectra are absorption features in the 1 $\mu$m region. The low reflectance of the sideromelane tuffs presents the illusion that their "1-$\mu$m" absorptions are weaker than the palagonite tuffs, but in fact the reverse is true.

The primary cause of the "1-$\mu$m" feature in the sideromelane tuffs is $Fe^{2+}$ in octahedral sites within the sideromelane producing a crystal field absorption. The 1-$\mu$m feature is a characteristic feature of such ferrous iron bearing minerals as olivine, pyroxene and even plagioclase. Indeed, point counts of thin sections indicate that approximately 10% of the sideromelane tuffs are discrete crystals, predominantly plagioclase with lesser amounts of olivine and clinopyroxene. Certainly these phases contribute to the observed 1 $\mu$m absorption, but are not by any means the primary cause.

The cause of the 1-$\mu$m feature in the palagonite tuffs is less well constrained. Ferric iron phases have an absorption in the 0.86 to 0.93 $\mu$m region caused by the $^6A_1 \rightarrow {}^4T_1$ [8]. For hematite this band occurs at 0.86 $\mu$m, for goethite ($\alpha$-FeOOH) at about 0.90-0.93 $\mu$m. As can be seen in Figure 2, some of the most oxidized tuffs from Cerro Colorado have band centers at about 0.92 $\mu$m. In thin section, the primary sideromelane in these tuffs has altered almost completely to palagonite. Thus one could be tempted to say that the ferric iron bearing phase is goethite; however, the 0.63 $\mu$m band characteristically associated with goethite is not present. It seems likely that for most of the palagonite tuffs the 1-$\mu$m feature is in fact a composite band formed by contributions from ferrous and ferric iron phases.

Figure 2 shows the band depth [9] of the 1-$\mu$m feature versus band center for 21 samples from Cerro Colorado and Pavant Butte. This figure clearly displays the shift in band center from the unoxidized sideromelane tuffs to the oxidized palagonite tuffs. Less striking, but also noticeable is a decrease in band depth with increasing oxidation. Band width also tends to decrease with increasing oxidation. The shorter band center and decrease in band width are indicative of the increasing influence of ferric over ferrous iron mineralogies. However, the decrease in band depth seems to indicate that some of the ferrous iron which had been contributing to the 1-$\mu$m band in the sideromelane tuffs is no longer contributing to the equivalent shorter wavelength band in the palagonite tuffs. This makes sense in two regards. First, unlike the absorption produced by ferrous iron, $Fe^{3+}$ bands are spin forbidden and thus are inherently weaker than the equivalent ferrous 1-$\mu$m band. Secondly, ferric iron mineralogies in palagonite can be "nanocrystalline"; i.e. with grain

---

[*] Clear vitric basaltic glass is known as sideromelane, devitrified glass as tachylite.

sizes less than 10 nm. In such cases the 0.86 or 0.89 μm band for hematite or goethite disappears [10]. Therefore, it seems likely that in the palagonite tuffs there is a combination of nanocrystalline ferric oxide phases contributing to the UV absorption edge but not to the 1-μm band, plus more crystalline ferric oxides which do contribute to that band as well as ferrous iron within unaltered sideromelane which is skewing the band center to longer wavelengths.

This work has obvious implications for spectroscopic observations of Mars. As was noted earlier, basaltic tephras are believed to be an important surface material on Mars. Likewise recent observations of Mars [11,12] have shown there to be absorptions in the same wavelength region being discussed here. The present work indicates that when ferrous and ferric iron phases are both present their combined spectral contribution is a single band in the vicinity of 1 μm. The center, depth and width of that feature has the potential to be used to gauge the relative proportions of ferrous and ferric iron phases. Certainly, this is an area where laboratory work examining the oxidation of artificial, or hand picked natural, glasses would prove fruitful.

REFERENCES: [1] Wohletz K.H. and Sheridan M.F. (1983) *Am.J.Sci* **283**, 385-413. [2] Fisher R.V. and Schmincke H.U. (1984) *Pyroclastic Rocks*. [3] Head J.W. (1974) *PLSC 5*, 207-222. [4] Evans D.L. and Adams J.B. (1979) *PLPSC 10*, 1829-1834. [5] Singer R.B. (1982) *JGR* **87**, 10159-10168. [6] Geissler P.E. et al. (1990) *JGR* **95**, 14399-14413. [7] Mustard J.F. and Pieters C.M. (1989) *JGR* **94**, 13619-13634. [8] Morris R.V. et al. (1985) *JGR* **90**, 3126-3144. [9] Clark R.N. and Roush T.L. (1984) *JGR* **89**, 6329-6340. [10] Morris R.V. and Lauer H.V. (1990) *JGR* **95**, 5101-5109. [11] Bell J.F. et al. (1990) *PLPSC 20*, 479-486. [12] Singer R.B. et al. (1990) *Bull.Am.Astron.Soc.* **22**, 1061.

Fig. 1: Reflectance spectra of tuffs from Cerro Colorado and Pavant Butte. In each figures, the palagonite (top) and sideromelane (bottom) tuff occured beside each other in outcrop. Arrows indicate band center.
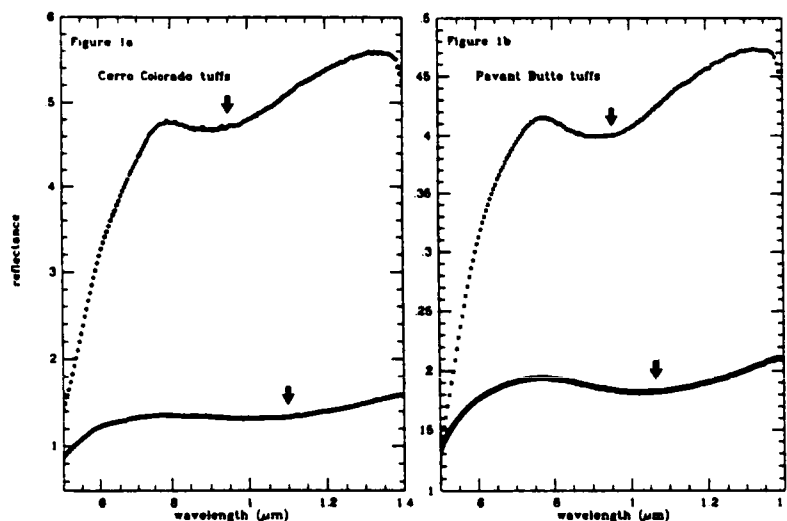


Fig. 2: Plot of band depth vs. band center. Palagonite tuffs cluster on the lower left and sideromelane tuffs on the right. The most highly oxidized tephras (shortest band centers) are from Cerro Colorado. The least oxidized tephras (longest band centers, deepest band depths) are from Pavant Butte. The 3 sideomelane tuffs in the upper right hand corner represent an earlier phase of the Pavant Butte eruption than those in the lower right.