



Allophane and palagonite: similar neoformation at low temperature.

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Weathering processes observed in various profiles of paleosols on basaltic pyroclastic from the Azores, Cameroon, Iceland, Galapagos Islands and Tenerife, are dominated by allophane neoformations associated with iron segregation. In all cases the parent material consists of vitric ashes, lapilli or scoria particularly sensitive to alteration. The morphology and fabric of the primary particles is well preserved within the allophane alteromorphs, even within the totally altered, highly vesicular scoria found below paleosols, more than one meter thick.

The first step of the alteration is a hydration (about 10%) of the beige-brown glass without important discoloration and associated with a slight leaching (a few percents) of cations and silica. A maximum of 15% of hydration was reached before a transformation into allophane. The alteromorphs formed consist of a yellow to orange highly hydrated (minimum 30 %) allophanic material. Na, K, Mg and Ca are totally leached, Ca remains as traces when P is adsorbed in some of the horizons. A limited cation-leached internal hypocoating at the glass surface with a relative enrichment of Fe and Al is evolving into a allophanic coating along borders. With increasing weathering in the deeper and older horizons, the dissolution is combined with desilication of the glass and concomitant with an Al and Fe relative enrichment, which is coherent with the observed neoformation of allophane, from the borders of the vitric material towards the inside. Besides the age, other factors influence the rate of weathering such as granulometry and vesicularity. The alteromorphs after lapilli or pumice are the end-product of the alteration of the glass. This is confirmed by the highly hydrated state (70 %) of the allophane alteromorphs after pumice attributed to the in situ alteration through a diffusion process. The chemical signature of allophanic varies from pure hydrated alumino-silicate to more or less Fe (Ti) enriched hydrated

alumino-silicate. Some coatings or alteromorphs are dark orange, possibly microlaminated. The high content of Fe and Ti (Fe/Al: 1.2 to 0.5) with occasionally 1 % of Mn, suggests mixed phases of allophane and oxhydroxides. When strong iron segregation occurs, the weathered orange lapilli show an onion-skin fabric in the mass, similar to the perlitic cracks resulting from the hydration/expansion of glass. The curved concentric micro-zones have refractive indices that increase with increasing Fe, Ti content. It is supposed that a strong hydration of the glass may have occurred originally creating mechanical micro or nano-zones that have been later altered into allophane.

The allophane alteromorphs display optical characteristics similar to those of palagonite. "Palagonite" (gel to fibro palagonite depending on the degree of crystallinity) is a mixing of phases resulting from the process of palagonitisation which is an alteration of the glass by sea-water or by unsalted-water, submitted to different temperature or pressure conditions. Several authors related the color of the palagonite to thermal conditions (ambient to high). The highly hydrated gel palagonite, related to low temperature alteration, is optical similar to the allophanic material observed in the weathered tephra of the paleosols: a clear yellowish to brownish isotropic and commonly concentrically banded material, in which the primary vitric morphology is preserved. Concentric banded layers of palagonite are also enriched with opaque minerals due to the chemical Fe and Ti segregation observed during the alteration. Palagonite was described as the first stable product resulting from the alteration of glass below water, forming a ring of insoluble material at the glass-fluid interface. In gel-palagonite spherical structures of 20 to 60 nm were observed by high resolution electron microscopy and interpreted as precursors of smectites. Proto-smectites have been chemically discriminated in the Azores samples as hydrated Mg alumino-silicate. It is now generally accepted that a dissolution-precipitation mechanism is responsible for palagonitisation, but mineralogical data on the neoformation are extremely rare. Amorphous "gel", palagonite is related to Si, Al, Mg, Ca, Na, K losses, H₂O gain and immobile Ti, Fe behaviour. The published results on REE mobility during palagonitisation are rather contradictory. More recently it has been correlated to the adsorption capacity of the secondary minerals.. In the case of the Azores allophanic horizon, the quantity of allophane is controlling the increasing amount of REE.

Even if similarities are obvious between amorphous palagonite and allophanic gel, differences remain in the chemical signatures. The microstructures observed by STEM on the allophanic gels are typical for the aggregates of hollow spherules of allophane rather than for the 20-60 nm spherical structures of palagonite. The chemical signature remains different with Al dominant towards Si, highly variable Fe and a total loss of cations. The incipient process of glass hydration/alteration however appears similar.