Formation of volcanic ash soils in the Matese Mountains of southern Italy

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Abstract
Over the past 40 ka, there have been many explosive eruptions in southern Italy from Campi Flegrei that have dispersed pyroclastic material in the southern Apennines surrounding the Matese Massif . A detailed mineralogical study was conducted on 5 pedons sampled on the Matese Massif to study volcanic ash soil genesis. All pedons contained vermiculite, mica, kaolinite and some interstratified mica-kaolinite. The diffraction patterns presented weak peaks, indicating a low mineral content and the presence of materials that did not diffract strongly, most likely allophane and unweathered volcanic glass and sanidine. The mica was most likely primary mica that crystallized along with the sanidine. The vermiculite was a weathering product of the mica. We assume that the finest ash cools faster, resulting in a glass, whereas the larger particles cool slower, resulting in sanidine and mica. Sanidine and mica weathering released K and Na ions, which leached from the profile, resulting in halloysite crystallization. We also identified gibbsite in the deepest horizons of 2 profiles. The sequence of pyroclastic deposits and the mineralogical evidence demonstrate the important contribution of the Campi Flegrei pyroclastic products on volcanic ash soil genesis in the southern Apennines.

Key words
Andic properties, halloisite, volcanic ash soils, aluminium oxides.

Introduction
The Matese Massif represents a wide calcareous relief located in southern Italy. The highest peaks are Mt. Miletto (2050 m), La Gallinola (1923) and Mt. Mutria (1823 m). The Matese Massif is part of the Mesozoic-Cenozoic carbonate platform domain. The geomorphologic features which characterize the Matese Massif and its northern border range from those typical of an upper mountain environment (glacial to periglacial landforms and deposits) to those of a fluvial to lacustrine environment. Its geomorphologic evolution appears strongly linked to tectonic and litho-structural controls, as well as to the high solubility of the carbonatic succession that has produced a rich karst landscape and diffuse endokarst phenomena. The Matese Massif represents one of the main karst aquifers of the Central-Southern Apennines. Groundwater percolates about 1500 m since it reaches the basal karst level. Over the past 40 ka, many eruptions of volcanoes in southern Italy were explosive and largely related to the Campi Flegrei and Somma-Vesuvius activity. During the Campi Flegrei, the higher magnitude eruptions produced the Campanian Ignimbrite (39 ka) and the Neapolitan Yellow Tuff (13 ka) as the result of several plinian and subplinian eruptions that resulted in a large amount of pyroclastitic material. The Campi Flegrei pyroclastic products were dispersed mainly eastward and north-eastward by the prevailing stratospheric wind regime and they mantle the southern Apennine Mountains surrounding the Matese Massif . The general sequence of pyroclastic deposits and dispersion, and the chemical and lithological evidence suggest an important contribution from Neapolitan Yellow Tuff (Tufo Giallo Napolitano) in this area. On the basis of paleoreconstructions, besides the described glacial deposits, two morainic arcs are present along the southern border of the Campitello plain. Older moraine deposits of pre-Würmian age are present along the northern border of the Matese Massif and reach minimum altitudes of about 800 m a.s.l. In this research a detailed chemical and mineralogical study was conducted on 5 pedons sampled on a selected area of the Matese Massif to study the characteristics of the volcanic ash in soil genesis and also to investigate the influence of the parent material and time on pedogenic processes under a Mediterranean climate.

Methods
Studied area
Five pedons were described by standard soil survey methodology. All analyses were performed on air-dried <2 mm soil (MIPAF, 2000). The Campitello Matese study site is characterized by small to large-scale surface karst features including bare rock outcrops, small karstic depressions (dolines), and sinkholes. The

MAT 8, MAT10 and MAT13 profiles occur at an elevation of 1624 m a.s.l. in a large doline. The climatic condition is moist (1874 mm) and cool (lowest medium annual temperatures of 7.2°C). MAT7 occurs in the same climate zone, but at 50 m lower elevation on a 37 % slope and in a different landscape. The present vegetation and land use are similar in MAT8, MAT10 and MAT13. The MAT9 profile was characterized by lacustrine sediments derived from pyroclastic material redeposited by turbidity currents. Mineralogical and geochemical analyses allow one to assign these pyroclastic materials to trachytes-trachyandesites. The criteria for andic soil properties were examined for the whole pedon and classified as Aluandic Andosols (WRB 2006).

Selective Dissolution
Iron, Al, and Si were extracted by ammonium oxalate (Fe_o, Al_o , Si_o); Fe and Al were also extracted by sodium pyrophosphate (Fe_p, Al_p). Iron, Al, and Si in solution were determined by ICP. Poorly crystallized aluminosilicate minerals (allophane and imogolite) were estimated by pH 3 NH_4-oxalate extraction.

Mineralogical data
The soil samples were treated with pH 5 Na-acetate to destroy carbonates and pH 8.5 Na-hypochlorite to remove organic matter before being dispersed ultrasonically in distilled water. They were then fractionated into <2 µm, 2 - 50 µm, and >50 µm fractions by sieving and repeated gravity sedimentation in distilled water adjusted to pH 10 with NaOH. The <2 µm fraction was used for X-ray diffraction (XRD) and differential X-ray diffraction (DXRD), as well as for selective dissolution by acid ammonium oxalate. Diffraction patterns were obtained using a PANalytical X'Pert PRO MPD x-ray diffraction system (PANalytical, Almelo, The Netherlands) equipped with a PW3050/60 θ-θ goniometer and a Co-target x-ray tube operated at 40 KeV and 35 mA. The diffraction patterns were collected from 2.1 to 80° 2θ at 0.05° steps with 60 sec measurement time per step. The data were analyzed with the X'Pert High Score Plus software package (PANalytical, Almelo, The Netherlands).

Results
Pedon characteristic
Pedons MAT7, MAT 8, MAT 10 and MAT13 are located in Campitello Matese on calcareous material. All soils are usually rich in organic carbon, with saturation base below to 50%, and with acidic pH.
The MAT 8 and MAT 10 pedons are deep and most likely reflective of repeated colluvial deposition in a doline environment. MAT8 has thick, black to dark brown granular A horizons, weakly-expressed Bw horizons with subangular blocky structure, and a long sequence of CB horizons. These horizons are quite homogeneous. In this pedon, the A is dark and granular while the Bw horizons have subangular blocky structure. Both the A and Bw horizons are very friable, highly permeable, and contain stratification.. The soil surface has thick, black to dark brown granular A horizons and weakly-expressed Bw horizons with subangular blocky structure. The permanent vegetation changes at higher altitudes (1650-1700 m. a.s.l.) from beech forest (Fagus sylvatica) to oak forest (Quercus pubescens), to chestnut forest (Castanea sativa) at 1000- 800 m. a.s.l. and follow the change from a udic to ustic pedoclimate. Soil temperature regimes change accordingly from thermic to mesic.

Chemical aspects
All horizons of pedons MAT7, MAT8, MAT13, MAT10 have oven-dry bulk densities of <0.80 kg dm^3 and a sand texture . This is typical for volcanic ash soils strongly influenced by non-crystalline materials and high soil organic matter concentrations (Shoji *et al.* 1993; Colombo *et al.* 2007). Water pH values range from 5.0 to 7.1 and are generally higher in surface horizons than in subsurface horizons. For all profiles and for all horizons, the sum (Al + 1/2Fe) extracted by oxalate is near the diagnostic 2% limit used to define andic soil properties in WRB and Soil Taxonomy. In profiles MAT8 and MAT13 the Al_p/Al_o ratio ranges from 0.38 to 0.85, suggesting the presence of active Al-humus complexes. The relative amounts of Al extracted by sodium pyrophosphate are correlated with Al-organo complexs. The Al_o concentrations are negatively correlated with pH in water (Figure 1). The values of Si_o are positively correlate with pH in NaF, indicating an increasing amount of allophane (<5 %) in some horizons. Ferrihydrite is also common but in low amount, with Fe_o ranging from 0.5% to 1 %.

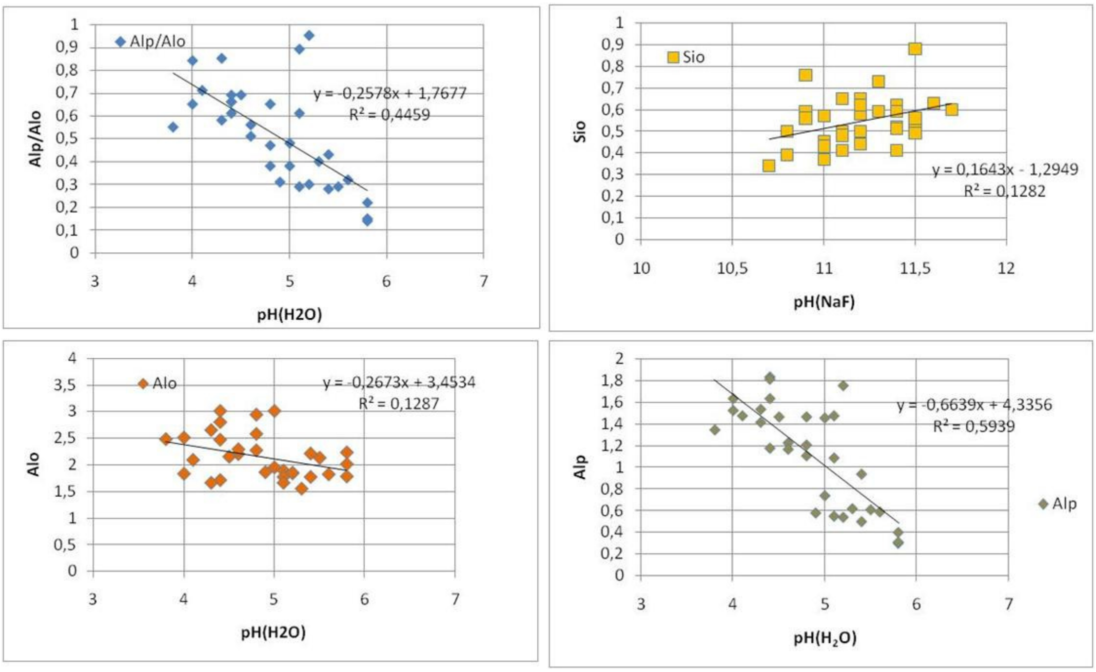

Figure 1. Correlation between Al and Si extracted by oxalate (in per cent), Al extracted with pyrophosphate (Al_p) and Al_p/Al_o ratio vs pH.

Mineralogical aspects

The clay minerals in the MAT7, MAT8 and MAT 13 profiles consist usually of vermiculite, mica and kaolinite and/or halloysite. Some hydroxy- interlayered vermiculite was also observed in the clay fraction. Mica and plagioclase are also present in all horizons. The highly ordered nature of the mica suggests its inheritance from the parent material, while the poor crystallinity of the 1.4-nm intergrade suggests a pedogenic origin (Vacca *et al.* 2003). Sanidine inherited from the parent material is revealed by a small peak at 0.62 nm present in many horizons of the MAT8, MAT13 and MAT10 profiles. The mica peaks are very weak in all patterns, while the vermiculite seems stronger in the MAT7 pedon in comparison with horizons above it. The presence of gibbsite in some horizons of MAT7 and MAT8 indicates intense (or long) leaching of these horizons compared to the ones above it. Again, the fact that these horizons were identified as buried horizons in the field is consistent with the presence of gibbsite. Presumably, these horizons were exposed to weathering for quite some time before they were buried by an additional ash fall. Some hydroxy interlayering in many pedons is indicated by a weak peak at 1.49 nm after heating to 100 C. The clay fraction of the MAT9 profile is dominated by kaolinite, mica, and vermiculite. In addition, the Bb2 horizon contains interstratified mica-kaolinite, a situation in which mica layers and kaolinite layers are stacked together in a random sequence. This is confirmed by the presence of a hump at about 0.80 nm that gets stronger on heating, but disappears after heating to 550 C. The interstratified mica-kaolinite is a weathering produce of mica. Traces of a partially dehydrated halloysite are also present in the CBb7 horizon and crystallized from the Al and Si released from the weathering of the sanidine and mica. The weathering of the sanidine and mica would have released K and Na ions, which have leached from the profile (Ugolini and Dahlgren 1991) This is consistent with the well-drained nature of the profile and the site. Primary minerals remaining in the < 2 µm fraction include K-feldspars (sanadine) and quartz. In the BW1 horizon some XRD lines also suggest the presence of analcime, a zeolite mineral.

Conclusion

The pedogenic environment of the studied soils is especially complex because of the heterogeneity of the stratified pyroclastic materials. Such stratification is a general condition in many volcanic areas (such as in the soils from the southern Apennine), it produces very different pedogenic way. The five profiles show different degrees of soil development, ranging from moderately weathered MAT7, MAT8, and MAT10, to poorly weathered MAT9. Despite such differences, all the soils exhibit common features such as the pedogenic redistribution of fine material.

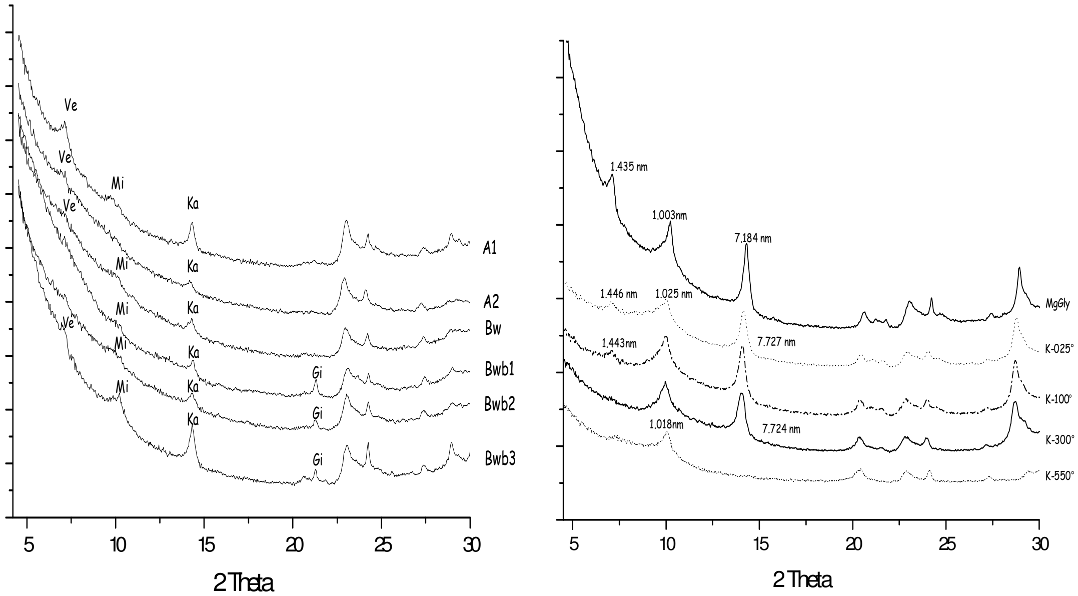

Figure 2. X-ray diffraction patterns (Co-Kα radiation) of the clay fraction of the 2Bb horizon of profile MAT 7 and MAT 13 (a) Ve_ vermiculite, Mi = mica, Ka = kaolinite.

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