# Clay minerals in South Australian Holocene basaltic volcanogenic soils and implications for halloysite genesis and structure*

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## Abstract

The clay mineralogical composition was determined of 8 soils formed from pyroclastic ejecta (tephra) from adjacent 5000-year old basaltic volcanoes at Mounts Gambier and Schank in South Australia. Both nanocrystalline (short-range order) and crystalline aluminosilicates and also Fe oxides and hydroxides were identified in the soils. Allophane generally occurred to a greater extent in the 4 soils derived from glass-rich Mt Schank tephra than in most of those from glass-poor Mt Gambier tephra. Ferrihydrite occurred along with allophane. Smectite, kaolinite, illite, and an interstratified kaolinite-smectite comprised the crystalline minerals in these soils. There was no evidence for halloysite. Unlike in New Zealand, decreased leaching resulted in Si-rich allophane, rather than halloysite, forming in place of the Al-rich form of the same mineral. This result may indicate that ferrous iron is an essential impurity in halloysite. It was likely absent from these soils because their high pH due to underlying calcareous rocks precludes its occurrence. The probable requirement of Fe(II) as an essential component of halloysites may have been overlooked because of oxidation consequent upon the inevitable drying of samples prior to analyses.

## Introduction

Southeastern South Australia experienced volcanic activity during the Pleistocene and Holocene periods (Lowe and Palmer, 2005). Its volcanoes form the western extension of the Newer Volcanics Province of western Victoria (Fig. 1). This study is concerned with the products of weathering of the youngest of the volcanoes in this province. These comprise two isolated basaltic Holocene eruption centres at Mounts Gambier and Schank, which are separated by about 10 km. They are near-contemporaneous and have been dated at about 5000 years old on the combined evidence of radiocarbon, thermoluminesence and paleomagnetic dating and they are therefore the youngest volcanoes on the Australian mainland.

Both volcanic complexes are underlain stratigraphically by consolidated calcareous, aeolian quartz-rich sands (Bridgewater Formation), and Oligocene-Miocene (Gambier) limestone. Some of the underlying calcareous material has become incorporated into both the pyroclastic eruptives and the resultant soils.

The climate in the region encompassing the volcanoes and associated soils comprises xeric moisture and mesic temperature regimes, with cool winters that largely bring moisture via drizzle and with very warm, dry summers. While the annual rainfall is around 700 mm, only about 280 mm of water drains through upper soil profiles, according to water balance studies. The drainage generally occurs over 3 to 10 weeks in winter and early spring.

Weathering of volcanic materials, and especially of their fragmental (pyroclastic) ejecta, hereafter tephra, leads commonly to the formation of either the aluminosilicate mineral allophane with short-range order (hereafter known as "nanocrystalline", following Churchman and Lowe, 2012), or the crystalline aluminosilicate mineral halloysite. Various oxides or oxyhydroxides of Fe are also formed.

All but one of the 8 pedons included in this study were classified as Andisols by Lowe and Palmer (2005), namely Haploxerands, Vitrixerands, or Melanoxerands (Takesako et al., 2010). Nonetheless, the conditions under which the soils were formed at Mounts Gambier and Schank are relatively uncommon for the formation of Andisols world-wide (McDaniel et al., 2012). Their volcanic parent material is basalt, but as tephra rather than the more typical lava. Also, pH values (in water) are near-neutral or alkaline, ranging from 6.4 to 8.5. The unusual combination of conditions for soil formation, including a xeric moisture regime and underlying calcareous country rock that is partially mixed with tephra in some places, has enabled examination to be made of some common generalizations concerning the products and processes of

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weathering of volcanic materials in many other studies worldwide (e.g. Parfitt et al., 1984; Takahashi et al., 1993; Churchman and Lowe, 2012).

**Materials and methods**

Five pedons (Nos. 1-6) were studied at Mt Gambier, two (Nos. 8 and 9) at Mt Schank and one (No. 7) midway between the two centres (Fig. 1). Their main physical and chemical properties and their primary mineralogies are described by Lowe and Palmer (2005).

The contents of allophane were determined by multiplying the content of Si that was extracted from a whole soil by an acid oxalate reagent ($Si_{ox}$) by a factor related to the Al:Si atomic ratio of the allophane, itself given by a ratio of the difference between $Al_{ox}$ and Al extractable by pyrophosphate to $Si_{ox}$, following Parfitt (1990).

Clay fractions were extracted from whole soils by sedimentation from suspensions of the soils following dispersion by shaking with sodium chloride, followed by the removal of excess salt by repeated centrifugation. Clay fractions were analysed by X-ray diffraction (XRD) both after air-drying and also immediately after additions of formamide to test for the possible occurrence of halloysite (Churchman et al., 1984).
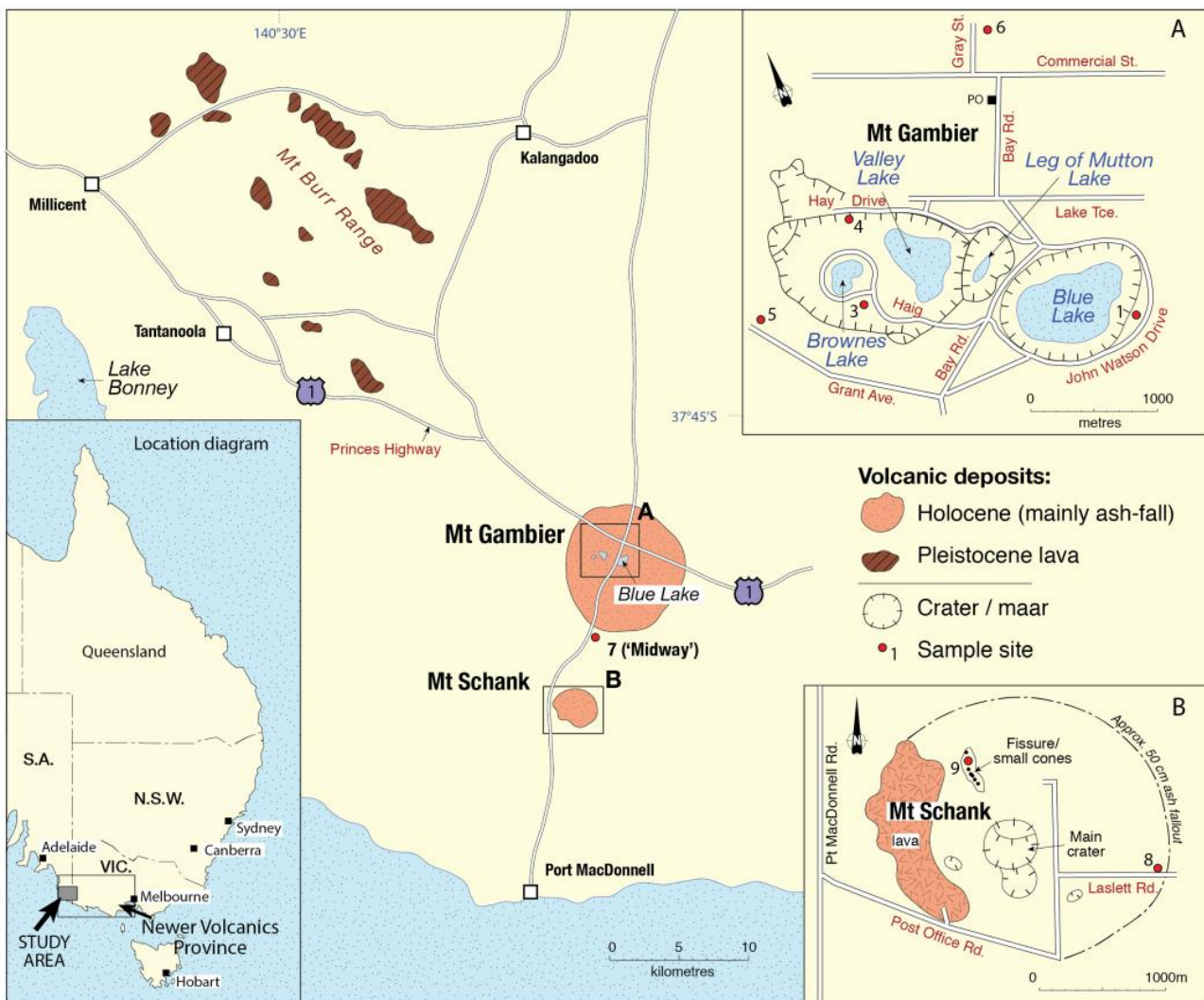


**Figure 1. Locations of pedons studied at Mounts Gambier and Schank. Symbols with ticks in inset maps A and B denote craters (after Lowe and Palmer, 2005).**

**Results**

The clay minerals found in the various soils included nanocrystalline and also crystalline phases. The principal nanocrystalline phases were allophane and ferrihydrite. There was variation in their occurrence both between sites and between horizons with depth in each profile. Allophane was a relatively insignificant proportion (<1.4%) of the whole soil throughout only one site (#1, Fig. 1) and in quite low (<2.2%) proportions within the profile at site #4. In one other soil, at site #3 (Fig. 1), the notably high concentration of allophane (~11%) occurred in a Bsm horizon at a considerable depth (~0.8 m) but was hardly present elsewhere in the profile. In the soils at the other 5 sites, high concentrations of allophane tended to occur in near-surface horizons. There was also a common trend in the Al:Si composition of the allophane in these soils. Typically, Al:Si was highest in the uppermost horizon. This ratio was generally about 1.7-1.8 at its highest in each profile, although the highest value for the ratio in the soil at site #9, in the scoria cone-derived tephra, was lower, at ~1.5.

Concentrations of ferrihydrite tended to parallel those of allophane, but it was almost always less concentrated than allophane in any particular horizon

It was observed that horizons containing high concentrations of $CaCO_3$ also contained low concentrations of allophane and ferrihydrite. The $CaCO_3$ was concentrated in the lower horizons of most of the soils near Mt Gambier. By contrast, soils developed on Mt Schank tephra had little or no $CaCO_3$ within their profiles. Nonetheless, some of the lower horizons within these soils were largely devoid of allophane and ferrihydrite.

XRD of clay fractions following the two different dispersion procedures showed that most horizons of all of the soils contained a common suite of crystalline clay minerals that comprised smectite, kaolinite, illite, and an interstratified kaolinite-smectite.

Formamide did not expand the 7 Å peak in the clay fractions from soils at any of the sites, indicating that there was no dehydrated halloysite in any of these samples. Halloysite that was hydrated in air-dried samples can also be discounted as a contributor to the (small) peaks for 10 Å spacings in patterns from some of the soils because solvation of hydrated halloysite with glycerol shifts the peak from 10 to 11 Å (MacEwan, 1946), and there were no peaks at 11 Å in clay fractions after addition of glycerol. It may therefore be concluded that halloysite has not formed in the soils at either Mt. Gambier or Mt. Schank.

**Discussion**

In soils formed on tephras in North Island, New Zealand, it is generally agreed (e.g. Parfitt et al., 1984; Churchman and Lowe, 2012) that both the form of allophane and also whether it is favoured compared with halloysite reflects the extent to which leaching removes Si from soil-forming solutions relative to Al. Although studies in New Zealand have generally shown that reductions in the degree of leaching of Si led to a change in the secondary product from Al-rich allophane to halloysite, in this system at both Mts Gambier and Schank, decreased leaching has produced Si-rich allophane rather than halloysite in place of the Al-rich form of the same mineral,.

It has been surmised that the defining characteristic of halloysite (cf. kaolinite) is its incorporation of interlayer water (e.g. Churchman and Carr, 1975). Bailey (1990) concluded that halloysite must have a higher layer charge than kaolinite in order to give rise to a more polar surface to its interlayer, hence allowing the attraction and retention of interlayer water upon its formation. Bailey (1990) further proposed that halloysite should have some tetrahedral Al replacing Si in the aluminosilicate layer in order to achieve a higher layer charge than in kaolinite. Later work (Newman et al., 1994) failed to find any more Al(IV) in several halloysites than in either well-crystallized or poorly-crystallized forms of kaolinite. We suggest instead that halloysite contains more ferrous iron in its octahedral layer than kaolinite (which may have none), thereby resulting in a higher (negative) layer charge, more polarity, and more attraction for polar water molecules than in kaolinite.

While ferrous ions are favored over ferric ions in wet conditions (where pE values are negative), they also become unstable in relation to solid phases such as siderite $FeCO_3$ (in a $CO_2$-rich system) and ferrihydrite $Fe_5HO_8.4H_2O$ (in a $CO_2$-poor system) as pH rises (Sposito, 2008). Assuming realistic values for the concentration of $Fe^{2+}$ and $CO_2$ partial pressure, ferrous ions are hardly present in solution in the pH 6-7 range and above. We may therefore conclude that they are hardly present in the suite of 8 soils examined here (which have pH values $\geq 6.4$ in water and $\geq 6.0$ in 0.02M $CaCl_2$). The lack of halloysite in these soils is consistent with a necessary requirement for ferrous ions for the formation of halloysite. It is also consistent

with the common occurrence of halloysite under acid conditions. The ease of oxidation of ferrous ions to ferric ions under oxidizing conditions would preclude the long-term retention of the ferrous form in the aluminosilicate layers. Oxidation of Fe(II) to Fe(III) may have occurred in these South Australian soils because of marked seasonal drying in the xeric moisture regime. More generally, drying of halloysite samples prior to their analyses may have generally led to oxidation of any incorporated ferrous iron, ensuring that this probable requirement for halloysites has inevitably been overlooked. This suggests that samples of halloysite which have never been dried should be analysed for ferrous iron.

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