Discovery of halloysite books in a ~270,000 year-old buried tephra deposit in northern New Zealand

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As part of a wider study examining the geomechanical properties, especially sensitivity, of sequences of Quaternary pyroclastic and associated deposits and buried soils in the landslide-prone western Bay of Plenty area near Tauranga, eastern North Island, we examined the mineralogy of a pale pinkish-grey tephra deposit directly beneath non-welded, siliceous Te Ranga Ignimbrite (~2 m thick) in a ~25 m high cutting at Tauriko. The pale tephra unit, ~0.5 m in thickness and at ~20 m depth, probably represents initial tephra fallout associated with the Te Ranga eruptive episode that has been dated at 0.274 ± 0.016 Ma (Briggs et al. 2005). The pale tephra unit overlies white to yellowish bedded and massive fluvial sands of the Matua Subgroup (Briggs et al. 1996), and contains ~7% clay (<2 µm), ~82% silt (2-60 µm), and ~11% sand (60-2000 µm) on the basis of lasersizer analysis. MgCl-saturated clay fractions (<2 µm) from 3 field-moist samples from the unit were separated by density (after dispersal in water using calgon, end-over-end shaking, and brief ultrasonication) and analysed by XRD using both glass-slide and ceramic-tile mounts, by analysis of acid oxalate extractions (AOE), and by SEM. Energy-dispersive X-ray (EDX)-derived elemental analyses were obtained on selected clays during SEM examination. Air-dried bulk samples (sand + silt + clay) were additionally analysed by XRD as dry powder mounts using aluminium holders, and via SEM. Fine-sand fractions were analysed as grain mounts using optical microscopy.

XRD (ceramic and glass mounts) showed that the clay fractions were dominated by hydrated halloysite. The AOE analyses indicated that nanominerals (allophane, ferrihydrite) were absent or negligible. That halloysite (rather than mica or kaolinite) was predominant was confirmed by the following XRD features. (i) A strong, well defined peak occurred between 9.82 and 9.92 Å, with no peak at ~7 Å (Fig. 1a). (ii) After the application of formamide, the 9.82-9.92 Å peak shifted to between 9.94 and 10.06 Å (i.e., the clay expanded). On heating at 110 °C for 1 hr, the peak shifted to between 7.2 and 7.3 Å, and after heating at 550 °C for 1 hr, it disappeared (Fig. 1b). (iii) Secondary halloysite peaks occurred at 4.4 Å (this peak being characteristically asymmetrical) and between 3.32 and 3.35 Å. The latter peak shifted to 3.6 Å with formamide treatment, and both secondary peaks collapsed when heated to 550 °C.

Whole (bulk) samples contained dehydrated halloysite – manifested by an XRD peak between 7.34 and 7.48 Å, an asymmetrical peak at 4.48 Å (slightly more intense than that at ~7 Å), a peak at 3.6 Å, and another between 2.37 and 2.4 Å – together with plagioclase, quartz, and tridymite. The asymmetry of the 4.48 Å peak and its greater height than the peak at 7 Å are both features consistent with halloysite rather than kaolinite being present. Kaolinite, if present at all (and in very small amounts in any event), would show up as a peak at ~7.15 Å but such a peak, if it exists, is masked by the dehydrated halloysite peak. Abundant volcanic glass, plagioclase, and quartz, as well as moderate amounts of hornblende, hypersthene, titanomagnetite, lithic fragments, and clay aggregates, were identified in fine-sand fractions. This mineralogical assemblage typifies that of many rhyolitic tephra deposits in central and eastern North Island, and is consistent with the mineralogy recorded for the Te Ranga Ignimbrite (Briggs et al. 1996).

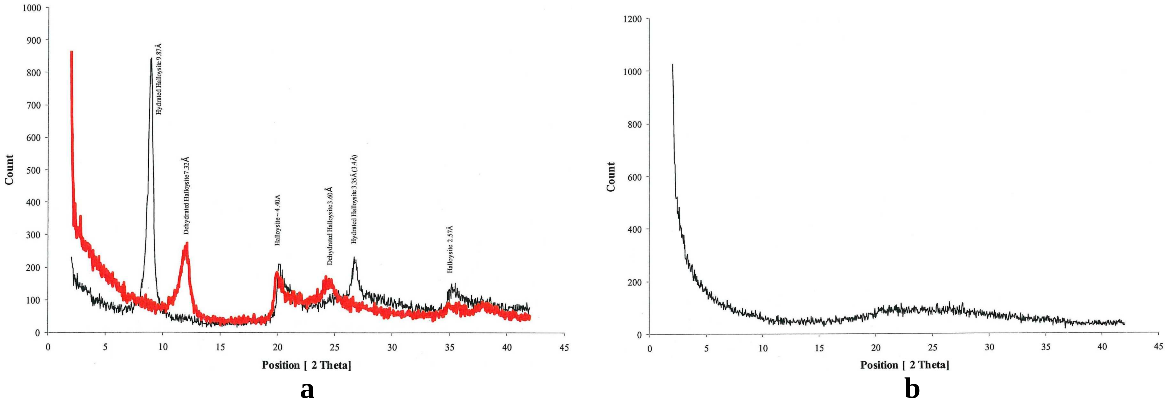
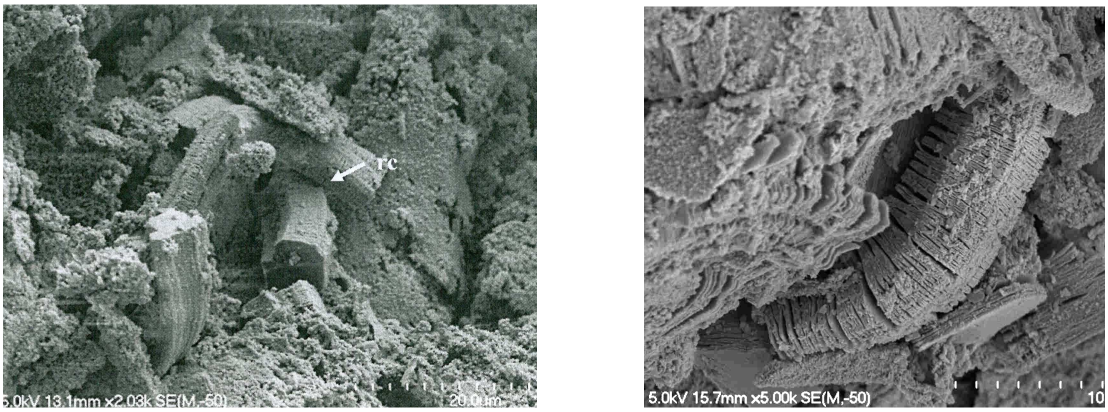


Fig. 1. (a) XRD traces of Tauriko clay fraction untreated (black) and after heating 110 °C (red). (b) XRD trace of same clay fraction after heating 550 °C.

SEM analyses of bulk samples and clay fractions revealed a range of clay particle morphologies including tubes (between ~0.3 and ~1 μm in length), small, irregular (polygonal) spheres (~0.1 to ~0.7 μm), and plates (<~0.5 μm), which are all classically associated with halloysite (e.g., Kirkman 1981; Dixon 1989; Joussein et al. 2005). But most surprising was the presence of plates stacked together as distinctive books (Fig. 2). Such books comprised up to ~30% of bulk samples and ~10% of the clay-fraction samples examined via SEM.

Book lengths ranged from ~1.5 to ~50 μm and most were curved. A variety of plate shapes occurred (irregular, quasi-hexagonal, and elongated), and plate widths ranged from ~1 to ~20 μm. Contacts between plates were normally tight (Fig. 2a) but some books displayed minor delamination at either plate edges or centres (Fig. 2b); some books were completely delaminated and contained infilling material (probably very small tubes, spheres, or plates). As far as we are aware, pure halloysite in book form has not previously been reported in the literature, such a morphology almost invariably being attributed previously to kaolinite. We unequivocally rule out kaolinite here, however, because our XRD analyses showed hydrated halloysite to be the only clay present in the Tauriko clay fractions. Further, because kaolinite gives a stronger reflection than halloysite for the same amount of material (Churchman et al. 1984), then even a small amount of kaolinite, if present (e.g., potentially intercalated with halloysite, as reported by Papoulis et al. 2004 – see below), would be expected to show up as a ~7 Å peak, but no such peak was evident in the clay-size fraction diffractograms. Dehydrated halloysite (7.33 to 7.41 Å peak) was the main clay identified in the bulk samples. In some cases, halloysite tubes up to ~3 µm long, possibly a secondary growth phase or the inception of further plate development, were arrayed on the edges of plates in the books; in places tubes were stacked much like individual plates (Fig. 3).



a **b**

Fig. 2. (a) Multiple curved halloysite books. (b) Curved halloysite book showing minor delamination of plates.

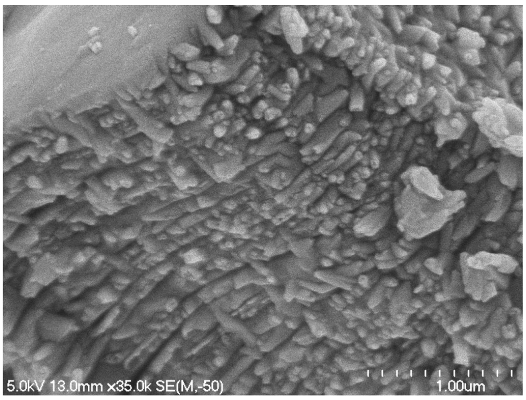


Fig. 3. Halloysite clay book with at least 24 individual plates seen edge-on and with small halloysite tubes emerging from the edges. At top right, tubes are stacked much like the individual plates

Previously, halloysite tubes had been reported as forming on the edges of, and in between, kaolinite plates as a result of loss of structural rigidity (e.g., Robertson and Eggleton 1991). However, Papoulis et al. (2004) invoked transformation from tubular halloysite to kaolinite via an unstable platy halloysite phase formed from "the interconnection of tubular halloysite to felted planar masses of halloysite" (p. 281). They suggested that resultant "halloysite-rich booklets" comprised both platy halloysite and newly-formed kaolinite together, and that eventually such halloysite-kaolinite booklets were "converted initially to a more stable but disordered kaolinite and finally to well formed booktype kaolinite" (p. 281). It may be that in our case this mechanism is fundamentally correct but that pure halloysite plates, thence pure halloysite books, are formed as an end point, i.e. without the coexistence of halloysite and kaolinite and without kaolinization. That the tephra bed at Tauriko occurs at depth within permeable, siliceous pyroclastic and volcaniclastic materials would imply that site wetness conditions needed to maintain halloysite genesis rather than kaolinite (Churchman et al. 2010) have prevailed.

EDX analyses of flat surfaces of plates in halloysite books in a Tauriko clay-fraction sample were compared with those of clusters of halloysite tubes in samples taken from another site in the area (Wyatt 2009). Previous studies have shown that structural Fe content is an important determinant of halloysite morphology especially with regard to plates and tubes (Papoulis et al. 2004; Joussein et al. 2005). Plates typically have relatively high Fe contents whereas tubes have much less. Although Si and Al contents were identical for both morphologies (books: SiO_2 47.7 ± 1.1 %, Al_2O_3 34.1 ± 0.5 %; tubes: SiO_2 50.7 ± 2.1%, Al_2O_3 34.2 ± 1.3 %), we found that the Fe content in the plates making up the books (Fe_2O_3 = 5.2 ± 0.2 %) was significantly larger than in the tubes (Fe_2O_3 = 3.2 ± 0.3 %). This enriched Fe content, consistent with ranges reported for plates, indicates that Fe has replaced Al in octahedral positions, hence reducing the mismatch with the tetrahedral sheet, lessening layer curvature, and thus generating flat plates.

In conclusion, although we have examined only 3 samples thus far at one site, it is evident that pure halloysite books (as well as halloysite tubes, irregular spheres, and plates) are present in the ~0.27 Ma tephra bed at Tauriko. We plan to examine more samples from the area to see if the novel halloysite book morphology occurs elsewhere. If such books are found (and positively identified as halloysite), then one implication is that some books identified in the past as kaolinite solely on the basis of their book-like morphology may have been misidentified. Further, it would appear that transformations whereby halloysite particles coalesce and convert into stacked halloysite plates (books) may take place in addition to transformations from halloysite to kaolinite.

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