Discovery of halloysite books in altered silicic Quaternary tephras, northern New Zealand

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ABSTRACT: Hydrated halloysite was discovered in books, a morphology previously associated exclusively with kaolinite. From ~1.5 µm to ~1500 µm in length, the books showed significantly greater mean Fe contents (Fe_2O_3 = 5.2 wt%) than tubes (Fe_2O_3 = 3.2 wt%), and expanded rapidly with formamide. They occurred, along with halloysite tubes, spheroids, and plates, in highly porous yet poorly-permeable, silt-dominated, Si-rich, pumiceous rhyolitic tephra deposits aged ~0.93 Ma (Te Puna tephra) and ~0.27 Ma (Te Ranga tephra) at three sites ~10–20 m stratigraphically below the modern land-surface in the Tauranga area, eastern North Island, New Zealand. The book-bearing tephras were at or near saturation, but have experienced intermittent partial drying, favouring the proposed changes: solubilized volcanic glass + plagioclase → halloysite spheroids → halloysite tubes → halloysite plates → halloysite books. Unlike parallel studies elsewhere involving both halloysite and kaolinite, kaolinite has not formed in Tauranga presumably because the low permeability ensures the sites largely remain locally wet so that the halloysite books are metastable. An implication of the discovery is that some halloysite books in similar settings may have been misidentified previously as kaolinite.

KEYWORDS: Halloysite, clay morphology, Fe content, pyroclastic, tephrochronology, Te Ranga tephra, Te Puna tephra, Quaternary

Halloysite is a 1:1 kaolin-subgroup clay mineral with a similar composition to kaolinite, but with interlayer H_2O ("water") that can easily be driven off, giving hydrated and dehydrated end members in a series of forms. It is this interlayer H_2O (or evidence of its removal) that characterises halloysite relative to kaolinite (Churchman & Carr, 1975). The fully hydrated form has a 1.0 nm (10 Å) basal spacing, and the fully dehydrated form has a basal spacing of 0.7 nm (7 Å). Halloysite can adopt a continuous series of hydration states, from 2 to 0 molecules of H_2O per $Si_2Al_2O_5(OH)_4$ aluminosilicate layer, and these are interpreted as a type of interstratification of the two end-member types (Churchman *et al*., 1972; Churchman & Lowe, 2012; Churchman, 2015; Joussein, 2016). Under ambient environmental conditions, dehydration of halloysite is an irreversible process (Churchman *et al*., 1972; Joussein *et al*., 2005; Keeling, 2015). However, the effective reversal of the basal-spacing change associated with the dehydration of halloysite by the addition of formamide provides a common test for distinguishing halloysites from kaolinite (Churchman *et al.*, 1984, 2016).

The first application of electron microscopy to a halloysite (Alexander *et al*., 1943) showed it to have particles with fibrous/tubular shapes. Subsequently, many halloysites were found to occur as tubes. However, halloysites have also been found to occur in many different shaped particles. Joussein *et al*. (2005) and Joussein (2016) characteriszed ten different types of morphologies for halloysites from reports in the literature. According to Churchman (2015), these may be grouped into four main morphological types, namely tubular, platy, spheroidal, and prismatic. Of these, the spheroidal form of halloysite occurs with a frequency comparable to that of the tubular form (Cravero & Churchman, 2016). Platy forms include a range of tabular shapes such as "crumpled lamellar" and "crinkled film" forms and all these invariably have a high Fe content (Bailey, 1990). The prismatic

73 form (e.g. Kogure *et al*., 2013) is probably a well-ordered refinement of the tubular form
74 that may occur in the dehydrated state of some halloysite samples (Churchman, 2015).
75 Some samples of halloysite comprise more than one morphological form co-existing
76 together (e.g. Churchman *et al*., 2016).

77 Halloysites are formed from many types of parent materials, but they are a common
78 product of the weathering of volcanic (including pyroclastic or tephric) materials (Joussein *et*
79 *al*., 2005; Churchman & Lowe, 2012). This paper describes the discovery of halloysite that
80 has formed from altered tephric materials to yield particles with book-like forms. Previously,
81 book morphologies for kaolin-group minerals have been exclusively associated with
82 kaolinite (e.g. Keller, 1978; Kirkman, 1981; Dixon, 1989; Joussien *et al*., 2005; Churchman *et*
83 *al*., 2016). Halloysite in book form has not been reported before (other than for this
84 particular occurrence in brief by Wyatt *et al*., 2010). Furthermore, it would appear that
85 changes whereby halloysite particles coalesce and convert into stacked plates (i.e. books) as
86 halloysite *per se* takes place in addition to parallel transformations on mineralogical
87 pathways from different morphological forms of halloysite to kaolinite books, as described
88 by Papoulis *et al*. (2004), and from tubular halloysite to kaolinite as outlined by Inoue *et al*.
89 (2012).

90 The present study initially outlines the geological and environmental settings, firstly
91 of the central North Island, New Zealand, then of the Tauranga area in western Bay of Plenty
92 where the halloysite books have been discovered. It then documents the three sites and
93 associated deposits where the books, some of sand-size, have been uniquely identified. The
94 analytical data that characterise the books using X-ray diffraction (XRD), scanning electron
95 microscopy (SEM), and energy-dispersive X-ray (EDX)-derived elemental analyses are then

presented. Finally, possible mechanisms that could give rise to such halloysite books are examined and a developmental model that attempts to explains their origins and evident metastability is presented and discussed.

GEOLOGICAL SETTING OF CENTRAL NORTH ISLAND, NEW ZEALAND

The New Zealand archipelago in the southwest Pacific bisects an obliquely-convergent plate boundary straddling the Pacific and Australian tectonic plates, and hence the central North Island is dominated by Quaternary volcanism and its products. The locus of volcanism for the past ~2 Ma has been the Taupo Volcanic Zone (TVZ) (Fig. 1). In contrast to the north-eastern and south-western parts of TVZ, which are dominated mainly by subduction-related andesitic stratovolcanoes (labelled 'A' in Fig. 1), the central TVZ (labelled 'R') is dominated by explosive, rhyolite calderas from which voluminous silicic, typically pumiceous pyroclastic density current or flow deposits (including ignimbrites), and widespread silicic pyroclastic fall deposits, have been erupted (e.g. Alloway *et al*., 2004, 2005; Briggs *et al*., 2005; Allan *et al*., 2008; Wilson *et al*., 2009). The pyroclastic deposits have formed extensive multi-layered landscapes in and adjacent to the TVZ consisting of sequences of ignimbrites interbedded with tephra-fall beds and reworked materials (volcaniclastic sedimentary deposits), and intervening buried soil horizons (palaeosols) that represent soil formation (pedogenesis) at the land surface at stable sites during periods of volcanic quiescence (Lowe & Palmer, 2005; Smith *et al*., 2015). The term "pyroclastic" encompasses all the clastic or fragmental (loose) materials explosively erupted from a volcanic vent and is similar in meaning to the term

118 “tephra” which comprises unconsolidated pyroclastic material of any composition or grain

119 size including volcanic ash (Lowe & Alloway, 2015).

120

121 **Fig. 1**. Map of North Island, New Zealand, showing general plate tectonic setting and location of

122 Taupo Volcanic Zone (TVZ) with respect to the Tauranga study area (after Leonard *et al*., 2010).

123 Locations of the three main study sites at Pahoia, Omokoroa, and Tauriko, and an auxiliary site at

124 Otumoetai, are shown in the inset map of the Tauranga area.

STRATIGRAPHY, COMPOSITION, AND CLIMATE OF QUATERNARY GEOLOGICAL DEPOSITS IN THE TAURANGA AREA AND OCCURRENCE OF THE HALLOYSITE BOOKS IN ALTERED RHYOLITIC TEPHRAS

Stratigraphy

The Quaternary stratigraphic sequences in the Tauranga area in western Bay of Plenty (Fig. 1) are complex and dominated by interdigitating pyroclastic and volcaniclastic deposits well exposed in paleo-sea-cliffs around Tauranga Harbour and in valley walls, landslide scarps, and road cuttings. Undifferentiated strongly-weathered Hamilton Ash beds (~0.35 Ma to ~0.05 Ma in age), the base of which is Rangitawa Tephra (~0.35 Ma), and younger tephra cover beds (≤~0.05 Ma), lie above a very well developed, dark brown clay-rich buried paleosol marking the top of the Pahoia Tephra deposits, a composite sequence consisting mainly of multiple distal rhyolitic tephra-fall deposits and ignimbrites dating from ~2.1 Ma to ~0.35 Ma (Pullar *et al*., 1973; Briggs *et al*., 1996; Lowe *et al*., 2001). The Pahoia Tephras and associated ignimbrites are interbedded with weakly consolidated volcaniclastic deposits of the Matua Subgroup, a widespread sedimentary sequence (within the Tauranga Group) that comprises fluviatile silts, sands, and gravels (i.e. mainly reworked pyroclastic and volcanic deposits) together with lignites, lacustrine silts, estuarine sands, and aeolian deposits, dating from ~2.1 Ma to ~0.05 Ma (Briggs *et al.*, 1996, 2006; Leonard *et al*., 2010). These intercalated pyroclastic, volcaniclastic, and sedimentary deposits underlie a landscape comprising a series of terraces and ignimbrite plateaux and an associated rolling to hilly topography together with steep-sided rhyolite-dacite domes and low-lying coastal dunes (Briggs *et al.*, 1996).

149 At some sites, such as Omokoroa Peninsula (Fig. 1), the Pahoia Tephra and Matua
150 Subgroup deposits attain a combined thickness of >12 m (Moon *et al.*, 2015). Two
151 widespread marker ignimbrites in the sequence are relevant here because the halloysite
152 books were discovered in coeval tephra-fall deposits associated with them: (1) partially- to
153 non-welded Te Puna Ignimbrite, which is dated at 0.929 ± 0.012 Ma, and (2) non-welded Te
154 Ranga Ignimbrite, which is dated at 0.274 ± 0.016 Ma (ages ± 1 standard deviation were
155 derived by $^{40}Ar/^{39}Ar$ analyses of feldspar separates: Briggs *et al*., 2005). These two
156 ignimbrites are the distal equivalents of widespread but as yet only tentatively correlated
157 ignimbrites derived from central TVZ (Briggs *et al*., 2005): Te Puna Ignimbrite may correlate
158 with Kidnappers Formation (C.J.N. Wilson *pers. comm*., 2016) and Te Ranga Ignimbrite with
159 Chimp Formation (Leonard *et al*., 2010).
160
161 *Field character and primary mineralogy and glass compositions of Te Puna and Te Ranga*
162 *tephras and associated ignimbrites*
163 In this study, pale cream-coloured and silt-dominated Te Puna and Te Ranga tephra
164 layers (these informal names used hereafter in the text) between ~0.5 m and ~0.8 m thick at
165 three sites, Pahoia, Omokoroa, and Tauriko (Fig. 1), were found to contain halloysite books.
166 These somewhat-weathered tephras, saturated and demonstrably containing solubilised
167 (ferrous) iron because they reacted positively to the Childs' (1981) test, were also identified
168 as being sensitive in a broader geotechnical study on slope failure and landsliding relating to
169 sensitive soil behaviour as described by Moon *et al*. (2015) and Moon (2016). The local
170 stratigraphy and field character of the relevant deposits at each of these sites are
171 exemplified in Fig. 2; further details are available in Wyatt (2009) and Cunningham (2012).
172

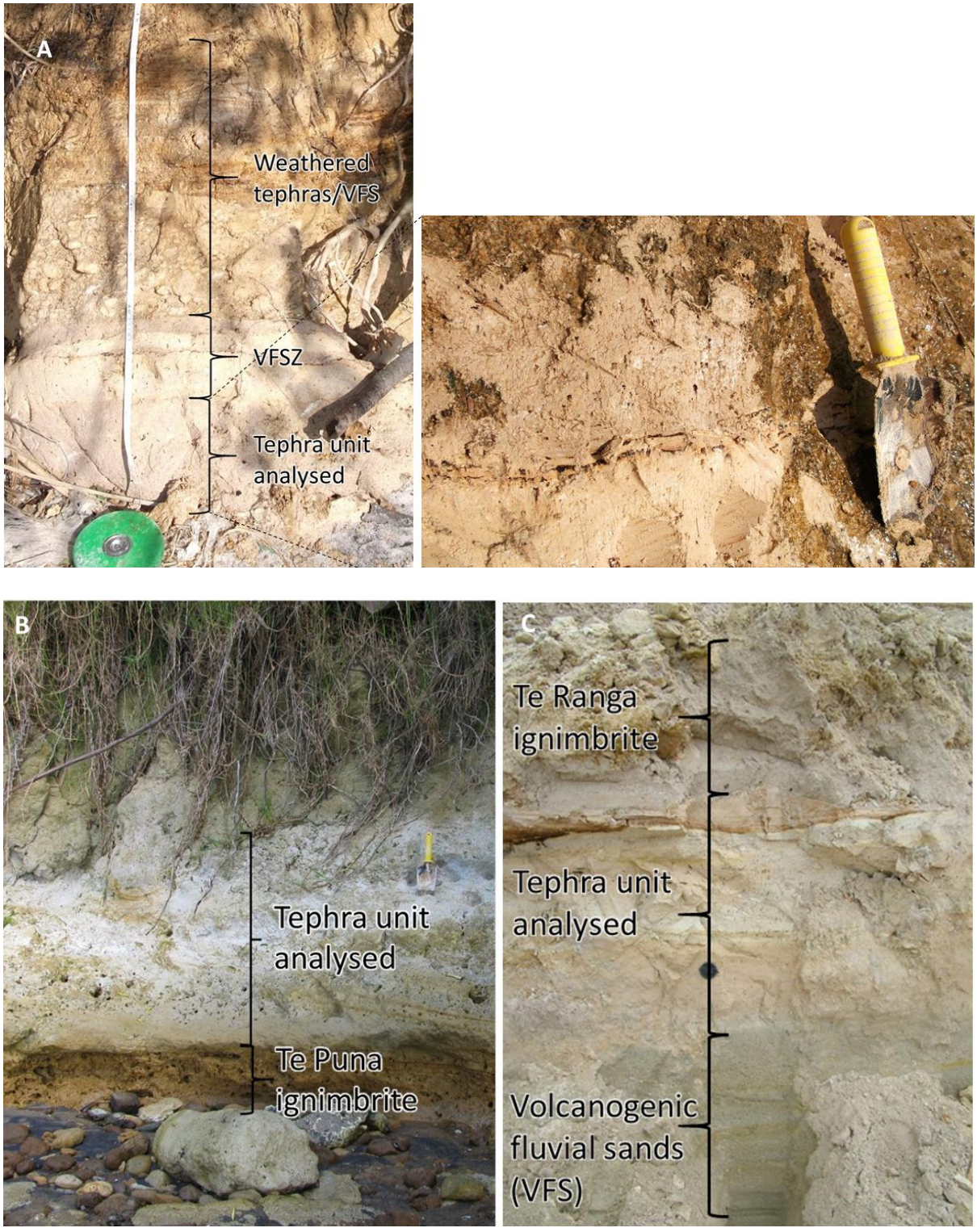

Fig. 2. Photos of three sites showing stratigraphic relations and field character of sensitive tephras of the Pahoia Tephra sequence that were sampled and shown to contain halloysite books, and encompassing deposits of the Matua Subgroup. VSF, volcanogenic fluvial sands; VSFZ, volcanogenic fluvial sands and silts. **A**, (Left) Pahoia site. The Te Puna tephra is ~0.5 m thick. Te Puna Ignimbrite (~0.93 Ma) crops out nearby. (Right) Close-up view showing wet character of Te Puna tephra and dark MnO_2 redox concentrations (segregations), some forming streaks where they have been cut.

Trowel is about 25 cm long. Photos: M.J. Cunningham. **B**, Omokoroa site. The Te Puna tephra is ~0.8 m thick and overlies Te Puna Ignimbrite (~0.93 Ma) as marked. Trowel is about 25 cm long. Photo: M.J. Cunningham. **C**, Tauriko site. The Te Ranga tephra is ~0.5 m thick, immediately underlies Te Ranga Ignimbrite (~0.27 Ma) and overlies volcanogenic fluvial sands as indicated, and contains MnO_2 redox concentrations evident as small dark "specks". Lens cap is ~5 cm in diameter. Photo: J.B. Wyatt. (For colour images, see the online version of this paper.)

At Pahoia (Fig. 2A), the book-bearing Te Puna tephra lies at the base of a coastal exposure (just above a shore platform close to sea level), ~10 m below the modern land surface. It is sandwiched between fluvially-reworked volcanicastic deposits closely associated with the Te Puna Ignimbrite and hence is dated at ~0.93 Ma. The Pahoia site is located at 37° 37' 38.30'' S, 176° 00' 25.00'' E.

At Omokoroa (Fig. 2B), at the base of another coastal exposure near sea level and ~14–15 m below the modern land surface, the book-bearing Te Puna tephra immediately overlies the Te Puna Ignimbrite and was deposited during the Te Puna eruptive episode. Thus it is also dated at ~0.93 Ma. The Omokoroa site is located at 37° 37' 40.96" S, 176° 02' 51.82" E.

At Tauriko (Fig. 2C), at an inland site on a cutting formed during excavations for housing and industrial developments, and ~20 m below the modern land surface at ~48 m above sea level, the book-bearing Te Ranga tephra immediately underlies the Te Ranga Ignimbrite and was deposited during the Te Ranga eruptive episode, and so this tephra is dated at ~0.27 Ma (Wyatt et al., 2010). The Te Ranga Ignimbrite is unusual in containing carbonised logs, the only ignimbrite in the region to do so, meaning it is readily identified in the field partly because of this distinctive property (Briggs *et al*., 1996; Wyatt, 2009). The Tauriko site is located at 37° 45' 00.51" S, 176° 05' 54.24" E.

206 Optical microscopic analysis of grain-mounted fine-sand fractions revealed that the
207 primary constituents of each of the two tephras generally comprised abundant volcanic
208 glass (Fig. 3A) (including bubble-wall, platy, and vesicular shards), some partially-dissolved
209 (Fig. 3B), with subordinate plagioclase feldspar and quartz; small quantities of hornblende,
210 hypersthene, and titanomagnetite (Fe-Ti oxides); and pumice clasts, rock fragments (lithics),
211 and clay aggregates (Wyatt, 2009; Cunningham, 2012). Small quantities of cristobalite and
212 tridymite were additionally identified by XRD analysis of bulk powdered samples in both
213 tephras. Traces of biotite were identified in some samples of the Te Puna tephra at Pahoia
214 and Omokoroa, but none was identified in the Te Ranga tephra at Tauriko. These
215 mineralogical assemblages are consistent with those of the equivalent ignimbrite units as
216 reported by Briggs *et al*. (1996).
217 Volcanic glass in the Te Puna tephra is likely to be compositionally similar to that of
218 coeval Te Puna Ignimbrite in which glass-rich matrices in pumice clasts (analysed via X-ray
219 fluorescence, data normalized) contained from 72.6 to 75.7 wt% SiO_2 (mean 74.1 wt %) and
220 from 13.6 to 14.5 wt% Al_2O_3 (mean 14.2 wt%) (n = 10) (Whitbread-Edwards, 1994; Briggs *et*
221 *al*., 1996).
222 Glass shards in the Te Ranga tephra (analysed by EDX, data normalized) contained
223 ~75 wt% SiO_2 and ~12 wt% Al_2O_3 (Wyatt, 2009). Analyses obtained by electron microprobe
224 of glass in Te Ranga Ignimbrite (data normalized) had similar contents of these oxides,
225 ranging from 75.4 to 77.9 wt% SiO_2 (mean 76.6 wt%) and from 12.3 to 13.8 wt% Al_2O_3 (mean
226 12.9 wt%) (n = 15) (Hollis, 1995).
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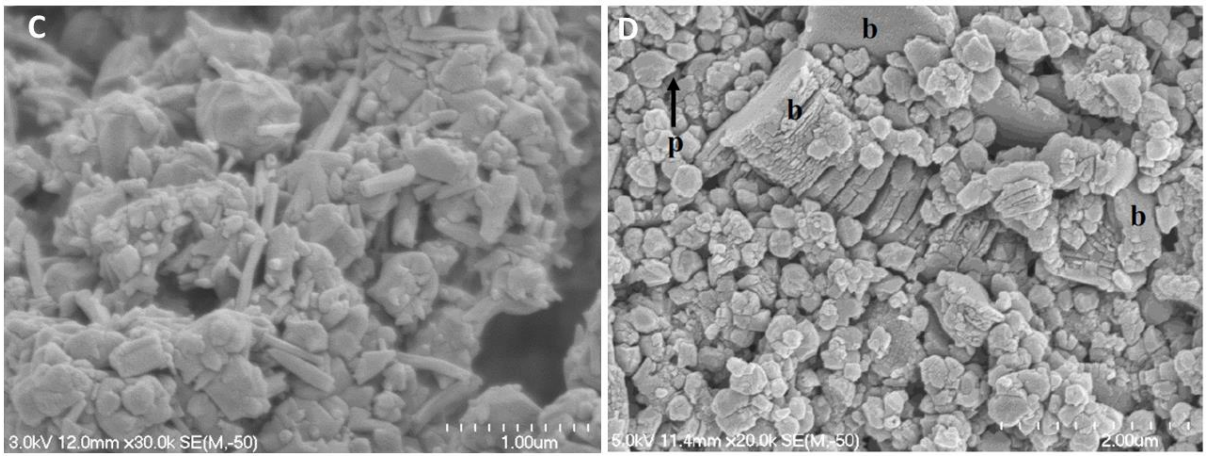
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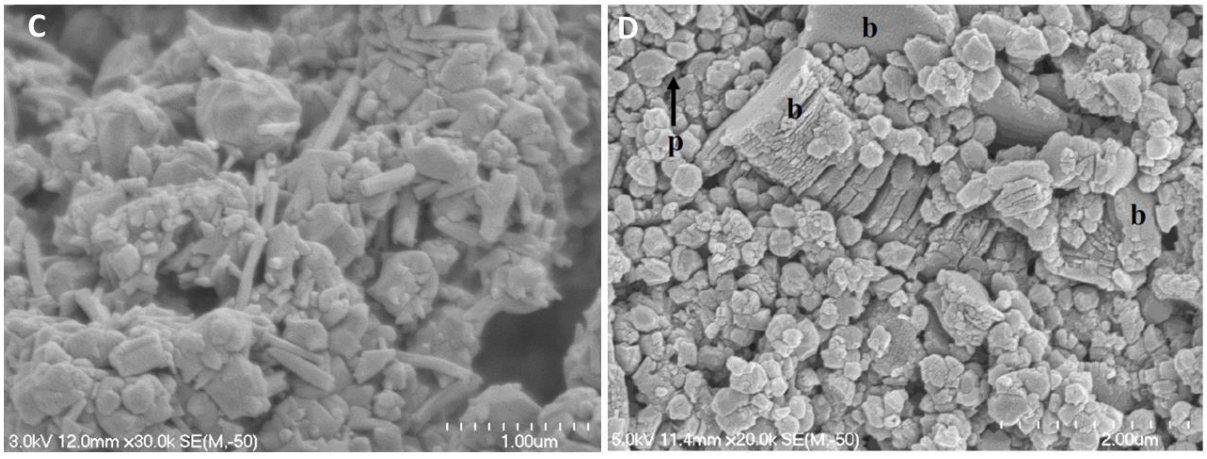
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231


E
5.0kV 12.0mm x1.10k SE(M,-50)
50.0um

232

Fig. 3. **A**, SEM image of a glass shard ~330 µm long, with a ~180-µm-long elongated central vesicle (from Te Ranga tephra, Tauriko site). **B**, SEM image of partially-dissolved glass shard with spheroidal halloysite infilling pits in the glass and dominating the surrounding material (from Te Puna tephra, Omokoroa site). **C**, SEM image of blocky-looking spheroidal halloysite with tubes seemingly "emerging" from them (from Te Ranga tephra, Tauriko site). **D**, 'Chunky-looking plates predominate together with a 'chunky' book (middle) with several proto-books forming to its right (from Te Ranga tephra, Tauriko site). **E**, SEM image depicting a wider view approximately 115 µm across dominated by numerous books, some curved (vermicular), with many ~2 to 3 µm in diameter and ~10 to 15 µm long. The large book at middle right (with another one partly hidden alongside) is ~30 µm long and consists of polygonal plates ~7.5 by 10 µm (from Te Ranga tephra, Tauriko site).

The abundant, silica-rich volcanic glasses and pumices in the Te Puna and Te Ranga eruptives qualify as "rhyolite" based on their total alkali and silica content (Le Bas *et al*., 1986). Many of the overlying pyroclastic and volcaniclastic deposits in the Pahoia Tephra/Matua Subgroup sequences in the Tauranga area have similar felsic and mafic mineralogical assemblages and are also quite silicic, being typically rhyolitic to dacitic in composition (Briggs *et al*., 1996, 2005).

Weathering and clay minerals

Soil formation and chemical weathering of the pyroclastic and volcaniclastic materials of the Pahoia Tephra/Matua Subgroup deposits, which encompass a wide range of physical and micromorphological properties and microenvironmental conditions, have generated in some units abundant clay minerals dominated generally by two contrasting aluminosilicates, halloysite and allophane (Lowe & Percival, 1993; Lowe & Palmer, 2005; Churchman & Lowe, 2012). Halloysite is especially common, and in Tauranga and further afield in central North Island it is dominated by three main morphologies, namely tubes, spheroids, and plates (Kirkman, 1977, 1980, 1981; Kirkman & Pullar, 1978; Churchman &

Theng, 1984; Lowe & Percival, 1993; Briggs *et al*., 1994; Churchman *et al.*, 1995). Examples of spheroidal and tubular halloysite at Omokoroa and Tauriko are shown in Figs. 3B and 3C, respectively, and halloysite plates are illustrated in Fig. 3D.

Climate

The climate in the coastal Tauranga area, described generally as temperate or sub-tropical with warm humid summers and mild winters, has a mean annual rainfall of ~1200 mm, a mean annual temperature of ~14.5 °C, and a mean soil temperature at 1-m depth of ≥~15.0 °C (Chappell, 2013). Rainfall at Tauriko is likely to be a little higher (~1300–1400 mm per annum) than at the two coastal sites. These climatic conditions are equivalent to an udic soil moisture regime (in which water moves entirely through the pedological soil profile in most years) and a thermic soil temperature regime as defined in *Soil Taxonomy* (Soil Survey Staff, 2014).

HALLOYSITE ANALYSIS AND IDENTIFICATION OF BOOK FORMS IN CLAY FRACTIONS AND BULK SAMPLES

Methods

Clay fractions (<2 μm) were separated centrifugally (after dispersal in water using Calgon [a commonly available dispersant used widely in soil particle-size analysis], end-over-end shaking, and brief ultrasonication) from each of the Te Puna and Te Ranga tephras sampled at Pahoia, Omokoroa, and Tauriko. $MgCl_2$ was used to flocculate clay fractions and these were pipetted onto ceramic tiles (Whitton & Churchman, 1987) and allowed to dry over distilled water for 24 hours to help prevent irreversible halloysite dehydration (Kirkman

& Pullar, 1978; Lowe & Nelson, 1994). The Mg-saturated clay fractions were analysed by XRD using a Philips PW analytical diffractometer over a scan-range from 2° to 40° 2θ. Samples (in triplicate) were scanned without treatment and then after heating at 110 °C for 1 h. Subsequently, the samples were heated to 550 °C for 1 hour and re-scanned. Finally, one drop of formamide was added to untreated samples and the samples re-scanned within ~1 to 3 h (Churchman *et al*., 1984).

Bulk samples (<2-mm size fractions) from each of the tephras at Pahoia, Omokoroa, and Tauriko were air-dried and analysed as powders in aluminium holders using XRD and with the same treatment and analyses as undertaken for the clay fractions. These bulk samples were analysed specifically to identify the common to abundant silt- to fine-sand-sized books within them (e.g. Fig. 3E).

Analyses by SEM and EDX were undertaken using an Hitachi S-4700 field emission scanning electron microscope with a Quorum Technologies cryo-system based at the Electron Microscope Facility, University of Waikato. Samples (mainly of bulk fractions) were mounted on carbon tape and coated in platinum and scanned at 3 kV to 5 kV. For EDX, an accelerating voltage of 20 kV was used. The EDX-based analysis of the books was straightforward because the relatively large, flat, end-plates of such books, targeted here, enabled the X-ray beam to encompass the entire surface area of the plate. On the other hand, the analysis of tubes was less precise because of the curved nature of the tube surfaces. Consequently, dense clusters of well-formed tubes were analysed using an X-ray beam about 1 μm in diameter, and so these assays carried some risk of scanning non-tubular material. Nevertheless, repeated analysis of the same cluster of tubes gave rise to statistically identical results for Fe content, and the findings are therefore likely to be reasonably reliable.

To determine if allophane and/or ferrihydrite were present, Tauriko samples were additionally analysed spectrophotometrically for Al_o, Si_o, and Fe_o after acid oxalate extractions (AOE) of these elements from bulk samples following the methods of Parfitt & Wilson (1985), Blakemore *et al*. (1987), and Parfitt & Childs (1988).

Grain size analyses were undertaken using a Malvern Mastersizer laser diffraction system.

Results

XRD

X-ray diffraction showed that the clay fractions (<2 μm) and bulk samples (<2 mm) from the Te Puna and Te Ranga tephras were dominated by hydrated halloysite. That halloysite rather than mica/biotite or kaolinite was predominant at all three sites was confirmed by the following XRD features based on the analysis of multiple samples. Examples are shown in Fig. 4.

(1) Typically a strong, well defined peak occurred between 9.82 and 10.14 Å, with no peak at ~7 Å, but in a few cases partial dehydration between 10 and 7 Å was evident as a shoulder to the main peak near 10 Å (e.g. Fig. 4, traces 2 and 4).

(2) After the application of formamide (and subsequent re-X-raying within 1–3 h), the ~10 Å peak expanded and enlarged (e.g. from 9.95 Å and a shoulder to 10.12 Å; Fig. 4, traces 1 and 3).

(3) On heating at 110 °C for 1 hr, the peak shifted to between 7.2 and 7.3 Å (Fig. 4, trace 6), and after heating at 550 °C for 1 hr, it disappeared (Fig. 4, trace 5). Trace 5 also confirms the lack of mica or biotite in the samples.

(4) Other halloysite peaks occurred at 4.4 Å (this peak being characteristically asymmetrical) (Fig. 4, traces 2, 4, 7) and at 3.56, 3.35, 2.56, and 2.34 Å. These peaks all disappeared when samples were heated to 550 °C (Fig. 4C).

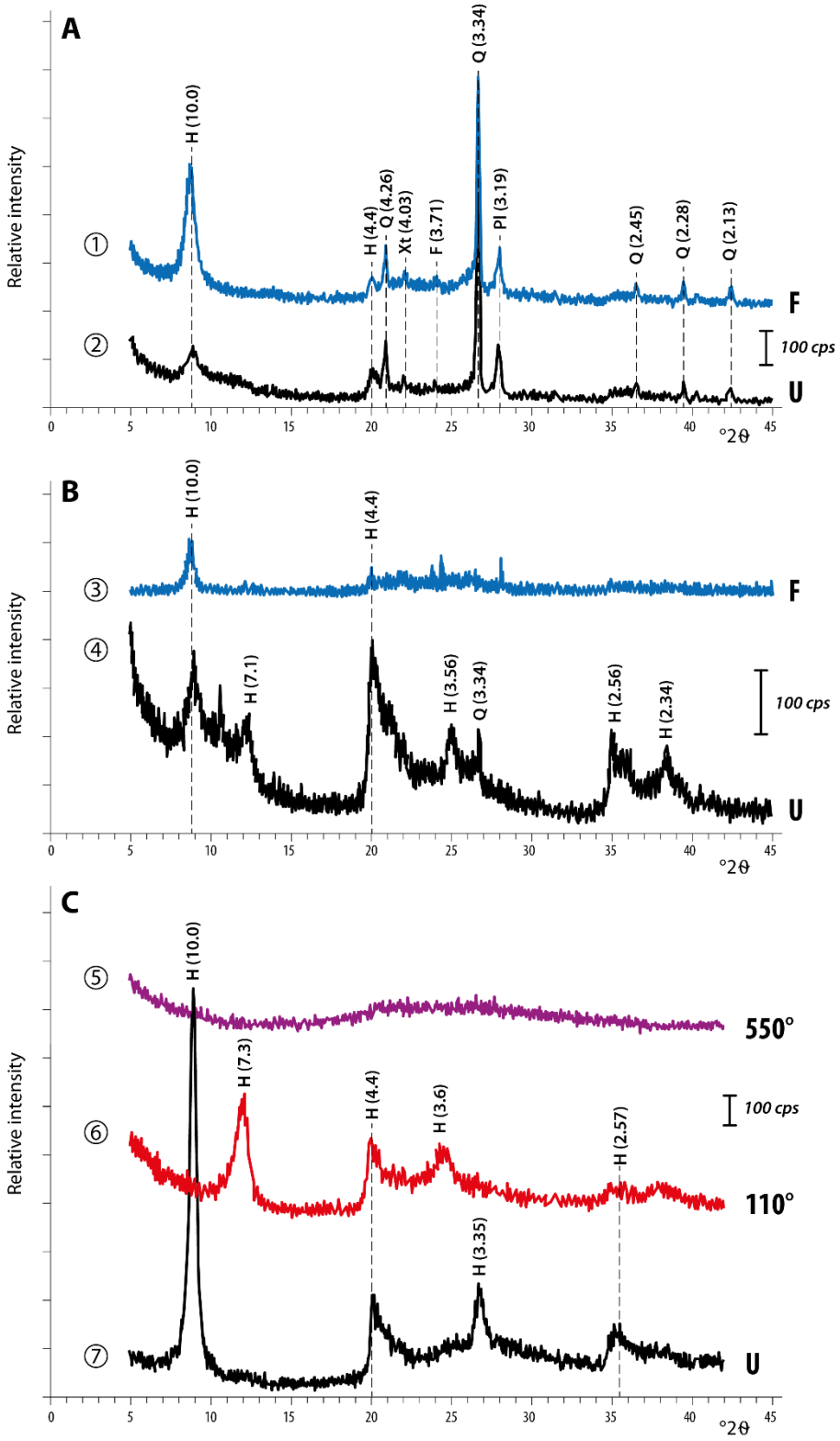


Fig. 4. XRD traces of clay fractions (<2 μm) and bulk samples (<2 mm). U, untreated; F, treated with formamide; 110°, heated to 110 °C; 550°, heated to 550 °C. Peaks identified (with basal spacings in Å) as follows: H, halloysite; Xt, cristobalite; F, feldspar; Q, quartz; Pl, plagioclase.
A, Clay fraction of Te Puna tephra from the Pahoia site. In trace 2, the squat hydrated halloysite peak at ~9.95 Å, and associated shoulder marking partial dehydration towards ~7 Å, shifted to ~10.12 Å and enlarged after formamide treatment (trace 1).
B, Bulk sample of Te Puna tephra from the Pahoia site (illustrated in Figs. 5A and 5C). In trace 4, the hydrated halloysite (10 Å) and dehydrated halloysite (7.1 Å) peaks, and also a broad band between them from partially dehydrated halloysite, all shifted to a single halloysite peak at 10.0 Å following formamide treatment (trace 3). Other samples gave similar results.
C, Clay fraction of Te Ranga tephra from the Tauriko site. The hydrated halloysite peak at ~9.87 Å in trace 7 has shifted to dehydrated halloysite at 7.32 Å after 110 °C heating (trace 6) and disappeared after 550 °C heating (trace 5). (For a colour version of this figure, see the online version of this paper.)

AOE

The AOE-based analyses of Te Ranga tephra at Tauriko indicated that both allophane and ferrihydrite were absent or undetectable. These analyses, together with SEM analyses, confirmed the negative NaF field-test responses attained for samples from all three sites (Fieldes & Perrott, 1966; Lowe, 1986).

SEM

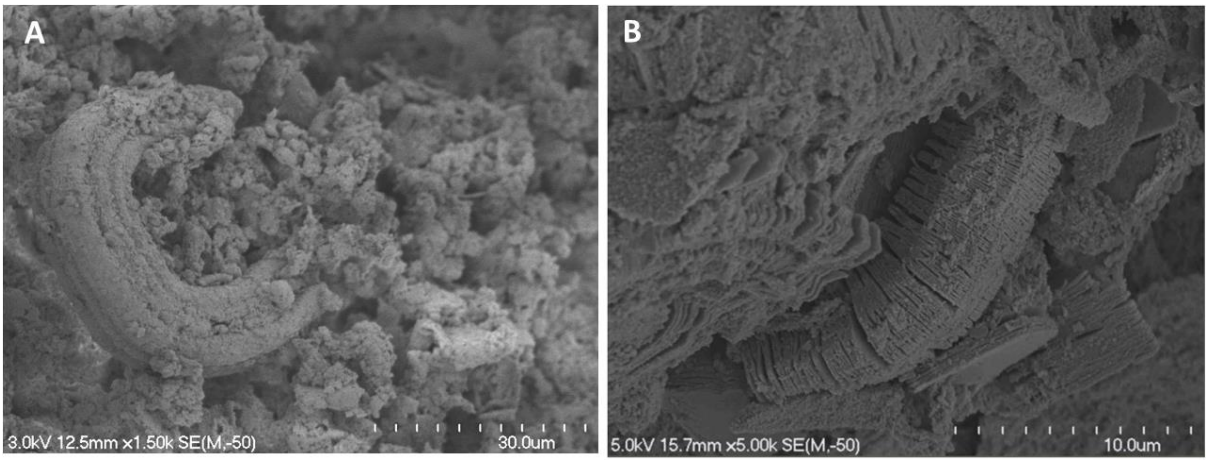
Bulk fraction SEM analyses showed several variations typical of halloysite particle morphologies, primarily as tubes (~0.1 to 1.0 μm in length) and small spheroids (~0.1 to 0.8 μm) together with plates (~0.5 to 30 μm) (e.g. Figs. 3B to 3D). Intermixed with these morphologies were books, ranging from about 10–20 % to very abundant, as exemplified in Te Ranga tephra at Tauriko in Fig. 3E in which the micrograph shows that ≥~50 % of the sample comprised books (estimated by comparison with area percentage charts, e.g.

364 Schoeneberger *et al.*, 2012). In clay fractions, books were estimated to comprise about 10 %
365 of samples. The books were commonly associated with grains of volcanic glass and
366 plagioclase feldspar as well as fine-grained halloysitic clay material.

367 Many books were curved, some twisted, and a variety of plate shapes occurred
368 including irregular or polygonal, quasi-hexagonal, and elongated (Fig. 3E, Figs. 5A to 5D).
369 Plates making up the books ranged from ~1 to ~20 µm in diameter (with similar sizes and
370 shapes expressed at each of the three sites). Books ranged mainly from ~1.5 to ~50 µm in
371 length, but some extraordinary "giant books", up to ~1500 µm long (i.e. ~1.5 mm), were
372 evident in samples of Te Puna tephra from Pahoia (Fig. 6). Contacts between plates
373 sometimes appeared tight (Fig. 6, top-left) as though they had been compressed, but other
374 books displayed partial delamination at either plate edges or centres (Figs. 5B, 5C, 5E), and
375 some books were completely delaminated. The edges of plates were sometimes seen to
376 consist of small stubby tubes (Fig. 5F), the importance of which is discussed later.

377 In conclusion, the XRD results exclude the possibility that the books in clay fractions
378 and bulk samples are kaolinite; rather, they are halloysite. Any kaolinite, if present at all,
379 was undetectable.

380

381 

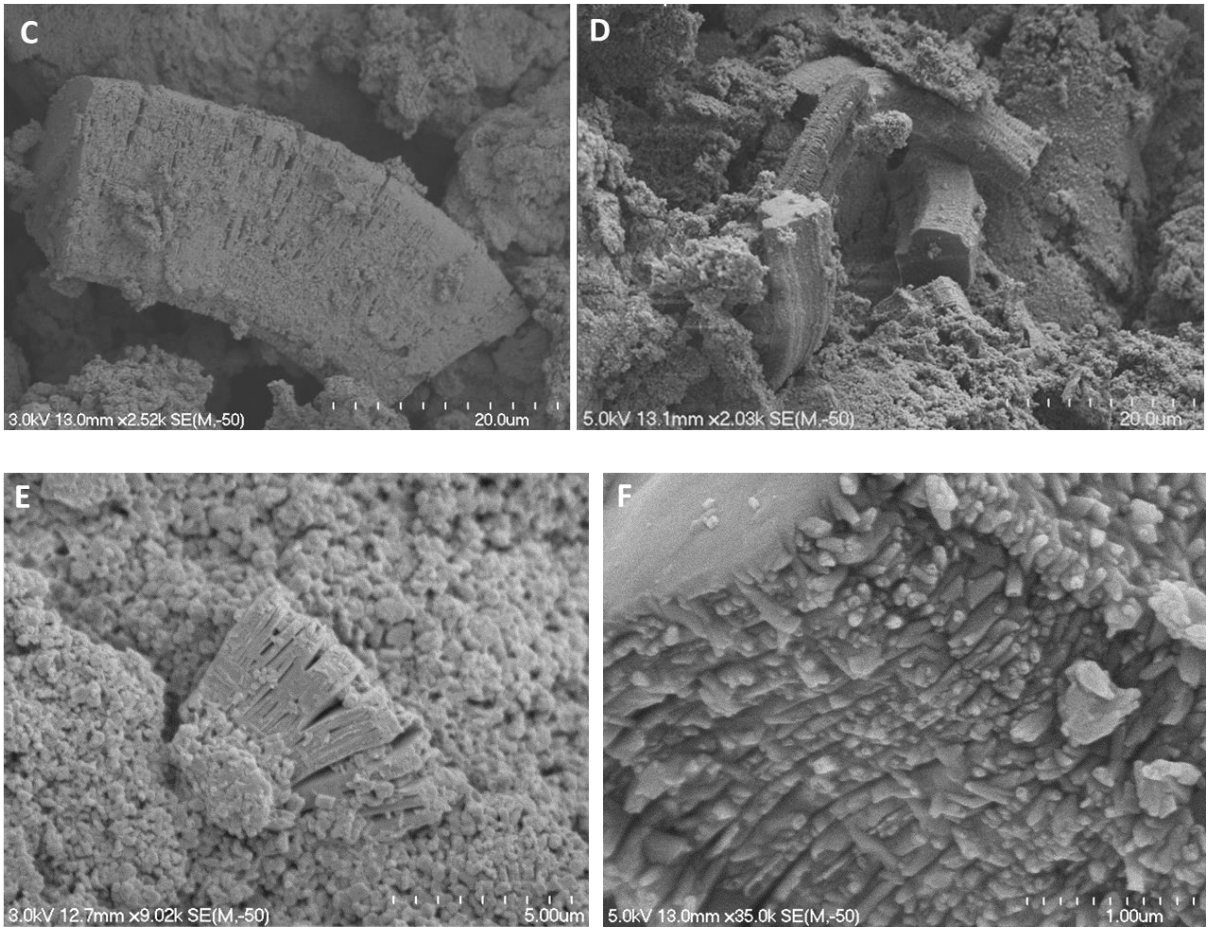


Fig. 5. SEM images of halloysite books in bulk samples (<2 mm) from altered tephra deposits in the Tauranga area. **A**, Curved vermicular book in Te Puna tephra (Pahoia site, same sample as depicted by XRD traces in Fig. 4B). **B**, Multiple books and plates in Te Ranga tephra (Tauriko site). The large curved book (centre) is ~18 µm long and ~6 µm wide and plates making up the book appear hexagonal. **C**, Book ~80 µm long and partially delaminated in Te Puna tephra (Pahoia site, same sample as depicted by XRD traces in Fig. 4B). **D**, Multiple curved (vermicular) books of differing sizes in Te Ranga tephra (Tauriko site), accounting for ≥~30% of the sample. **E**, Book with spheroidal particles visible in the gaps between some de-laminating plates, and spheroids and tubes on the edges of the plates. Spheroids, tubes, and some plates dominate the background particles from Te Puna tephra (Omokoroa site). **F**, Close-up of part of a book from Te Ranga tephra (Tauriko site) with at least 24 individual plates, the flat surface of one being visible at top left. Stacked tubes up to 0.3 µm long are essentially aligned with the plates, and on the edges of plates as seen at upper-right.

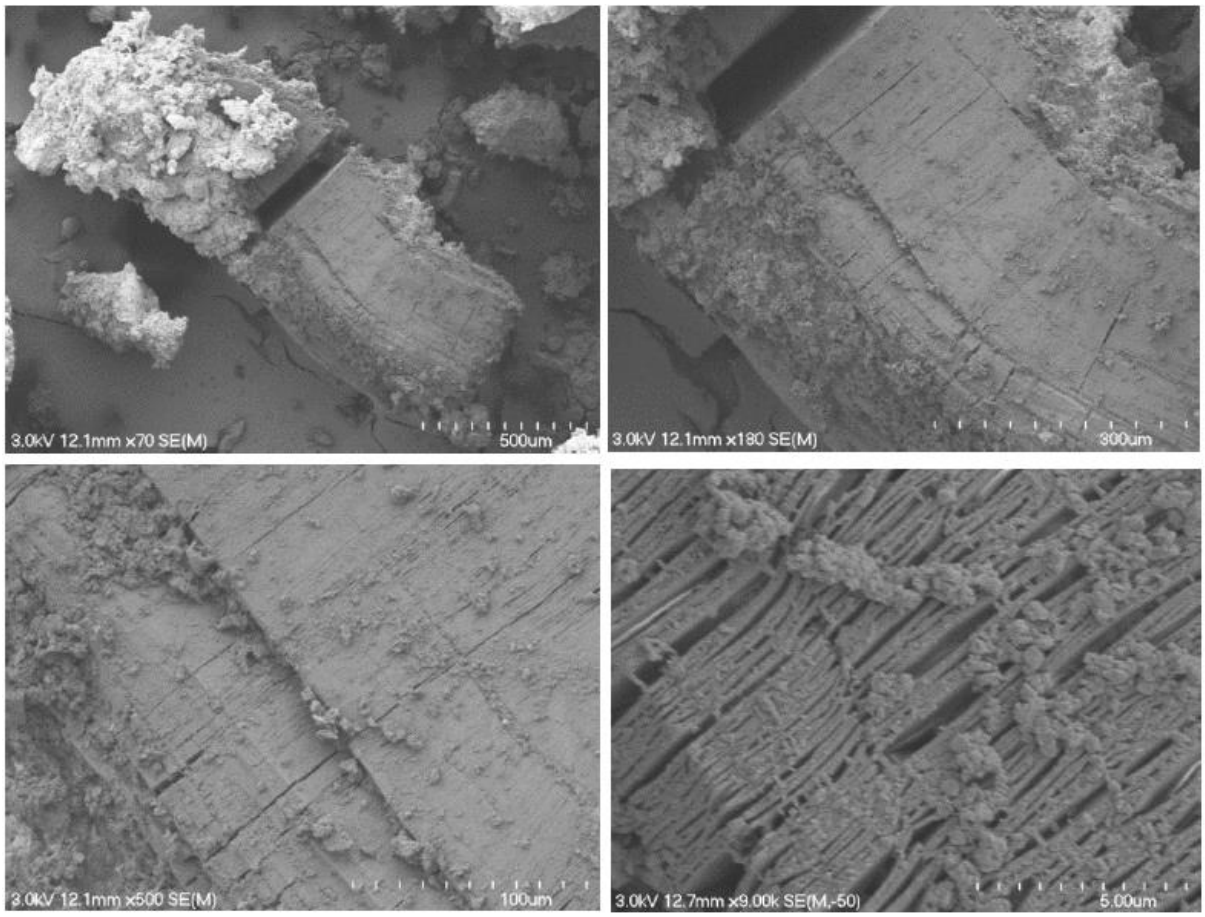


Fig. 6. Top-left – image of a very large, tightly laminated book (in two pieces) in Te Puna tephra (Pahoia site). This giant book is ~1500 μm in length (~1.5 mm). Enlargements of the book surface are shown, with increasing magnification, in images at top-right, bottom-left, and bottom-right. The bottom-right image clearly shows the top edges of partly-separated multiple plates or "leaves" (the plates are ~0.2 μm thick on average) forming the book, with small halloysite tubes evident on many of the plate edges or bridging gaps between them, together with clumps of mainly spheroidal halloysite to the right.

EDX

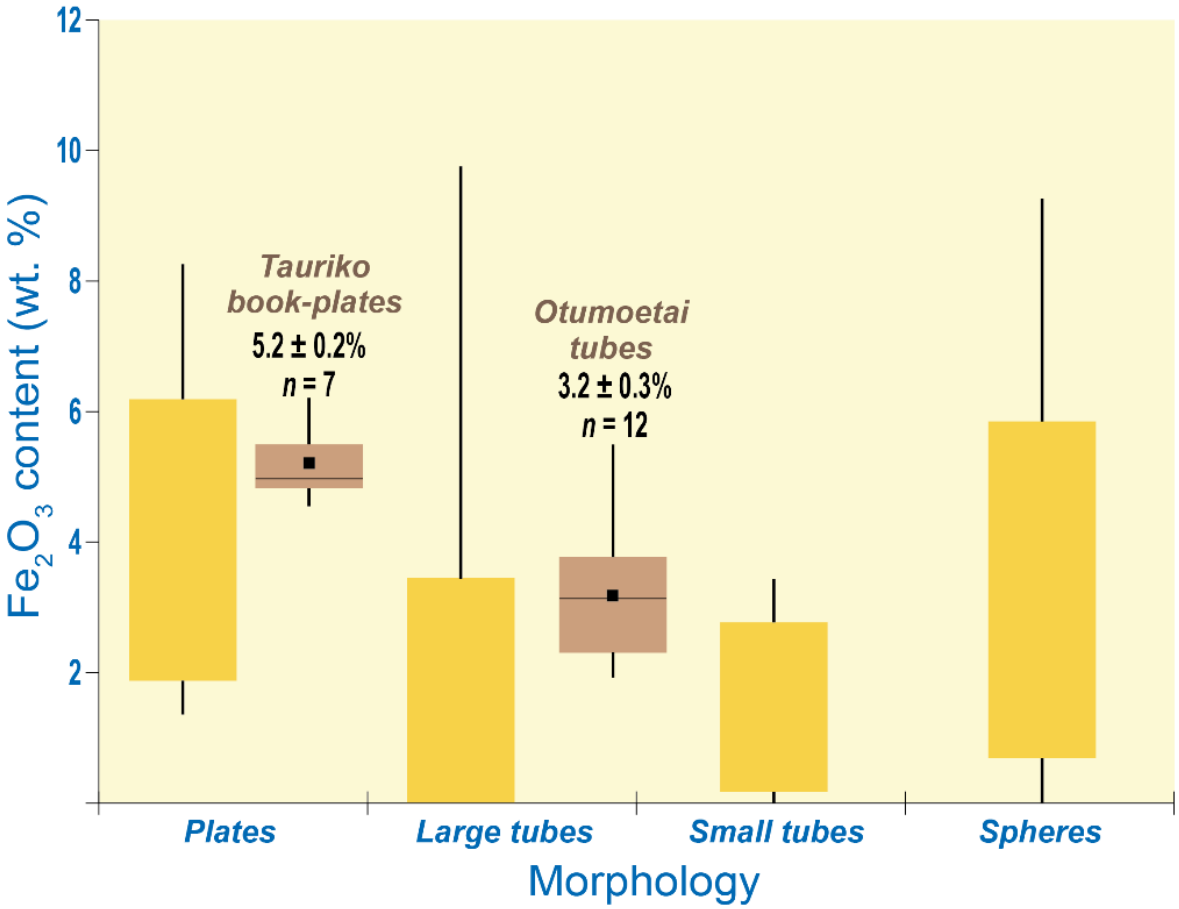
EDX analyses of flat surfaces of plates in halloysite books in bulk samples from Te Ranga tephra at Tauriko and from Te Puna tephra at Pahoia were compared with analyses of clusters of halloysite tubes in an uncorrelated Pleistocene tephra deposit of the Pahoia tephra sequence sampled near the base of two contiguous landslide scarps at Grange Road, Otumoetai (Fig. 1). Located at 37° 40' 46.00" S, 176° 08' 33.37" E, this pale, sensitive, silt-

413 rich tephra deposit is ~16 m below the modern land surface and older than ~0.35 Ma in age
414 on the basis of tephrochronology (Lowe *et al*., 2001; Wesley, 2007). Analyses by XRD and
415 SEM (not reported) showed that clays in this uncorrelated tephra at Otumoetai were
416 dominated by hydrated halloysite (Wyatt, 2009).

417 At Tauriko, Pahoia, and Otumoetai, mean Si and Al contents were essentially
418 identical for both book (plate) and tube morphologies, and consistent with their kaolin-
419 subgroup classification. For example, books in Te Ranga tephra at Tauriko (n = 7): SiO_2 = 47.7
420 ± 1.1 wt%, Al_2O_3 = 34.1 ± 0.5 wt%; tubes in the Pleistocene tephra at Otumoetai (n = 12):
421 SiO_2 = 50.7 ± 2.1 wt%, Al_2O_3 = 34.2 ± 1.3 wt%.

422 Previous studies have suggested that structural Fe content is an important
423 determinant of halloysite morphology especially with regard to plates and tubes (Tazaki,
424 1982; Noro, 1986; Papoulis *et al.*, 2004; Joussein *et al*., 2005; Churchman *et al.,* 2016;
425 Joussein, 2016). Plates typically have relatively high Fe contents whereas tubes have lower
426 Fe contents (Fig. 7). Our findings are consistent with this trend: mean Fe content in the book
427 plates in Te Ranga tephra at Tauriko (Fe_2O_3 = 5.2 ± 0.2 wt%) (n = 7) was significantly greater
428 than that in the tubes in the Pleistocene tephra at Otumoetai (Fe_2O_3 = 3.2 ± 0.3 wt%) (n =
429 12) on the basis of a Student t-test ($p < 0.0001$).

430 This enriched Fe content, broadly supported by additional analyses of the book
431 plates in the Te Puna tephra from Pahoia (mean Fe_2O_3 = 4.4 ± 1.28 wt%) (n = 7)
432 (Cunningham, 2012), is consistent with ranges documented for single plates in the literature
433 (Fig. 7), and supports the assumption that Fe has replaced some Al in octahedral positions.
434



435

436 **Fig. 7**. Box plots showing Fe contents (expressed as Fe_2O_3) of halloysite book-plates of Te Ranga
437 tephra samples, Tauriko site, and of halloysite tubes of an uncorrelated Pleistocene tephra sample,
438 Otumoetai site, as determined by EDX analyses (mean values shown as black squares, median values
439 by grey lines, ± standard errors). Fe contents (as Fe_2O_3) of plates, tubes, and spheres of halloysite
440 derived from data compiled by Joussein *et al.* (2005) are shown for comparison. (For a colour version
441 of this figure, see the online version of this paper.)

442

443

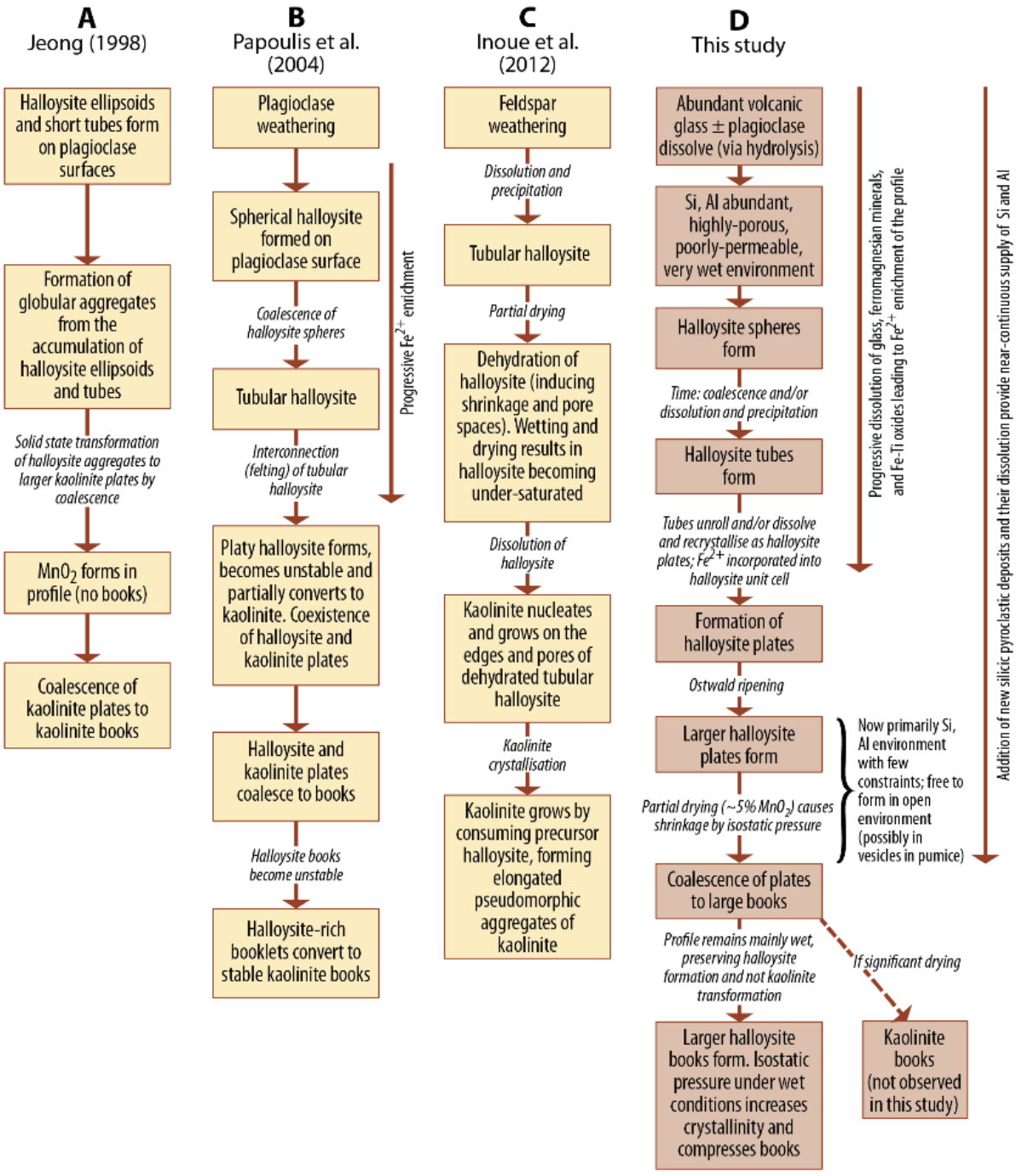
444 *Grain size*

445 Generally, the grain-size analyses of the tephras under study (Fig. 2) showed they
446 were predominantly silts (confirming field-based evaluations), and typically contained ~8%
447 clay sized material (<2 μm), ~70% silt-sized material (2-60 μm), and ~12% sand-sized
448 material (60-2000 μm) (Wyatt, 2009; Cunningham, 2012).

DISCUSSION

Proposed model for development of halloysite books

The presence of halloysite in book form is unique given that this morphology has not previously been reported for this clay mineral. Historically, halloysite has been recorded as a transitional form in the transformation of biotite (mica) to kaolinite books, or during the formation of "vermicular kaolinite" or kaolinite books from halloysite tubes (Figs. 8A, 8B) (Jeong, 1998; Papoulis *et al.*, 2004). An important related paper is that of Inoue *et al*. (2012) who described the "cannibalistic" transformation of halloysite to kaolinite via the nucleation and growth of primary halloysite, its subsequent dissolution, and then crystallization as "lath-shaped oriented (or pseudomorphic) aggregates of kaolinite after halloysite" (p. 388) (Fig. 8C). In the current study, the paucity (in Te Puna tephra) or lack of biotite (in Te Ranga tephra) in the primary mineral assemblages of the two parent tephras indicates that solid-state transformations from biotite to halloysite books are very unlikely to have occurred, although interstratified micaceous-kaolinite intergrades have been recorded in weathered biotite-rich tephras in western North Island (Lowe & Percival, 1993; Briggs *et al*., 1994; Lowe *et al*., 2001). Papoulis *et al.* (2004) described the coalescence or "felting" of halloysite tubes to form (unstable) halloysite books which ultimately transitioned to kaolinite (Fig. 8B).



468

469 **Fig. 8.** Schematic models of processes giving rise to kaolinite or kaolin-subgroup book formation as
470 determined in three previous studies (A–C), and the postulated model for the formation of halloysite
471 books conceived in the current study (D). The route to the formation of halloysite books (and
472 potentially kaolinite) is speculative but, arguably, it is consistent with the geological situation and
473 local environmental conditions as indicated (see text). (For a colour version of this figure, see the
474 online version of this paper.)

475

In the Tauranga study, the halloysite in book form does not appear to be unstable but on the contrary persists in various book lengths in fine-grained deposits of contrasting ages dating back to nearly 1 Ma. The presence of the books as halloysite on its own (rather than co-existing with kaolinite) implies that the mechanism for their formation must be unique to the environment to allow the books to form and persist as metastable products. Thus it is considered that the books have resulted from neoformation, not transformation, via the dissolution of the main primary mineral constituents and then subsequent precipitation (crystallisation) as halloysite in a series of morphological forms relating to progressive weathering (Fig. 8D) that probably correspond (except for the kaolinitic endpoint) to the sequence described by Papoulis *et al.* (2004) (Fig. 8B). The tephras contain abundant siliceous (rhyolitic) volcanic glass together with mainly plagioclase feldspar, which dissolve to produce large amounts of Si together with plentiful Al in soil solution. Fragmental glass shards and crystals of plagioclase have very large surface areas (especially the vesicular pumiceous glass), and are thermodynamically unstable and readily dissolved quickly via hydrolysis where the dominant proton donor is carbonic acid, H_2CO_3 (formed from dissolved CO_2 via soil organism respiration) (Ugolini & Sletten, 1991; Gislason & Oelkers, 2003; Churchman & Lowe, 2012). Hydrolysis liberates cations, such as Na^+, Ca^{2+}, and K^+ (which occupy intermolecular space amidst loosely linked SiO_4 tetrahedra in the glass) and Si^{4+} into interstitial pore water, and (with Al^{3+}) leads to the rapid precipitation of secondary minerals from such soil solutions (Daux *et al*., 1994; Hodder *et al*., 1996; Shikazono *et al.*, 2005; Churchman & Lowe, 2012). That the halloysite in Tauranga likely derives largely from the products of the dissolution of abundant glass fragments together with loose feldspar grains (Fig. 8D) contrasts with other models for its development in which

499 halloysite is depicted as emanating from the dissolution of feldspars alone from (hard) rock
500 (Figs. 8A–C).

501 A silica-rich environment favours the formation of halloysite rather than allophane,
502 as expressed by the Si-leaching model (summarised by Churchman & Lowe, 2012). Under
503 this model, both allophane and halloysite can form directly from the synthesis of the
504 products of dissolution of volcanic glass and primary minerals via different pathways
505 according to local environmental conditions (Parfitt *et al*., 1983, 1984; Lowe, 1986; Hodder
506 *et al*., 1990; Vacca *et al*., 2003). Halloysite formation is favoured by a Si-rich environment (Si
507 concentrations > ~10 ppm) or a wet, even "stagnant", moisture regime, whereas allophane,
508 conversely, forms preferentially in free-draining situations where Si concentrations in soil
509 solution are low (< ~10 ppm), allowing development of Al-rich allophane (Singleton *et al*.,
510 1989; Alloway *et al*., 1992; Churchman *et al*., 2010; Churchman & Lowe, 2012). Thus,
511 halloysite forms preferentially in the Tauranga region where the weathering and dissolution
512 of mainly rhyolitic pyroclastic deposits, including Hamilton Ash beds and upper Pahoia
513 Tephras, have provided an additional source of Si that has slowly migrated (leached) in soil
514 solution (probably as monosilicic acid, $Si(OH)_4$) into the lower deposits including the Te
515 Ranga and Te Puna tephras through long periods of time (≥~270,000 years) to continue
516 precipitation and re-precipitation processes, as discussed further below.

517 The continuing deposition of siliceous tephras through time in Tauranga, therefore,
518 has generated a thickening overburden and hence potential ongoing supply of silica and
519 alumina (e.g. Lowe, 1986; Wada, 1987) (Fig. 8D). Such a situation is comparable (but over a
520 much longer time-scale) to the dissolution kinetic-fluid flow coupling model developed by
521 Shikazono *et al.* (2005) to explain the ongoing generation and downward migration of
522 monosilicic acid from the weathering of multiple mid- to late-Holocene basaltic tephras

accumulated layer by layer in central Japan. In this model, rainwater penetrates downwards through a "unit reservoir" (i.e. a glass-dominated tephra layer), and reacts with the volcanic glass, which dissolves and crystallises as halloysite; the soil water then moves downward through a new unit reservoir of freshly-deposited glass at the land surface. Measured concentrations of Si in soil water through the entire sequence in Japan were mostly 25 to 35 ppm (the range was 10 to 45 ppm) (Shikazono *et al*., 2005), consistent with the formation there of halloysite that increased in abundance with depth and also compatible with the Si-leaching model outlined earlier.

Critically, the high porosity and yet low permeability of the Te Puna and Te Ranga tephra deposits at Tauranga, between ~10 and ~20 m below the modern land surface and beneath the Pahoia Tephra/Matua Subgroup deposits, have resulted in consistently high natural moisture contents with limited water movement (Smalley et al., 1980; Moon *et al*., 2015). Therefore Si has effectively accumulated because of both a sluggish permeability and a dissolution kinetic-fluid flow mechanism that provided a perpetual source of Si.

Formation of differing halloysite morphologies

In such a locally very wet environment enriched in silica at Tauranga, the formation of halloysite is thermodynamically and kinetically favoured (Churchman *et al*., 2010). Initially, halloysite spheroids are formed from solution, probably reflecting rapid solubilisation of the abundant glass and with the solution near the glass being supersaturated with silica (e.g. Lowe, 1986; Nagasawa & Noro, 1987; Adamo *et al*., 2001; Papoulis *et al*., 2004; Shikazono *et al*., 2005; Joussein, 2016; see also Cravero & Churchman, 2016). Given enough time, these spheroids reform either by coalescence, as invoked by Paoulis *et al*. (2004), or by dissolution and precipitation, or both, to form halloysite tubes

547 (Figs. 3C–D; Fig. 8D) (Churchman, 2015; Cravero & Churchman, 2016). In some cases,
548 halloysite tubes up to ~0.5 µm long, possibly new growth phases marking the inception of
549 further plate development, were arrayed along the edges of plates in the books (Fig. 6,
550 bottom-right), and in places tubes were stacked much like individual plates (Fig. 5F).
551 Previously, halloysite tubes have been reported as forming on the edges of, and in between,
552 kaolinite plates as a result of loss of structural rigidity (e.g. Robertson & Eggleton, 1991).
553 However, Papoulis *et al.* (2004) proposed that tubular halloysite transformed to kaolinite via
554 an unstable platy halloysite phase formed from "the interconnection of tubular halloysite to
555 felted planar masses of halloysite" (p. 281). They suggested that resultant "halloysite-rich
556 booklets" comprised both platy halloysite and newly-formed kaolinite together, and that
557 eventually such halloysite-kaolinite booklets were "converted initially to a more stable but
558 disordered kaolinite and finally to well-formed book-type kaolinite" (p. 281). In the
559 Tauranga study, the first part of this mechanism seems feasible, i.e. halloysite tubes unroll
560 and coalesce into plates, possibly via "felting". The stacked tubes on the edges of the plates
561 evident in Fig. 5F may reflect this postulated unrolling process. However, at the same time,
562 the rapid weathering of glass, ferromagnesian minerals, and Fe-Ti oxides (from the original
563 pyroclastic materials) enriches the profile with percolating ferrous iron. (The deposition
564 occasionally of very thin andesitic tephras over the region, such as occurred during the
565 1995-96 Mt Ruapehu eruptions, e.g. Cronin *et al*., 2003, provided another potential source
566 of iron.) That such Fe^{2+} is abundant was demonstrated by the positive Childs' (1981) tests
567 applied in the field. As noted earlier in the section on EDX, mean Fe content in the book
568 plates in Te Ranga tephra at Tauriko was significantly greater than that in the tubes in the
569 Pleistocene tephra at Otumoetai (Fig. 7). This enriched Fe content, consistent with ranges
570 reported for single plates and with previous analyses on tubular halloysite in the Bay of

571 Plenty by Soma *et al*. (1992), suggests that Fe has replaced Al in octahedral positions hence
572 reducing the mismatch with the Si tetrahedral sheet, lessening layer curvature by unrolling
573 and flattening, thus generating plates. Consequently, it is considered viable that the tubes
574 may be dissolving in the Fe-rich solution and re-crystallising as plates because of the
575 incorporation of Fe^{2+} into the unit cells (Fig. 8D). It is uncertain therefore which (if any) of
576 these two processes (morphological development via unrolling and "felting", or
577 neoformation) predominates in generating the halloysite plates.

578 Mechanisms for the formation of the halloysite books, which comprise plates aligned
579 or stacked in parallel, and their enlargement in some cases to dimensions exceeding 1000
580 μm in length, are entirely speculative at this point. It is suggested that the edges of the
581 plates may enlarge directly via the tube-unrolling mechanism solicited above (Fig. 5F) or,
582 where essentially confined in voids such as vesicles, they may grow in the manner of
583 Ostwald ripening (e.g. Dahlgren *et al.*, 2004) (Fig. 8D). The mechanism envisaged here is very
584 slow crystallisation via dissolution and re-precipitation so that the plates grow incrementally
585 larger and become slightly more crystalline over a very long time. The process is likely to be
586 exceptionally slow because of the very small difference in free energy between the
587 antecedent and subsequent phases of dissolving and re-crystallising halloysite.

588 The alignment of plates in the form of books themselves is not well understood,
589 even for kaolinite in the absence of precursory micas (e.g. Churchman *et al*., 2010), and
590 hence it is conjected that the intermittent drying of the tephra deposits in which the books
591 occur may have promoted shrinkage by isostatic pressure between the plates, allowing
592 them to coalesce and amalgamate to form books (Fig. 8D). With a return to wet conditions,
593 isostatic pressure increases crystallinity and compresses the books (e.g. see tightly
594 laminated book in Fig. 6). Such mechanisms have been described, for example, by Aparicio

595 *et al.* (2009) and Brigatti *et al.* (2013). The partial drying of the host tephra deposits is shown
596 by the scattered MnO_2 redox concentrations, generally small masses or concretions up to
597 ~5 mm in diameter, which indicate prior oxidation of the deposits by seasonal drying (e.g.
598 Vespraskas *et al*., 2004; Schoeneberger *et al*., 2012; Vespraskas & Vaughn, 2015).
599 Churchman *et al*. (2010) used the occurrence of such MnO_2 concentrations in some
600 saprolites in Hong Kong to trace a history of dehydration, leading to conditions favouring
601 the formation of kaolinite rather than halloysite. The abundance of MnO_2 at Tauranga
602 (estimated by comparison with area percentage charts, e.g. Schoeneberger *et al.*, 2012),
603 although relatively low with typically up to ~5% in the Te Puna and Te Ranga tephras (e.g.
604 Fig. 2A), nevertheless is a notable feature. These quantities suggest that the tephras and
605 associated deposits were only partially and intermittently dried. That the drying is short-
606 lived is viewed as critical for the development of halloysite books, because complete drying
607 would deter the formation of all forms of halloysite (Churchman *et al*., 2010, 2016).
608 Moreover, if the tephra deposits were completely dehydrated, the halloysite books would
609 become unstable and transform to kaolinite (kaolinite is thermodynamically favoured over
610 halloysite, e.g. Percival, 1985; Joussein *et al*., 2005), as suggested by the models of Jeong
611 (1998) and Papoulis *et al.* (2004) (Figs. 8A–B).
612 The timing of partial drying is uncertain because it may simply represent occasional
613 seasonal drying, but on a longer time-scale the MnO_2 concentrations may reflect drying
614 episodes during glacial periods which were drier than today (e.g. Stevens & Vucetich, 1985;
615 Kohn *et al*., 1992; Newnham *et al.*, 1999; Stephens *et al*., 2012; Eaves *et al*., 2016). At
616 Tauriko, the Te Ranga tephra (dated at ~0.27 Ma) has experienced generally cold and dry
617 glacial climates during marine oxygen isotope stages (MOIS) 8, 6, and 2, whereas at both

618 Omokoroa and Pahoia, the Te Puna tephra (dated at ~0.93 Ma) has experienced another
619 eight glacial stages dating back to around MOIS 24.
620
621 *Summary of proposed model and conditions for formation and persistence of halloysite*
622 *books*
623 The primary mineralogical and fragmental character (i.e. predominance of rhyolitic
624 glass shards with plagioclase and mafic crystals) and the micro-environmental conditions
625 associated with the fine-grained, pumice-bearing Te Puna and Te Ranga tephras at Pahoia,
626 Omokoroa, and Tauriko in Tauranga (Si-rich, Fe^{2+}-rich, highly porous yet poorly-permeable,
627 permanently near or at saturation but with occasional drying out) seem to have kinetically
628 favoured the pathway: solubilized glass + plagioclase → halloysite spheroids → halloysite
629 tubes → halloysite plates → halloysite books (Fig. 8D). It is suggested that the halloysite
630 plates, thence halloysite books, are formed as the metastable end-point, i.e. without the
631 coexistence of halloysite and kaolinite, and without the ultimate kaolinization that was
632 described by Papoulis *et al.* (2004) (Fig. 8B), because evidence for the occurrence of
633 kaolinite in the book-bearing tephras is entirely lacking. That transformation to
634 thermodynamically-favoured kaolinite is not occurring is attributable to the site remaining
635 wet most of the time, a condition that favours hydrated halloysite instead of kaolinite
636 (Churchman *et al*., 2010; Churchman & Lowe, 2012). Although the proposed pathway above
637 is presented perforce as a "linear" succession, the concomitant existence of the different
638 halloysite morphologies in the Te Puna and Te Ranga tephras at Tauranga indicates that the
639 set of processes that allow each morphology to form is continuing iteratively but
640 presumably against a pervasive very long-term trend to attain the remarkably large
641 metastable book forms.

642 *Diagenesis or pedogenesis?*

643 The tephra deposits in which the halloysite books occur are only weakly to
644 moderately weathered (clay contents were typically ≤10 %) and lack pedogenic features
645 (aside from the MnO_2 concentrations that can occur in both geological and pedological
646 environments). At both Omokoroa and Tauriko, the book-bearing deposits (Te Puna and Te
647 Ranga tephras) occur stratigraphically well below buried soil horizons (~8 m and ~11 m
648 below, respectively). Although the Te Puna tephra at Pahoia is overlain (within ~1 m) by a
649 buried soil (paleosol), it is itself only barely weathered and is best considered a geological,
650 not pedological, unit comparable to those at Omokoroa and Tauriko. Thus it is evident that
651 the halloysite books are formed in a relatively simple, geological environment via diagenesis
652 (i.e. the post-depositional alteration of a sedimentary or volcanic/pyroclastic deposit at low
653 temperature) rather than in a surface soil via pedogenesis. This interpretation is expressed
654 in the model developed for their formation involving the slow migration and accumulation
655 of abundant silica in soil solution (Fig. 8D) and is supported by the relatively large sizes
656 attained by many of the books. Such large sizes tend to be characteristic of clay mineral
657 particles formed in "clean" geological environments rather than the much smaller clay
658 mineral particles typically formed in the "heterogeneous milieu" of pedogenic soils at or
659 near the land surface (Chadwick & Chorover, 2001; Churchman, 2010; Churchman & Lowe,
660 2012).

661 Similar observations about halloysite crystal size were made by Kirkman & Pullar
662 (1978), who studied hydrated halloysite in a "wet" sequence of partly weathered Middle to
663 Late Quaternary-aged rhyolitic pyroclastic "white tuff" deposits and associated paleosols in
664 eastern Bay of Plenty (see also Manning, 1996). They found that halloysite particles in

665 geological units (referred to as “basal [ash] clays” in their paper) were large, usually up to
666 ~0.5 μm but often ~1 μm in diameter, and undistorted, whereas halloysite particles in the
667 paleosols (“paleosol clays”) in the sequence were invariably somewhat smaller and
668 distorted. Intriguingly, an unusual cube-shaped particle amidst halloysite spheroids in an
669 electron micrograph of one of the deposits was remarked upon by Kirkman & Pullar (1978,
670 p. 5): although they described it as “probably amorphous”, the particle has plate-like
671 features ~1.5 μm across with straight edges and may instead be a halloysite book. Kirkman
672 & Pullar (1978) also speculated that the sizes of the halloysite particles in their study were
673 ultimately determined by the supply of Al, which in the Tauranga study does not seem to be
674 limiting with respect to the formation of the very large books.

675

676 *When did the halloysite books form?*

677 It is known from tephrochronology that the halloysite books at Pahoia and
678 Omokoroa formed since ~0.93 Ma and those at Tauriko since ~0.27 Ma, the latter age
679 indicating therefore that books can form within ~270,000 years. That these two ages differ
680 implies, however, that time (other than being necessarily abundant) is not the only critical
681 factor in the formation of the books because landscape and stratigraphic position (~10–20
682 m below the modern land surface) and geohydrological conditions, together with a humid
683 climate, seem to provide the necessary local kinetic environmental conditions as described
684 earlier. Nevertheless, time is important in at least three ways, being required for (1) the
685 ongoing accumulation of the siliceous pyroclastic and volcaniclastic deposits as an
686 “overburden” to provide a self-replenishing source of downward-migrating Si , along with
687 ample Al, in soil solution; (2) the processes involving dissolution of the volcanic glass and

688 feldspars in the overburden and then the synthesis of halloysite in its various forms; and (3)
689 potentially very slow Ostwald ripening and other processes (Fig. 8D) that allow book growth,
690 especially to giant size as at Pahoia, where they occur in the ~0.93-Ma Te Puna tephra.

691 Halloysite can form quickly in temperate, humid environments if conditions are
692 suitable, and remain as a (meta)stable and persistent phase for long periods (e.g. McIntosh,
693 1979; Lowe, 1986; Lowe & Percival, 1993; Joussein *et al*., 2005; Churchman & Lowe, 2012).
694 However, it is contended in the current study that the great abundance of time has been
695 essential to enable the formation of the halloysite books via an iterative set of processes as
696 noted earlier (Fig. 8D), and that the books have probably been forming continuously over
697 hundreds of thousands of years.

698

699 *Are more halloysite books waiting to be discovered?*

700 It is hypothesised that halloysite books may also be found not only in other porous
701 yet poorly-permeable deposits in the Pahoia Tephras and Matua Subgroup in similar geo-
702 hydrological juxtapositions several tens of metres below the modern land surface, but also
703 in comparable deposits and palaeo-environments elsewhere in North Island, and potentially
704 beyond New Zealand. For example, large (sand-sized) kaolinite books identified by Salter
705 (1979) as b-axis disordered "books and stacks" occurred in three units of the very strongly
706 weathered sequence of Kauroa Ash beds aged between ~1.7 Ma (beds K3, K4) and ~1.3 Ma
707 (bed K12, a correlative of Ongatiti Ignimbrite) in western North Island (Briggs *et al*., 1989;
708 Lowe *et al*., 2001; Alloway *et al*., 2004). However, the clay-rich Kauroa Ash beds are
709 dominated by abundant halloysite tubes (Kirkman, 1980; Briggs *et al*., 1994), and the
710 presence of halloysite tubes mainly on the edges of, and occasionally between, very thin

plates comprising the large books observed by Salter (1979) suggests that the identity of some books may need to be re-evaluated in light of the findings reported in the current paper.

Similarly, Jeong (1998) relied mainly on particle morphology (and specifically the vermicular form, e.g. see p. 271) to identify kaolinite, and so there is the possibility that at least some of the “vermicular kaolinite” he described may be halloysite.

CONCLUSIONS

The identification of halloysite books is a novel discovery that has been unveiled with a proposed mechanism for their development and persistence. It is evident that the books, some “giant” in size (i.e. fine sand), in two altered, fine-grained rhyolitic tephras (Te Puna tephra, ~0.93 Ma; Te Ranga tephra, ~0.27 Ma) in the Tauranga area of eastern North Island, New Zealand, are composed essentially entirely of halloysite and are metastable because they have not transformed to kaolinite, contrary to findings from other studies elsewhere (Fig. 8). It is suggested that kaolinite has not formed in Tauranga because the low permeability of the tephras and associated deposits ensures that the sites largely remain locally wet. The findings of this study challenge the notion that book morphologies are always kaolinite in altered tephra deposits and hence indicate that books may have been incorrectly identified in the past.

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