Tales of the unexpected: halloysite delivers surprises and a paradox*

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Introduction

Despite being first described nearly 200 years ago (Bethier, 1826; Joussein et al., 2005), halloysite still has the capacity to surprise. We report here the remarkable discovery in New Zealand of two new morphologies for this 1:1 Si:Al layered aluminosilicate member of the kaolin subgroup. One discovery was entirely serendipitous, thus lending validity to the famous phrase attributed to scientist Isaac Asimov (1920-1992) (Wainer and Lysen, 2009):

> *The most exciting phrase to hear in science, the one that heralds new discoveries, is not "Eureka" but "That's funny..."*

Moreover, the recognition of one of the new morphologies of halloysite helped enable a long-standing problem regarding the geotechnical property of sensitivity and its impact on landsliding in the Tauranga region, eastern North Island, to be solved. Such landsliding has commonly been attributed (possibly erroneously) to the dominance of nanocrystalline allophane, the clay commonly associated with halloysite in many weathered pyroclastic sequences and volcanogenic soils in North Island (Moon et al., 2015; Moon, 2016). In this article, we briefly summarise the circumstances and implications of the two discoveries relating to halloysite morphology, one published in *Clay Minerals* and the other in *Geology*, and a third study (also in *Clay Minerals*) relating in part to the formation of halloysite.

In doing so, we mark publication of a collection of 16 articles, and an editorial, on halloysite published in volume 51, issue 3, of the journal, *Clay Minerals* (Churchman et al., 2016a). In the editorial, entitled "The rise and rise of halloysite", Churchman et al. (2016b) have documented the remarkable actual and prospective uses of halloysite and show the exponential rise in numbers of papers relating to this clay since about 2005. Up until then, the main application of halloysites had been as an alternative raw material to kaolinite for the ceramics industry. In New Zealand, the main supplies derive from the Matauri Bay halloysite deposits in Northland, the world's dominant source (e.g. see Brathwaite et al., 2012; Walrond, 2016). But halloysite, especially its nanotubular form, has potential uses in nanocomposites with polymers, as carriers for active agents (e.g. in medicine, agriculture, and environmental remediation), and possibly for other medical uses in addition to drug delivery (e.g. in wound dressing and tissue engineering scaffolds), as anti-inflammatory agents, in water filtration, for the uptake of spilled oil, and various other promising applications (Churchman and Pasbakhsh, 2015; Churchman et al., 2016b).

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Discovery of halloysite in book form

Whilst examining clays in the weathered volcanogenic and tephra sequences, and paleosols, that underlie the landscape of the Tauranga region, masterate student at Waikato University, Justin Wyatt, using scanning electron microscopy (SEM) in 2008, came across what appeared to be classic 'kaolinite' book forms in samples from a somewhat-weathered tephra (dated at ~0.27 Ma) in a section at Tauriko where a new subdivision was being developed (Figs. 1, 2). However, on analysis by X-ray diffraction (XRD), Justin found that the books seemed to be hydrated halloysite, not kaolinite. "That's funny…", he thought, because Justin, despite an exhaustive search of the literature, could find no mention of halloysite being reported in book form. Jock Churchman in Adelaide was contacted and he agreed with Justin's conclusion that books invariably were seen to be kaolinite, and subsequently a short, preliminary paper was presented in 2010 at a meeting in Brisbane following the World Soil Congress in that city (Wyatt et al., 2010).

Fig. 1. SEM image showing multiple curved (vermicular) halloysite books of differing sizes in ~270,000 year-old Te Ranga tephra (Tauriko site, Tauranga). From Cunningham et al. (2016, p. 360).

Waikato University colleague Vicki Moon, like Justin, was primarily interested in explaining the properties of the altered tephras and associated deposits with the view towards explaining pervasive and problematic landsliding in the Tauranga region, which seemed to be related to some layers that were very sensitive (Moon et al., 2013, 2015; Moon, 2016). Sensitivity is defined as the loss of strength (of earth material) upon remoulding, and is quantified as the ratio of undisturbed to remoulded undrained strength where both strengths are determined at the same moisture content. Values of <2 are insensitive, 4–8 are considered sensitive, 8–16 are extra sensitive, and >16 are referred to as 'quick clays' (Moon et al., 2015).

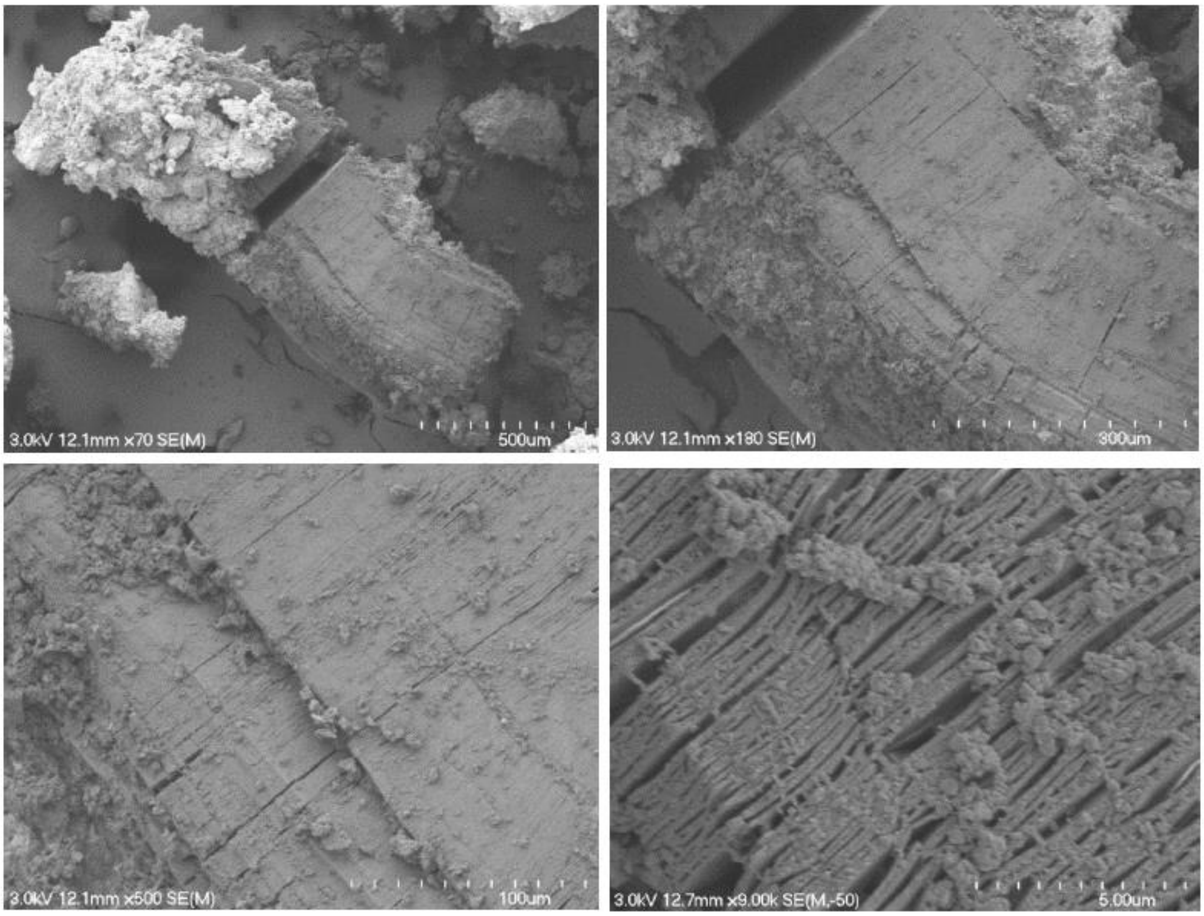

Fig. 2. SEM image of a giant, tightly laminated halloysite book (in two pieces) in ~930,000 year-old Te Puna tephra (Pahoia site, Tauranga). This book is ∼1500 µm long (∼1.5 mm). Enlargements of the book surface are shown, with increasing magnification, in images at top-right, bottom-left, and bottom-right. From Cunningham et al. (2016, p. 361).

Vicki subsequently asked another masterate student at Waikato University, Michael Cunningham, to work on more sites around Tauranga Harbour. Occurrences of the book morphology were identified at two more locations and they were characterised in detail using XRD and other methods; all were shown to be halloysite, not kaolinite. In the resulting paper by Cunningham et al. (2016), the books were described as ∼1.5 to ∼1500 µm in length and they occurred in highly porous yet poorly permeable, altered, siliceous rhyolitic tephra deposits aged ∼0.93 Ma (Te Puna tephra) or ∼0.27 Ma (Te Ranga tephra) ∼10 to 20 m stratigraphically below the modern landsurface. Unlike parallel studies elsewhere involving both halloysite and kaolinite (e.g. Papoulis et al., 2004), kaolinite has not formed in Tauranga presumably because the low permeability ensures that the sites largely remain locally wet so that the halloysite books are metastable.

An implication of the discovery therefore is that some halloysite books may have been misidentified previously as kaolinite on the basis of morphology alone (Cunningham et al., 2016).

Discovery of halloysite mushroom-cap-shaped spheroids and a new attraction-detachment model that explains high sensitivity and proneness to landsliding in altered tephras

In a detailed geotechnical study involving the INTERCOAST collaboration between Bremen University, Germany, and University of Waikato, Hamilton, the properties of the volcanogenic and tephra deposits and paleosols in a drill core associated with a coastal landslide (also referred to as a flow slide because of very long run out distances) at Bramley Drive, Omokoroa Peninsula, Tauranga, were examined (Fig. 3). A white, clayey silt layer, ~0.3 m thick, at 23 m depth in the core (also exposed in the scarp, e.g. Gulliver and Houghton, 1980) was identified as being highly sensitive (Smalley et al., 1980), and it had a very high concentration of spheroidal halloysite.

Fig. 3. Landslide at Bramley Drive, Omokoroa, photographed in October 1979, barely two months after the initial main failure event on 9 August that year. The landslide, ~60 m across, had a run out distance of at least 150 m from the base of the slope; the cliff edge receded by ~20 m, forcing the eventual removal of five houses in close proximity to the main scarp (Gulliver and Houghton, 1980; Moon, 2016). The slide was reactivated in May 2011 and in April and August 2012, causing further regression of the scarp. Photo: D.J. Lowe.

Examining SEM micrographs of the spheroids before and after remoulding (kneading of samples by hand), PhD student at Bremen University, Max Kluger, noticed something odd about the before-and-after images. “Das ist merkwürdig…”, he mused. The spheroids seemed to look different depending on the remoulding. In the undisturbed state, they were distinctly aggregated into networks of well-connected particles but, after remoulding, most of the aggregates were broken apart into small, loose clusters or individual halloysite particles (Fig. 4). Max noticed that individual spheroids had distinctive “deformities” in the form of openings on one side and that these openings were previously hidden by contact with other spheroids. The deformities gave the particles an ovate “mushroom cap” appearance, and thus a new halloysite morphology, mushroom-cap-shaped (MCS) spheroids, was documented for the first time (Fig. 5). Point-counting individual spheroids in both undisturbed (aggregated) and remoulded (disaggregated) samples showed that the observable MCS spheroids increased around tenfold in abundance, from ~4 % to ~45%, respectively (Kluger et al., 2016).

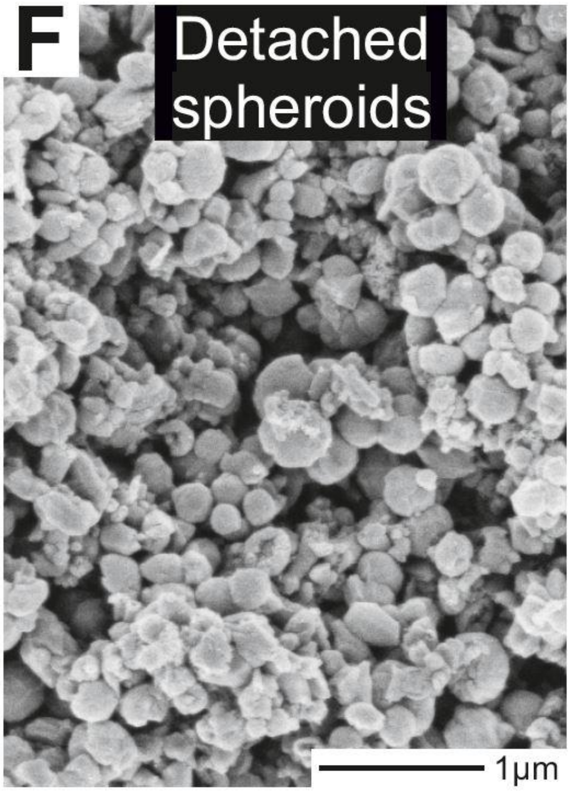

Fig. 4. SEM images of mainly detached or only weakly connected mushroom-cap-shaped halloysite spheroids after remoulding. These samples are from the sensitive layer that failed in the landsliding at Omokoroa (from Kluger et al., 2016).

Because this particular morphology overwhelmingly occurred in the highly sensitive slide-prone layer, it was suggested that this unique particle shape controlled the mechanical behavior of the flow slide (Kluger et al., 2016). New work on the molecular-level structure of halloysite (Churchman et al., 2016c, reported below) has shown that at pH values between ~2 and ~8, the Al-octahedral (aluminol) sheet has a net positive charge and a Si-tetrahedral (silanol) sheet a net negative charge (see also charge density-functional modelling for halloysite nanotubes by Guimarães et al., 2010). The halloysite spheroids observed at Omokoroa are almost certainly composed of concentrically stacked 1:1 layers, i.e., with an onion-like structure, as shown in numerous studies (e.g. Wada et al., 1977; Kirkman, 1981; Berthonneau et al., 2015). Hence it was suggested that if sufficient numbers of positively charged openings are exposed, the electrostatic interactions between them and the negative exterior silanol surfaces would allow the MCS spheroids to form stacked aggregates. If the paired silanol and aluminol sheets exposed in the openings are neutral overall, then a net increase in particle attraction will still occur because electrostatic repulsion is reduced and the larger contact areas lead to higher van der Waals’ forces (Kluger et al., 2016).

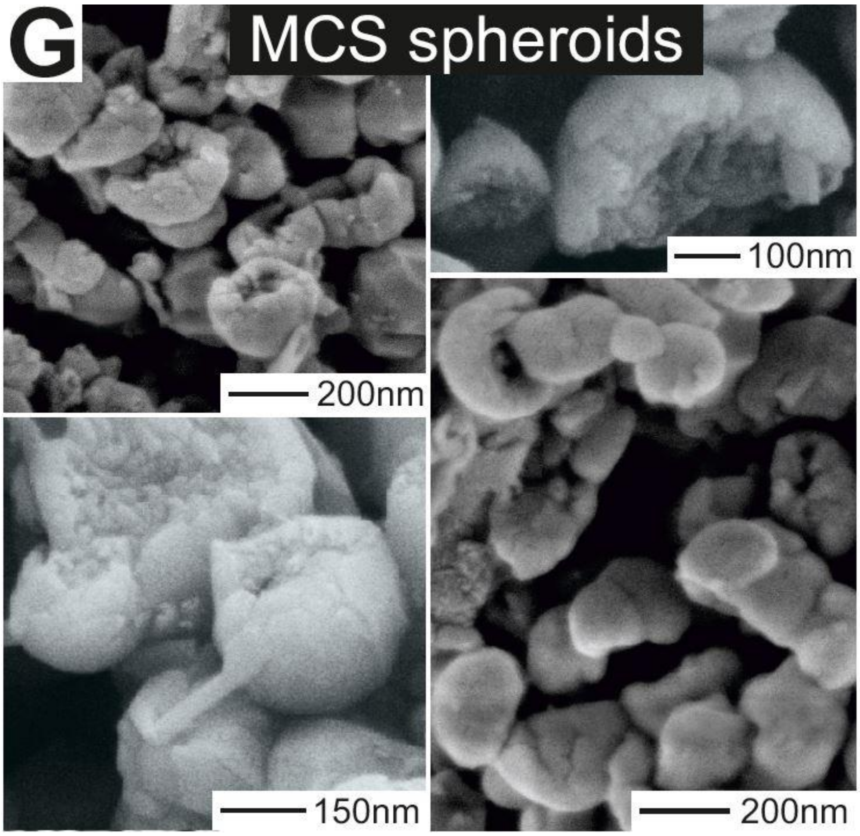

Fig. 5. SEM images of individual mushroom-cap-shaped halloysite spheroids with their distinctive openings on one side clearly visible (from the sensitive layer at Omokoroa) (from Kluger et al., 2016).

Thus the landsliding took place at Omokoroa (and potentially elsewhere around Tauranga) because a layer dominated by MCS halloysite spheroids was highly sensitive. That high sensitivity in turn was explainable by the attraction-detachment model that relates to charge distributions on the MCS spheroids. The attractive forces between the openings (weakly positively charged or neutral) and the convex exterior surfaces (negatively charged) are demonstrably strong enough to allow for the formation of aggregates, but also permit easy disaggregation by mechanical detachment during shear, leading to flow sliding in the presence of abundant water (Kluger et al., 2016).

How the lack of halloysite in basaltic ash-derived soils at Mounts Gambier and Schank in South Australia helped explain water intercalation in halloysite

We studied the volcanic-ash soils formed at the mid-Holocene basaltic volcanoes of Mount Gambier and Mount Schank in southeast South Australia during David Lowe's sabbatical leave at CSIRO Soils Division, Adelaide, in 1991-1992 (e.g. Figs. 6, 7). Yet around 25 years later the soil mineralogy provided unexpected insight into halloysite's formation and molecular-scale structure, notably how different halloysites may employ a range of mechanisms for adsorbing and retaining interlayer H_2O, which is the defining feature of (hydrated) halloysite (Churchman and Carr, 1975; Churchman and Lowe, 2012). How interlayer H_2O fitted into halloysite was a question that Jock had been pondering for nearly 50 years. Paradoxically, it was a *lack* of halloysite in the South Australian ash-derived soils that provided the key to answering it.

Fig. 6 (**left**). Profile of soil (Humic Vitrixerand) mainly on basaltic ash at Brownes Lake near Mt Gambier, South Australia (marks on auger at 10-cm intervals) (from Churchman et al., 2016c, p. 400). **Fig. 7** (**right**). Profile of soil (Thaptic Haploxerand) on basaltic ash over a buried soil on aeolian sand at Laslett Road near Mt Schank, South Australia (knife ~25 cm long) (from Churchman et al., 2016c, p. 400)

Apart from informing the identification of Andisols in Australia, a surprise in itself to most pedologists (Lowe and Palmer, 2005; Takesako et al., 2010; McDaniel et al., 2012), the clay mineralogy of the soils at Mounts Gambier and Schank seemed to conform to the New Zealand-developed Si-leaching model: the concentration of Si in the soil solution is controlled largely by the rate of leaching of the parent volcanic ash, its composition, and its drainage (Parfitt et al., 1983; Lowe, 1986; Singleton et al., 1989). A threshold of ~250 mm leaching marks the transition from conditions favouring halloysite formation to those favouring allophane. That is, >~250 mm throughput of leachate results in allophane, whereas ⩽~200 mm gives rise to halloysite (Parfitt et al., 1984). In the soils at Mounts Gambier and Schank, under a xeric moisture regime and mesic temperature regime (Soil Survey Staff, 2014), the flow of water through the upper horizons is ~280 mm/year, typically for ~3–10 weeks during winter or early spring, similar to the upper threshold for halloysite formation in New Zealand. There is considerably less flow through the lower horizons in the South Australian soils, ~100 mm/year, which should favour halloysite formation (Churchman and Lowe, 2012).

However, XRD peaks near 7 Å for clays from many of the soil samples were observed but the basal spacing did not expand beyond ~7 Å when formamide was applied, indicating the absence of halloysite (Churchman et al., 2016c). “That’s funny…”, thought Jock and David: the conditions are apparently conducive to the formation of Al-rich allophane in upper horizons, but the limited leaching over the non-winter months seems to have favoured formation of Si-rich allophane (and phyllosilicate clays) instead of halloysite in lower horizons. The soils almost invariably contained kaolinite and illite, accompanied sometimes by a smectitic phase, including interstratified kaolinite-smectite and/or illite-smectite, as well as allophane. Hence it seemed unlikely that Si concentrations were sufficiently low to limit halloysite synthesis (cf. Wilson et al., 2017). Furthermore, halloysite had been identified in soils on ash and volcanogenic materials under xeric moisture regimes in northern California (Takahashi et al., 1993). But the South Australian ash soils, with no halloysite, have high pH values (up to 8.7) whereas those from northern California have pH values of 5.3–6.9 (Churchman et al., 2016c). The high pH of the soils at Mounts Gambier and Schank is related to calcareous materials underlying both volcanic complexes, with the ash deposits and soils containing up to ~60% of exotic, non-volcanic materials, including xenolithic limestone fragments (Churchman and Lowe, 2012).

Churchman et al. (2016c) consequently proposed that pH plays a key role in the formation of halloysite, especially in the interlayer uptake of H_2O. The proposal is based on the difference in charge characteristics between the silica tetrahedral sheet and the alumina octahedral sheet. Various studies (including those of Vergaro et al., 2010; Abdullayev and Lvov, 2013, 2015) have shown that the two structural sheets have a different pattern of pH-dependent charge (as invoked, critically, by Kluger et al., 2016, in the Tauranga landsliding study noted above). The octahedral sheet is positively charged at all pH values below ∼8, whereas the tetrahedral sheet is negatively charged at all pH values above ∼2. It was therefore suggested by Churchman et al. (2016c) that the two sheets making up a layer of halloysite have opposite charges between pH ∼2 and ∼8. Consequently, the alumina sheet would attract the oxygen “end”, and the silica sheet the hydrogen “end”, of H_2O molecules. This process generates a driving force for the uptake and retention of interlayer H_2O by halloysite. Although kaolinite has the same sheet structure as halloysite to provide the same driving force, H_2O molecules are not retained in the interlayer space of kaolinite because of the lack, or erratic supply, of water during its formation (Churchman et al., 2010; Gupta and Miller, 2010). This new hypothesis is consistent with observations that halloysites tend to occur in acidic environments.

An alternative (or additional) mechanism to explain why halloysite formation rarely occurs under alkaline conditions was also proposed following the work on the Mount Gambier and Mount Schank Andisols (Churchman and Lowe, 2014). It was argued that after its formation but prior to drying, halloysite contains ferrous ions in its octahedral sheet. The replacement of Al^{3+} by Fe^{2+} in this sheet raises the layer charge and cation exchange capacity. Ferrous ions are favoured over ferric ions under wet conditions but become unstable in relation to solid phases as pH rises. Ferrous ions, therefore, are rarely found in solutions of pH ≥ 6. The absence of halloysite in the ash-derived soils at Mounts Gambier and Schank may thus be linked to the requirement for ferrous ions during the formation of halloysite (Churchman et al., 2016c).

These two hypotheses replaced one put forward by Bailey (1990), who proposed that H_2O was brought into the interlayers of halloysites together with hydrated cations in order to satisfy a small negative charge resulting from the replacement of Si (4+) by some Al (3+). However, using ^{27}Al-NMR, Newman et al. (1990), also in New Zealand, found that halloysites had no more tetrahedral Al than kaolinites, contrary to Bailey’s hypothesis. Further, Bordallo et al. (2008), using quasi-elastic nuclear scattering, found that, unlike montmorillonite, halloysites had no cations in their interlayers. So everything but the kitchen sink has been thrown at the problem of the interlayer water in halloysite without a satisfactory explanation until now, we would claim.

Conclusions

Firstly, always expect the unexpected: there is an infinite capacity to discovery in the sciences, including the geosciences, as illustrated by these three case studies. Secondly, could these advances and applications relating to halloysite, arguably now a 'supermineral' that is intimately associated with extensive volcanogenic deposits in North Island, together with new work relating to halloysite's 'ally', allophane (e.g. Huang et al., 2016a, 2016b; Taylor et al., 2016), herald a much-needed resurgence in clay mineralogy in the geosciences (including soil science) in New Zealand and elsewhere? We hope so.

Acknowledgements

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References

Abdullayev, E., Lvov, Y. 2013. Halloysite clay nanotubes as a ceramic "skeleton" for functional biopolymer composites with sustained drug release. *Journal of Materials Chemistry B*, **1**, 2894–2903.

Abdullayev, E., Lvov, Y. 2015. Halloysite tubule nanoreactors in industrial and agricultural applications. Pp. 363–382 in Pasbakhsh, P., Churchman, G.J. (eds), *Natural Mineral Nanotubes*. Apple Academic Press, Oakville, Canada.

Bailey, S.W. 1990. Halloysite – a critical assessment. Pp. 89-98 in Farmer, V.C., Tardy, Y. (eds), *Proceedings of the 9th International Clay Conference 1989*. Sciences Géologiques Mémoire, **86**, Strasbourg, France.

Berthier, P. 1826. Analyse de l'halloysite. *Annales de Chimie et de Physique*, **32**, 332–335.

Berthonneau, J., Grauby, O., Jeannin, C., Chaudanson, D., Joussein, E., Baronnet, A. 2015. Native morphology of hydrated spheroidal halloysite observed by environmental transmission electron microscopy. *Clays and Clay Minerals*, **63**, 368–377.

Bordallo, H.N., Aldridge, L. P., Churchman, G.J., Gates, W.P., Telling, M.T.F., Kiefer, K., Fouquet, P., Seydel, T., Kimber, S.A.J. 2008. Quasi-elastic neutron scattering studies on clay interlayer-space highlighting the effect of the cation in confined water dynamics . *Journal of Physical Chemistry C*, **112**, 13982–13991.

Brathwaite, R.L., Christie, A.B., Faure, K., Townsend, M.G., Terlesk, S. 2012. Origin of the Matauri Bay halloysite deposit, Northland, New Zealand. *Mineralium Deposita*, **47**, 897–910.

Churchman, G.J., Carr R.M. 1975. The definition and nomenclature of halloysites. *Clays and Clay Minerals*, **23**, 382–388.

Churchman, G.J., Lowe, D.J. 2012. Alteration, formation, and occurrence of minerals in soils. Pp. 20.21–20.72 in Huang, P.M., Li, Y., Sumner, M.E. (eds), *Handbook of Soil Sciences: Vol. 1 Properties and Processes* (2nd ed). CRC Press, Boca Raton, USA.

Churchman, G.J., Lowe, D.J. 2014. Clay minerals in South Australian Holocene basaltic volcanogenic soils and implications for halloysite genesis and structure. Pp. 3–6 in Gilkes, R. (ed), *Proceedings of the 23rd Biennial Australian Clay Minerals Society Conference*, University of Western Australia, Perth. Published at http://www.smectech.com.au/ACMS/ACMS_Conferences/ACMS23/Program/Abstracts/S1-0220Churchman20and%20Lowe.pdf

Churchman, G.J., Pasbakhsh, P. 2015. Current trends in research and application of natural mineral nanotubes. Pp. 481–488 in Pasbakhsh, P., Churchman, G.J. (eds), *Natural Mineral Nanotubes.* Apple Academic Press, Oakville, Canada.

Churchman, G.J., Pontifex, I.R., McClure, S.G. 2010. Factors affecting the formation and characteristics of halloysites or kaolinites in granitic and tuffaceous saprolites in Hong Kong. *Clays and Clay Minerals*, **58**, 220–237.

Churchman, G.J., Pasbakhsh, P., Hillier, S. (eds) 2016a. [Special issue on halloysite.] *Clay Minerals*, **51 (3)**, 303–528.

Churchman, G.J., Pasbakhsh, P., Hillier, S. 2016b. [Editorial] The rise and rise of halloysite. *Clay Minerals*, **51**, 303–308.

Churchman, G.J., Pasbakhsh, P., Lowe, D.J., Theng, B.K.G. 2016c. Unique but diverse: some observations on the formation, structure, and morphology of halloysite. *Clay Minerals*, **51**, 395–416.

Cunningham, M.J., Lowe, D.J., Wyatt, J.B., Moon, V.G., Churchman, G.J. 2016. Discovery of halloysite books in altered silicic Quaternary tephras, northern New Zealand. *Clay Minerals*, **51**, 351–372.

Guimarães, L., Enyashin, A.N., Seifert, G., Duarte, H.A. 2010. Structural, electronic, and mechanical properties of single-walled halloysite nanotube models. *Journal of Physical Chemistry C*, **114**, 11358–11363.

Gulliver, C.P., Houghton, B.F. 1980. Omokoroa Point land stability investigation. *Report prepared by Tonkin & Taylor for Tauranga County Council* [New Zealand]. Reference no. 4487/2. 54 pp.

Gupta, V., Miller, J.D. 2010. Surface force measurements at the basal planes of ordered kaolinite particles. *Journal of Colloid and Interface Science*, **344**, 362–371.

Huang, Y-T., Lowe, D.J., Churchman, G.J., Schipper, L.A., Cursons, R., Zhang, H., Chen, T.-Y., Cooper, A. 2016a. DNA adsorption by nanocrystalline allophane spherules and nanoaggregates, and implications for carbon sequestration in Andisols. *Applied Clay Science,* **120**, 40-50.

Huang, Y-T., Lowe, D.J., Zhang, H., Cursons, R., Young, J.M., Churchman, G.J., Schipper, L.A., Rawlence, N.J., Wood, J.R., Cooper, A. 2016b. A new method to extract and purify DNA from allophanic soils and paleosols, and potential for paleoenvironmental reconstruction and other applications. *Geoderma,* **247**, 114–125.

Joussein, E., Petit, S., Churchman, G.J., Theng, B., Righi, D., Delvaux, B. 2005. Halloysite clay minerals – a review. *Clay Minerals*, **40**, 383–426.

Kirkman, J.H. 1981. Morphology and structure of halloysite in New Zealand tephras. *Clays and Clay Minerals*, **29**, 1–9.

Kluger, M.O., Moon, V.G., Kreiter, S., Lowe, D.J., Churchman, G.J., Hepp, D.A., Seibel, D., Jorat, M.E., Mörz, T. 2016. A new attraction-detachment model for explaining flow sliding in clay-rich tephras. *Geology* (in press), DOI: 10.1130/G38560.1

Lowe, D.J. 1986. Controls on the rates of weathering and clay mineral genesis in airfall tephras: a review and New Zealand case study. Pp. 265–330 in Colman, S.M., Dethier, D.P. (eds), *Rates of Chemical Weathering of Rocks and Minerals*. Academic Press, Orlando, USA.

Lowe, D.J., Palmer, D.J. 2005. Andisols of New Zealand and Australia. *Journal of Integrated Field Science*, **2**, 39–65.

McDaniel, P.A., Lowe, D.J., Arnalds, O., Ping, C.-L. 2012. Andisols. Pp. 33.29-33.48 in Huang, P.M., Li, Y., Sumner, M.E. (eds), *Handbook of Soil Sciences*: *Vol. 1 Properties and Processes* (2nd ed). CRC Press, Boca Raton, USA.

Moon, V. 2016. Halloysite behaving badly: geomechanics and slope behaviour of halloysite-rich soils. *Clay Minerals*, **51**, 517–528.

Moon, V.G., Cunningham, M.J., Wyatt, J.B., Lowe, D.J., Mörz, T., Jorat M.E. 2013. Landslides in sensitive soils, Tauranga, New Zealand. Pp. 537–544 in Chin, C.Y. (ed), *Proceedings 19th New Zealand Geotechnical Society Symposium "Hanging by a thread – lifelines, infrastructure, and natural disasters"*, Queenstown, November 2013. The Institution of Professional Engineers New Zealand.

Moon, V.G., Lowe D.J., Cunningham M.J., Wyatt J., Churchman G.J., de Lange W.P., Mörz T., Kreiter S., Kluger M.O., Jorat M.E. 2015. Sensitive pyroclastic- derived halloysitic soils in northern New Zealand: interplay of microstructure, minerals, and geomechanics. Pp. 3–21 in Rotonda, T., Cecconi, M., Silvestri, F., Tommasi, P. (eds), *Volcanic Rocks and Soils*. Proceedings of the International Workshop on Volcanic Rocks and Soils, Lacco Ameno, Ischia Island, Italy. Taylor and Francis, London, UK.

Newman, R.H., Childs, C.W., Churchman, G.J. 1994. Aluminium coordination and structural disorder in halloysite and kaolinite by ^{27}Al NMR spectroscopy. *Clay Minerals*, **29**, 305-312.

Papoulis, D., Tsolis-Kataga, P., Katagas, C. 2004. Progressive stages in the formation of kaolin minerals of different morphologies in the weathering of plagioclase. *Clays and Clay Minerals*, **52**, 275–286.

Parfitt, R.L., Russell, M., Orbell, G.E. 1983. Weathering sequence of soils from volcanic ash involving allophane and halloysite, New Zealand. *Geoderma*, **29**, 41–57.

Parfitt, R.L., Saigusa, M., Cowie, J.D. 1984. Allophane and halloysite formation in a volcanic ash bed under differing moisture conditions. *Soil Science*, **138**, 360–364.

Singleton, P.L., McLeod, M., Percival, H.J. 1989. Allophane and halloysite content and soil solution silicon in soils from rhyolitic volcanic material, New Zealand. *Australian Journal of Soil Research*, **27**, 67–77.

Smalley, I., Ross, C.W., Whitton, J. 1980. Clays from New Zealand support the inactive particle theory of soil sensitivity. *Nature*, **288**, 576–577.

Soil Survey Staff 2014. *Keys to Soil Taxonomy*, 12th ed. USDA Natural Resources Conservation Service, USA, 362 pp.

Takahashi, T., Dahlgren, R.A., van Susteren, P. 1993. Clay mineralogy and chemistry of soils formed in volcanic materials in the xeric moisture regime of northern California. *Geoderma*, **59**, 131–150.

Takesako, H., Lowe, D.J., Churchman, G.J., Chittleborough, D. 2010. Holocene volcanic soils in the Mt Gambier region, South Australia. In Gilkes, R.J., Prakongkep, N. (eds), *Proceedings of the 19th World Congress of Soil Science "Soil Solutions for a Changing World"*, 1-6 August, 2010, Brisbane, Symposium 1.3.1 Pedogenesis: ratio and range of influence, pp. 47-50. Published at http://www.iuss.org/19th%20WCSS/Author_Main.html

Taylor, M.D., Lowe, D.J., Hardi, P., Smidt, G., Schnug, E. 2016. Comparing volcanic glass shards in unfertilised and fertilised Andisols derived from rhyolitic tephras, New Zealand: evidence for accelerated weathering and implications for land management. *Geoderma,* **271**, 91–98.

Vergaro, V., Abdullayev, E., Lvov, Y.M., Zeitoun, A., Cingolani, R., Rinaldi, R., Leporatti, S. 2010. Cytocompatibility and uptake of halloysite clay nanotubes. *Biomacromolecules*, **11**, 820–826.

Wada, S.-I., Aoki, K., Wada, K. 1977. The interior structure of spherical halloysite particles. *Clay Science*, **5**, 113–121.

Wainer, H., Lysen, S. 2009. That's funny… A window on data can be a window on discovery. *American Scientist*, **39**, 272–275.

Walrond, C. 2016. "Rock, limestone and clay – Types of clay". In *Te Ara*, the Encyclopaedia of New Zealand. http://www.TeAra.govt.nz/en/rock-limestone-and-clay/page-7 (accessed 15 November 2016).

Wilson, S.G., Lambert, J.-J., Nanzyo, M., Dahlgren, R.A. 2017. Soil genesis and mineralogy across a volcanic lithosequence. *Geoderma*, **285**, 301–312.

Wyatt, J., Lowe, D.J., Moon, V.G., Churchman, J.G. 2010. Discovery of halloysite books in a ~270,000 year-old buried tephra deposit in northern New Zealand. Pp. 39-42 in Churchman, G.J., Keeling, J.L., Self, P.G. (eds), *Extended abstracts, 21st Biennial Australian Clay Minerals Society Conference*, QUT Gardens Point, Brisbane, 7-8 August, 2010. Published at http://www.smectech.com.au/ACMS/ACMS_Conferences/ACMS21/ACMS21.html