Clay Minerals, (2016) **51**, 309–324

Global occurrence, geology and characteristics of tubular halloysite deposits

IAN WILSON[1,*] AND JOHN KEELING[2]

[1] *Withielgoose Farmhouse, Withiel, Bodmin, Cornwall PL30 5NW, UK*
[2] *Geological Survey of South Australia, Department of State Development, Adelaide, South Australia*

(*Received 29 October 2015; revised 25 May 2016; Associate Editor: Steve Hillier*)

ABSTRACT: Halloysite with tubular morphology is formed in a wide range of geological environments from the alteration of various rock types. Intrusive acidic coarse-grained rocks, such as granites, pegmatites and anorthosite, with large potash and sodic feldspars contents, are subsequently altered to kaolinite, halloysite and other clay minerals by weathering or shallow hydrothermal fluid activity. Processing to separate the halloysite-kaolinite fraction from the altered host rock provides a product which can be used as a paper filler and in ceramics and fibreglass, among other uses, with various deposits in Brazil, China, Thailand and elsewhere. In the Kerikeri-Matauri Bay district of Northland, North Island, New Zealand, volcanic alkali rhyolite was extruded as domes and cooled rapidly with fine-grained feldspar subsequently altered to halloysite. The IMERYS plant in Matauri Bay separates the clay from the quartz-cristobalite matrix with an ~20% yield of halloysite. The principal market is for high-quality porcelain and bone china that require low levels of Fe_2O_3 and TiO_2. Deposits with high levels of halloysite occur in China, Turkey and the USA. The Dragon mine in Utah, USA was recently reopened by Applied Minerals Inc. and now produces halloysite from zones of up to 100% white halloysite. Smaller occurrences of tubular halloysite are mined in China, Turkey and elsewhere from masses of comparatively pure clay that appear to have crystallized directly from solutions in which Al and Si were soluble.

KEYWORDS: halloysite, Dragon mine, Turkey, Matauri Bay, New Zealand, China, geological occurrence, chemical analyses, tubular halloysite uses.

Halloysite is a 1:1 aluminosilicate clay mineral with chemical formula $Al_2Si_2O_5\ (OH)_4.2H_2O$ when fully hydrated. Halloysite was named by Berthier in 1826 in honour of Belgian geologist Jean Baptiste Julien d'Omalius d'Halloy who previously collected samples from an occurrence near Liége in Belgium. Aspects of the mineralogy, occurrence and modification of halloysite clay minerals were reviewed by Joussein *et al.* (2005) and the main properties of halloysite are summarized in Table 1; the focus of this paper is tubular halloysite deposits with relevance to existing and emerging markets.

The hydrated form of halloysite is denoted as halloysite-(10 Å) and the dehydrated form as halloysite-(7 Å), also referred to historically as 'metahalloysite'. Halloysite-(10 Å) is the primary form that crystallizes with H_2O molecules in the interlayer space and this 3 Å thickness of interlayer H_2O is easily and irreversibly lost resulting in collapse of the interlayer spacing from 10 Å to ~7.2 Å to give halloysite-(7 Å). This is illustrated for a sample of soft white halloysite with 40% moisture collected underground at the Dragon mine of Applied Minerals in Utah, sealed immediately in a plastic container, and analysed at the then Macaulay Institute (now James Hutton Institute, Aberdeen, UK) with 40 XRD scans

*E-mail: ian.r.wilson@btinternet.com
DOI: 10.1180/claymin.2016.051.3.12

TABLE 1. Some properties of tubular halloysite.

Property	Details
Chemical formula	$Al_2Si_2O_5(OH)_4.2H_2O/Al_2Si_2O_5(OH)_4$
Hydrated halloysite	10 Å Halloysite
Dehydrated halloysite	7 Å Halloysite
Molecular weight	294.2 (hydrated), 258.2 (dehydrated)
CAS Registry Number	1332-58-7
Density (gm/cm^2)	2.1 (hydrated)–2.6 (dehydrated)
Hardness (Moh's)	1–2
Refractive index	1.534
Tubular shape maintained until	900°C
Cation Exchange Capacity	5 to ~20 meq/100 g
Morphology	Tubular-cylindrical and polygonal
Range of size of tubes	Lumen diameter = 5–30 nm Outer diameter 50–200 nm (0.05–0.20 μm) Length 50–30,000 nm (0.05–30 μm)
BET surface area	23–89 m^2 g^{-1}
Transparency	Colourless, UV transparent

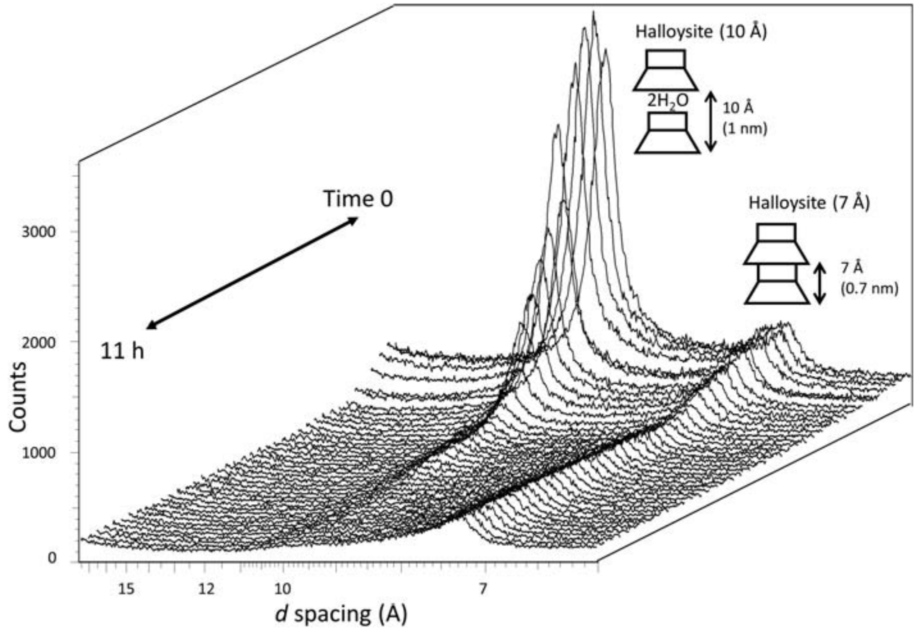

FIG. 1. Dehydration of halloysite 10 Å to the halloysite 7 Å form as shown by continuous recording of XRD data (40 scans) over an 11 h period under ambient laboratory conditions (lab temperature ≈ 20°C, relative humidity ≈ 40%). The as-received wet starting sample is a mixture of 10 and 7 Å forms. Note that the initial background is greater due to the moist nature of the sample and so the 7 Å peak intensity also appears to decrease with time. Figure courtesy of Steve Hillier, James Hutton Institute, Aberdeen, UK.

collected over a period of 11 h on exposure to air, to record the transformation from halloysite-(10 Å) (1 nm) to halloysite-(7 Å) (0.7 nm), as shown in Fig. 1.

When pure, halloysite is white or has a pale bluish tinge, but other colours are common including light-brown and dark-brown (goethite) and reddish (hematite) all due to varying levels of coloured impurities and in some instances to partial substitution of Al by Fe in the crystal lattice. Particulate manganese minerals such as lithiophorite and cryptomelane are also encountered in some halloysite samples, resulting in black-coloured patches.

The habit of tubular halloysite can be quite variable in terms of length, thickness and inner pore diameter but two distinct types are often encountered, one with circular cross section and cylindrical form, and one as polygonal prismatic cylinders with angular flat faces (Kogure *et al.*, 2013; Hillier *et al.*, 2016). Many deposits show variable mixtures of the two types. Cylindrical and polygonal prismatic halloysite each show a distinctive X-ray diffraction (XRD) pattern, Fourier Transform infrared (FTIR) spectrum, particle size range, and cation exchange capacity (CEC, Hillier *et al.*, 2016). Cylindrical tubes tend to have the largest surface area and porosity whilst polygonal halloysite tubes have smaller values for both of these properties.

TYPES OF DEPOSITS

Halloysite is encountered in a wide range of geological environments from the alteration of various rock types. Intrusive acidic rocks types such as granites, pegmatites and anorthosites are coarse-grained as they cooled slowly with potash and sodic feldspars subsequently being altered to kaolinite, halloysite and other clay minerals either by weathering or the combination of circulating hydrothermal and meteoric fluids. In New Zealand extrusive volcanic porphyritic rhyolite has a fine-grained groundmass as it cooled quickly. The feldspars forming porphyritic grains and in the groundmass were subsequently altered to halloysite by percolating fluids. In China, Turkey and the USA, zones of up to 100% halloysite are present and formed as a result of precipitation from fluids carrying Al and Si in solution and derived largely from volcanic and igneous activity.

Deposits described in the following sections are grouped by those with high concentrations of halloysite that can be mined selectively, high-quality halloysite that can be separated with processing, and selected other deposits and occurrences where halloysite and kaolinite are often mixed.

DEPOSITS WITH LARGE HALLOYSITE CONTENTS

Deposits which contain large amounts of halloysite are mined currently in the USA, China and Turkey.

Dragon mine, Utah, USA

Dragon mine is located in the Tintic District of north central Utah, some 60 miles southwest of Salt Lake City. The geology and details of alteration and mineralization at the Dragon mine are described by Cook (1957), Kildale & Thomas (1957), Morris (1964, 1985) and Wilson (2004a, 2015). The host rocks are Upper Cambrian Ajax Dolomite and Opex Formation with underlying Middle Cole Canyon Dolomite and Tintic Quartzite (Fig. 2). Volcanic andesites and latites near the Dragon mine were extruded at ~33.8 Ma with intrusion of Silver City Monzonite from 33.6 to 33.0 Ma. Extensive iron oxide deposits probably formed during the latter stages of the monzonite activity at ~33 Ma. Volcanic activity continued in the Tintic area over the period 33.9 to 18 Ma (Ken Krahulec, Utah Geological Survey, pers. comm.).

There are two main clay bodies at the Dragon mine – West and East as shown in Fig. 2. Dragon was originally an iron ore mine and subsequent mining of halloysite was mainly from underground during 1947–1976 with 1.35 million tons mined by Filtrol. Halloysite was extracted using a square-set method (5.2 × 6.0 × 7.8 ft) and hand-drills and was transported to the surface *via* a shaft and then loaded onto a lorry, which delivered raw clay to the Filtrol plant in Salt Lake City for processing into a fluid cracking catalyst (FCC) for the petroleum industry. Halloysite was replaced by synthetic zeolite catalysts in the early 1970s and the mine was closed. In 2003 exploration commenced at Dragon mine to determine available halloysite resources, with drilling campaigns in 2003, 2005 and 2006. In 2008 Applied Minerals Inc. was established, taking over the mine and resources from Atlas Mining. Further drilling was carried out in 2008–2010 in the lead up to development of an underground mine in August 2010. Drilling from 2003 to September 2015 totalled 38,410 ft (11,707 m) with all cores logged and characterized for their mineralogy and chemistry. The Western area mine is mainly monzonite with the feldspars altered to kaolinite and illite-smectite. Iron oxides (mainly hematitic) were found to have precipitated extensively in faults and fractures from hydrothermal fluids. The alteration of monzonite at the contact with the iron ore is a mix of halloysite,

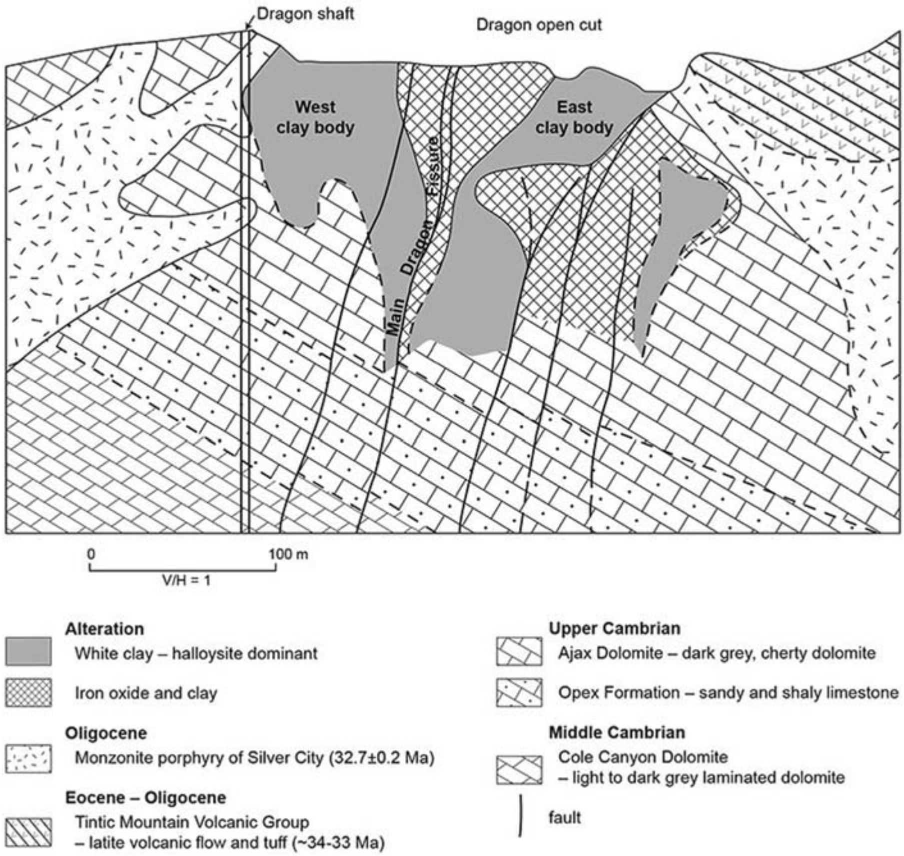

FIG. 2. Geological section, approximately west–east, through the Dragon mine, Tintic mining district, Utah, showing the distribution of halloysite ore zones – redrawn from Kildale & Thomas (1957) and Morris (1985).

kaolinite and alunite. The alunite can be removed by a wet process to leave a clay fraction containing halloysite and kaolinite. The Eastern area (underlying the old Dragon open iron ore pit) is mainly an iron ore (dominantly goethite), which formed extensively within faults and fractures. The iron alteration zones include areas where dolomite is replaced by large zones of white (and some iron-stained) clay with up to 100% halloysite formed by precipitation of Al-Si from acidic solutions circulating through the fractures.

Current processing is dry milling of selected halloysite to give a range of products marketed under the DRAGONITE™ label for various markets including flame retardant in plastics, nucleating agent in plastics, coating and additives, cosmetics, catalysts, ceramics, water purification, extended relief carriers, ceramic proppants and other uses.

The chemistry and mineralogy of eight halloysite samples from the surface and underground from East and West ore zones of the Dragon deposit are shown in Table 2. These include some very pure samples with three of the eight samples recording ~100% halloysite and five samples showing minor to trace amounts of kaolinite, quartz, alunite, jarosite and gibbsite. Other accessory minerals in the less pure halloysite include phosphate minerals (woodhouseite, wavellite and tinticite) and manganese minerals (lithiophorite, todorokite and cryptomelane). The Brunauer Emmett Teller (BET) surface area of the halloysite products ranges from 40 to 76 m^2/g. White, pure halloysite shows high brightness values due to low levels of Fe_2O_3 and TiO_2, and is mined selectively and stockpiled separately from coloured halloysite that is iron-stained mainly by goethite and hematite.

The morphology of the halloysite tubes is dominantly cylindrical with some polygonal; examples of both types are shown in Fig. 3.

TABLE 2. Chemistry, mineralogy and surface area of halloysite from Dragon Mine, Utah (beneficiated powder product).

Sample Number	1	2	3	4	5	6	7	8
Locations	Dragon East Area				Dragon West Area			
XRF – Chemistry (wt.%)								
SiO_2	45.04	45.67	44.61	46.33	46.45	45.24	45.21	45.35
Al_2O_3	39.32	38.72	38.32	39.01	37.98	38.45	38.72	38.22
Fe_2O_3	0.12	0.26	0.47	0.14	0.19	0.10	0.16	0.12
TiO_2	0.04	<0.05	<0.05	<0.05	0.05	0.01	<0.05	<0.05
K_2O	0.08	0.05	<0.05	0.01	<0.05	<0.05	<0.05	<0.05
Na_2O	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
P_2O_5	0.01	0.13	<0.05	0.04	0.17	0.02	0.16	2.02
S	0.01	0.01	0.05	0.06	0.07	0.08	0.01	0.03
LOI	14.89	14.90	16.15	14.34	15.05	15.41	15.45	14.21
XRD – mineralogy (wt.%)								
Halloysite	92.3	99.7	94.6	99.9	100	100	100	94.6
Kaolinite	7.7	trace	4.5	0	0	0	0	0.9
Quartz	0	0.3	0.6	0.1	trace	0	trace	0.5
Alunite	0	0	0	0	0	0	0	0.3
Jarosite	0	0	0.3	0	0	0	0	0.5
Gibbsite	0	0	0	0	0	0	0	3.2
BET Surface Area (m^2/g)	47			76	40		67	

Sample details of white halloysite:
Dragon East Area.
1. Borehole DDH 11-2015, Depth 502–506 ft.
2. Borehole UG 1, Depth 54–59 ft.
3. Borehole DDH 35-2012, Depth 120–158 ft.
4. Underground sample.
5. Surface sample near old shaft, Dragon West Area.
6. Surface sample.
7. West pit, centre of surface outcrop.
8. West pit, east of surface out crop.

China

In China there are small deposits of halloysite in Guizhou, Yunnan and Hunan provinces (Wilson, 2004b). In Guizhou there are four areas of halloysite in Dafang, Qingxi, Sunyi and Shijin. Dafang has many occurrences of halloysite as a result of alteration of volcanic rocks adjacent to limestone. Alumina-silica-rich solutions passed along fractures and faults and on cooling and/or interaction with limestone precipitated halloysite. The halloysite is often iron-stained and local farmers carry out mining. The deposits are very pockety and mining is done in circular pits ~1–2 m wide and down to depths of 5–10 m. One or two people work in one small area and hand-pick halloysite on the basis of colour; probably only 10–20% is whitish with the rest being iron-stained. The selected material at ~25–30% moisture is bagged and taken to an area where the clay is allowed to dry somewhat before further hand-picking. The clay is then taken to the village where a team do further hand-sorting. Very little is wasted at this stage as all the iron-stained halloysite is sold for general ceramics. The whiter halloysite is sold in lumps for use in porcelain and bone china. The lump halloysite is generally hard and whitish with some a bluish colour. Grade A with medium-grinding has 94–99% <2 µm, surface area from 60–70 m^2/g, 0.10% Fe_2O_3 and <0.01 TiO_2 with LOI 15–16%. The product is ~99% halloysite with 1% quartz. Less pure halloysite has accessory minerals such as alunite, goethite and manganese minerals.

Some of the halloysite has a bluish tinge, which disappears on drying. Production from the area is small, perhaps only 2000 tonnes/annum (tpa), and the halloysite is utilized, mainly by ceramic companies in

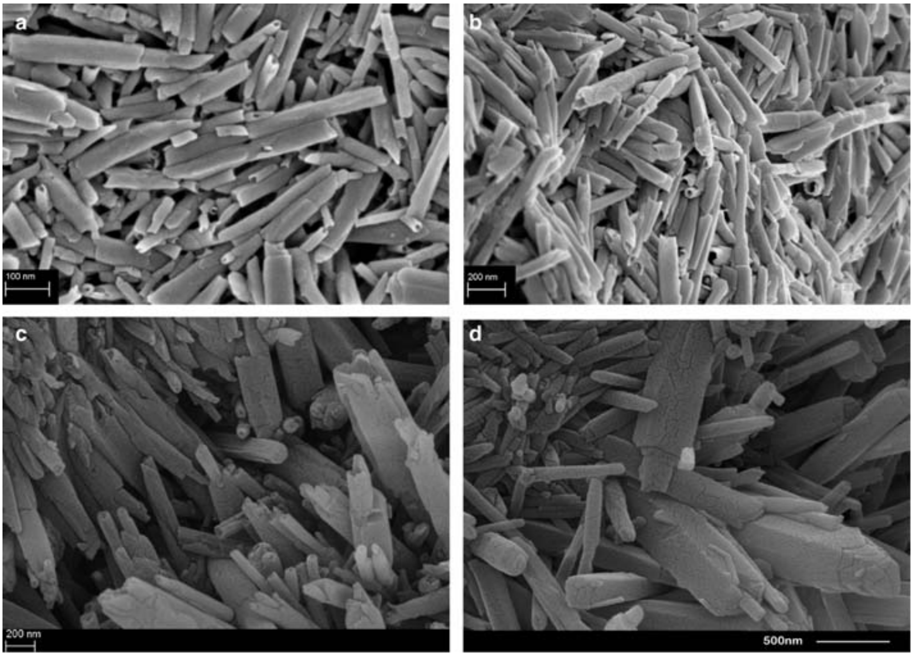

FIG. 3. SEM images of varying morphologies of halloysite from Dragon mine, Utah. (a) Cylindrical tubes – underground from J1 location. (b) Cylindrical tubes – underground 300 ft level. (c) Cylindrical and polygonal tubes – Dragon pit centre outcrop. (d) Polygonal tubes – diamond drill hole 4-2009, 235 ft.

TABLE 3. Chemistry, mineralogy, and surface area of Chinese halloysite (beneficiated powder product).

Province	Guizhou	Yunnan				
Locations	Dafang	Yilliang	Weining	Bifa - white	Bifa - Blue	Wan Jar
XRF - chemistry (wt.%)						
SiO_2	42.29	45.86	44.03	44.39	44.56	44.59
Al_2O_3	36.62	37.01	38.56	38.90	39.18	38.73
Fe_2O_3	0.08	0.10	0.15	0.33	0.05	0.11
TiO_2	0.01	<0.05	<0.05	0.07	<0.05	<0.05
K_2O	0.03	<0.05	<0.05	0.20	<0.05	<0.05
Na_2O	0.14	<0.05	<0.05	<0.05	<0.05	<0.05
P_2O_5	0.02	<0.05	<0.05	<0.05	<0.05	<0.05
S	0.10	0.01	0.01	0.02	0.01	0.04
LOI	15.86	16.81	16.76	16.02	16.16	16.40
XRD - Mineralogy (wt.%)						
Halloysite	98.5	99.9	99.9	99.8	100	100
Kaolinite	1.4	0	0	0	0	0
Quartz	0.1	0.1	0.1	0.1	0	0
Gibbsite	0	0	0	0.1	0	0
BET Surface Area (m^2/g)	50–60	48				

China, to enhance fired brightness and to increase the strength of the porcelain body, due to its inherent fineness and large surface area. Some of the halloysite is also exported to Japan and Korea for use in bone china and porcelain.

The chemistry, mineralogy and BET surface area of the Dafang halloysite from Guizhou Province is shown in Table 3 together with results from four deposits in Yunnan Province at Yiliang, Weining, Bifa and Wen Jar. Dafang has 98.5% halloysite, 1.4% kaolinite and 0.1% quartz with small Fe_2O_3 and TiO_2 contents and large BET surface area of 60 m^2/g.

The deposits in Yunnan are small in scale and are exploited by means of a combination of small trenches and adits into the hillsides. Hand-picking selects the whitish and a light-bluish halloysite, which probably represents just 10–15%, with consistent low levels of Fe_2O_3, TiO_2, K_2O, Na_2O, P_2O_5 and sulfur. All the samples have large halloysite contents (98.5–100%) with minor amounts only of kaolinite, quartz, alunite and gibbsite.

Chinese halloysite deposits contain mainly halloysite with tubular cyclindrical morphology; examples of the cylindrical form from Dafang (Guizhou) and of the prismatic/polygonal form from Yiliang (Yunnan) are shown in Fig. 4.

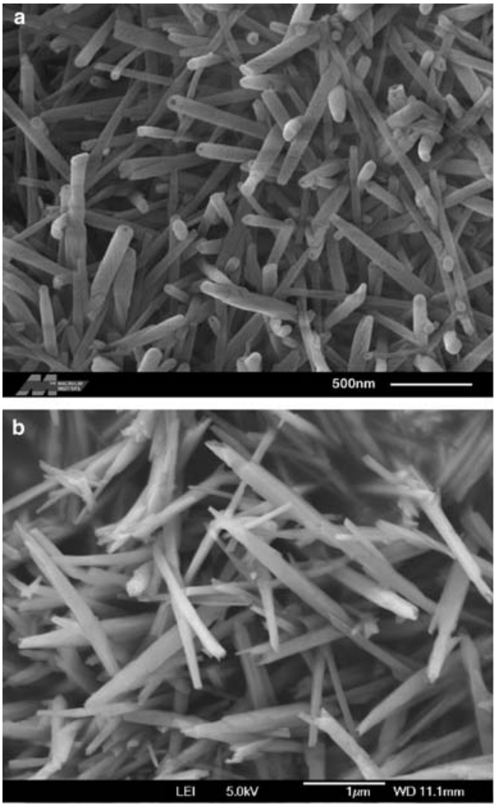

FIG. 4. SEM images of: (a) halloysite with tubular cylindrical morphology from Dafang halloysite, Guizhou; and (b) halloysite with tubular prismatic/polygonal morphology from Yiliang halloysite, Yunnan.

Turkey

Turkey has many small occurrences of halloysite in the Biga Peninsula, which were formed by acid sulfate hydrothermal alteration of andesitic tuffs (Ece *et al.*, 2008).

Eczacibaşi Esan extracts halloysite from five different locations in northwest Turkey. There are two principal pits at Turplu and Taban with three smaller occurrences at Ilicaoba, Kanasu-Kabalkar and Şahbas, all in the province of Balikesir. The production of high-quality halloysite is estimated at 5000 tpa and some of the product is shipped from Bandirma. The extraction is from open pits with small-scale galleries and shafts. Excavators are used to strip the overburden and the whitish halloysite exposed is hand-picked.

All of the Turkish halloysite deposits are associated with Miocene volcanics of NW Anatolia and formed at the contact between Jurassic limestone and the andesitic volcanics. The larger Taban deposit is stratiform between a limestone basement and the overlying volcanics. The volcanics are altered by hydrothermal activity with the formation of halloysite probably by precipitation directly from Al and Si-rich acidic fluids. Pyritization on the margins of the halloysite bodies, recrystallization of the limestone, and dissemination of manganese minerals at the contact with the limestone are all part of the process that results in halloysite precipitation. Alunite, gibbsite and illite are accessory minerals found with the halloysite. Details of selected deposits are as follows:

Turplu, ~25 km west of Balikesir, has two main quarries. Minor amounts of gibbsite are the main accessory mineral found with halloysite, with some of the volcanics altered to kaolinite. The production from Turplu is estimated at up to 2000 tpa. Hard, hand-picked whitish halloysite from No 2 mine is up to 100% halloysite in small samples but often quartz, alunite and gibbsite are present as accessories. A small part of the deposit has low Fe_2O_3 at 0.15% with TiO_2 at 0.01% and for slightly iron-stained halloysite the Fe_2O_3 is 0.45%. The halloysite surface area is 70–75 m^2/g with tubular cylindrical morphology. The clay mineralogy and chemistry of halloysite and alunite

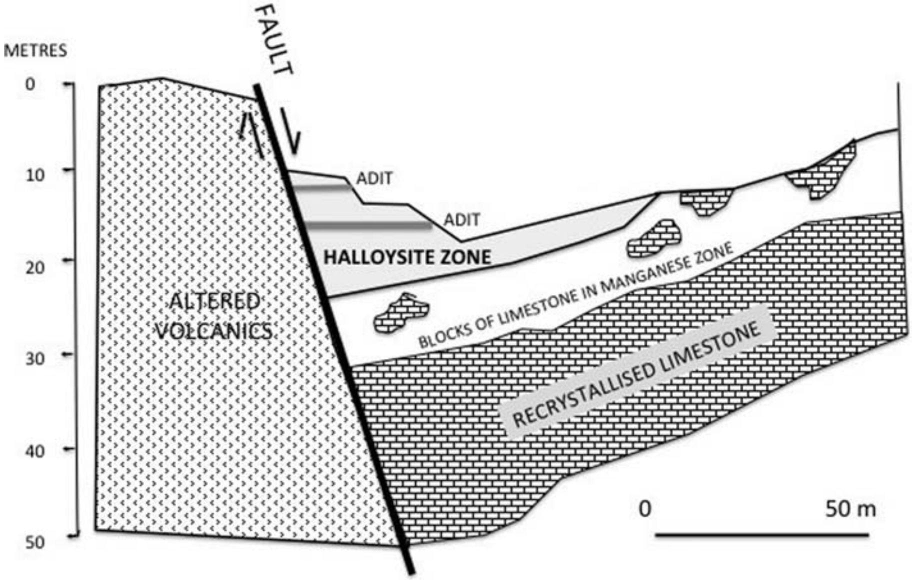

FIG. 5. Geological sketch section of Taban halloysite deposit, Turkey.

in the Turplu area were described in a study by Ece & Schroeder (2007).

At Taban, halloysite occurs in five different locations along a N20E striking fault zone of ~600 m with extraction of clay from three pits. The whitish halloysite is 15 m thick and is mined in adits and at the surface. A cross-section of the Taban deposit is shown in Fig. 5 with altered volcanics in faulted contact with recrystallized limestone at the base, passing upwards into a Mn-rich zone with entrained blocks of limestone, in turn overlain by the stratiform halloysite layer. Geophysical studies and drilling are carried out in the summer to locate additional resources along the fault zone. Electron microscopy by Saklar *et al.* (2012) of halloysite from the high-grade Taban deposit, ~3.7 km southeast of the town of Tabanköy, recorded tubular particles up to 5 μm long, but more typically between 0.1 and 1.0 μm in length and 0.04–0.05 μm in diameter. Chemical analysis of commercial halloysite product from the district, reported by Saklar *et al.* (2012), were SiO_2 46.22%, Al_2O_3 37.30%, Fe_2O_3 1.02% and TiO_2 0.21%. Acid leaching experiments on a sample from Taban deposit showed that much of the iron oxide was leachable, and was present mainly as goethite (Saklar *et al.*, 2012).

Other deposits are at Ilicaoba, Kanasu-Kabalkar and Şahbas with levels of production dependent upon sales. Hand-picked, soft, whitish halloysite from Ilicaoba mine has some zones with low Fe_2O_3 at 0.17% with TiO_2 at 0.01% and for iron-stained halloysite the Fe_2O_3 is 0.86%. The surface area ranges from 47 to 74 m^2/g.

All the deposits with high levels of halloysite in USA, China and Turkey are geologically similar in that limestone and/or dolomite are generally the host rock or proximal to the halloysite, and igneous intrusions and altered volcanic rocks are present with indication of fluid circulation and concentration of manganese and iron minerals. All areas have undergone major and minor faulting with indication of circulating Al-Si-rich solutions resulting in the precipitation of halloysite adjacent to dolomite/limestone and, in the case of the Dragon mine, as large halloysite zones within and adjacent to massive iron oxides. Deposits in China and Turkey are generally small, distributed in veins and pockets whilst the Dragon ore body is on a larger scale and associated with extensive carbonate replacement and large deposits of iron oxide (both goethite and hematite).

HIGH-QUALITY HALLOYSITE SEPARATED BY PROCESSING

New Zealand

The Kerikeri-Matauri Bay area of Northland, North Island, New Zealand, is located 240 km northeast of Auckland. Halloysite deposits in the region have been

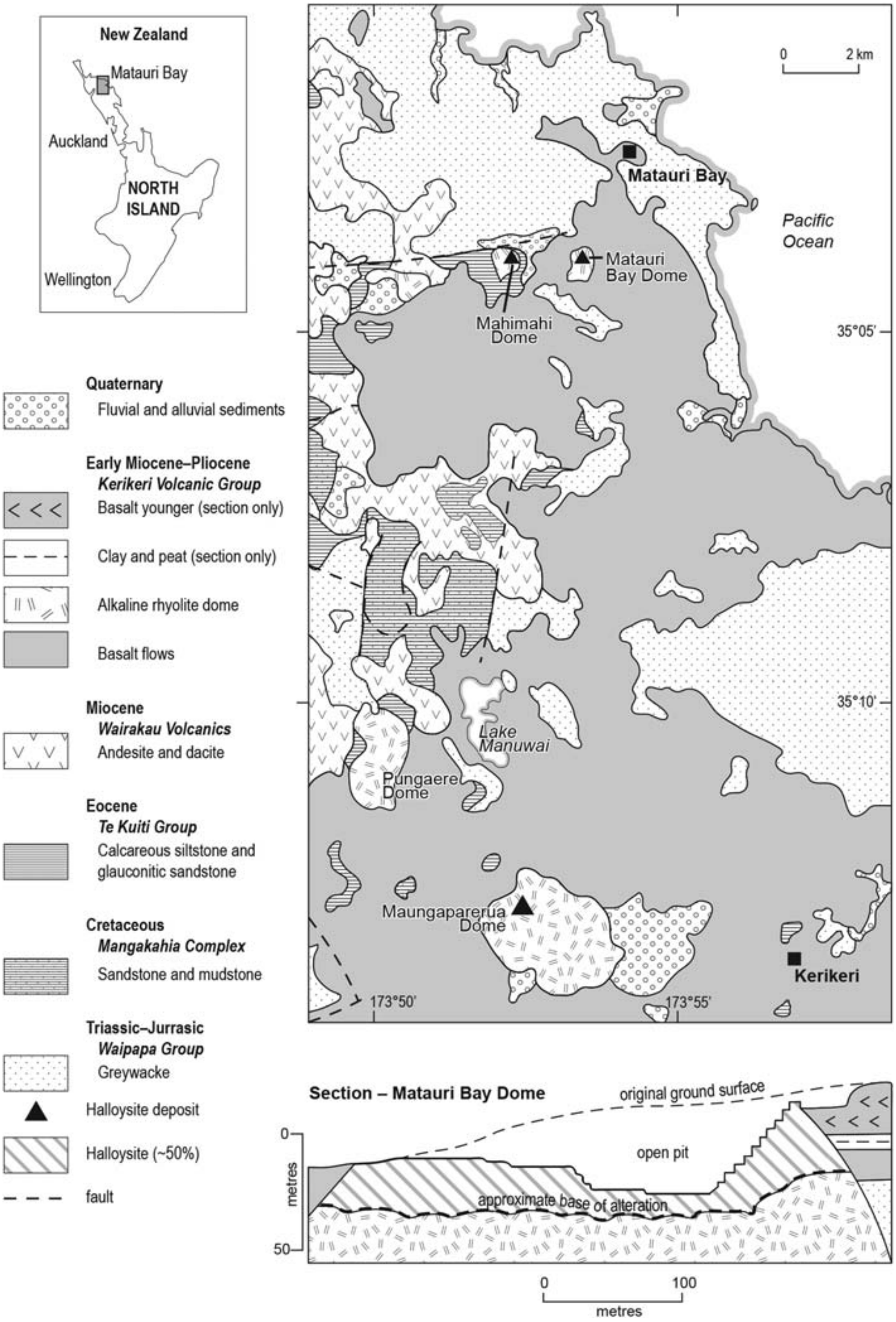

FIG. 6. Location of halloysite rhyolite domes from Northland, New Zealand.

mined and processed since the late 1940's (Townsend, 1989; Harvey & Murray, 1993; Townsend *et al.*, 2006). The halloysite deposits are hosted by alkaline rhyolite domes of Late Miocene age with the location of Matauri and Mahimahi Domes near Matauri Bay and Maungaparerua Dome near Kerikeri shown in Fig. 6.

In 1969 a wet process plant was installed at the Matauri Bay deposit and since the mid-1970s this has been the main supplier of halloysite worldwide. The operation was acquired in 2000 by IMERYS from former operators New Zealand China Clays Ltd (NZCC). IMERYS Tableware NZ Ltd currently mines raw clay from open-pit mines in the Matauri Bay and Mahimahi rhyolite domes. The rhyolite at Matauri Bay is flow foliated and spherulitic with phenocrysts of quartz, sanidine and plagioclase and minor fine-grained cristobalite and tridymite in a groundmass of quartz and feldspar (Brathwaite *et al.*, 2012). Alteration of feldspar phenocrysts and groundmass to halloysite is extensive throughout the upper 10–30 m of the rhyolite and has been attributed to hydrothermal alteration and/or weathering under subtropical climatic condition (Harvey, 1980; Townsend, 1989; Harvey *et al.*, 1990). Brathwaite *et al.* (2012) suggested that the Matauri Bay halloysite deposit was formed solely by weathering, rather than by acid-sulfate hydrothermal alteration. The absence of sulfate and phosphate minerals and hydrogen and oxygen isotope compositions of Matauri Bay halloysite are interpreted by them as being most consistent with halloysite having formed in equilibrium with meteoric waters.

Raw clay is blended from stockpiles and wet ground in a pan mill to <5 mm. This is followed by autogenous grinding at high solids content and then hydrocyclones, settling boxes and centrifuges are used to reduce levels of fine-grained silica. The beneficiated clay is thickened, then dewatered by filter pressing and the filtercake is either extruded at 37% moisture or shredded and dried to produce granules and powders with 3–4% moisture content (Luke, 1997; Townsend & Marsters, 2002). NZCC Premium grade halloysite is mainly destined for use in bone china and porcelain manufacture with key properties of high brightness, high translucency, reduction of fired sag, and low iron and titania. A typical analysis of NZCC Premium halloysite has low Fe_2O_3 (0.25%) and TiO_2 (0.07%) which gives rise to high fired brightness of 97.0% (1180°C) and 98.7% (1280°C), fine particle size of 95% <2 μm with 0.5% >10 μm. The BET specific surface area is 27.8 m^2/g. The typical product is 88% halloysite, 2% kaolinite, and 10% quartz/cristobalite. NZCC halloysite is a mixture of tubular cylindrical and polygonal morphologies (Fig. 7) with some spheroidal halloysite and platelets of kaolinite. Most of the halloysite is exported primarily for use in quality tableware, porcelain and bone china with ~15% for technical ceramics for use in molecular sieves and in manufacture of honeycomb catalyst supports (Harvey & Murray, 1997; Christie *et al.*, 2000; Clarke, 2008).

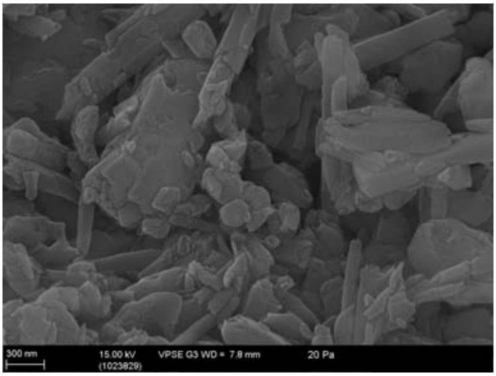

FIG. 7. SEM image of halloysite from Matauri Bay, Northland, New Zealand

In addition to the Matuari Bay and Mahimahi deposits, the Maungaparerua rhyolite dome is also altered extensively to a mixture of quartz, halloysite and allophane with minor plagioclase feldspar (Murray *et al.*, 1977). Iron oxide and titania contents are generally greater than those of Matauri Bay and Mahimahi deposits (Townsend *et al.*, 2006) due to eruption through overlying basalt (rich in titania and iron) which became assimilated into the rhyolite. The large iron and titania contents in the halloysite make it unsuitable for bone china and porcelain manufacture.

OTHER HALLOYSITE AND MIXED HALLOYSITE-KAOLINITE DEPOSITS

Despite the small number of high-grade deposits identified, halloysite with kaolinite is distributed widely across a range of geological environments. This is reflected in the deposits listed in Table 4 and the descriptions below, which while not comprehensive, provide an overview of companies, locations, types of deposit, mineralogy, main markets and estimated capacities for existing operations.

Argentina

Halloysite mined in Argentina at Mamil Choique and Buitrera in the southwest of the province of Rio Negro was reported by Cravero *et al.* (2012) to be a late Paleogene weathering product of ignimbrites and pyroclastics of rhyolitic composition. Mamil Choique halloysite is dominantly spheroidal with minor kaolinite; Buitrera halloysite occurs mostly as short tubes

TABLE 4. Some halloysite and mixed halloysite-clay deposits.

Country	Company/ Location	Type of deposit	Mineralogy	Markets	Capacity (tpa)
Argentina	Piedra Grande, Chubut Province	Altered volcanics	Halloysitic clay	Mainly ceramics	25,000
Australia	Minotaur, Poochera, South Australia	Altered granite	Kaolinite + Halloysite	Ceramics and fillers	Pilot plant
	Maralinga, Camel Lake, South Australia	Altered clay sediment	Halloysite		Prospect
Brazil	Various, Minas Gerais	Altered pegmatites	Halloysite + Kaolinite	Fillers, ceramics	50,000
	Ceramica Oxford, Santa Catarina	Altered rhyolites	Halloysite + Kaolinite	Ceramics	40,000
	Mineração Horii, Jundiapeba, SP	Altered granite	Kaolin + Halloysite	Fibre glass, ceramics	80,000
	Various, Encruziilhada, RGS	Altered anorthosite	Halloysite + Kaolinite	Ceramics, fillers	–
China	Longyan Kaolin, Longyan, Fujian	Altered granite	Kaolin + Halloysite	Ceramics – porcelain	50,000
	China Clay Co, Suzhou, Jiangsu	Altered volcanics	Mainly Halloysite	Mainly ceramics	100,000
	Changning, Jiepai, Liling, Hunan	Altered granites	Kaolin + Halloysite	Mainly ceramics	100,000
Mexico	Various locations	Altered volcanics	Halloysite + Kaolin	Ceramics	
Poland	KH Dunino Sp, Krotoszyce, Legnica	Weathered basalt	Kaolinite + Halloysite	Absorption, liners	3000
South Korea	Various, Handong-Sancheong area	Altered anorthosite	Mainly Halloysite	Ceramics	
Thailand	Imerys-MRD, Ranong Province	Altered granite	Mainly Halloysite	Sanitaryware,	73,000
USA	IM-Minerals, Bovil deposit, Idaho	Weathered granite	K-feldspar, halloysite	Being studied	Not known

that appear to crystallize on the surface of partly dissolved volcanic glass (Cravero *et al.*, 2012).

Australia

Occurrences of halloysite, associated with alunite have been reported from sites of acid groundwater discharge in Cenozoic palaeochannel sands and palaeocoastal deposits along the inland margin of the extensive Eucla Basin in southern Australia (King, 1953). Up to 4 m of halloysite was intersected during drilling for lignite in Eocene sands near a small playa lake, Camel Lake site, 63 km east of Maralinga (Keeling *et al.*, 2010). Samples from just below the surface of the dry lake bed produced halloysite composed of regular cylindrical tubes, 1 μm average length and a BET surface area of ~77 m^2/gm (Pasbakhsh *et al.*, 2013). Contaminants are alunite, gypsum and halite, with sandy patches and irregular hematite and goethite staining. The halloysite is considered to have replaced illite-smectite clay beds, below flat-lying Miocene dolomitic limestone, through the action of acid groundwater from underlying oxidized lignitic and pyritic sands (Keeling, 2015). Resources of halloysite are potentially large but the site is remote and drilling is required to test for extensions under areas of thin dune sand cover. Large resources of kaolinite in deeply weathered Mesoproterozoic granites were outlined during the 1980s by English China Clays Ltd drilling on northwestern Eyre Peninsula, South Australia. This included areas with large halloysite contents in the Tomney East and Tomney West localities of the Poochera kaolin district (Janik & Keeling, 1996). The thickness of kaolinization at

Tomney exceeds 20 m but halloysite yields were typically low at <20% and the raw clay was mostly a mixture of fine-grained halloysite with coarse kaolinite as thick stacks of platelets (Ferris & Keeling, 1993). Small zones and layers of pure white halloysite were encountered in the weathered profile in Archean greenstone at the Patch nickel mine in Western Australia. The halloysite is unusual in that the morphology consists of regular thin tubes ~30 nm in diameter and up to 30 μm long with a large cation exchange capacity (CEC) of 20 meq/100 g for the wet clay (Norrish, 1995).

Brazil

Mixed kaolinite and halloysite is typical of kaolin mined from small deposits in weathered pegmatites in the Minas Gerais district of Brazil, from weathered granitic basement in the São Paulo region, and weathered anorthosite at Encruzilhada, east of Porto Alegre, Rio Grande do Sul (Wilson *et al.*, 2006). The morphology of halloysites from these deposits is generally tubular and their characteristics were described by de Souza Santos (1993). A tubular kaolin from Piedade, São Paulo, Brazil, was described by de Souza Santos *et al.* (1965) as distinctly fibrous in appearance and composed of aggregated tubular halloysite many microns long, and between 0.03 μm and 0.15 μm wide. The clay occurred as infill in 1–3 cm-wide cracks in weathered porphyritic granite. Mineração Horii Ltda, Jundiapeba, east of São Paulo has been a major producer of kaolin in southern Brazil for paper filler clays, ceramics and fibreglass. These include deposits containing mixtures of kaolinite and halloysite. For 20 years from 1981–2001 filler clay was supplied to major paper groups and this business came to a halt with the switch to using PCC as the filler. However, Horii continues to provide a clay product for paper but the main output is for fibre glass, ceramics and other uses.

China

China is today a major kaolin producer, supplying mainly internal markets for paper-manufacture and the ceramics industry (Wilson, 2004b). Halloysite is present with kaolinite in residual kaolins extracted from the Longyan area in Fujian Province. The Longyan kaolin deposit is a whitish coarse-grained mix of tubular halloysite and stacky kaolinite platelets from alteration of feldspar in the granite. The clay is used primarily in tableware and porcelain due to the low levels of iron and titania in the altered granite. Altered Jurassic volcanics mined in the Suzhou district in Jiangsu Province are dominantly halloysite with some kaolinite and alunite; the latter is found in hard white nodules that are easy to separate.

Japan

Japanese halloysite clays are widespread, associated with weathering and/or hydrothermal alteration of Pliocene andesite lavas, andesitic breccias and Pleistocene pyroclastic deposits. These have been described by Nagasawa (1978, 1992). The area east-northeast of Nagoya in central Japan is an important source of kaolin clay, from Pliocene sediments with intercalated altered volcanic tuff, and from weathered granitic basement of Cretaceous age. Sedimentary *Kibushi* clay, a kaolinitic ball clay with organic matter, and *Gaerome* clay, a kaolinitic sand, both contain minor amounts of halloysite. Post-depositional alteration of intercalated pyroclastic tuff deposits has produced a dominantly halloysite or mixed halloysite/kaolinite clay. Halloysite in the sediments is typically in the form of short tubes, <0.5 μm long. Altered interbedded pyroclastics contain mostly spheroidal halloysite, together with platy forms and short tubes, which in places appear to have evolved from spheroidal halloysite (Nagasawa & Miyazaki, 1975). Kaolin in the weathered granite is a mixture of kaolinite and short and long halloysite tubes, which can exceed 5 μm in length. Hydrothermal kaolin with a large halloysite content is mined at various sites, including the Omura and Okuchi mines on Kyushu, Japan's southernmost main island, and at the Joshin mine in the northern part of the Gumma Prefecture in central Japan (Harvey, 1996).

Poland

Minor halloysite production in Poland has come from the Dunino deposit near Legnica in Lower Selesia. The clay is a mixture of tubular, spheroidal and platy halloysite, with some kaolinite, and is the weathering product of basalt (Komusiński *et al.*, 1981; Matusik *et al.*, 2009). Contaminants include hematite, iron hydroxides and siderite.

South Korea

The Sancheong district of South Korea has a long history of kaolin production, including clays with large amounts of halloysite. These formed by weathering of late Palaeoproterozoic anorthosites intruded into

TABLE 5. Some present and future uses and applications for halloysite.

Market sector	Present and future uses and applications for halloysite
Controlled release	Halloysite nanotube (HNT): compounds can be loaded into tubes and released at a predictable rate
Environmental remediation	Sequester pollutants from oil spills, power plants and mine sites.
	Used for oil, toluene, phenols, heavy metals and uranium
Oil remediation	Deep-water environment: absorbed de-emulsified and dispersed micro-droplets of oil will float
	Will absorb and with action of bacteria, 98% of the oil will degrade within 7 days
	Marshland Environment: will absorb oil and will prevent penetration to subsurface
Agriculture	Can load, store and release agricultural agents uniformly. Avoids need for frequent spraying.
	Agents for pesticides, fertilizers, insecticides, fungicides, herbicides, vitamins and hormones
	Applications: crops, tree crops, plants, shrubs, trees and control of fleas and ticks on animals
Paint and Coatings	Loading of biocides for sustained release protection against microbial growth and corrosion
Fluid Cracking Catalysts (FCC)	Used in conversion of gas, oils and residues to light olefin, high octane and distillates
	Tubular shape, pore-size, thermal stability and large surface area ideal to remove impurities
Catalysts	Molecular sieves: binder for zeolites to enhance drying of natural gas and air separation of liquid
	Hydrocracking Catalysts and supports: removes impurities such as metals, sulfur, nitrogen
Polymer Composites	1% in polypropylene (PP) improves mechanical properties with modulus increased by 20–25%
	Strength increased by >20% and impact resistance increased by 40%. Cycle-time reduced by 15%.
	Effective in processing of injection and blow moulding, automotive parts and household appliances.
	Loading of 1% in polyethylene (PE) similar to improvements in PP
Flame retardant plastics	Halloysite (15% lattice water) not released until 400°C – good for plastic processed at higher temperature
	Can be used as stand-alone or in conjunction with flame retardant components
Cosmetics	White, pure halloysite performs as a non-irritating skin cleanser with cosmetic agents added to tube.
	Possibilities include skin and sun care, hair, oral, colour cosmetics, detergents and bug repellents
Ceramics	Porcelain/Bone China – low iron and titania on firing body will give good translucency
	Fine particle size halloysite has significant strength and is used to blend with kaolin in ceramic bodies
	Sanitaryware – halloysite with long tubes often have good casting properties. Other markets.
Pharmaceuticals	Appropriate drugs loaded into halloysite tubes (HNT) and are released at a constant rate. Non-toxic
	Loaded with antibacterial and antiseptic agents, enzymes and proteins. Sustained-released capsules

gneissic rocks over an area of ~150 km^2 (Jeong, 1998). The anorthosites are predominantly medium to coarse-grained plagioclase feldspar, of labradorite composition, which was altered extensively by weathering under humid, temperate climatic conditions. The resulting clay is a mixture of kaolinite and halloysite that precipitated from solution and progressively filled microfractures formed by plagioclase dissolution. The halloysite is present predominantly as tubes 1–12 μm long and 0.1–0.3 μm in diameter; spheroidal forms are a minor component only (Khan & Kim, 1991). Zones of large halloysite content are concentrated in areas of more fractured rock and sites of increased porosity arising from dissolution of feldspar grains (Jeong & Kim, 1993; Jeong, 1998). Vermiculite, illite, chlorite-vermiculite and iron oxides are present as minor alteration mineral phases (Jeong & Kim, 1992).

Thailand

Halloysite is a major component of kaolin product derived from hydrothermally altered granite in Ranong Province in Thailand, an important source of dominantly halloysite clay used particularly for sanitaryware. Ranong halloysite is tubular and reportedly up to 20 μm long, which gives the clay excellent casting properties for sanitaryware ceramics manufacture (Wilson, 2013).

In the Thung Yai district, pinkish clay lenses of dominantly halloysite clay were reported by Bordeepong *et al.* (2011). These occur within 6–8 m thick kaolinitic clays that underlie sedimentary ball clay resources on the flood plain of the Tapi River in southern Thailand. The halloysite is tubular, ranging from 0.5 to 4 μm in length, 0.08 to 0.2 μm in diameter, and has high Fe_2O_3 (2.27%) and TiO_2 (2.72%) contents.

DEVELOPMENT OF NEW MARKETS FOR HALLOYSITE

The tradional uses of halloysite were limited mainly to ceramics and, in the past, catalysts. Research on halloysite (as a naturally occurring nanotube), over the past 20 y, has contributed some 700 published papers with over 9000 citations in the fields of Chemistry, Material Science, Polymer Science and Engineering.

Many of the potential new markets require comparatively pure halloysite such as those found in China, Turkey and the USA. A list of present and future uses and applications for halloysite is given in Table 5. The resource potential for halloysite in China and Turkey remains unclear, though existing deposits are quite small and pockety and need to be hand-picked to supply a high-quality product. The high grades sought by many evolving new applications are represented by only a small proportion of known resources. Lower-grade bulk resources might still be used in less demanding applications, although the price differential is substantial. Developments in beneficiation are needed to unlock the potential of more widespread mixed deposits where it may be feasible to separate halloysite from kaolinite. Exploration and characterization of halloysite deposits requires a very detailed drilling and testing program. Deposits need to be studied extensively by trenching, drilling and fully characterized in order to plan effective R&D and product development to meet the demands of changing and emerging markets.

ACKNOWLEDGEMENTS

Andre Zeitoun (President & CEO) and Eric Nedreberg (Operations Manager) of Applied Minerals. Inc are thanked for opportunities to visit Dragon mine, Utah over many years. Alex Ball and Tomasz Goral (Imaging and Analysis Centre, The Natural History Museum London) are thanked for the SEM images in Fig. 3a,b and Evelyne Delboss (James Hutton Institute, Aberdeen) for SEM images in Fig. 3c,d, Fig. 4a,b and and Fig. 7. Thanks to many mine owners and companies in various countries for permission to visit their halloysite deposits. Constructive comments and suggestions from reviewers Peter Ryan and Colin Harvey and editorial assistance from Steve Hillier are gratefully acknowledged.

REFERENCES

Bordeepong S., Bhongsuwan D., Pungrassam T. & Bhongsuwan T. (2011) Characterization of halloysite from Thung Yai district, Nakon Si Thammarat Province, in southern Thailand. *Songklanakarin Journal of Science and Technology*, **33**, 599–607.

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.

Christie T., Thompson B. & Brathwaite R. (2000) *Mineral Commodity Report – Clays.* New Zealand Institute of Geological and Nuclear Sciences, Lower Hutt, New Zealand.

Clarke G. (2008) Tubular clays. *Industrial Minerals*, March, 58–59.

Cook D.R. (1957) Ore deposits of the main Tintic mining district. Pp. 57–79 in: *Geology of the East Tintic*

Mountains and Ore Deposits of the Tintic Mining Districts (D.R. Cook, editor). Guidebook to the Geology of Utah, 12, Utah Geological Society, USA.

Cravero F., Maiza P.J. & Marfil S.A. (2012) Halloysite in Argentinian deposits: origin and textural constraints. *Clay Minerals*, **47**, 329–340.

de Souza Santos P. (1993) The use of clay particle morphology studies to characterize industrial clay deposits; examples from Brazil. *Clay Minerals*, **28**, 539–553.

de Souza Santos P., Brindley G.W. & de Souza Santos H. (1965) Mineralogical studies of kaolinite-halloysite clays: Part III. A fibrous kaolin mineral from Piedade, São Paulo, Brazil. *American Mineralogist*, **50**, 619–628.

Ece Ö.I. & Schroeder P.A. (2007) Clay mineralogy and chemistry of halloysite and alunite deposits in the Turplu Area, Balikesir, Turkey. *Clays and Clay Minerals*, **55**, 18–36.

Ece Ö.I., Schroeder P.A., Smilley M.J. & Wampler J.M. (2008) Acid-sulphate hydrothermal alteration of andesitic tuffs and genesis of halloysite and alunite deposits in the Biga Peninsula, Turkey. *Clay Minerals*, **43**, 281–315.

Ferris G.M. & Keeling J.L. (1993) *Review of exploration for kaolin near Poochera, northern Eyre Peninsula, South Australia.* Department of Mines and Energy, South Australia, Report 93/18.

Harvey C.C. (1980) *A study of alteration products of acid volcanic rocks from Northland, New Zealand*. PhD Thesis, Indiana University, Illinois, USA, 322 pp.

Harvey C.C. (1996) Halloysite for high quality ceramics. Pp. 71–73 in: *Industrial Clays*, 2nd ed. (T. Kendall, editor). Metal Bulletin Plc, London.

Harvey C.C. & Murray H.H. (1993) The geology, mineralogy and exploitation of halloysite clays of Northland. Pp. 233–248 in: *Kaolin Genesis and Utilization* (H.H. Murray, W.M. Bundy & C.C. Harvey, editors). Clay Minerals Society, Boulder, Colorado, USA.

Harvey C.C. & Murray H.H. (1997) Industrial Minerals in the 21st Century: a perspective of exploration, technology and utilization. *Applied Clay Science*, **11**, 285–310.

Harvey C.C., Townsend M.G. & Evans R.B. (1990) The halloysite clays of Northland New Zealand. Pp. 229–238 in: *Proceedings Australasian Institute of Mining and Metallurgy Annual Conference.*

Hillier S., Brydson R., Delbos E., Fraser T., Gray N., Pendlowski H., Phillips I., Robertson J. & Wilson I. (2016) Correlations among the mineralogical and physical properties of halloysite nanotubes (HNTs). *Clay Minerals*, **51**, 325–350.

Janik L.J. & Keeling J.L. (1996) Quantitative determination of halloysite using FT-IR PLS analysis and its application to the characterisation of kaolins from north-western Eyre Peninsula, South Australia. CSIRO, Division of Soils, Divisional Report 129.

Jeong G.J. (1998) Vermicular kaolinite epitactic on primary phyllosilicates in the weathering profiles of anorthosite. *Clays and Clay Minerals*, **46**, 509–520.

Jeong G.J. & Kim S.J. (1992) Kaolinites in the Sancheong kaolin, Korea: their textures, chemistry and origins. Pp. 129–135 in: *Clay Minerals, Their Natural Resources and Uses* (K. Nagasawa, editor). Proceedings, 29th International Geological Congress Workshop WB-1.

Jeong G.J. & Kim S.J. (1993) Boxwork fabric of halloysite-rich kaolin formed by weathering of anorthosite in the Sancheong area, Korea. *Clays and Clay Minerals*, **41**, 56–65.

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

Keeling J.L. (2015) The mineralogy, geology and occurrences of halloysite. Pp. 96–115 in: *Natural Mineral Nanotubes: Properties and Applications* (P. Pasbakhsh & G.J. Churchman, editors). Apple Academic Press Inc., Oakville, Canada.

Keeling J.L., Self P.G. & Raven M.D. (2010) Halloysite in Cenozoic sediments along the Eucla Basin margin. *MESA Journal*, Department of Primary Industries and Resources, South Australia, **59**, 9–13.

Khan A.M. & Kim S.J. (1991) Mineralogy of halloysite from Suryun, Korea. *Geological Bulletin, University of Peshawar*, **24**, 63–70.

Kildale M.B. & Thomas R.C. (1957) Geology of the halloysite deposit at the Dragon Mine. Pp. 94–96 in: *Geology of the East Tintic Mountains and Ore Deposits of the Tintic Mining Districts* (D.R. Cook, editor). Guidebook to the Geology of Utah, **12**, Utah Geological Society, USA.

King D. (1953) Origin of alunite deposits at Pidinga, South Australia. *Economic Geology*, **48**, 689–703.

Kogure T., Mori K., Drits V.A. & Takai Y. (2013) Structure of prismatic halloysite. *American Mineralogist*, **98**, 1008–1016.

Komusiński J. Stoch L. & Dubiel S.M. (1981) Application of electron paramagnetic resonance and Mössbauer spectroscopy in the iInvestigation of kaolinite-group minerals. *Clays and Clay Minerals*, **29**, 23–30.

Luke, K.A. (1997) Geology and extraction of the Northland halloysite deposits. Pp. 193–198 in: *New Zealand Minerals & Mining Conference Proceedings*, Ministry of Commerce, Wellington, New Zealand.

Matusik J., Gaweł A., Bielańska E., Osuch W. & Bahranowski K. (2009) The effect of structural order on nanotubes derived from kaolin-group minerals. *Clays and Clay Minerals*, **57**, 452–464.

Morris H.T. (1964) *Geology of the Eureka Quadrangle Utah and Juab Counties, Utah.* Geological Survey

Bulletin 1142-K, United States Government Printing Office, Washington.

Morris H.T. (1985) Geology, ore bodies and halloysite deposits of the Tintic Mining District, Pp. 40–53 in: *Field Trip Guidebook, Clay and Clay Minerals.* Western Colorado and Eastern and Central Utah. International Clay Conference, Denver.

Murray H.H., Harvey C. & Smith J.M. (1977) Mineralogy and geology of the Maungaparerua halloysite deposit in New Zealand. *Clays and Clay Minerals*, **25**, 1–5.

Nagasawa K. (1978) Weathering of volcanic ash and other pyroclastic materials. Pp. 105–123 in: *Clays and Clay Minerals of Japan* (T. Sudo & S. Shimoda, editors). Developments in Sedimentology **26**, Elsevier, Amsterdam.

Nagasawa K. (1992) Geology and mineralogy of kaolinitic clay deposits around Nagoya. Pp. 1–15 in: *Clay Minerals, Their Natural Resources and Uses* (K. Nagasawa, editor). Proceedings, 29th International Geological Congress Workshop Kyoto, WB-1, Hammatsu, Japan.

Nagasawa K. & Miyazaki S. (1975) Mineralogical properties of halloysite related to its genesis. Pp. 257–265 in: *Proceedings International Clay Conference*, 1975 (S.W. Bailey, editor). Applied Publishing Ltd, Wilmette, Illinois, USA.

Norrish K. (1995) An unusual fibrous halloysite. Pp. 275–284 in: *Proceedings 10th International Clay Conference Adelaide, Australia* (G.J. Churchman, R. W. Fitzpatrick & R.A. Eggleton, editors). CSIRO Publishing, Melbourne, Australia.

Pasbakhsh P., Churchman G.J. & Keeling J.L. (2013) Characterisation of properties of various halloysites relevant to their use as nanotubes and microfibre fillers. *Applied Clay Science*, **74**, 47–57.

Saklar S., Ağrili H., Zimitoğlu O., Başara B. & Kaan U. (2012) The characterisation studies of the northwest Anatolian halloysites/kaolinites. *Mineral Research and Exploration Bulletin (Turkey)*, **145**, 48–61.

Townsend M.G. (1989) Halloysite clay deposits in Northland. Pp. 39–43 in: *Mineral Deposits of New Zealand* (D. Kear, editor). Monograph, **13**, Australasian Institute of Mining and Metallurgy, Melbourne.

Townsend M.G. & Marsters S. (2002) Northland halloysite – past, present and future. Pp. 139–142 in: *Proceedings of the AusIMM 2002 Annual Conference*, publication series 6/02, Australasian Institute of Mining and Metallurgy, Melbourne.

Townsend M.G., Luke K.A. & Evans R.B. (2006) Recent developments in the exploration and uses of halloysite clay deposits in Northland. Pp. 59–64 in: *Geology and Exploration of New Zealand Mineral Deposits* (A.B. Christie & R.L. Brathwaite, editors). Monograph, **25** Australasian Institute of Mining and Metallurgy, Melbourne.

Wilson I.R. (2004a) Special clays from attapulgite to sepiolite. *Industrial Minerals*, November, 54–61.

Wilson I.R. (2004b) Kaolin and halloysite deposits of China. *Clay Minerals*, **39**, 1–15.

Wilson I.R. (2013) Asia kaolin market dominated by China. *Industrial Minerals*, March, 23–31.

Wilson I.R. (2015) Worldwide halloysite deposits, production and market developments. *Industrial Minerals*, February, 48–52.

Wilson I.R., de Souza Santos H. & de Souza Santos P. (2006) Kaolin and halloysite deposits of Brazil. *Clay Minerals*, **41**, 697–716.