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The rise and rise of halloysite

G. JOCK CHURCHMAN[1,*,†], POORIA PASBAKHSH[2,*,†] AND STEPHEN HILLIER[3,4,*,†]

[1] *School of Agriculture, Food & Wine, University of Adelaide, SA 5005, Australia*
[2] *School of Engineering, Monash University Malaysia, Bandar Sunway, 47500, Selangor, Malaysia*
[3] *The James Hutton Institute, Craigiebuckler, Aberdeen AB15 8QH, Scotland*
[4] *Department of Soil and Environment, Swedish University of Agricultural Sciences (SLU), SE-75007, Uppsala, Sweden*

THE ISSUES

Up until about 2005, the main application of halloysites had been as an alternative raw material to kaolinite for ceramics. Since then, however, there has been an exponential increase in studies aimed at applications of halloysite nanotubes, now widely referred to as HNTs (Fig. 1). The readily available and relatively cheap nanotubular forms of halloysite have potential uses in nanocomposites with polymers, as carriers for active agents, *e.g.* in medicine, agriculture, cosmetics and environmental remediation, as well as in nanotemplating, as supports for catalyst immobilization and as heterogeneous catalysts (Pasbakhsh *et al.*, 2013; Churchman & Pasbakhsh, 2015; Yuan *et al.*, 2015). They also hold promise for other medical uses besides drug delivery, *e.g.* in wound dressing and tissue engineering scaffolds (Lecouvet, 2015; Abdullayev, 2015), as anti-inflammatory agents (Cervini-Silva *et al.*, 2015) and in water filtration (Makaremi *et al.*, 2015). Indeed, many niche uses for halloysite, especially following their functionalization with chemical and biochemical agents, continue to be proposed and studied. These include their use for the storage of gases, including oxygen (Cavallaro *et al.*, 2014) and hydrogen (Jin *et al.*, 2015), as environmental and bio-sensors (Abdullayev, 2015; Sheng *et al.*, 2015), and for the uptake of spilled oil (Cavallaro *et al.*, 2015). A further remarkable feature is that the number of patents filed that include the word ‘halloysite’ in the title or the abstract closely parallel the rising trend in the number of halloysite scientific papers (Fig. 1). Since 2005, the number of patents has virtually equalled the number of papers on HNTs. These observations provide clear evidence that research on halloysite is readily translated into important new technologies, perhaps to a greater extent than the research on any other clay mineral.

Some of the prospective uses for halloysite are described in papers in this Special Issue of *Clay Minerals*. The issue arose out of a scientific session held during ‘Euroclay 2015’, the conference of the European Clay Groups Association (ECGA) held at Edinburgh University in July 2015, jointly with The Clay Minerals Society 52nd Annual meeting. The session was entitled ‘Halloysite: a unique, diverse and widely useful natural nanomaterial’ and was supported generously by Applied Minerals which owns and operates the Dragon halloysite mine in Utah. One of the primary aims of the session was to bring together scientists involved in all aspects of halloysite research; the broad spread of topics in this special issue reflects that aim.

The trends in Fig. 1 and the details which give rise to them have professional, personal and political implications. Professionally, it may be fun for workers or authors in this field to place their papers on the graph in Fig. 1. If you published before 2005, you may get some mathematical satisfaction to know that you occupied a large part of the whole topic for that/those years, especially if they fell before 1980. However, you should get more satisfaction to be publishing in the field now, when there are colleagues, collaborators and competitors in halloysite studies to be found worldwide and, consequently, a plethora of ideas to work on.

Personally, the reach of the possible applications of HNTs is such that many authors and readers alike may be affected by them. To take the possible role of the mineral in the treatment of cancer, for example, this illness is bound to continue to strike many, thanks to

*E-mail: jock.churchman@adelaide.edu.au; pooria.pabakhsh@monash.edu; stephen.hillier@hutton.ac.uk
†Guest Editors
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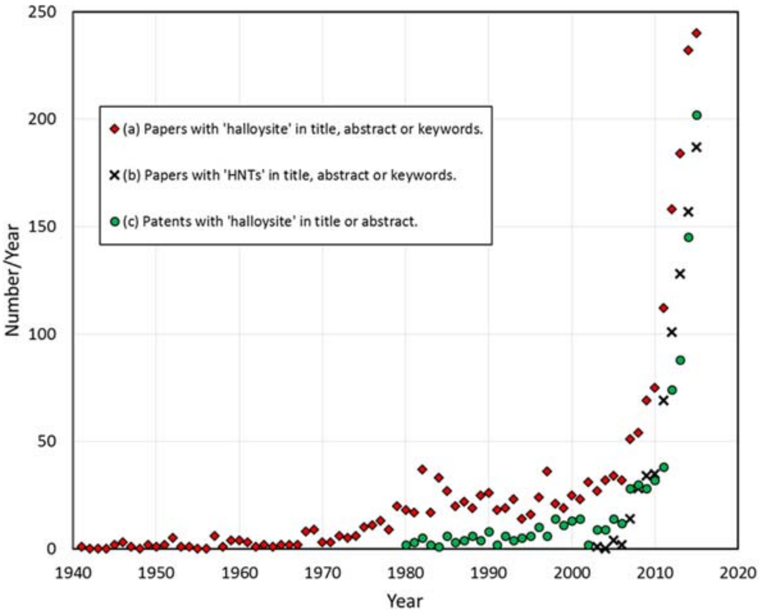

FIG. 1. Numbers of scientific papers published each year up to 2015 according to the appearance of (a) halloysite (diamonds) or (b) halloysite nanotubes (HNTs) in the Article Title, Abstract or Keywords (both sourced from Scopus© database) and (c) numbers of patents filed per year with halloysite in Article Title or Abstract (source Espacenet).

increased ageing and perhaps also other aspects of the modern world. Those who have already succumbed have been subjected to systemic treatments with overall chemotherapy. It is a sledgehammer designed to crack nuts, so to speak, and it is painful and debilitating, with possible long-term negative effects, even if successful. It is a source of some hope, combined with professional satisfaction, to hear about the role that halloysite may have to play in targeted drug delivery and/or the extraction of cancer cells from circulation through the body.

And then there are the political implications. Unfortunately, funding imperatives mean that scientists must play the political game, at least to some extent. The steep increase in applications for, and interest in, halloysite that is illustrated by Fig. 1 shows that a material that once had limited known uses, but, in addition, a high curiosity value thanks mainly to its unusual morphology (*e.g*. Hofmann *et al.*, 1962), has blossomed within use-oriented disciplines (nanoscience and nanotechnology) that did not exist just a few years ago. This illustrates the broader issue for administrators of science and funding agencies to raise with their political masters of the value of supporting research without obvious extensive practical applications in the hope that persistence and intensive study have a chance of reaping large rewards. The story of halloysite and HNTs once again shows that many of the best returns from investment in research can come from apparently irrelevant studies that are largely driven by the curiosity of scientists, admitted frankly to often be their own deepest motivation for research. The history of science is replete with examples of this (*e.g*. Holmes, 1965; Chambers, 1997; Gribben, 2002; Bryson, 2003; Wikipedia).

These examples include the case of Henry Cavendish (1731–1810), who was so motivated by curiosity alone that he hardly published anything, yet first isolated carbon dioxide and hydrogen and accurately obtained the weight of the Earth. They also include that of James Hutton (1726–1797), the founder of Geology, with all-encompassing ideas that were unheralded in his time, but have become of fundamental importance since. Then there was Alexander Fleming, whose accidental discovery of penicillin in 1928 has led to many millions of lives being saved and extended ever since. More recently, John O'Sullivan and colleagues at CSIRO in Australia, working on a failed experiment in radio-astronomy in the 1990s, incidentally completed the requirements for the development of Wi-Fi that is now proving so useful everywhere. It seems that many of the most outstanding discoveries often come along when the objectives are either vague, non-practical or aimed in other directions. Even so, "chance favours the prepared mind", according to Louis Pasteur in 1854 (Wikiquote) and discoveries tend to be made by those who are observant and have open flexible minds. Who knows where halloysite will ultimately prove most useful? Already the possibilities exceed anything that was thought of in 1980, let alone as recently as 2005. At least the field has been well prepared by those who have devoted their time and thoughts to this most interesting mineral in the past.

THIS ISSUE

Seven of the papers in this special issue were presented at Euroclay 2015 in Edinburgh. However, such is the rate of acceleration in the output of halloysite research (Fig. 1) that nine other papers have been included to complete this issue in order to keep pace with this trend. The papers are presented in the sequence: (1) geology and occurrence (one paper); (2) types, mineralogy and properties (six papers); (3) applications (six papers); and (4) applied studies (three papers).

Wilson & Keeling's (2016) paper describes the characteristics of most known commercial, or potentially commercial, halloysite deposits, in terms of both their geological settings and also some of the main commercially important properties of the halloysites mined. These properties include their purity, composition, shape, colour and admixed minerals.

Hillier *et al.* (2016) next survey the mineralogical properties of a wide range of HNTs. These authors describe systematic relationships between features in their X-ray diffraction patterns and infrared spectra that reflect variations in the size, shape and other physical characteristics of the HNTs. Larger prismatic tubular halloysites are interpreted as forming from smaller cylindrical tubular halloysite as a result of continued growth. The relationships elucidated between mineralogical characteristics and physical properties of HNTs should lead to a more systematic understanding of the natural variation in their properties and hence improved prediction of their behaviour. They should therefore assist in the selection and assessment of suitable HNTs for specific technical applications.

Not all halloysites are tubular and Cunningham *et al.* (2016) describe the novel occurrence in vermicular 'book' form of halloysite in tuffs from New Zealand. They propose a mechanism for their formation that involves transformations from spherical, tubular and also platy forms. The book form is classically attributed to kaolinite. This observation again reminds us that morphology alone is not an unequivocal indicator of mineralogy.

Gray *et al.* (2016) found that surveys of the somewhat disparate published data on the cation exchange capacity (CEC) of halloysite, *e.g.* by Bailey (1990) and Joussein (2005), show values encompassing a wide range, from ~2 to 60 cmol(+) kg^{-1}. Through the systematic measurement of the CEC of a selection of seven pure halloysites, all in their 7 Å (dehydrated) form, these authors provide a much needed CEC baseline study including the effects of pH on CEC. Most CEC derives from pH variable sites, and variation between samples is mainly related to differences in specific surface area.

The adsorption properties and characteristics of the surface sites of halloysite are key for many applications of HNTs and Maziarz & Matusik (2016) investigate the adsorption of Pb(II), Cd(II), Zn(II) and As(V) on acid-activated, calcined and untreated samples of mixed halloysite/kaolinite ores from a Polish commercial deposit. Both acid activation and calcination enhances the adsorption of the bivalent metal cations, whereas As(V) adsorption was greatest on the untreated halloysite.

Through a mix of review and new data, Churchman *et al.* (2016) explore various aspects of the formation, structure and morphology of halloysite, placing emphasis on its diversity. The role of water, pH and other variables in the formation of halloysite, particularly in soils, is reviewed. In addition, the opposite charges on silanol and aluminol surfaces across the interlayer space over all but extreme pHs are suggested as a new idea for a driving force behind the intercalation of water in halloysite. Intercalation with organic molecules is employed to probe the structure of halloysite, and the contrasting behaviour with that of kaolinite together with some similarities to that of dickite seems to provide further support for a distinctive 2-layer periodicity in the layer stacking sequence of halloysite. The various roles of Fe in influencing halloysite morphology either by isomorphous substitution or as external accessory Fe-oxides are also reviewed, pointing to a complex topic to unravel.

In another review, Cravero & Churchman (2016) explore the occurrence and formation of spherical halloysites. Consideration is given to such factors as their origins, relationships with volcanic glass and allophane, with crystalline rocks, with iron, rock fabric and organic matter as possible contributors to the occurrence of halloysite with spherical, spheroidal and related shapes. This review concludes that much still remains to be learnt about spherical halloysite, as for other forms of the mineral.

Six papers are all concerned with the nanotechnological applications of HNTs, which has been the main driver of the recent surge in research and technology activity that is shown in Fig. 1. Konnova *et al.* (2016) describe how the deposition of magnetically modified HNTs onto yeast cells is achieved without compromising their viability. Such nanocoated cells are a step in the development of "cyborg" microorganisms laden with their HNTs "backpacks".

Khunová *et al*. (2016) also describe an application involving magnetically modified halloysite nanotubes (mHNTs). Its successful incorporation into a biodegradable polymer (poly ε-caprolactone) produces a nanocomposite with magnetic properties that can be useful in many potential applications.

The application of sodium perfluorooctanoate-modified HNTs in paper conservation is described by Cavallaro *et al.* (2016). Paper coated with a dispersion of HNTs showed improved mesoscopic structure, thermal stability and wettability. These improved properties are correlated with the loading, and consequently to the affinity between the fluorinated modified HNTs and the paper cellulose. The HNTs also contribute a flame retardant effect.

Liu *et al.* (2016) review aspects of recent research progress on polysaccharide-HNT composites for biomedical applications. Interfacial interactions, preparation methods, structure and properties of the composites are covered and some new data on biocompatibility are presented. Previous studies have shown that the biocompatibility of HNTs is often seen to be very good and hence they may be put to many uses in this field. Nonetheless, these authors identify biocompatibility as an area where more research effort is required.

Hanif *et al.* (2016) review HNTs as a delivery system with applications in anticancer therapy, sustained and controlled release drug delivery systems, cosmetics, delivery of proteins, vaccines and genes. These authors identify some characteristics of HNTs that are relevant to their use in these applications along with some of the methods for loading the tubes. They identify drug delivery as a research field that is likely to continue to expand.

In a further review, Pasbakhsh *et al.* (2016) cover a range of uses of HNTs in industry, medicine and the environment, with a particular focus on their multifunctional roles as both carriers and for enhancing material properties. The compositions include chitosan/HNT membranes as bone tissue scaffolds, polylactic acid (PLA)/HNTs membranes for food packaging applications and their antimicrobial activities, instrumented impact properties of epoxy/HNT nanocomposites and the role of HNTs in the self-healing of epoxy composites, polyacryronitrile (PAN)/HNT membranes for use in water filtration, and HNTs/alginate beads in the adsorption of contaminants such as lead.

Three papers cover aspects of halloysite applied to, or already present, in soils. Radziemska *et al.* (2016) examine the effects of additions of halloysite and calcined halloysite on the bioavailability of Ni added to soils and its uptake by Indian mustard (*Brassica juncea L.*). In a controlled experiment they show that the soil amendments reduce the Ni concentration in the plants, as well as affecting biomass and the patterns of uptake of some other heavy metals already occurring in the soil.

The final two papers of the special issue have a focus on spherical halloysite and particularly its geotechnical importance. Shaller *et al.* (2016) describe an investigation into the sudden and catastrophic failure of a dam holding water for crops on the island of Kauai, Hawaii. Seepage of deoxygenated waters through the 115-year-old dam appears to have altered the volcanic basaltic rocks and pyroclastic deposits rapidly (in a geological sense) to spherical halloysite, and has also removed Fe oxides. The poor strength of the resulting halloysite-rich zones, including spherical particles with little if any inter-particle bonding, reduced the ability of the dam to resist hydrostatic loads continuously acting on the dam and this was the principal contributor to its failure.

Finally, Moon (2016) presents a detailed review of the role of halloysite in landslides which are particularly common in weathered pyroclastics. Halloysite mineral morphology has been found to affect the rheology of remoulded suspensions, with tubular minerals having a greater viscosity and undrained shear strength than those with spherical morphologies. The review includes a survey of laboratory-measured physical parameters such as Atterberg limits and shear strength.

In summary, the aim of the Euroclay 2015 halloysite session was to bring together people and ideas from all areas of halloysite and HNT research so that they could share their different perspectives on this fascinating and often also puzzling mineral. We hope and trust that this special issue provides a lasting legacy of that aim with something for everyone interested in halloysite. It may also spark an interest in halloysite from those concerned with its many novel applications and could also lead to new and useful applications for a mineral that is already proving useful as a nanomaterial in many fields. From whichever sphere of interest they come, we hope that this collection of papers will not only provide readers with a snapshot of research on halloysite as it was in 2016, but will also pose some curly questions leading to research resources becoming channeled in the direction of halloysite.

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