

The origin of spheroidal halloysites: a review of the literature

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ABSTRACT: Tubular halloysite has many applications as a nanomaterial. Spheroidal halloysite (SPH) is the other most common form of halloysite. Its mode of formation has had different explanations, including association with allophane, or more generally, following weathering of volcanic glass. Some SPHs have formed from minerals in crystalline rocks, sometimes as an early stage of evolution into plates and/or tubes of halloysite and ultimately to kaolinite. Spheroidal halloysites can show a range of Fe contents and can occur with other forms of halloysite; they have often formed in confined environments whereas tubular halloysites apparently form in more open spaces. They have also formed on microbes or where there is a significant amount of organic matter. Generally, SPHs have often formed by rapid dissolution of volcanic glass and primary minerals. The SPHs can persist over time. They have few active edges, so interparticle interaction is poor, causing low viscosities in clay-water suspensions, poor soil stability and low adsorption capacities.

KEYWORDS: spheroidal halloysite, allophane, iron content, microbes, organic matter, volcanic glass.

Berthier (1826) described a waxy material collected by J.J. d’Omalius d’Halloy in Angleur, Liege, Belgium and named it halloysite (Daltry & Deliens, 1993). From then until 1934 the mineral was regarded as an amorphous substance with no characteristic structure or shape. An early worker (Mellor, 1908) described it as irregularly shaped, amorphous granules, with irregular surfaces and a sponge-like structure. It was later found that halloysite can adopt different forms, including elongated tubes, short tubes, spheroidal, squat cylinders, plates, *etc.* (Joussein *et al.*, 2005).

It is the tubular form that has attracted most interest for new technological applications. There is increasing research interest in new industrial applications for this form of halloysite where greater use is made of its natural tubular morphology, nano-scale diameter and contrasting chemistry and electrical charges on

external and internal surfaces. Halloysite nanotubes, commonly referred to as HNTs, have potential applications as microfibre fillers, carriers for the supply and controlled or sustained release of active agents for drug delivery and anticorrosion coatings, in nanoreactors or nanotemplates, and for the uptake of contaminants or pollutants (Pasbakhsh *et al.*, 2013). In a critical review, Yuan *et al.* (2015) described this form of halloysite as a “natural nanosized tubular clay mineral that has many potentially important uses in different industrial fields”.

For these reasons halloysite studies have focused on the tubular form and have left aside interest in other forms of halloysite, such as the spheroidal form, SPH, which is the other most common form of the mineral. From the early works of Sudo (1953) to the more recent studies of Cravero *et al.* (2009, 2012, 2014), SPH has been described as being associated with different rocks and environments and different mechanisms of formation have been proposed. According to Churchman (2000), SPH might reflect particular

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modes of formation. As discussed by Churchman & Lowe (2012), it has been associated more frequently with a fast dissolution of volcanic glass and recrystallization from supersaturated solution. The association of SPH with allophane, the Fe in its structure, specific physical environments, and biological activity, are all given as causes involved in controlling this shape of halloysite (see the reviews by Joussein *et al.*, 2005 and Churchman & Lowe, 2012 for appropriate references).

On the other hand, little is known of the possible uses that SPH could have in industry. Theng *et al.* (1982) demonstrated that phosphate adsorption by halloysite is related to particle morphology: SPH adsorbed almost half of that adsorbed by tubular forms. This is because SPH particles have few, if any, edge sites at which phosphate can adsorb. Shape is also the cause of the Newtonian flow behaviour (Theng & Wells, 1995) of SPH suspensions for which shear stress increases linearly with shear rate throughout because the clusters of spherules making up the network can presumably roll over one another like ball bearings

without the action of attractive or repulsive forces. This is a major problem in soils composed of SPH, which have a high sensitivity and little interparticle interaction (Smalley *et al.*, 1980; Moon *et al.*, 2015). Some soils in New Zealand are very sensitive because SPHs are dominant or common (Smalley *et al.*, 1980; Moon *et al.*, 2015).

The scope of the present study was to review what is known about the genesis and properties of SPH, trying to shed some light on these topics and to show the latest advances which may inspire clay researchers to continue with studies on the origin of SPH and to investigate its possible applications.

DISTINCTION AND OCCURRENCE

In a comprehensive review of halloysite, Joussein *et al.* (2005) concluded that there were ten different morphological forms of the clay mineral. Churchman (2015) summarized these into three or four general types: tubular, platy, spheroidal and prismatic. The

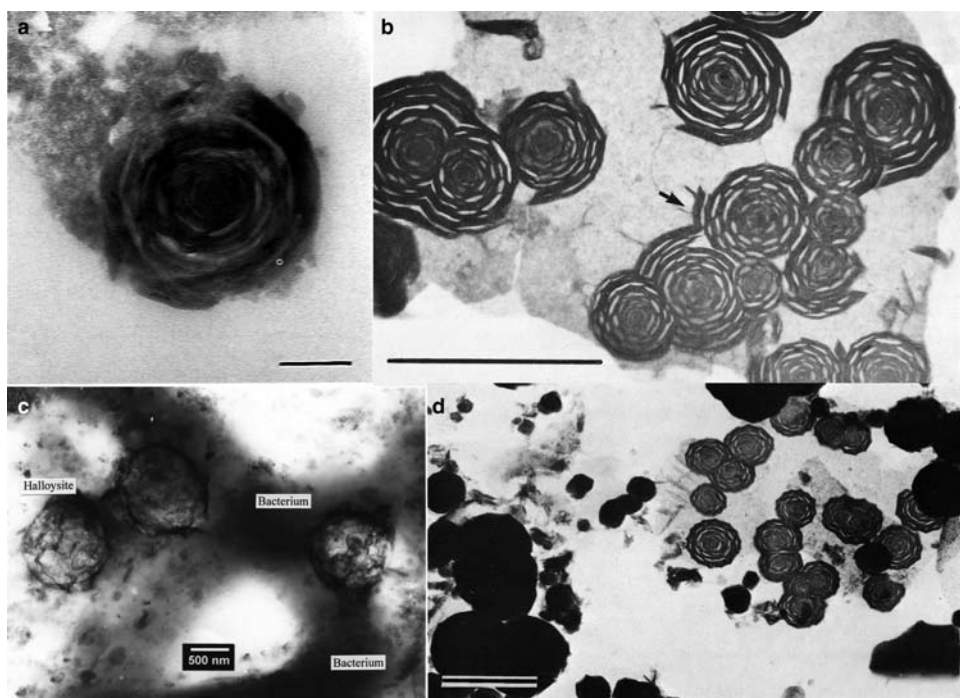


FIG. 1. TEM images of SPHs: (a) from Opotiki in New Zealand, showing probable allophane on the surface of SPH; scalebar = 0.1 μm (from Churchman *et al.*, 1995); (b) halloysite disks associated with silica flakes (mostly to the right) alongside halloysite squat cylinders (mostly to the left); the arrow indicates whorls growing around several disks; scalebar = 1 μm (from Kirkman, 1977); (c) bio-halloysite in clay bubbles on the surface of bacillus-type bacteria (from Tazaki, 2005); and (d) disks associated with silica flakes; scalebar = 1 μm (from Kirkman, 1977). Parts a, b and d reproduced with kind permission of the Mineralogical Society; part c reproduced with the kind permission of The Clay Minerals Society.

spheroidal type included the following shapes identified by Joussein *et al.* (2005): pseudospheroidal and spheroidal; cylindrical, disk; spherulitic, irregular lath with rolling edge; glomerular or “onion-like”, together described in a total of 28 reports, compared with 32 reports of the tubular types (Churchman, 2015). Actually, those are not different shapes, but are different descriptions by various authors for halloysite particles that present this particular morphology; hence all those terms have to be considered as synonyms for “spheroidal”. As described by Bailey (1990), spheroidal morphology (including rounded, ball, cabbage-like, *etc.*) consists of layers that are rolled up within the spheroid, like the structure of an onion. Upon dehydration, openings could develop between these layers, giving the aspect of disks.

Illustrations of some of the range of morphologies of SPH as seen in both transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are shown in Figs 1 and 2, respectively.

Spheroidal halloysite and HNT can be found in different environments and are formed by different processes (Joussein *et al.*, 2005); they are most commonly found in quaternary soils formed by weathering of volcanic ash, however. Spheroidal

halloysite has also been reported in older sequences as in Minnesota (Cretaceous) (Parham, 1970) and Patagonia (Early Tertiary) (Cravero *et al.*, 2009).

ORIGIN

Different sources and genetic pathways have been proposed for SPH. Table 1 summarizes information regarding parent rock and proposed processes of formation as well as the locality and references for many different SPHs.

From the early studies and, up until the work of Tazaki in the early 1980s, the differences in the processes of formation referred largely to the presence or absence of allophane as the precursor of SPH (Sudo & Takahashi, 1955; Sieffermann & Millot, 1969; Askenasy *et al.*, 1973; Kirkman, 1977; Tazaki, 1982; Nagasawa & Noro, 1987).

Since Tazaki (1982) proposed that Fe in octahedral sites has an influence on the morphology of halloysite, many studies have supported this idea (*e.g.* Churchman & Theng, 1984; Nagasawa & Noro, 1987) whereas others found quite the opposite (Papoulis *et al.*, 2004), with no involvement at all of Fe in the formation of SPHs (Adamo *et al.*, 2001;

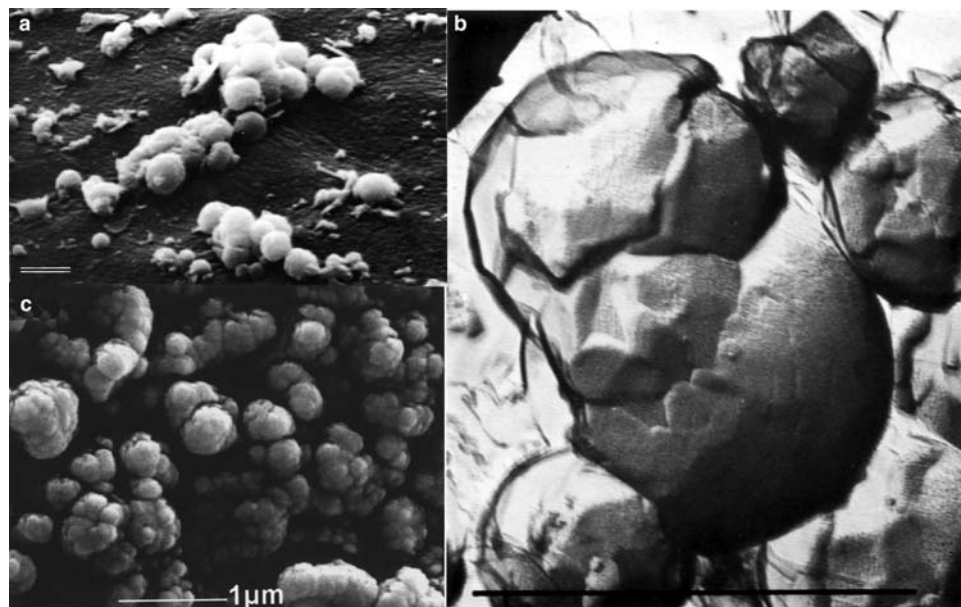


FIG. 2. SEM images of SPHs: (a) groups of SPH as squat cylinders; and (b) carbon replica of fine clay showing layered structure and intergrowth of squat cylinders; scalebars = 1 μm (both from Kirkman, 1977); (c) unification of spheres of halloysite and conversion of SPH to tubular halloysite in the 2nd stage of weathering (from Papoulis *et al.*, 2004). Parts a and b reproduced with kind permission of the Mineralogical Society of Great Britain & Ireland; part c reproduced with kind permission of The Clay Minerals Society.

TABLE 1. Summary information on origin of SPHs.

Rock type (and age)	Process	Locality	References
Subsoil from volcanic ash and pumice	Weathering	New Zealand	Birrell <i>et al.</i> (1955)
Glassy tuff	Weathering, related to allophane	Japan	Sudo & Takahashi (1955)
Mugearite	Weathering, direct precipitation	Hawaii	Nakamura & Sherman (1965) (as cited by Askenasy <i>et al.</i> , (1973)
Basalt	Weathering, associated with allophane	Cameroon	Sieffermann & Millot (1969)
Pumice beds Pliocene	Leaching by groundwaters	Japan	Nagasawa (1969)
Clays in sedimentary sequence	Weathering during the Cretaceous	Minnesota	Parham (1970)
Rhyolitic tephra and palaeosol	Weathering, <2500 y BP	New Zealand	McIntosh (1979)
Subsoil derived from Quaternary volcanic deposits	Weathering, related to allophane, from confined vesicles	Guatemala	Askenasy <i>et al.</i> (1973)
Soil clays	Weathering, porous volcanic glass, uniform confinement pressure	Mexico	Dixon & McKee (1974)
Saprolite from rhyolite and gabbro	Weathering	Japan	Nagasawa, unpublished data mentioned in Nagasawa & Miyazaki (1976)
Volcanic glass <i>via</i> allophane	Replacement of allophane	Japan	Nagasawa & Miyazaki (1976)
Rhyolitic tephra	Grown from allophane	New Zealand	Kirkman (1975, 1977, 1981)
Saprolite from granite	Alteration in fissures, coexisting forms (SPH + HNT)	Germany	Wilke <i>et al.</i> (1978)
Soils in tephra	Coexisting forms (SPH + HNT) Greater amount in humus horizons, no allophane	Japan	Saigusa <i>et al.</i> (1978)
Metakaolin	Rehydration of a metakaolin by groundwaters	Australia	Loughnan & Roberts (1981)
Granite, pumice grains and ashes	Weathering-allophane-crinkly films with >10% Fe spheroidal, tubular, Fe-free (iron reduction)	Japan	Tazaki (1982)
Rhyolite and andesite	More structural Fe content in spheroids (Embryonic halloysite) Weathering, in paddy soil	New Zealand	Churchman & Theng (1984)
Pumice	(Embryonic halloysite) Weathering, in paddy soil	Japan	Wada <i>et al.</i> (1985)
Andesitic volcanic ash	(Embryonic halloysite) Weathering	Ecuador	Wada & Kakuto (1985)
Pyroclastic	(Halloysite B) Allophane to halloysite, high Fe content	Japan	Nagasawa & Noro (1987)
Volcanic glass	Marine environment		Imbert & Desprairies (1987)
Basaltic ash	Weathering, role of Fe is not clear	Vanuatu	Quantin & Rambaud (1987)
Trachytic pumice	Weathering SPH directly from glass (Fe and K, formed mixed layer?)	Italy, volcano	Quantin <i>et al.</i> (1988)
Probably pyroclastic debris in coals	Higher Si and Fe than coexisting kaolinites	Sydney, Australia	Ward & Roberts (1990)
(Review)	SPH likely from dissolution-precipitation of amorphous particles in starting material	(Global)	Bailey (1990)

(continued)

TABLE 1. (contd.)

Rock type (and age)	Process	Locality	References
Soils from crystalline and metamorphic rocks	A horizons contain SPH or other mineralogical forms associated with allophanic forms (allophane-like particles, crinkly films), while B and C horizons contain HNT; organic matter can protect allophane (often in aggregates) and inhibit tube growth	Spain	Romero <i>et al.</i> (1992)
Anorthosite	Weathering plagioclase, from spheres to plates	Korea	Jeong & Kim (1993)
Experimental, from obsidian	From allophane to SPH		Kawano & Tomita (1995)
Laterites over basalts	HNT less Fe than SPH. Evolution from halloysite to Fe-kaolinite	Brazil	de Oliveira <i>et al.</i> (1997)
Pyroclastic deposits, Quaternary volcanism	SPH more dense and compact material, HNT: loose material	Italy	Adamo <i>et al.</i> (2001)
Volcanic glass from scoriated basalt and scoria	SPH and ellipsoidal 10 Å halloysite formed by solid-phase transformation of volcanic glass – as crinkly, sheet-like particles formed by precipitation on vesicle walls	Israel-Lebanon, <i>etc.</i> (Golan Heights)	Singer <i>et al.</i> (2004)
Felsic amphibolite	Weathering plagioclase, different steps. SPH near the fresh rock, kaolinite more weathered; SPH is the most Al-rich and Fe-poor. Chemical composition of ambient solutions is considered to mainly dictate the nature of solid phase	Greece	Papoulis <i>et al.</i> (2004)
Bacteria in soils	Microbial activity in nucleation		Tazaki (2005)
Saprolite-Trachydacitic lava (glass)	(Embryonic halloysite). Weathering	Italy	Certini <i>et al.</i> (2006)
Pyroclastic rocks Eocene	SPH associated with denser rocks	Argentina	Cravero <i>et al.</i> (2012)

Cravero *et al.*, 2016), and some (Johnson *et al.*, 1990) even found SPH with almost no iron in the structure.

Another explanation for SPH formation lies in the control that the physical characteristics of the host rock and the environment may have on the morphology, mainly relating to porosity, confining pressure, *etc.* (Dixon & McKee, 1974; Kirkman, 1977; Adamo *et al.*, 2001; Cravero *et al.*, 2012).

Some authors (Romero *et al.*, 1992; Tazaki, 2005) have also found that organic matter and microbial activity influence the formation of halloysites with spheroidal morphologies.

Relationship with volcanic glass/allophane

The transformation of allophane to SPH has been reported in Quaternary soils derived from different rocks although volcanic glass is the principal precursor

(Sudo & Takahashi, 1955; Sieffermann & Millot, 1969; Askenasy *et al.*, 1973; Kirkman, 1977; Tazaki, 1982; Nagasawa & Noro, 1987; Romero *et al.*, 1992).

Sudo & Takahashi (1955), based on SEM images, proposed that, in the initial stage, extremely fine particles of allophane (0.02 µm in mean diameter) coagulate into rounded grains that change into an aggregate of 10 Å halloysite with a low degree of crystallinity and containing shapes like twisted fibres or curled hairs. With progressive crystallization, extremely fine fibres with sharp edges and rounded grains change into aggregates consisting entirely of well crystallized halloysite minerals. As crystallization advances further, some of the crystals of hydrated halloysite may change into the dehydrated form with an accompanying greater degree of crystallinity. Sieffermann & Millot (1969) found in soils developed on basalts in zones with a dry season, that halloysite

can form in two habits: (1) as tubes only; the exclusive occurrence of tubes often coincides with the presence of amorphous material rich in thread-like, fine, fibrous particles, which may be imogolite, and (2) as globules with defined form and crystallinity; these occur in soils in which allophanes predominate as amorphous flakes. Based on the presence of amorphous material that was removed by NaOH treatment, Askenasy *et al.* (1973) considered that allophane is present in the interior of the spheres (see Fig. 1a). Kirkman (1977) reported that dilute alkali dissolves the interior of the squat cylinders of halloysite and Churchman *et al.* (1995) found that halloysite from the same region as Kirkman's (1977) samples, *i.e.* Opotiki halloysite, shows an amorphous, large-surface-area material, which is probably allophane, surrounding particles of SPH (see Fig. 1a). However, Dixon & McKee (1974), although considering allophane as a precursor, show how SPH was initiated in porous volcanic particles, and proposed that the spherical shape could be produced by the relatively uniform confining pressure experienced there. Nagasawa & Miyazaki (1976) went further and generalized that halloysites derived from the alteration of volcanic glass are spheroidal while those derived from feldspars are tubular or lath-shaped, although, in the same paper, these authors noted rounded forms in saprolites derived from rhyolite and gabbro. In 1987, Nagasawa & Noro suggested that these rounded forms might be due to a high Fe content.

Kirkman (1981) re-examining material from weathered rhyolitic tephra that was studied by Kirkman (1977), but after freeze-etching to preserve interlayer H₂O in the halloysite, found that their shapes were best described as squat ellipsoids but also observed that

some of them had given rise to elongate outgrowths. However, whereas squat ellipsoids were most common as products of pre-formed allophane, elongate ellipsoids or tubes were generally formed from feldspars.

On the other hand, Saigusa *et al.* (1978) considered it highly improbable that SPH particles were formed by aggregation of allophane spherules which were then transformed to tubular particles. In buried soils from Nambu and Ninokura tephtras, Japan, the central core of SPH with a diameter of ~ 150 Å showed neither a layer structure nor the presence of allophane spherules. Because the average diameter of allophane spherules has been estimated to be 50 Å (Henmi & Wada, 1976), at least several could be present in the core if it did consist of aggregated spherules. Both forms of halloysite, spheroidal and tubular, would seem to have formed simultaneously in those soils.

Furthermore, spheroidal forms of halloysite are often formed rapidly upon the deposition and weathering of volcanic materials. McIntosh (1979) found that halloysite largely comprising particles with a circular to spiral outline formed from pumice and a palaeosol developed from rhyolitic tephra within the past 2500 y. Koji Wada and co-workers identified a mineral which they named "embryonic halloysite" in a paddy soil from volcanic ash in Japan (Wada *et al.*, 1985), and also in a soil in Ecuador from andesitic volcanic ash (Wada & Kakuto, 1985). Both embryonic halloysites showed spherical particles, apparently dominant in the Japanese soil, but accompanied by thin flakes and rolled plates in that from Ecuador. The embryonic halloysite from both Japan and Ecuador contained a high proportion of oxalate-extractable "amorphous" material. Nonetheless, according to both

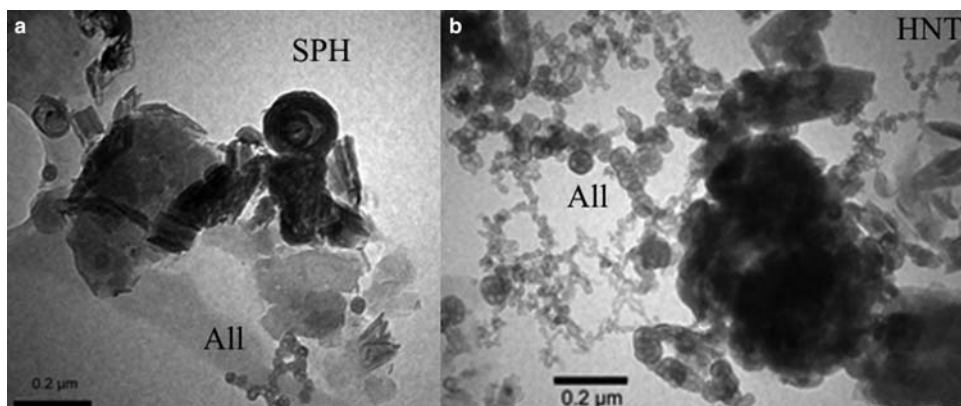


FIG. 3. Halloysites from Mamil Choique deposits, Argentina: (a) SPH and allophane (All); (b) allophane (All) and short tubes (HNT).

Wada *et al.* (1985) and Wada & Kakuto (1985) this did not indicate their formation from allophane. Certini *et al.* (2006) described the formation of embryonic halloysite (spheroids) and gibbsite from the weathering of trachyte-derived soils and saprolites in Italy, where allophane is scarce or absent.

Bailey (1990) considered that the formation of SPH occurred in the same way as the process described by Tomura *et al.* (1985) for a spheroidal kaolinite. The spheroids appeared to form by a dissolution-precipitation mechanism from the amorphous particles of the starting material. This particular mechanism could explain the prevalence of SPH in altered volcanics. The dissolution rate of glass is faster than for crystalline minerals, and the solution around the glass will therefore be highly supersaturated.

The possible transformation of allophane to halloysite has been a matter of some debate. Churchman & Lowe (2012) explained the two schools of thought in this matter: one that predominated until the 1980s which considered that allophane altered to halloysite *via* solid-phase transformation with time (Fieldes, 1955), and the other, postulated by Parfitt *et al.* (1983), which considered that it is the concentration of Si and the availability of Al in the soil which controls the formation of the alteration product, and thus halloysite can form directly from glass.

Halloysites from the Mamil Chioque deposits, formed by alteration of acid pyroclastic rocks during the early Paleocene, show the coexistence of allophane together with spheroidal and short tubes of halloysites (Fig. 3), but no clear path of evolution from one to the other is seen.

Association with crystalline rocks

Most of the halloysites derived from crystalline rocks such as granites, rhyolites or metamorphic rocks, are tubular in shape, a form which is apparently favoured when feldspars are altered (Nagasawa & Miyazaki, 1976; Nagasawa & Noro, 1987).

Romero *et al.* (1992) found abundant gels and halloysite on representative samples of soils developed on crystalline rocks which was considered quite unusual. An analogy was drawn with what occurs on volcanic rocks, where the source of clay is glass. Wilson & Tait (1977) also identified an important halloysite formation on crystalline rocks in NE Scotland, but they have interpreted this as the result of ancient weathering in warmer conditions. They found that organic matter favours high hydrolysis and gel production, and also its conservation and slow transformation in the soil. Thus 1:1 clays like halloysite

can be neofomed from gels in conditions very similar to those involved in volcanic rocks.

Jeong & Kim (1993) describe the different steps in the weathering of plagioclase to give a boxwork texture. Halloysite evolves from spheres to plates and then to tubes, after more open spaces become available. Papoulis *et al.* (2004) found a similar evolution during the weathering of plagioclase: SPH is found near the fresh rock, and, with progressive weathering, SPH converts to tubular halloysite (Fig. 2d). As weathering advances, tubular halloysite converts to platy halloysite, which in turn converts to kaolinite. The chemical composition of the ambient solutions is considered to be the main factor dictating the nature of the solid phase that forms.

Relationship with iron

Tazaki (1982) described the transformation of sheet aggregates of allophane into crinkly films which eventually grow into spheroidal particles. Tazaki claims to show this evolution in one sample, but are those particles part of an evolution or do they each represent different responses to other factors? What she found is that there are differences in the chemical composition among the different morphologies: larger Fe contents were found in crinkly films than in SPHs and those were larger than in tubular forms.

Churchman & Theng (1984) found a similar trend of chemical properties of halloysites in relation to their morphology and remarked on the possible connection between Fe content and particle shape. They suggested that under conditions conducive to halloysite formation, a low concentration of Fe in the system tends to favour crystallization into long tubes. Nagasawa & Noro (1987) concluded that halloysite morphology is controlled by structural Fe. Halloysites formed by weathering of pyroclastics that show different morphologies, mainly spheroidal, in the area of Nagoya, Japan, contain a larger amount of structural Fe than halloysites formed as a weathering product of feldspar that adopts a tubular morphology.

Papoulis *et al.* (2004) found the opposite trend: SPH was the most Al-rich and Fe-poor in the processes of alteration from SPH to platy kaolinite.

From data in the literature, Joussein *et al.* (2005) reached the conclusion that platy forms always contain relatively large amounts of Fe, while tubular particles are relatively Fe-poor whereas SPHs exhibit a wide range of Fe contents, from almost zero up to quite large values. But the Fe content does not appear to influence the formation of SPHs significantly.

Spheroidal halloysite may also occur in association with other shapes of halloysite, including tubular (e.g. Churchman & Theng, 1984; Nagasawa & Noro, 1987; Cravero *et al.*, 2014). Churchman *et al.*, (2016, this issue) report that spheroidal particles tended to have larger Fe contents, possibly including Fe oxyhydroxides, than tubular particles in mixtures. Spheroidal particles from Patagonia (Cravero *et al.*, 2016) show that halloysite derived from different deposits had small Fe contents (0.5–1.5% in samples with 90–70% of halloysite), and there were no differences associated with different morphologies. The greater Fe values found in some localities are related to the presence of smectite associated with halloysite (from ~3% up to ~20% of Fe₂O₃, depending on the amount of smectite). A smectite, a ferruginous beidellite, was formed with the Fe released from the process that formed the halloysite (Cravero *et al.*, 2014). Analysis by EDS of SPHs from those deposits in Patagonia (Fig. 4) confirm that there is no detectable Fe, similar to the halloysite from Indiana studied by Johnson *et al.* (1990).

Relationship with the fabric of the source rock

Scanning electron microscopy of halloysite-bearing weathered pyroclastic deposits of the Roccamonfina volcanic area in southern Italy, showed that halloysite with tubular morphology occurred in the free spaces, whereas halloysite with spheroidal morphology occurred in the cavities of vesicular pumices (Adamo *et al.*, 2001). The same spatial relationship was found by Cravero *et al.* (2012) in halloysites formed by weathering of volcanic-pyroclastic rocks. Spheroidal halloysites are associated with denser textures, while tubes are formed in cavities. The availability of open spaces to form tubular halloysite had already been mentioned during feldspar alteration (Jeong & Kim, 1993; Papoulis *et al.* 2004). Dixon & McKee (1974) related the formation of SPH to their precipitation in vesicles under uniform pressure. Kirkman (1977) found that flattened spheres or “disks” of halloysite formed sandwiched between silica flakes (Fig. 1b,d). These occurred alongside SPHs and SEM showed these to occur in three dimensions as squat cylinders in this (Fig. 2a,b) and other occurrences (Fig. 2c).

Relationship with microorganisms and organic matter

The influence of microbial activity in SPH formation was demonstrated by Tazaki (2005) through the

interaction between clays and microbes in microbial films from laboratory cultures derived from natural sediment (see Fig. 1c). The biological formation of primitive clay bubbles and the growth of a transitional product of spherical bio-halloysite were achieved. Romero *et al.* (1992) found in soils that A horizons could contain SPH or other mineralogical forms associated with allophanic forms (allophane-like particles, crinkly films), while B and C horizons contained tubular halloysites. One explanation is given by the role of organic matter which is always more abundant in A horizons, and which can protect allophanes (often in aggregates) and inhibit the crystal growth of tubes. Wilson *et al.* (2008) studied the influence of fungal activity in the breakdown and dissolution of primary minerals in soils. Ferromagnesian minerals were slightly altered, apparently to embryonic halloysite (spheroidal). However, Wilson *et al.* (2008) found no evidence for microorganisms as effective agents of the mineral weathering and suggested that the association with clay minerals is indirect.

Origin of spheroidal shape

Few authors have examined the mechanism which causes the spheroidal shape adopted by many halloysites. To Kirkman (1977, 1981), continuous dislocation leads to spiral growth, which, he contended, occurs rather than circular growth in the formation of both spheroids (or squat ellipsoids) and tubes (or elongate ellipsoids) of halloysite. The symmetry of squat ellipsoids is often broken by protuberances caused mainly by inclusions of e.g. glass, allophane, ferrihydrite or feldspar (Kirkman, 1981). These do not occur in tubes or elongate ellipsoids according to Kirkman (1981). He contended that only allophane develops into halloysites with squat ellipsoids whereas elongate ellipsoids (tubes) may grow from within the grains of a primary mineral such as feldspar. These ideas require further examination.

SUMMARY

Reaching a conclusion about how SPHs have formed is not easy, and there is no agreement on a unique pathway. From the review of the literature above, it is proposed that SPH is frequently associated with a fast dissolution of volcanic glass and a recrystallization from a supersaturated solution. When either volcanic glass (more frequently) or a feldspar (and other primary

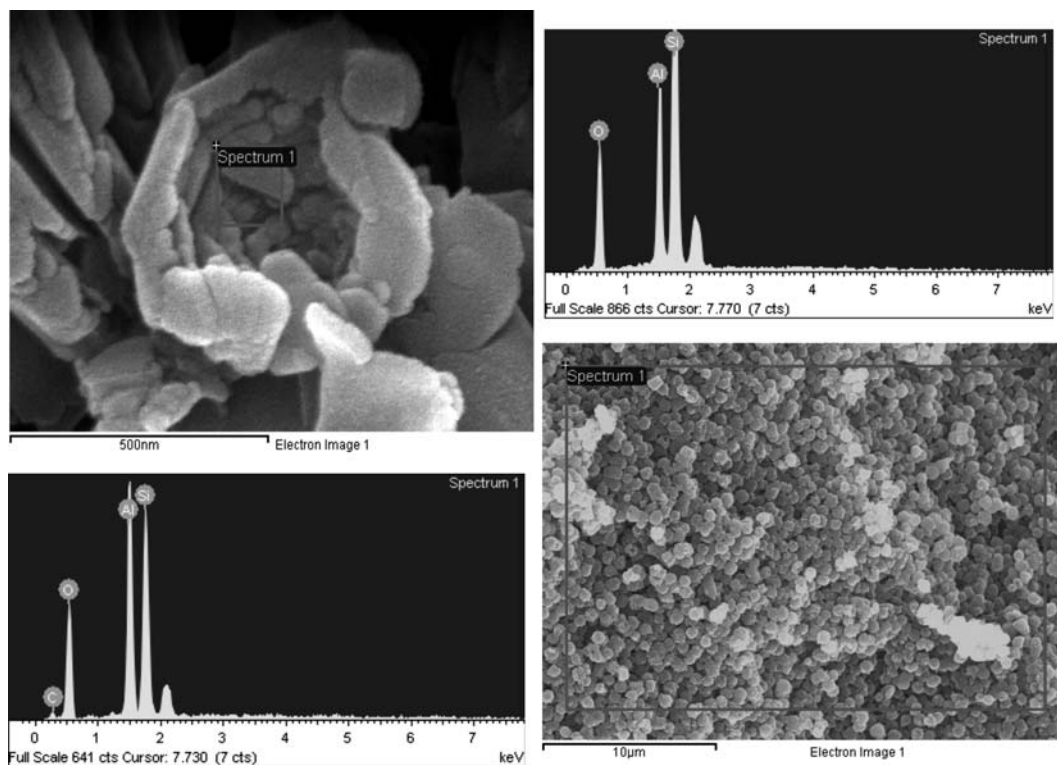


FIG. 4. SPH from Mamil Choique deposits, Argentina: SEM and EDS analyses. No iron was found in this SPH.

minerals) weathers, and the medium becomes enriched in Si and Al, depending on the relationship of these elements, either allophane, or halloysite or both, can form. If the dissolution is fast, only halloysite will form; whereas, if the process is slow, allophane will form first, and, halloysite may form after allophane. The morphology of the halloysite formed will depend on the space into which halloysite crystals can grow. If they are physically constrained, such as in vesicles under confined pressure, between cleavage faces or within silica flakes, SPH will develop whereas tubular halloysite could form in more open spaces, or by the coagulation of spheres as the alteration process proceeds and more open spaces develop.

The presence of SPH in old weathered areas, such in Minnesota (Parham, 1970) and Patagonia (Cravero *et al.*, 2009) clearly indicate that SPH can persist without transforming either to other morphological forms of halloysite or to kaolinite. In Patagonia, the climate changed from temperate humid to semi-arid after the rise of the Andes. These changes in climate would have inhibited any further alteration after SPH formation.

Kirkman's (1977, 1981) hypotheses for the mechanism causing spheroidal growth rather than tubular growth of halloysites await rigorous testing.

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