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OCCURRENCE OF SPHERICAL HALLOYSITE IN BITUMINOUS COALS OF THE SYDNEY BASIN, AUSTRALIA

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Abstract—Spherical halloysite aggregates have been identified for the first time in mineral matter isolated from bituminous coals. The spherules, found in Permian coals of the Sydney basin, New South Wales, range from 0.4 to 0.6 μm in diameter and have a delicate ring-like structure that helps to confirm the halloysite identification. They appear from their location to be related to influxes of pyroclastic debris, either directly or from nearby soils, into the original peat accumulation. Analytical electron microscopy indicates higher proportions of Si and Fe than coexisting particles of hexagonal platy kaolinite, and electron diffraction reveals a typical disordered halloysite structure. The aggregates are larger than those normally reported in soils, and comparison to growth rates in soils suggests development over a significantly longer time than that expected for accumulation of the host coal seams. The buckled structure in the ring-like pattern and the related crude polyhedral outlines probably reflect shrinkage with dehydration during the coalification process, but it may also be due to the different sample preparation techniques.

Key Words—Coal, Energy-dispersive X-ray spectroscopy, Halloysite, Morphology, Sphere, Transmission electron microscopy.

INTRODUCTION

The Sydney basin in southeastern Australia (Figure 1) is a fault-bounded Permo-Triassic foreland basin; Permian granitic intrusions and evidence of a contemporaneous subduction zone occur beyond the basin margin on the northeastern side. An extenxive coal-bearing sequence dominates the upper part of the Late Permian basin fill, which was deposited essentially in fluvial to delta-plain environments, with some alluvial fan development (Hunt and Hobday, 1984). Bentonite horizons also occur in this sequence in the northern part of the basin (Holmes, 1983; Roberts and Loughnan, 1989) providing evidence of at least some syndepositional volcanic activity.

The coals themselves are mainly of high-volatile bituminous rank, with the mean maximum vitrinite reflectance (Ro_{max}) of the seams at economic depths ranging from 1.0% in the east to 0.6% in the west (Hunt and Hobday, 1984). Most have a relatively high proportion of inherent mineral matter. The mineral fraction is typically dominated by kaolinite and a range of regular to irregular mixed-layer clay minerals; smectite is also present in some of the coals from the northern margin areas (Ward, 1978, 1989).

TEM studies as part of a general analysis of the mineral matter of Sydney basin coals (Ward, 1989) have shown at least two seams in the northern part of the basin to contain small, spherical aggregates (Figure 2) resembling those described in the literature as "chestnut shell-like particles" of halloysite (Sudo and Yotsumoto, 1977), "spherulitic halloysite" (Sudo *et al.*, 1981), "spheroidal halloysite" (Glasmann, 1982), and "spherical halloysite" (Tomura *et al.*, 1983). They are, however, slightly larger than the halloysite of this form usually reported in sedimentary materials (Wada, 1987).

Such particles have been identified in several different areas in soils and sediments derived from volcanic materials (Nagasawa and Miyazaki, 1976; Sudo *et al.*, 1981), but this is both the first reported occurrence in the sedimentary strata of the Sydney basin and the first in any ancient coal seams. As well as helping to understand the origin of the mineral matter in the coals concerned, their presence therefore provides additional data on the form and mode of occurrence of spherical halloysite aggregates in a wider geological context.

EXPERIMENTAL

The mineral fraction was isolated from coal samples from different parts of the Sydney basin (Figure 1) by oxidizing the organic matter at a temperature of about 120°C in an electronically excited oxygen plasma (Gluskoter, 1965). This technique, widely used in coal research for mineral-matter studies, destroys the organic matter under vacuum and leaves the minerals originally in the coal as a residue in essentially unaltered from. The mineralogy of the residues was determined by X-ray powder diffraction (XRD) using a Philips system and both powder-mount and oriented-aggregate techniques.

The morphology of the clay particles in the mineral residues was also investigated using a JEOL transmission electron microscope (TEM). The mineral matter isolated from each of the coals was dispersed in distilled water using an ultrasonic bath, and a drop of the suspension was placed on a carbon-coated collodion film supported by a copper grid. The grid and attached sus-

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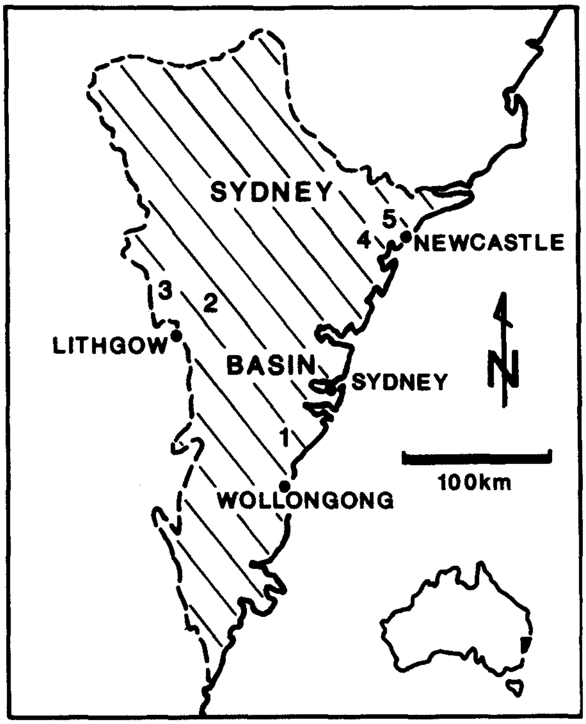

Figure 1. Location of samples studied in the Sydney basin. 1, Bulli seam, Iluka DDH 21; 2, Katoomba seam, Clarence Colliery; 3, Lithgow seam, Fernbrook Colliery; 4, Dudley seam, Pacific Colliery; 5, Victoria Tunnel seam, John Darling Colliery.

pension were then air-dried before being placed in the TEM sample chamber. Electron diffraction studies and qualitative chemical analysis using an energy-dispersive X-ray (EDX) system were made on individual particles.

RESULTS

Clay minerals in the coals

Spherical aggregates, identified on morphological grounds as halloysite, were noted as minor constituents in the mineral fraction isolated from two of the coal seams studied: the Dudley seam and the Victoria Tunnel seam of the Newcastle Coal Measures in the northern part of the basin (Figure 1). XRD of these materials (Ward, 1989; Ward *et al.*, 1989) showed them to be made up mainly of kaolinite (some of which was well crystallized) and a smectite mineral, with irregular mixed-layer clay and minor amounts of chlorite also being present in oxidation residues from the Dudley seam. A small amount of quartz was identified in the coal from both seams, along with abundant calcite and dolomite in several of the Victoria Tunnel samples (Ward *et al.*, 1989) and siderite and apatite in some of the Dudley seam material (Ward, 1989).

The other coals studied for the present paper, taken from the Bulli, Katoomba, and Lithgow seams of the Illawarra Coal Measures in the southern and western parts of the basin, were not found to contain spherical halloysite aggregates when viewed under the TEM. Although of essentially the same age as the coals studied from the north, the first two of these have a mineral assemblage made up almost entirely of well-crystallized kaolinite and a minor amount of quartz (Ward, 1989). The third contains abundant kaolinite, minor quartz, and a distinctive regularly interstratified illite/smectite/chlorite resembling material described from elsewhere in the associated sequence by Loughnan and Craig (1961).

Spherical halloysite aggregates

Morphology. The halloysite in the Dudley and Victoria Tunnel seams typically occurs as spherical to concentric ring-like particles, with diameters normally between 0.4 and 0.6 μm (Figure 2). This is larger than the diameters of about 0.2 μm reported for the spherulitic halloysite by Sudo and Yotsumoto (1977) and Kohyama *et al.* (1982), and may be a significant indicator of the time required for their formation (Wada, 1987).

Some of the particles have the appearance of peeling spheroids, with individual layers exfoliating from the central body (Figure 2a). Gaps also occur between some of the individual rings; these gaps are not symmetrical, but typically show some branching and locally link adjacent ring-like layers. Unlike tubular halloysite, which tends to be hollow in the center, the central portion of the spheroidal bodies is generally solid. Some appear to have a polyhedral outline. Clusters of the aggregates also occur (Figures 2b to 2d), with individual aggregates having a crudely polyhedral form. The spherical halloysite aggregates coexist with other clay minerals, notably smectite (Figure 2e) and hexagonal platy kaolinite (Figure 2f), which Ward (1989) suggested were of volcanic and authigenic origin, respectively.

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Figure 2. Transmission electron micrographs of spherical halloysite aggregates isolated from coal seams. Scale bars represent 2000 Å. (A) spherical halloysite with outer rings partly broken away, Dudley seam; (B) two spherical halloysite aggregates, with outer layers showing crude polyhedral outline, Dudley seam; (C) cluster of spherical halloysite aggregates, with crude polyhedral outlines, Victoria Tunnel seam; (D) cluster of spherical halloysite particles, Victoria Tunnel seam; (E) spherical halloysite (H) associated with smectite (S), Victoria Tunnel seam; (F) spherical halloysite (H) and well-crystallized kaolinite (K), Victoria Tunnel seam.

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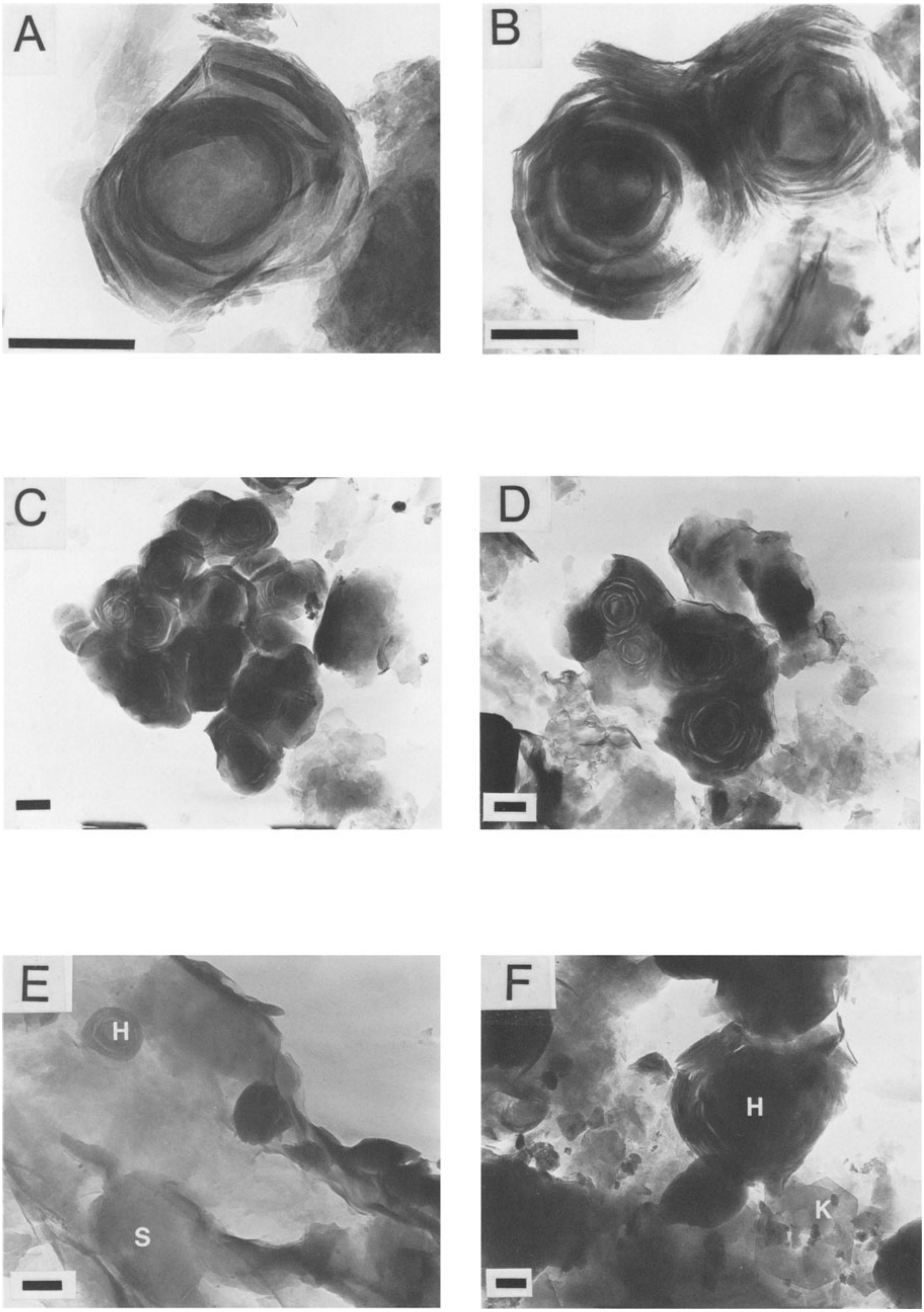

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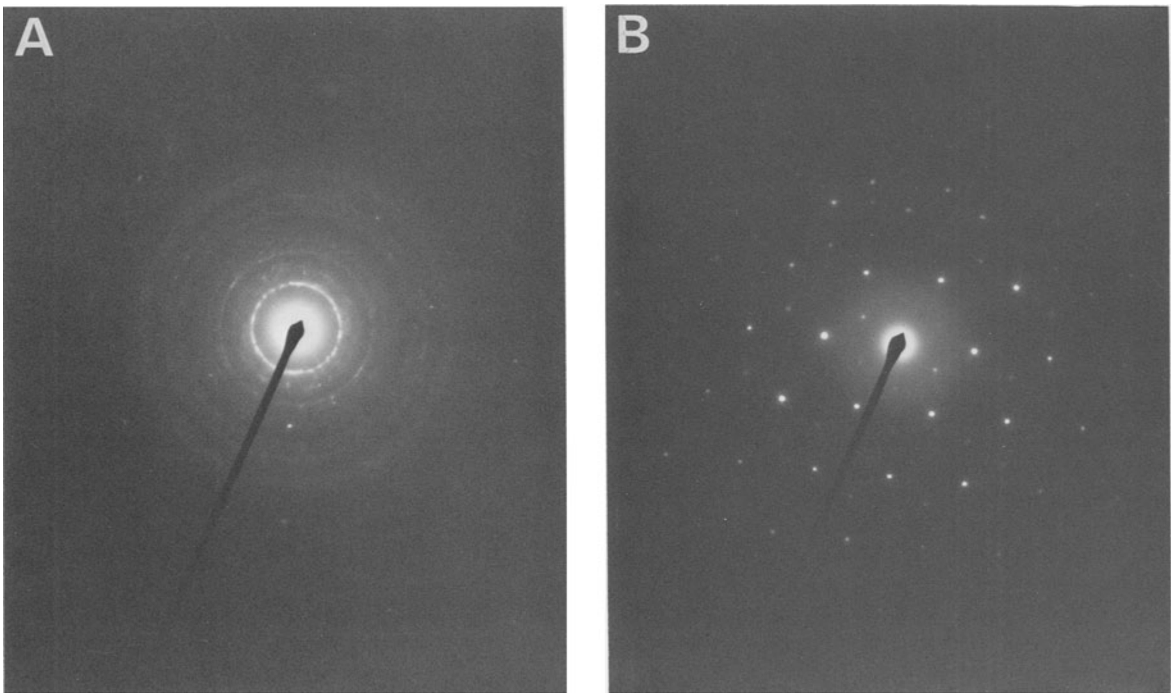

Figure 3. Electron diffraction patterns of (A) spherical halloysite aggregates and (B) well-crystallized kaolinite, Victoria Tunnel seam.

Electron diffraction. Electron diffraction patterns obtained from different parts of various aggregates in the mineral fractions (Figure 3a) are similar to the patterns reported for spherical halloysite by Sudo *et al.* (1981). They show broad and very weak diffraction rings, which Brindley and De Kimpe (1961) indicated were diagnostic. The hexagonal-spot electron diffraction pattern obtained from one of the platy kaolinite particles in the Victoria Tunnel seam is also shown for comparison in Figure 3b.

Elemental analysis. Typical EDX data for spherical halloysite aggregates and well-crystallized kaolinite particles isolated from the Victoria Tunnel seam are shown in Figure 4. The halloysite particles appear to have a lower Al/Si ratio than the kaolinite and also to contain some Fe, features consistent with the observations on spherical halloysite of Tazaki (1982). A small amount of potassium is also present, the most likely source of which, if not the halloysite, is the coexisting mixed-layer clays or smectite.

ORIGIN OF THE HALLOYSITE NODULES

Spherical halloysite is a common component of soils derived from the weathering of volcanic ash and pumice (Aomine and Wada, 1962; Sudo and Yotsumoto, 1977; Kirkman, 1981; Glasmann, 1982; Wada, 1987). The leaching of silica and bases from the ash is thought initially to form allophane and imogolite (Wada, 1987), with the halloysite developing slowly from these components at depth. The proximity of the occurrences in the Sydney basin to the active northern margin, and the occurrence in the host coals of smectite and discrete bentonite beds, also suggest a volcanic origin for the halloysite aggregates described here.

Wada (1987) indicated that incorporation of Al in soil humus may inhibit formation of the halloysite precursors (allophane and imogolite) in surface weathering conditions, a factor that may have been significant if the volcanic ash fell directly into the peat-forming swamp. Breakdown of the ash to form the halloysite and its precursors could, however, have occurred at depth in the peat bed, in which new humus was no longer forming. Alternatively, the halloysite could have been formed in less organic-rich volcanic soils developed outside the swamp environment and washed in with other detrital components of the mineral matter. The fact that the aggregates were not disintegrated by the ultrasonic treatment used in sample preparation suggests that they were capable of surviving such a transportation process.

Drawing on the occurrence of spherical halloysite in soils of different ages, Wada (1987) also suggested that the size of the aggregates is related to the length of time over which they developed. Wada's data suggest that

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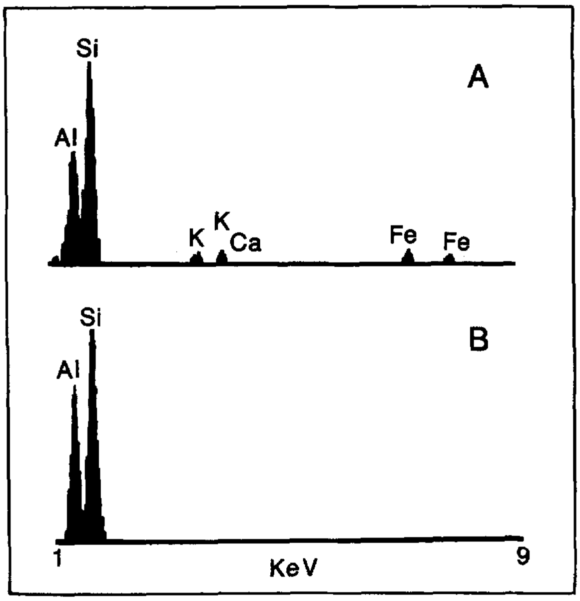

Figure 4. Energy-dispersive X-ray spectra from (A) spherical halloysite aggregates and (B) well-crystallized kaolinite, Victoria Tunnel seam.

the aggregates in the Sydney basin coals developed over at least 30,000 and possibly more than 100,000 years. Such an interval, particularly at the upper level, could significantly exceed the time required to build up the coal seams themselves. Stach *et al.* (1982) indicated from typical peat accumulation rates and compaction factors that one meter of bituminous coal probably represents accumulation over 6000 to 9000 years, and the Dudley and Victoria Tunnel seams where sampled are only 2 and 3 m thick, respectively.

Halloysite(10Å) is very susceptible to dehydration in dried air, in a vacuum (Kohyama *et al.*, 1978), or at moderately high temperatures in atmospheric conditions, forming halloysite(7Å). Kohyama *et al.* (1978) showed that this dehydration causes halloysite to segregate into "units," with crevices developing between them. Tomura *et al.* (1983) noted similar changes in morphology for spherical halloysite and indicated that the changes can be used to distinguish spherical halloysite from otherwise similar spherical kaolinite bodies.

The oxygen-plasma ashing process used to isolate the mineral matter from the coal or dehydration of the material in the vacuum chamber of the TEM could have converted halloysite(10Å) to halloysite(7Å) and produced the separated ring-like structures and polyhedral outlines noted in the Sydney basin aggregates. The process of rank advance, however, also involves subjecting the coal to burial temperatures >100°C for considerable periods (Hood *et al.*, 1975), and, thus, could have produced the same features in the halloysite, regardless of the sample preparation technique.

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