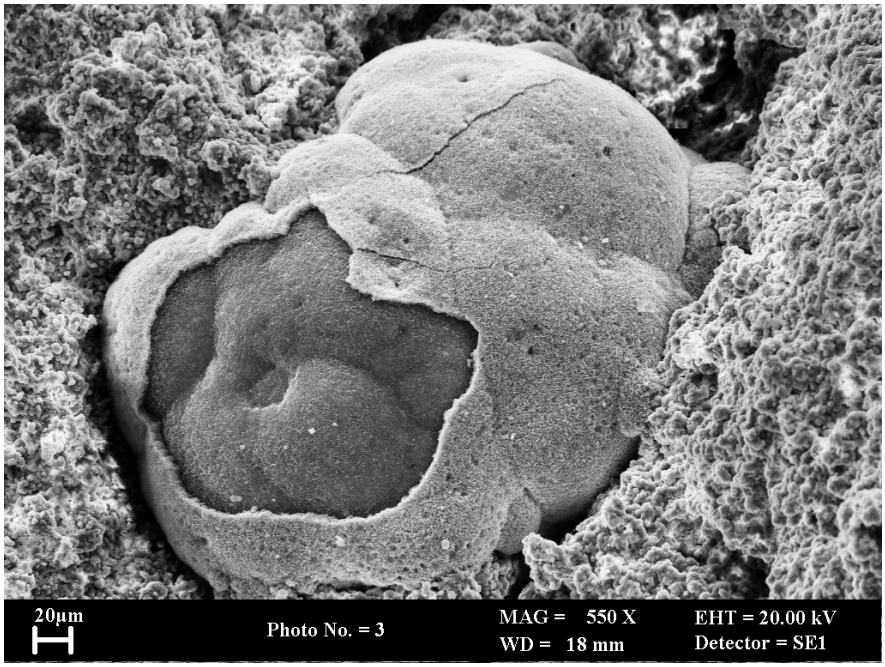
British Geological Survey
NATURAL ENVIRONMENT RESEARCH COUNCIL

Mineralogical analysis of Chalk solution pipe mineralisation, Aldworth, Berkshire

Integrated Geoscience Surveys Southern Programme

Internal Report IR/02/047



BRITISH GEOLOGICAL SURVEY

INTERNAL REPORT IR/02/047

Mineralogical analysis of Chalk solution pipe mineralisation, Aldworth, Berkshire

S J Kemp

Key words

Chalk, solution pipe, mineralisation, gibbsite, Mn oxyhydroxide, hydrated alumino-silicates

Front cover

Spheroidal intergrowths of Mn oxyhydroxide and gibbsite crystals developed within a coarser-grained gibbsite matrix.

Bibliographical reference

KEMP, S.J. 2002. Mineralogical analysis of Chalk solution pipe mineralisation, Aldworth, Berkshire. *British Geological Survey Internal Report*, IR/02/047. 18pp.

Keyworth, Nottingham British Geological Survey 2002

BRITISH GEOLOGICAL SURVEY

The full range of Survey publications is available from the BGS Sales Desks at Nottingham and Edinburgh; see contact details below or shop online at www.thebgs.co.uk

The London Information Office maintains a reference collection of BGS publications including maps for consultation.

The Survey publishes an annual catalogue of its maps and other publications; this catalogue is available from any of the BGS Sales Desks.

The British Geological Survey carries out the geological survey of Great Britain and Northern Ireland (the latter as an agency service for the government of Northern Ireland), and of the surrounding continental shelf, as well as its basic research projects. It also undertakes programmes of British technical aid in geology in developing countries as arranged by the Department for International Development and other agencies.

The British Geological Survey is a component body of the Natural Environment Research Council.

Keyworth, Nottingham NG12 5GG

☎ 0115-936 3241 Fax 0115-936 3488
e-mail: sales@bgs.ac.uk
www.bgs.ac.uk
Shop online at: www.thebgs.co.uk

Murchison House, West Mains Road, Edinburgh EH9 3LA

☎ 0131-667 1000 Fax 0131-668 2683
e-mail: scotsales@bgs.ac.uk

London Information Office at the Natural History Museum (Earth Galleries), Exhibition Road, South Kensington, London SW7 2DE

☎ 020-7589 4090 Fax 020-7584 8270
☎ 020-7942 5344/45 email: bgslondon@bgs.ac.uk

Forde House, Park Five Business Centre, Harrier Way, Sowton, Exeter, Devon EX2 7HU

☎ 01392-445271 Fax 01392-445371

Geological Survey of Northern Ireland, 20 College Gardens, Belfast BT9 6BS

☎ 028-9066 6595 Fax 028-9066 2835

Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB

☎ 01491-838800 Fax 01491-692345

Parent Body
Natural Environment Research Council, Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU

☎ 01793-411500 Fax 01793-411501
www.nerc.ac.uk

Foreword

This report is the published product of a study by the British Geological Survey (BGS) and forms part of the Core Strategic (Lands and Resources) Programme.

Acknowledgements

G Turner is thanked for his assistance with scanning electron microscopy.

Contents

FIGURES

PLATES

Summary

This report describes the results of laboratory characterisation of mineralisation exposed in Upper Chalk solution features, near Aldworth, Berkshire. X-ray diffraction and scanning electron microscopy reveal that the mineralisation is predominantly formed of gibbsite with poorly crystalline hydrous alumino-silicates (halloysite and possibly allophane). Black microspheres which speckle the surface of the mineralisation are formed of sub micron-sized crystals of Mn oxyhydroxide intergrown with gibbsite. When fractured, the Mn oxyhydroxide microspheres reveal a fibro-radiating morphology and are rich in cobalt.

The mineralisation is thought to have developed from the interaction between acidic, sulphate-bearing groundwater generated in the overlying Tertiary pyrite-bearing sands and clays with the Upper Chalk. Similar mineralisation has been studied by the author at Newhaven, Sussex. The lack of $Al(OH)_3$ polymorphs other than gibbsite suggest that groundwater flow in the solution feature remained unimpeded. The Aldworth features and mineralisation probably formed from pre-existing joints, post-Lambeth Group deposition, under wetter, possibly warmer climatic conditions than today.

1 Introduction

This report presents the results of mineralogical analysis carried out on samples of mineralisation taken from linear Chalk solution features near Aldworth, Berkshire [SU 5431 7907]. The features, from near the Lambeth Group and clay-with-flints/Upper Chalk interface, were exposed during initial, shallow (30-40 cm) excavations for a Transco pipeline. The samples were submitted for analysis by D Aldiss and R Marks (BGS).

In the field, the stripped ground shows 3 m bands of Chalk together with orange brown sands with clays. The stripes generally have a wedge cross section with the sand and clay pinching out with depth. The sands and clays in the wedge are highly distorted with slump structures. Close to the Chalk contact there is often a layering parallel to the contact in which the sampled mineralisation has developed. The deposit contains a few nodular and unbroken flints. The linear nature of the features would seem to suggest that they have developed from fractures in the Chalk.

The sampled mineralisation is composed of a soft, friable mass of variously translucent, white, beige and buff coloured material which is speckled with black microspheres.

2 Methods

2.1 X-RAY DIFFRACTION ANALYSIS

For XRD analysis, small c.5 mg portions of sample were removed with a scalpel, ground to a powder in an agate pestle and mortar and deposited onto the surface of a 'zero-background' silicon crystal using a single drop of acetone. Analysis was carried out using a Philips PW1700 series diffractometer using Co-Kα radiation and operating at 45kV and 40mA. Diffraction data were analysed using Philips X'Pert software coupled to an International Centre for Diffraction Data (ICDD) database running on two Gateway personal computers. The silicon substrate mount was scanned from 2-50 °2θ at a scanning speed of 0.55°2θ/minute.

2.2 SCANNING ELECTRON MICROSCOPY

For SEM analysis, several portions of the sample were removed and mounted on aluminium stubs using carbon-based Leit-C cement. Once dry, the stubs were coated with a layer of carbon approximately 25 nm thick in an Edwards 306A carbon evaporation coater. The stub was then examined in a Leo 435VP Scanning Electron Microscope operated in Secondary Electron Imaging mode at 20 KV. Semi-quantitative chemical analysis was performed on individual mineral grains using a Link Analytical Energy-Dispersive Spectrometer (EDS).

3 Results

Under the SEM, the mineralisation is predominantly composed of subhedral plates, typically 2-5 µm in diameter which EDS indicates is composed of Al and O only (Plates 1 and 2). XRD analysis (Figure 1) reveals that this phase is gibbsite [$Al(OH)_3$]. (Note, EDS does not detect elements lower than atomic number 6, carbon).

In places the gibbsite plates are coated in a very fine-grained gel-like material (Plates 3 and 4) that EDS suggests is composed of Al, O and variable, minor Si. XRD analyses of a particularly white area of the mineralisation identified the presence of hydrated halloysite [$Al_2O_3.2SiO_2.4H_2O$] which would fit with such a chemistry. Despite the very broad, low

intensity XRD peaks generated by this material suggesting a lack of crystal order, halloysite was identified by its characteristic peak spacings and their collapse to smaller spacings on heating to 175°C/2hours (e.g. d_{001} collapses from c.10Å to 7.1Å, Figure 2). Even more poorly crystalline or X-ray amorphous alumino-silicates such as allophane or imogolite may also be present in the samples but could not be definitively identified. The gel appears intensely cracked, possibly due to drying during specimen preparation and 'charges' in the SEM due to poor conduction.

XRD analysis of carefully-extracted and cleaned black microspheres reveals a gibbsite and ?todorokite [$(Mn,Ca)Mn_5O_{11}.4H_2O$] mineralogy (Figure 3). Mn minerals typically yield diffuse and poorly defined XRD patterns, particularly where they have developed under soil formation processes. In addition, Mn minerals produce strong secondary fluorescence when examined with the Co radiation used in this study. Todorokite was therefore only tentatively identified on the basis of diffuse peaks at c.9.4 and 4.74Å. SEM examination shows that the microspheres typically reach 100 µm in diameter but often coalesce to form larger aggregates (Cover and Plate 5). Where fractured, the fibro-radial structure of the microspheres is exposed (Plates 5, 6 and 7). High magnification photomicrographs show that the microspheres are composed of sub micron-sized intergrowths of platey Mn oxyhydroxide (?todorokite) crystals and more equant, subhedral gibbsite crystals. EDS indicates that the microspheres also contain appreciable Co. In some cases, the microspheres are coated with and are therefore post-dated by a layer of cracked alumino-silicate gel.

4 Discussion

4.1 PREVIOUS OCCURRENCES

Several accounts of deposits immediately overlying the Chalk and filling solution cavities have previously been published (e.g. Thorez *et al.*, 1971, Hodgson *et al.*, 1967). Early accounts of mineralisation formed in such cavities from southern England were made by Perceval (1871) and Howell (1872). They described the occurrence of nodular masses of 'websterite' (aluminite, $Al_2(SO_4)(OH)_4.7H_2O$) and a 'black lignite-like coating' which was found to '…consist of manganese with a certain proportion of cobalt'. These authors also described compact nodules consisting of an intimate mixture of gibbsite and allophane from localities in the Brighton area.

More recently, aluminite and other aluminium minerals including gibbsite and alumino-silicate gels have been described from similar mineralisation near Newhaven, Sussex by Wilmot and Young (1985) and Kemp and Pearce (1991). These authors explained the formation of Chalk solution hollows by groundwater percolation through the overlying Tertiary beds which then exploited pre-existing hollows and joints in the Chalk. Collapse of Tertiary material into the hollows ensured that they remained as pathways for groundwater flow. Reactions between groundwater, the pipe infill sediments and surrounding chalk were also responsible for the mineralisation.

4.2 PARAGENESIS

Wilmot and Young (1985) suggested that oxidation of abundant pyrite in the overlying Tertiary clays produced highly acidic, sulphate-rich groundwaters (pH<4). The downward movement of such acidic water would have leached aluminium and other cations (but only minor silicon) from the clay-rich beds. Reaction between these waters and the chalk would cause dissolution of the chalk, precipitation of selenite [$CaSO_4.2H_2O$] and an increase in pH. The removal of sulphate and increasing pH would result in decreasing aluminium solubility and the precipitation of aluminium hydroxides such as gibbsite when sulphate/aluminium ratios fall below 0.5 (Adams and Hajek, 1978). Such reactions are today engineered in ALDs (anoxic limestone drains) for the amelioration of acid mine drainage (e.g. Robins *et al*. 1999, Yun *et al.*, 2001). Gibbsite continues to form where groundwater continues to percolate and the pH remains below 7.

Where the pH rises due to temporary groundwater ponding, other polymorphs such as nordstrandite [$Al(OH)_3$] become dominant.

An iron pan formed of fibro-radial Fe oxyhydroxide (Kemp and Pearce, 1991) and a manganiferous crust within the Newhaven solution pipes also probably formed due to rising pH since the solubilities of iron and manganese also decrease with rising pH. A lack of silica deposition provided further evidence for increasing pH due to its increased solubility. Wilmot and Young (1985) could not produce a precise identification for hydrous alumino-silicate gels, some of which were admixed with gibbsite, but state that such species are also likely to form at pH <5.

This model would also seem appropriate for development of the Aldworth mineralisation. Pearce *et al.* (1999) noted the occurrence of pyrite in the Upnor and Reading formations (Lambeth Group) that overlie the Chalk in excavations for the nearby Newbury-bypass. Oxidation of this pyrite would have produced the necessary acidic groundwaters which could then exploit linear fractures in the underlying Chalk, enlarging them to produce linear solution features. The lack of the high pH $Al(OH)_3$ polymorphs suggest that unlike those at Newhaven, the groundwaters at Aldworth remained relatively free-flowing and acidic resulting in the predominant precipitation of gibbsite and alumino-silicate gels. The fibro-radial fabrics in the Mn oxyhydroxide/gibbsite microspheres probably indicate subtle variations in fluid chemistry and/or pH. Under relatively high pH conditions, the fibrous crystals would continue to form from solution, but a sudden lowering of pH would curtail precipitation. Precipitation would then recommence with rising pH. The source of the cobalt associated with the Mn oxyhydroxide and also mentioned by Perceval (1871) is unknown but may also have been scavenged from the overlying Tertiary clays. The late coatings of alumino-silicate gel observed on some of the Mn oxyhydroxide/gibbsite microspheres is a further indication of variations in the chemistry and/or pH of the groundwaters over time.

4.3 TIMING OF SOLUTION FEATURES AND MINERALISATION DEVELOPMENT

Wilmot and Young (1985) reasoned that the solution hollows at Newhaven formed well before their exposure in the cliffs and that the mineralisation formed either during hollow formation or later when groundwater was still moving through the system. Due to a lack of significant modern groundwater flow, they were not thought to be forming at the present day.

The similar features and mineralisation seen at Aldworth would seem to suggest a similar timing for their formation. The requirement for acidic groundwaters and the distorted, slumped nature of the overlying Lambeth Group sediments (R. Marks, *pers. comm.*) suggest that the solution features formed after deposition of the Lambeth Group. The linear nature of the features suggests that in the Aldworth area, the hollows formed by exploitation of the main joint direction in the Chalk in this area. The required groundwater flow probably resulted from a wetter, possibly warmer climatic period.

5 Conclusions

- Mineralisation in Chalk solution features near Aldworth, Berkshire is predominantly formed of subhedral gibbsite platelets together with a gel-like hydrated alumino-silicate and fibro-radial growths of Mn oxyhydroxide and gibbsite.
- The linear solution features probably developed from pre-existing joints due to the movement of acidic, sulphate-bearing groundwaters formed in the overlying pyrite-bearing Lambeth Group sediments.
- The mineralisation formed from the reaction of acid groundwaters with the solution feature infill and underlying Chalk. The lack of $Al(OH)_3$ polymorphs other than gibbsite suggest that groundwater flow in the solution feature remained unimpeded. The fibro-radial fabrics of the Mn oxyhydroxide/gibbsite microspheres probably indicate subtle variations in fluid chemistry and/or pH of the groundwater.
- Studies of similar mineralisation from Chalk solution features in southern England suggest that it is not forming at present. The features and mineralisation probably formed post-Lambeth Group deposition under wetter, possibly warmer climatic conditions than today.

References

Most of the references listed below are held in the Library of the British Geological Survey at Keyworth, Nottingham. Copies of the references may be purchased from the Library subject to the current copyright legislation.

ADAMS, F and HAJEK, B F. 1978. Effects of solution sulphate, hydroxide and potassium concentrations on the crystallisation of aluminite, basaluminite and gibbsite from dilute aluminium solutions. *Soil Science*, **126**, 169-172.

HOWELL, J. 1872. On the minerals lately found in the drainage-works at Brighton. *Report British Association*. Brighton 1872, 108-109.

KEMP, S J, and PEARCE, J M. 1991. A mineralogical and geochemical study of pyrite alteration: implications for trace element mobility and radionuclide migration. *British Geological Survey Technical Report*, WG/91/29.

PEARCE, J M, KEMP S J and HARDS, V L. 1999. The mineralogy and petrography of the Lambeth Group from the London and Hampshire basins. *British Geological Survey Technical Report*, WG/98/4R.

ROBBINS E I, CRAVOTTA C A, SAVELA C E and NORD G.L. 1999. Hydrobiogeochemical interactions in 'anoxic' limestone drains for neutralization of acidic mine drainage. *Fuel,* **78** (2): 259-270.

THOREZ, J P, BULLOCK, P, CATT, J A AND WEIR, A H. 1971. The petrography and origin of deposits filling solution pipes in the Chalk near South Mimms, Hertfordshire. *Geological Magazine,* **108**, 413-423.

PERCEVAL, S G. 1871. On the occurrence of websterite at Brighton. *Geological Magazine*, **8**, 121-122.

WILMOT, R D and YOUNG, B. 1985. Aluminite and other aluminium minerals from Newhaven, Sussex: the first occurrence of Nordstrandite in Great Britain. *Proceedings of the Geological Association*, **96**, 47-52.

YUN S T, JUNG H B and SO C S. 2001. Transport, fate and speciation of heavy metals (Pb, Zn, Cu, Cd) in mine drainage: Geochemical modeling and anodic stripping voltammetric analysis. *Environmental Technology* **22** (7): 749-770

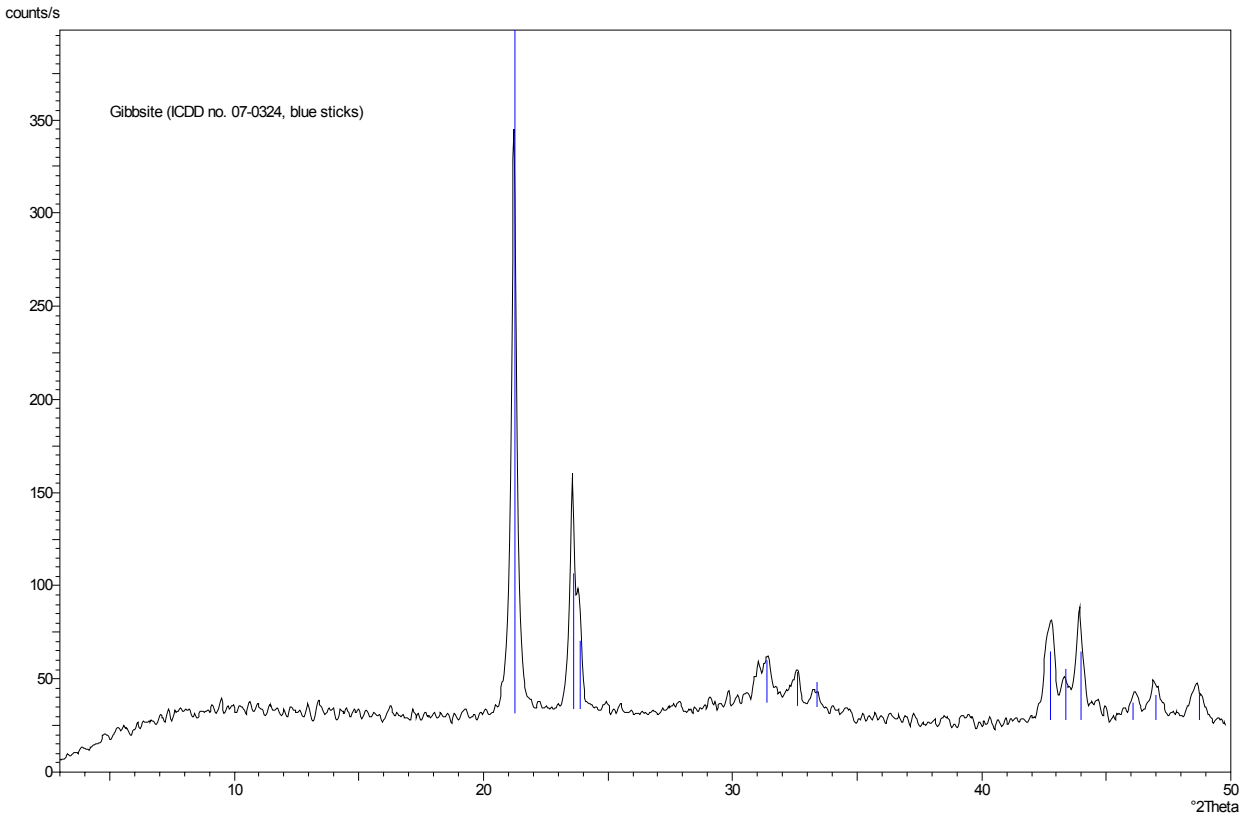


Figure 1. X-ray diffraction trace for beige-coloured material compared to gibbsite standard 'stick' pattern. Vertical axis = intensity (counts per second), horizontal axis = °2θ Co-Kα.

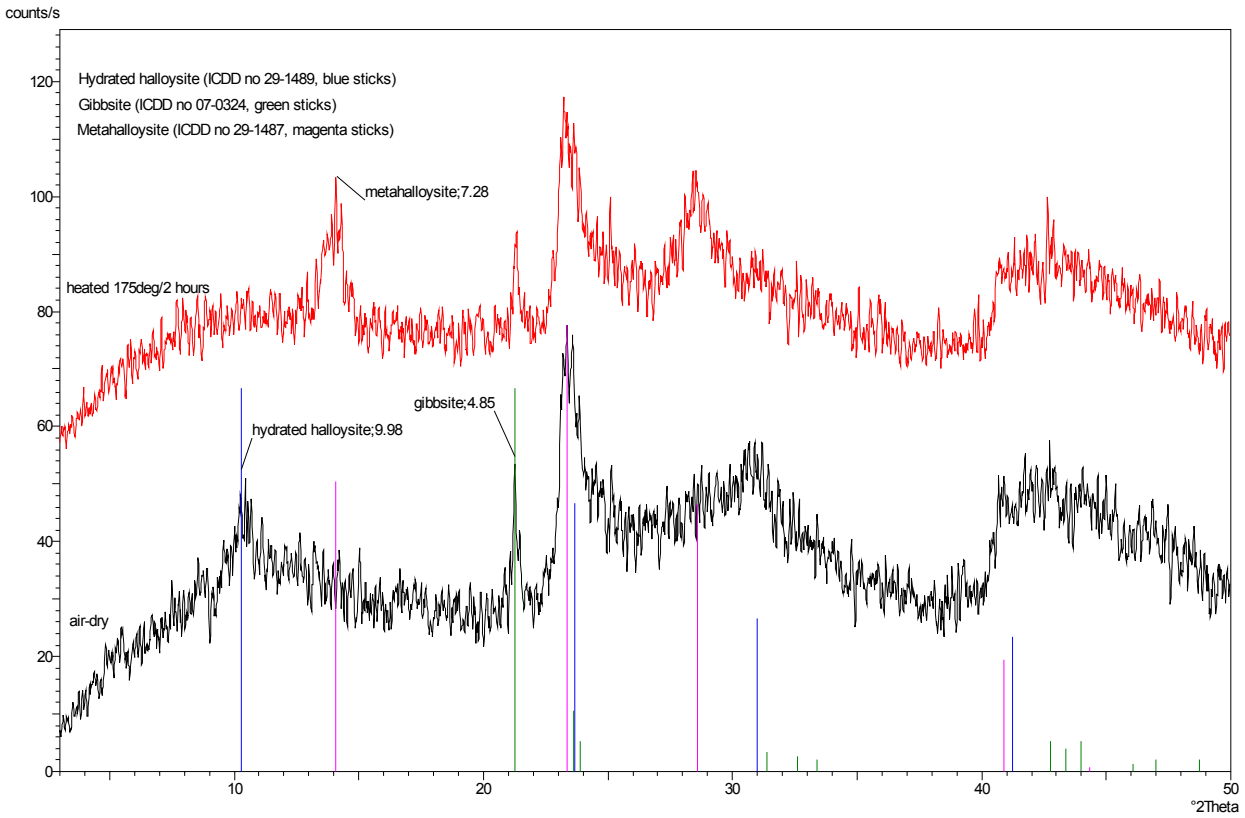


Figure 2. X-ray diffraction traces for white material compared to hydrated halloysite, metahalloysite and gibbsite standard 'stick' patterns. Black trace = air-dry, red trace = heated 175°C/2hours. Vertical axis = intensity (counts per second), horizontal axis = °2θ Co-Kα.

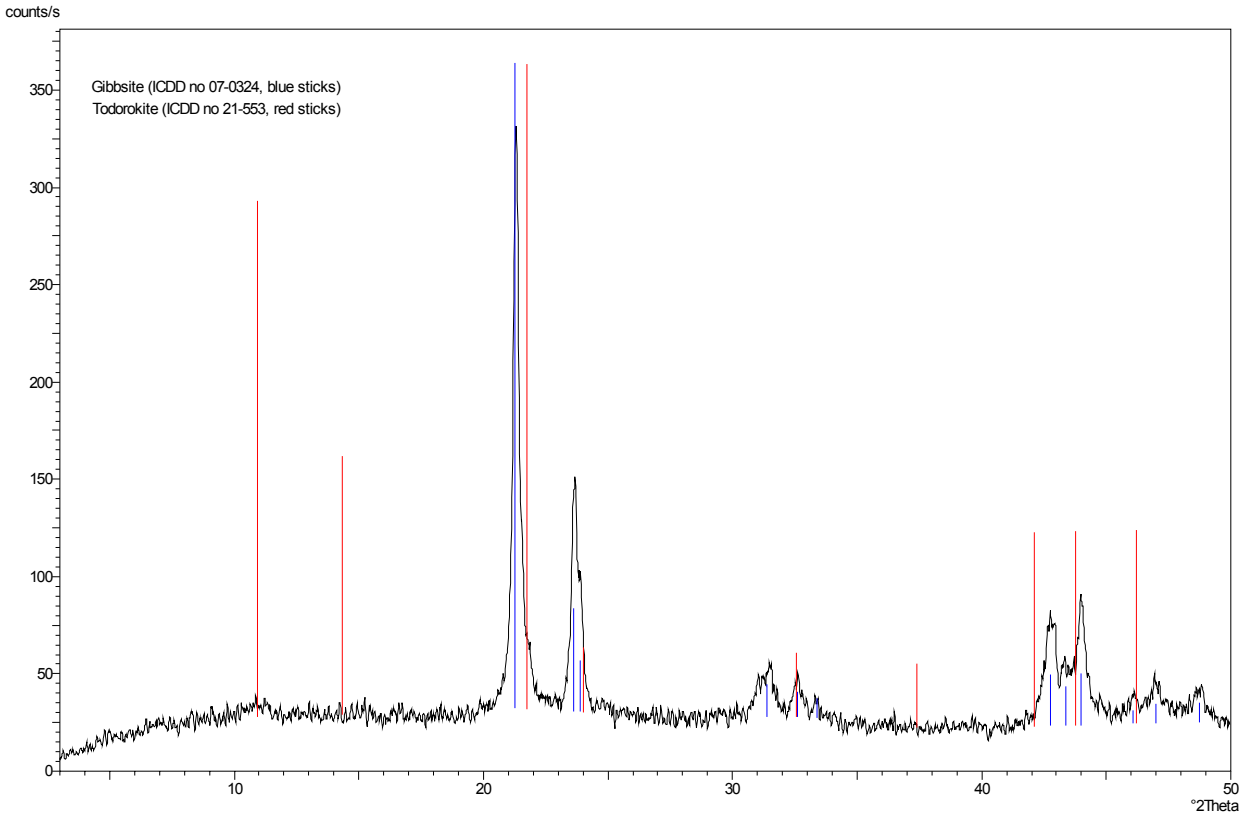


Figure 3. X-ray diffraction trace for black microspheres compared to todorokite and gibbsite standard 'stick' patterns. Vertical axis = intensity (counts per second), horizontal axis = °2θ Co-Kα.

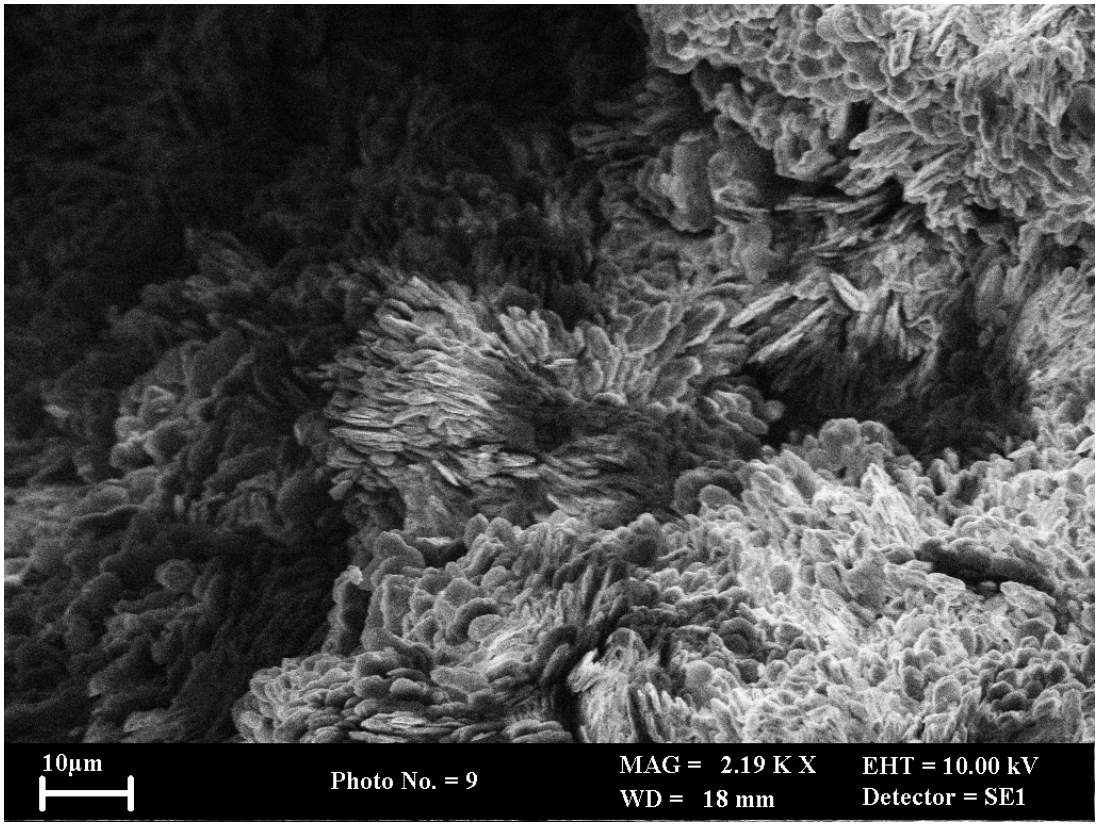


Plate 1. Scanning electron photomicrograph showing extensive development of subhedral gibbsite plates.

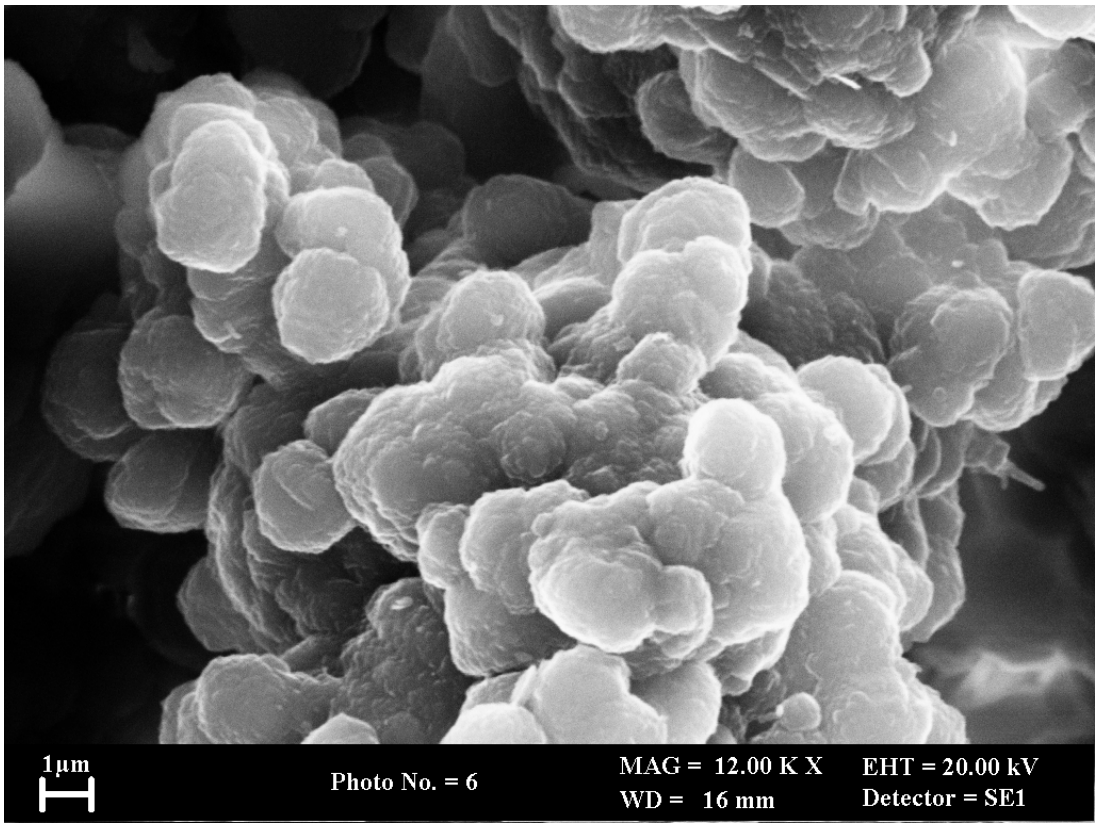


Plate 2. Scanning electron photomicrograph showing high magnification view of subhedral gibbsite plates.

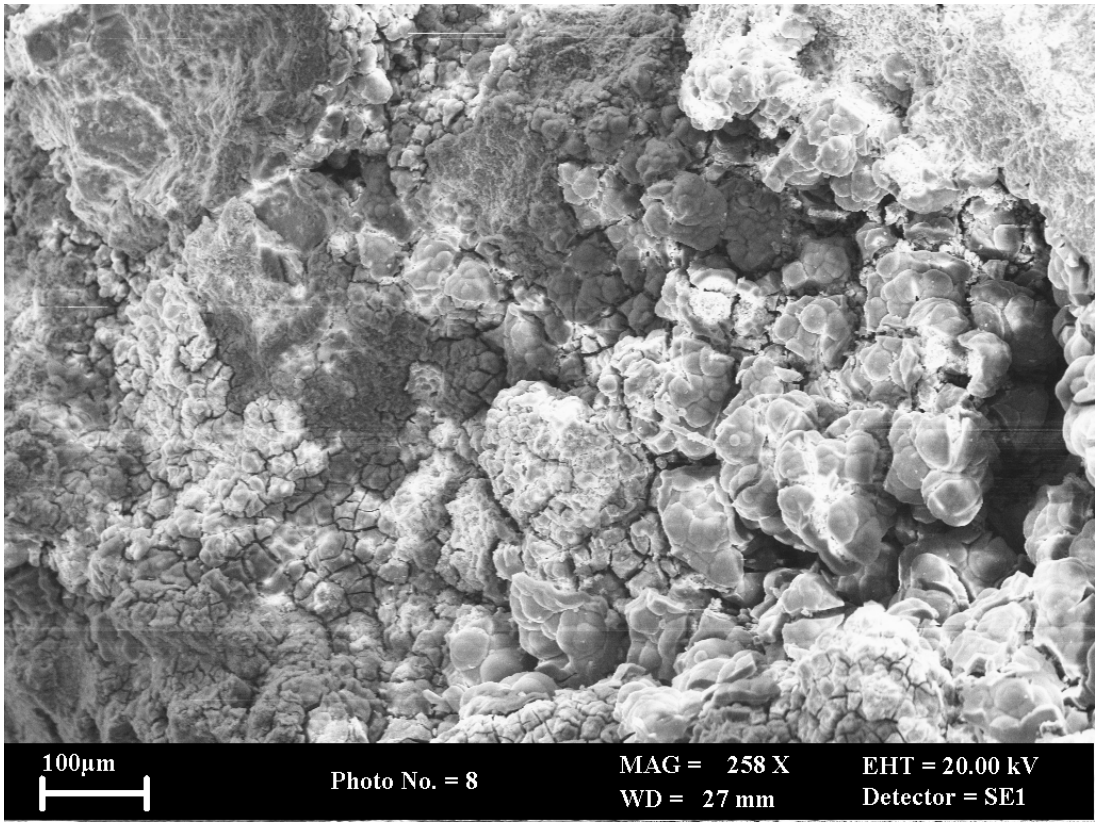


Plate 3. Scanning electron photomicrograph showing development of very fine-grained alumino-silicate gel.

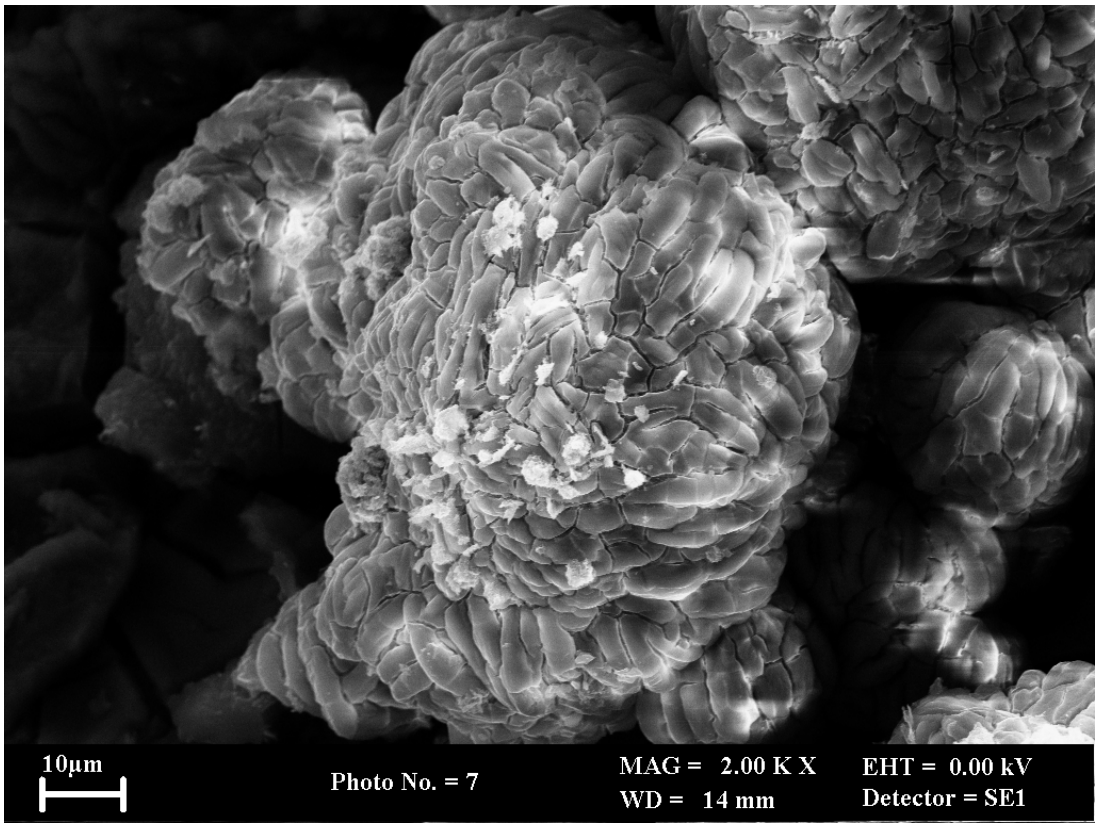


Plate 4. Scanning electron photomicrograph showing development of very fine-grained alumino-silicate gel.

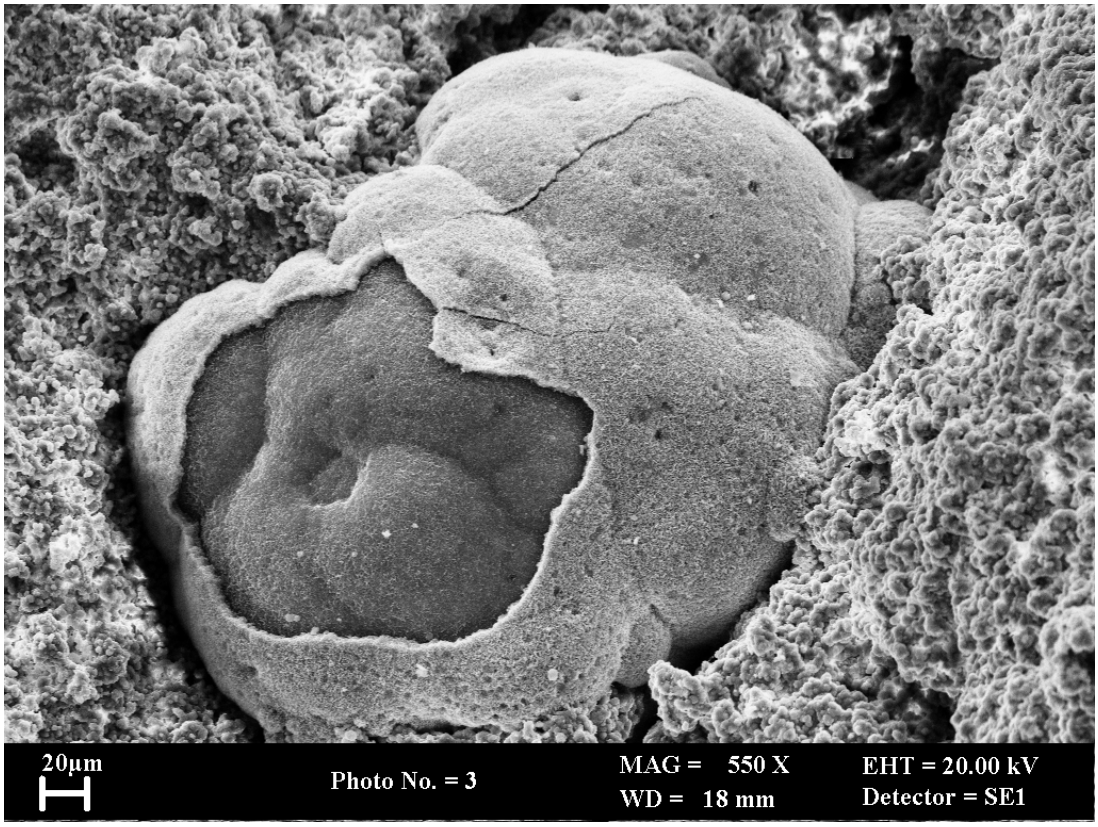


Plate 5. Scanning electron photomicrograph showing coalesced Mn oxyhydroxide/gibbsite microspheres.

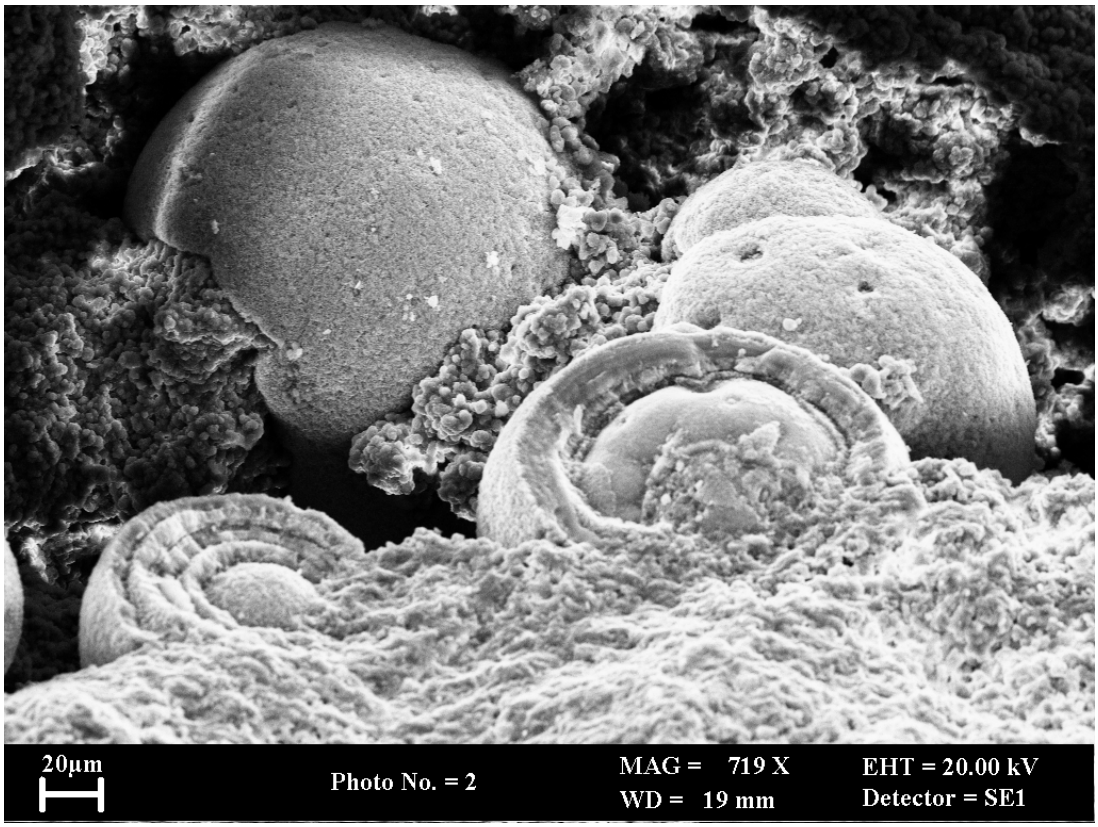


Plate 6. Scanning electron photomicrograph showing the internal fibro-radial structure of fractured Mn oxyhydroxide/gibbsite microspheres.

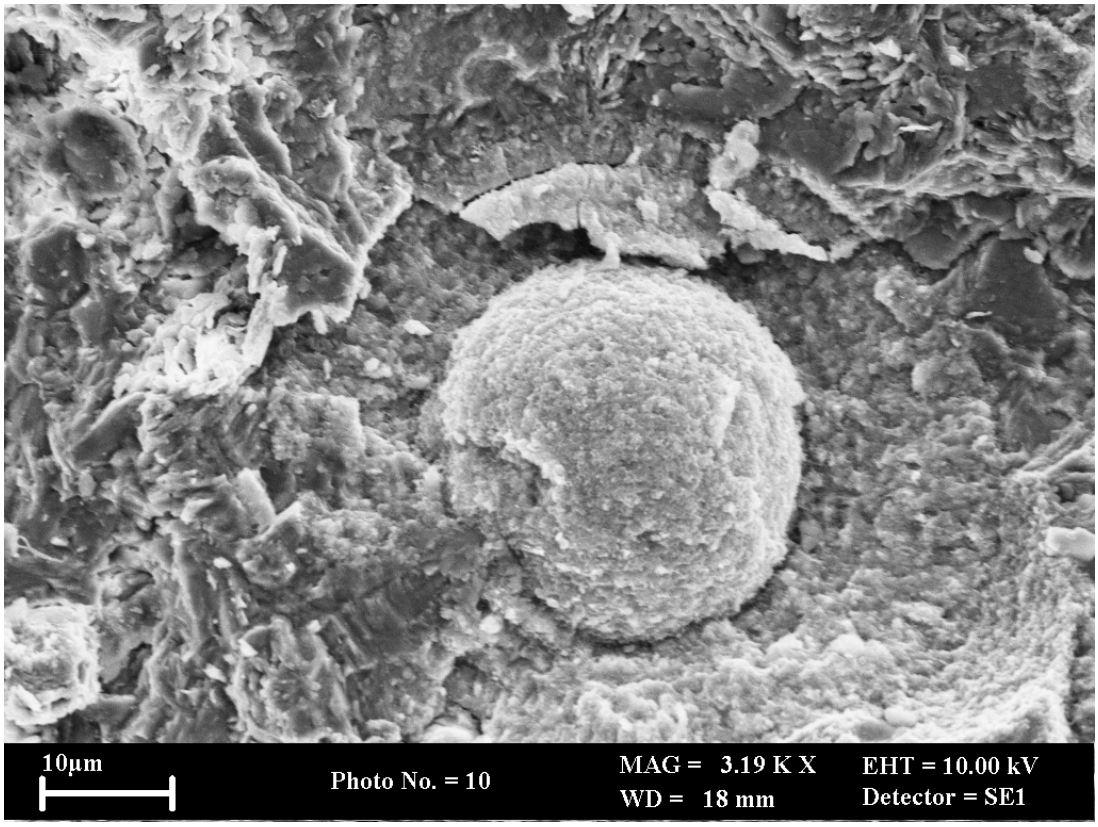


Plate 7. Scanning electron photomicrograph showing a higher magnification view of the internal fibro-radial structure of a fractured Mn oxyhydroxide/gibbsite sphere.

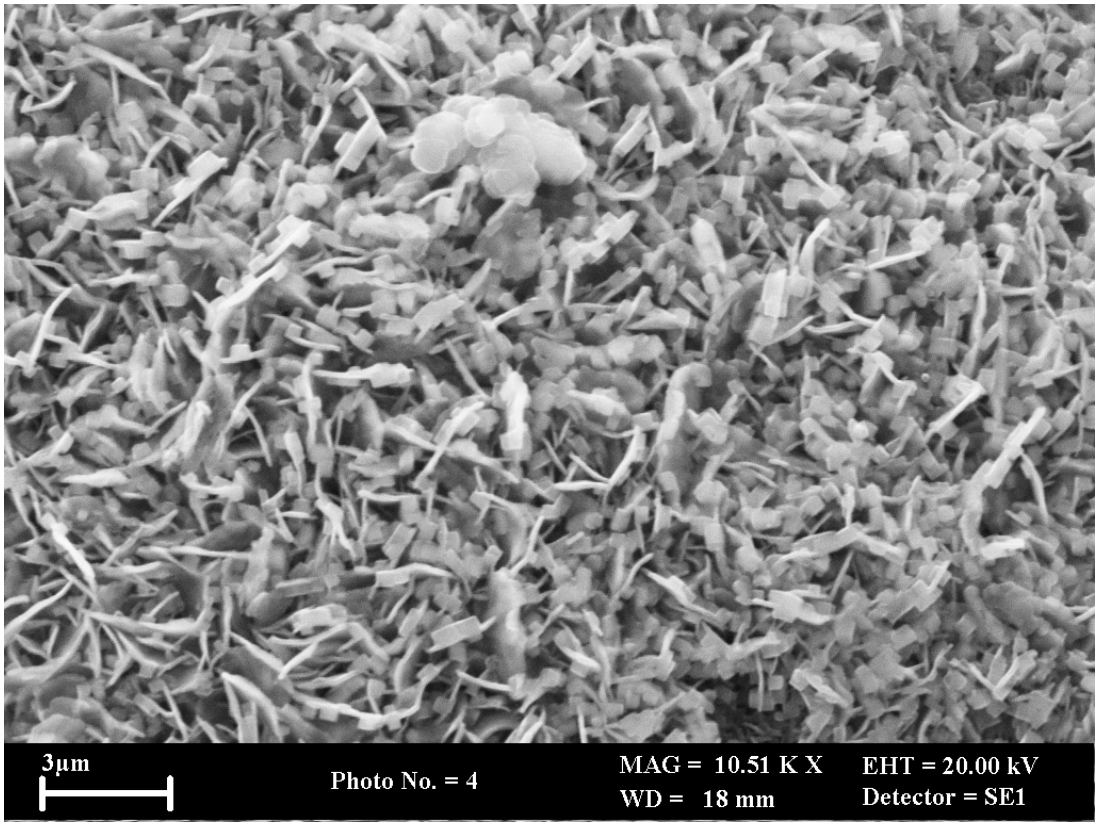


Plate 8. Scanning electron photomicrograph showing a high magnification view of intergrowing Mn oxyhydroxide plates and subhedral, equant gibbsite crystals.