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Keywords

region, sydney, stalactites, silica, australia, within, south, formation, alunite, eastern, GeoQUEST

Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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Alunite formation within silica stalactites from the Sydney Region, South-eastern Australia

Robert A.L. Wray¹

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This paper presents X-ray diffraction and SEM evidence for the formation of alunite, and possibly small quantities of natroalunite, within opal-A stalactites formed on quartz sandstone near Sydney in south-eastern, Australia. Alunite has been reported as a speleogenetic mineral from sediments within a number of caves around the world, but this is believed to be the first report of speleothemic alunite in opaline silica speleothems. Individual alunite crystals have not been visually identified, but SEM X-ray element mapping suggests the alunite has formed amongst kaolinite clay. Sedimentary alunite and natroalunite formation is usually associated with the reaction of sulphuric acid on illite, smectite and kaolinite clay materials. In this location groundwater sulphate levels are not high, but evaporative concentration of stalactite drip-water containing small amounts of sulphuric acid generated by oxidization of pyrite might lower the pH to a level sufficiently acidic for conversion of kaolinite or illite to alunite. The ferrolisis of hydrous Fe^{2+} -oxides, or the biochemical activities of bacteria or other micro-organisms, also provide conceivable pathways for the generation of pH sufficiently low to contribute to alunite formation. The occurrence of alunite in these silica stalactites, whilst unusual, is consistent with the normal silica stalactite-forming process in this region, and in accord with observations of the authigenic formation of alunite and groundwater opal in weathering profiles elsewhere.

Keywords: alunite, natroalunite, opal-A, apeleothem, atalactite

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INTRODUCTION

The formation of alunite within stalactites at normal atmospheric temperatures (10 to 30°C) has to our knowledge not been reported previously. This paper presents evidence for the authigenic formation of alunite, and possibly lesser quantities of natroalunite, within small opal-A stalactites from the Sydney region in south-eastern Australia. Based on microscopic and preliminary geochemical evidence a possible formative mechanism can be suggested.

Alunite, hydrous potassium aluminium sulphate ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$), is a member of a solid solution series of sulphuric acid indicator minerals that include natroalunite ($\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$) and jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), which respectively substitute Na^+ for K^+ and Fe^{3+} for Al^{3+} (Dill, 2001). Chitale & Güven (1987) classify the term 'alunite' as members in which $\text{K} > \text{Na}$, and 'natroalunite' those in which $\text{Na} > \text{K}$.

Alunite typically forms by the reaction of sulphuric acid, produced by the oxidation of sulphides, with potassium- and aluminium-rich rocks or clays (Khalaf, 1990; Hill & Forti, 1997; Dill, 2001; Polyak & Provencio, 2001; Deyella et al., 2005; Mutlua et al., 2005; Ece & Schroeder, 2007; Ece et al., 2008). It is therefore a relatively common geothermal or hydrothermal-alteration product (Raymahashay,

1968; Stoffregen et al., 1994; Deyella et al., 2005; Mutlua et al., 2005; Ece & Schroeder, 2007; Ece et al., 2008). But alunite also forms in low-temperature supergene (Bird et al., 1989, 1990; Stoffregen & Alpers, 1992) and sedimentary/diagenetic or deep-weathering environments (Goldbery, 1980; Chitale & Güven, 1987; Khalaf, 1990; Alpers et al., 1992; Long et al., 1992; Thiry et al., 2006; Blanco et al., 2008).

In the context of caves and cave deposits, primary speleogenetic (formed within caves) alunite-group minerals have been found in the wall and floor sediments of a number of caves worldwide, where they are regarded as a clear indicator of the alteration of smectite, illite and kaolinite by sulphuric acid (Hill & Forti, 1997; Polyak & Provencio, 2001). Probably the best examples are found within the caves of the Guadalupe Mountains in New Mexico, including Carlsbad Cavern and Lechuguilla Cave (Polyak & Güven, 1996; Polyak et al., 1998; Polyak & Provencio, 2001). The timing of origin of some of these caves has been determined by $^{40}\text{Ar}/^{39}\text{Ar}$ dating of this alunite to over 11 Ma (Polyak et al., 1998; Polyak & Provencio, 2000).

However Hill & Forti (1997), in their benchmark review of cave minerals, note that alunite is very rarely found as an authigenic speleothemic mineral (formed within speleothems). They only report one instance of alunite-bearing stalactites, from a Sicilian lava tube where the mineral appears to have formed at elevated temperature. Further, there appears to be

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only one previous known instance of low-temperature speleothem alunite (Martini, 1980; Martini et al., 1997); in the Eastern Transvaal, where alunite is found as powdery pale-green nodules in gypsum-rich 'speleothems' on cave sediments, but not in silica stalactites. This depositional environment and possible genesis pathways are in some ways similar to the present location. To our knowledge natroalunite has not been reported in any cave or speleothem context (Hill & Forti, 1997).

Most speleothems are composed of calcium carbonate. However small opal-A stalactites are found at a number of locations around the world (Urbani, 1976; Briceño & Schubert, 1990; Wray, 1997a; Carreño & Urbani, 2004; Wiegand et al., 2004; Young et al., 2009) and their occurrence and formation on quartz sandstones within the Sydney region has previously been discussed (Wray, 1997a,b, 1999). However the presence of alunite within some of these stalactites has not previously been described. This may also be the first report of low-temperature alunite in stalactitic speleothems.

FIELD LOCATION

Opal-A stalactites are widespread, but not particularly common, on some quartz sandstones of the Sydney region in south-eastern Australia. However alunite-bearing stalactites have to date only been found within a single sandstone overhang-cave near Bundanoon, approximately 200 km southwest of Sydney. The climate is humid temperate with an annual precipitation of just over 1000 mm distributed evenly throughout the year.

This medium-sized (approx. 20 m x 5 m x 2 m) cave is at approximately 630 m elevation and has formed at the foot of a 15 m high cliff in the quartzose fluvio-deltaic Mid-Triassic Hawkesbury Sandstone.

This sandstone is an essentially flat-lying, crossbedded, very fine to pebbly quartz arenite that averages more than 75% detrital and overgrowth quartz, 2% feldspars and mica, and 2% rock fragments (Standard, 1969). Kaolinite and minor illite matrix clays are generally up to 20% of the total rock composition (Bayliss et al., 1965; Pells, 1977). Siderite accounts for around 1% to 4% of the total, but quantities of calcite (<0.1%) or other minerals are very low (Standard, 1969; Herbert & Helby, 1980).

About 2 to 3 m below this cave is a disconformable boundary to underlying estuarine/marine sandstones, mudstones, black shales and coal of the Permian Illawarra Coal Measures. Sulphur-rich minerals including pyrite are common within these underlying rocks (Standard, 1969; Herbert & Helby, 1980).

SPELEOTHEM DESCRIPTIONS

In the Sydney region dissolved silica precipitates from evaporating groundwater as a range of small speleothems including stalactites, or much rarer stalagmites and flowstones. These speleothems are clearly forming under atmospheric conditions (Wray, 1997a,b, 1999). The alunite-bearing stalactites discussed here are of identical appearance and microscopic structure to the region's other silica

stalactites and appear to form in a similar manner (Wray, 1997a,b, 1999). They are typically 1 mm to 50 mm in length, 0.5 mm to about 5 mm in diameter, and display either a gently tapering conical form or an irregular branching coral-like configuration. Very tiny droplets of groundwater may sometimes be seen on some of these stalactites.

ANALYTICAL METHODS

Ten stalactites, samples of the Hawkesbury Sandstone to which they were attached, and groundwater from nearby springs were collected for laboratory analysis. Optical thin-sections of the stalactites were examined under ordinary and polarised light, and freshly broken samples were viewed with a scanning electron microscope (SEM) equipped with an X-ray energy-dispersion detector (EDS) for elemental analysis and mapping. X-ray powder diffraction (XRD) and X-ray fluorescence (XRF) were used for mineral and elemental identification. Other chemical analysis were performed by ICP-OES, CNS analyser and electron microprobe. The chemical composition of springwater was determined by ion-chromatography.

RESULTS

Stalactite X-ray diffraction

The Hawkesbury Sandstone is a relatively mature quartz sandstone, and Dill (2001) notes that pure sandstones that are not highly weathered or hydrothermally altered rarely contain alunite-group minerals. Such is the case with the sandstone to which these alunite-bearing stalactites were attached, and no alunite minerals have been previously found within this sandstone. X-ray diffraction spectra of the whole rock at this site only showed peaks of quartz, kaolinite, a little illite, and possibly a trace of muscovite and siderite.

Evidence for alunite and possibly smaller amounts of natroalunite within these stalactites is provided by five independent X-ray diffraction spectra, including at least three duplicates (Fig. 1). No other Sydney region silica speleothem has displayed similar patterns.

Very clear diffraction peaks of quartz (chalcedony) were obtained from each analysed stalactite. These were therefore used as an internal diffraction standard between individual samples.

Each of the XRD spectra shows the broad diffuse opal-A hump (Jones & Segnit, 1971; Finlayson & Webb, 1985) and the sharp peaks of quartz (chalcedony) and kaolinite typical of other Sydney region silica stalactites (Wray, 1997b, 1999). But what is unusual are prominent peaks at 4.96 Å, 3.49 Å, 2.99 Å, 2.29 Å and 1.92 Å. Although some minor alunite peaks are not discernable above the opal-A background, and whilst there is not a perfect match with all peaks, the general pattern fits that of alunite, and no other explainable mineral seems to fit such a peak pattern.

Samples 5, 9 and 10 show additional, less clear, peaks at 4.90 Å, 3.49 Å, 2.97 Å, 2.96 Å, 2.22 Å and 1.89 Å which may suggest the presence of some natroalunite (Brindley & Brown, 1980). However the diffraction patterns are not sufficiently clear for unambiguous identification of natroalunite.

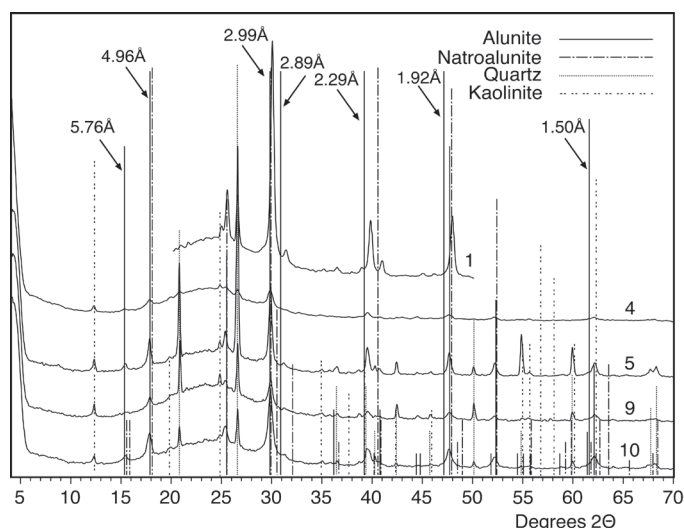


Fig. 1. X-ray diffraction spectra of five opal-A stalactites (BUND1, 4, 5, 9 and 10). The d-spacings of major alunite peaks are indicated. The individual spectra have been vertically offset for clarity. Note the broad amorphous opal-A hump between approximately 15° and 35° and the sharp peaks of alunite, quartz and kaolinite. Also note the variations in peak intensity between samples, and how BUND1 appears to possibly contain natroalunite. The spectrum for BUND1 was only measured between 20° and 50°.

This XRD evidence appears to suggest the identification of alunite, and perhaps also natroalunite, but it is also possible that based on their solid solution series chemistry (Dill, 2001) and similar D-spacings a proportion of an intermediate alunite/natroalunite end-member may also be present. Either way, such minerals have not been identified in silica speleothems before.

Stalactite microscopic examination

Optical thin-section and SEM examination showed these stalactites to be visually identical to those reported for other similar silica stalactites from this region (Wray, 1997b, 1999). Optically the microscopic structure is complex and composed of many distinct wavy 0.007 mm to 0.15 mm thick layers of dark grey to red-brown amorphous opal-A, alternating with layers of a mixture of opal-A and colourless, fibrous, length-fast, crypto-crystalline chalcedony. These layers are arranged annularly around the central stalactite axis and parallel to the stalactite surface, but there is no central drip-water hole. Significant amounts of kaolinite along with red-brown and opaque amorphous iron oxides and hydroxides are common within the opal-A layers, as are numerous other opaques (moss, bacteria, dust, etc.) (Wray, 1997b, 1999).

SEM examination showed a very large number of irregularly packed, 0.5 µm to 15 µm-sized grains of non-biogenic opal-A (Fig. 2). These silica 'flecks' appear to be precipitating from evaporating silica-rich water, and over time may slowly 'mature' by Ostwald-type paragenesis to crypto-crystalline chalcedony (Wray, 1999). These observations are similar to those found for silica stalactites elsewhere in the world (Urbani, 1976; Briceño & Schubert, 1990; Carreño & Urbani, 2004; Wiegand et al., 2004).

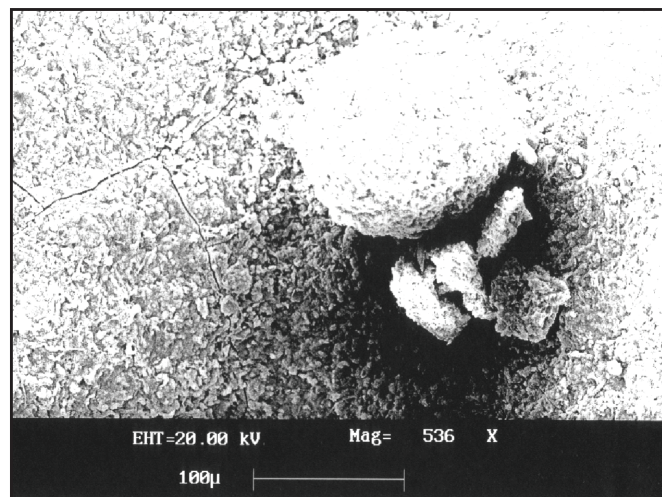


Fig. 2. SEM micrograph of the surface of a silica stalactite (BUND1) composed of an large number of small, irregularly packed, 0.5µm to 15µm-sized grains of amorphous opal-A. No 1µm or smaller, pseudo-cubic alunite crystals were found within this opaline material. Note the desiccation cracks that have formed as the opal-A has dehydrated, and the large spherical masses presumably formed when opal-A precipitated around material, possibly quartz sand grains, adhering to the stalactite surface.

In low-temperature settings, alunite usually occurs as microscopic 1µm or smaller, white, pseudo-cubic crystals (Kerr, 1977; Stoffregen & Alpers, 1992; Stoffregen et al., 1994; Hill & Forti, 1997; Polyak & Provencio, 2001). They are thus of similar or smaller size than the opal-A grains, and despite extensive searching no discrete alunite crystals were visually identified either in thin-section or under the SEM.

In a further attempt to identify alunite crystals within this stalactite material, SEM-EDS X-ray spectra and element mapping were utilised to find areas containing sulphur and potassium. Element maps and X-ray spectra (Fig. 3) of the same powdered material used for the XRD analysis confirm that the elemental composition of the stalactites is dominated by silicon, aluminium and oxygen, but also significant amounts of sulphur (around 2% - 4%) and potassium (around 1% - 3%) are found (Fig. 3). Areas of sulphur concentration were identified and visually searched in detail for alunite crystals, but without success, even under high magnification.

These results suggest that the alunite is not to be found as discrete concentrations of crystals, but seems to be concentrated into areas also high in silicon, oxygen, potassium and aluminium (Fig. 3), namely the kaolinite clay.

Stalactite chemical analysis

Various other chemical analysis were also performed; electron microprobe analysis of a polished sample of BUND1 (Tab. 1), XRF analysis of BUND3, and ICP-OES and CNS analysis for sulphur of five of the powdered XRD samples (BUND5-10) (Tab. 2). These results all confirm that the major element of the stalactites is silica, but they also contain quantities of aluminium, potassium and sodium, small amounts of magnesium, iron, phosphorus, and sulphur, and traces of several minor elements.

Table 1. Electron microprobe chemical analysis of two transects across BUND1 stalactite perpendicular to long axis. Total excludes H₂O.

Sample	SiO ₂ (%)	Al ₂ O ₃ (%)	K ₂ O (%)	Na ₂ O (%)	FeO (%)	MgO (%)	CaO (%)	TiO ₂ (%)	Total (%)
MP1/1	86.5	1.31	0.06	0.36	0.11	0.06	0.03	0.00	88.43
MP1/2	78.2	1.93	0.08	0.19	0.23	0.04	0.04	0.06	80.85
MP1/3	67.3	1.24	0.06	0.08	0.16	0.01	0.02	0.02	68.89
MP1/4	90.2	2.32	0.11	0.35	0.00	0.09	0.01	0.02	93.10
MP2/1	84.7	1.75	0.04	0.13	0.13	0.06	0.09	0.00	86.90
MP2/2	89.5	1.61	0.09	0.47	0.14	0.05	0.03	0.00	91.89
MP2/3	86.0	1.11	0.06	0.31	0.06	0.09	0.15	0.03	87.84
MP2/4	88.7	1.28	0.08	0.24	0.10	0.06	0.07	0.02	90.55
MP2/5	81.0	4.91	0.38	0.05	0.74	0.16	0.10	0.02	87.36
MP2/6	101.0	0.13	0.00	0.00	0.27	0.12	0.02	0.06	101.61

Table 2. Elemental chemical analysis of silica stalactites. BUND3 by XRF, BUND5 to 10 by ICP-OES, with Total Sulphur by CNS analyzer.

Sample	Al (%)	S (%)	K (%)	Fe (ppm)	Na (ppm)	Ti (ppm)	Ca (ppm)	Mg (ppm)	P (ppm)	Sr (ppm)
BUND3	4.85	nm	1.45	4195	nm	420	0	4884	1048	144
BUND5	6.00	2.83	1.66	2960	2710	790	810	1020	815	252
BUND6	4.95	1.58	1.16	2310	4060	545	740	1260	175	136
BUND7	5.95	2.59	1.55	1800	4060	505	445	1080	265	148
BUND8	3.55	0.40	0.38	1380	3010	500	625	1190	135	94
BUND9	4.30	1.22	0.86	1270	3070	595	390	1110	115	97
BUND10	6.10	3.54	1.97	4280	4440	575	455	1110	195	169

nm = not measured.

Table 3. Chemical analysis of spring waters by ion chromatography. Duplicate analyses on each water sample.

Sample	pH	Eh (mV)	Temp (°C)	F (ppm)	Cl (ppm)	Br (ppm)	NO ₃ (ppm)	NO ₂ (ppm)	SO ₄ (ppm)
Springs									
1a	6.52	+156	18.1	0.233	28.474	0.061	0.069	0.796	2.092
1b				0.220	27.274	0.057	0.053	0.840	2.040
2a	6.42	+154	18.1	0.240	29.870	0.056	0.049	0.862	2.540
2b				0.236	24.839	0.052	0.054	0.702	2.042
3a	5.94	+152	17.2	0.269	25.035	0.032	0.111	0.844	2.025
3b				0.238	29.499	0.049	0.038	0.856	2.262
4a	5.84	+146	17.1	0.251	30.306	0.048	0.047	0.967	2.350
4b				0.143	34.540	0.060	nd	1.108	2.636
5a	4.65	+153	17.1	0.263	30.528	nd	0.091	0.748	2.384
5b				0.293	30.078	0.057	0.042	0.811	2.389
6a	6.07	+125	16.9	0.245	30.513	0.053	0.047	0.967	2.447
6b				0.248	29.909	0.045	nd	0.835	2.488
7a	6.27	+110	16.9	0.260	28.684	0.051	0.039	0.838	2.383
7b				0.270	29.449	nd	0.090	0.921	2.330
8a	6.19	+113	16.9	0.237	32.033	0.059	0.001	0.991	2.662
8b				0.236	30.416	0.051	nd	0.977	2.381
Surface Stream									
9a	5.08	+133	17.5	0.251	30.921	0.047	nd	1.004	2.449
9b				0.242	30.349	0.045	0.052	0.779	2.400

nd = not detected.

Water chemistry

Although evaporation of tiny droplets of seepage water precipitating opal-A is the prime process controlling silica speleothem growth (Wray, 1997a,b, 1999), the tiny size of these drops prohibits direct measurement of their chemistry. However movement of water through the Hawkesbury Sandstone is common, and within a few hundred metres of the stalactite cave several perennial springs of significant flow volume resurge at the closely-underlying disconformable boundary between the sandstone and the lower estuarine/marine units.

Water from eight of these springs and a nearby surface creek flowing on the sandstone were analysed by ion chromatography (Tab. 3). They were all slightly to moderately acid (pH 4.65 to 6.52), and well-oxidised with Eh between +110 mV and +156 mV. Dissolved SO₄²⁺ concentrations ranged between 2.03 ppm and 2.66 ppm (Av. 2.35 ppm, Sd. 0.19), similar to those of other natural surface and groundwaters in the surrounding region (Johnson & Johnson, 1972; Johnson, 1984).

As these sulphate concentrations are not high, alunite is presumably not precipitating directly from these groundwaters; large alunite deposits in hot springs and hyper-saline sedimentary environments usually display sulphate concentrations 2 to 3 orders of magnitude higher (Raymahashay, 1968; Alpers et al., 1992; Long et al., 1992). If, however, other factors such as evaporative concentration of groundwater forming the stalactites, or oxidation of reduced iron-bearing waters, are considered, these concentrations may be sufficient for the formation of alunite under favourable conditions.

DISCUSSION

Various XRD spectra and SEM-EDS spectra and element maps all suggest the presence of small quantities of alunite and the possibility of natroalunite within these stalactites. Although the formation of these sulphate minerals within silica stalactites is seemingly unusual, their presence is not inconsistent with general opal-alunite relationships elsewhere; for example, Barnes & Townsend (1982), Bird et al., (1990), Dill (2001), Thiry et al. (2006) and Blanco et al., (2008) all report the co-formation of alunite and non-speleothem groundwater opal in soil and weathering profiles.

Authigenic speleogenetic alunite-group minerals in cave sediments, and their more widespread presence in weathering profiles, are usually taken as clear indicators of the reaction of sulphate-acidified groundwater on kaolinite, illite, smectite clays or mica (Keller et al., 1967; Goldbery, 1980; Chitale & Güven, 1987; Rouchy & Pierre 1987; Polyak & Güven, 1996; Hill & Forti, 1997; Polyak et al., 1998; Polyak & Provencio, 2001; Blanco et al., 2008), or reactions of acidic solutions with shale matrix, dolomite, or by evaporation (Martini, 1980). Therefore the presence of alunite within these stalactites, but not within the overlying sandstone or any other Sydney-region speleothem so far studied, strongly suggests that it is an authigenic speleothemic product formed by highly localised, but conceivable, geochemical factors.

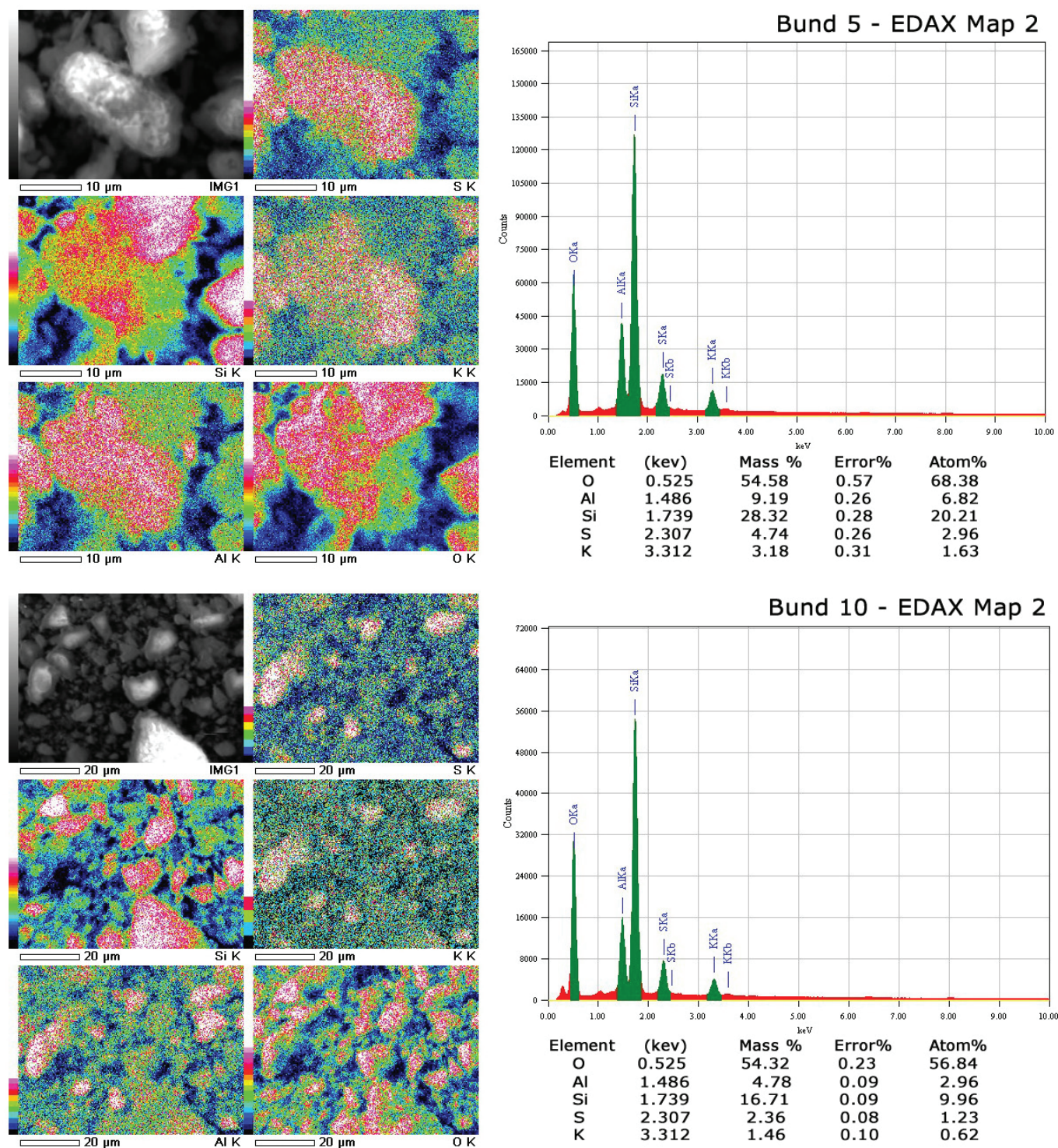


Fig. 3. SEM energy dispersive X-ray spectra and element maps of powdered samples BUND5 and BUND10, the same sample material used for XRD analysis. Element maps for S, Si, K, Al and O. Table indicates relative percentages of selected elements. Sulphur (alunite) is concentrated into certain areas, those also typically high in Si, K, Al and O, presumably the kaolinite clay. However, even at higher magnification, individual pseudo-cubic alunite crystals were not visible.

Goldbery (1978, 1980) identified three critical stages or conditions for the generation of diagenetic non-hydrothermal alunite. Firstly, generation of H_2S and/or pyrite under anaerobic conditions (stage 1), followed by a change to oxidising conditions and the formation of sulphuric acid (H_2SO_4) (stage 2), and finally (stage 3) the alteration of clay minerals (presumably kaolinite and/or illite in this instance) by the sulphuric acid generated in stage 2.

Each of Goldbery's stages is plausible here. Sulphur-bearing minerals are rare within the Hawkesbury Sandstone, but pyrite is quite common within the closely underlying estuarine/marine sediments (Standard, 1969; Herbert & Helby, 1980) and spring waters contain modest levels of dissolved sulphate. Well-oxidised conditions are evidenced by the relatively high Eh of the springwaters, very tiny evaporating water droplets on the stalactites, and

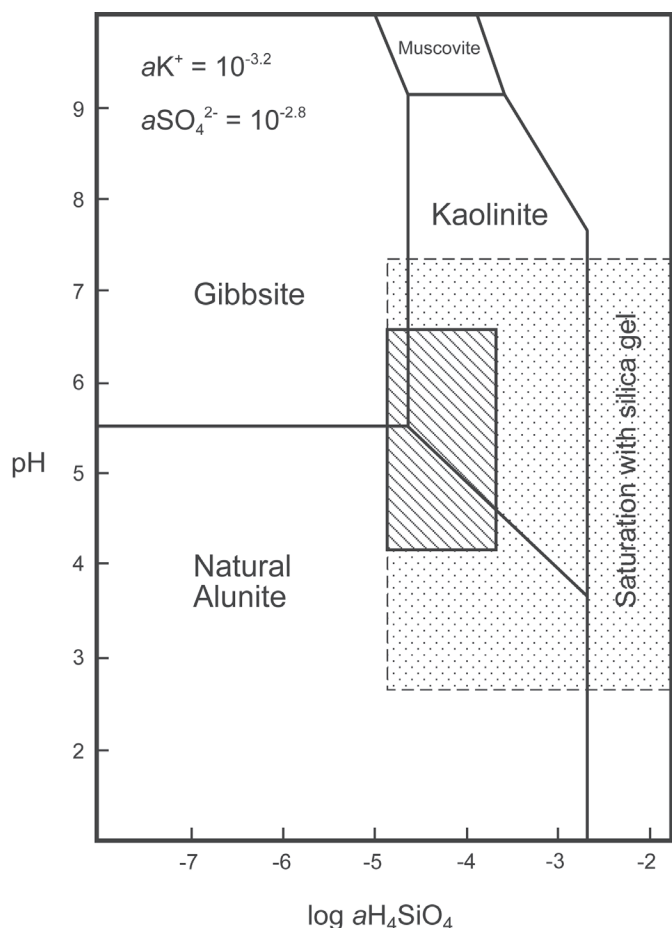


Fig. 4. Stability fields of amorphous silica, gibbsite, kaolinite, muscovite, and natural alunite at 25°C in acid environments (after Raymahashay, 1968, Table 10). Shaded area shows the expected range of geochemical conditions within these stalactites. Hatched zone shows range of pH and dissolved silica reported in local surface and groundwater.

by the common presence of oxidised iron minerals throughout the stalactites. The generation of acid conditions may particularly be encouraged if Ca^{2+} and Mg^{2+} levels are low, as they are here. Clay minerals such as kaolinite and illite necessary for the acid-alteration pathway are plentiful throughout the sandstone, and common within the stalactites.

Thus an acidic-reaction pathway before silica saturation is reached and opal-A precipitates is compatible with the alteration of kaolinite to alunite by sulphate-rich groundwater suggested by Raymahashay (1968). The activities of K^+ , SO_4^{2-} , H_4SiO_4 and pH are the controlling factors (Raymahashay, 1968; Chitale & Güven, 1987), and the equilibrium may shift to the right or left, with kaolinite being converted to alunite releasing additional silica for opal formation, or alunite replaced by kaolinite removing silica from solution.

At 25°C, the thermodynamic stability fields of kaolinite and alunite (Raymahashay, 1968) show that alunite will not form in near-neutral pH solutions (Fig. 4). However at low silica concentrations below a pH of about 5.5, alunite is more stable than kaolinite, but will convert to kaolinite as the H_4SiO_4 concentration increases toward saturation and opal-A

precipitation (i.e. during evaporation of the tiny water droplets seen on stalactites). The H_4SiO_4 activity of the stability boundary between alunite and kaolinite increases with decreasing pH (Fig. 4) (Raymahashay, 1968), therefore, if the pH drops below about 3.7, alunite or natroalunite might conceivably form within these stalactites and persist right up to the point of silica saturation and opal-A precipitation, and some might remain preserved within the opal-A mass rather than reverting to kaolinite. The range of measured springwater pH and typical dissolved silica concentrations in the region fall within the thermodynamic stability fields of this opal-A-kaolinite-alunite system.

An alternative to sulphate-derived acid conditions may come from the oxidation and hydrolysis (ferrolysis) of hydrous Fe^{2+} -oxides. Mann (1983), Thiry et al. (2006) and Blanco et al. (2008) have all suggested that in weathering profiles ferrolysis of dissolved Fe^{2+} compounds can provide pH sufficiently low for the conversion of kaolinite to alunite coincident with the precipitation of opal-A. Such a process where anoxic iron-rich groundwater mixes with oxygenated waters may account for the opaque iron materials within the stalactites (Tab. 1 and 2), and could conceivably lead to the acidic conditions needed for alunite formation.

Another possibility is some form of micro-chemical action by bacteria or other micro-organisms in the precipitation of alunite. Microbial communities are abundant in many active H_2SO_4 caves today, and their excretions are believed to have played an important role in the alteration of clays and other insoluble minerals during speleogenesis (Engel et al., 2000; Hose et al., 2000; Polyak & Provencio, 2001). It was not possible to examine either of these possible alternatives in detail here, but they represent avenues for potentially fruitful future study.

The exact mechanism for the formation of the small quantities of natroalunite that are suggested is uncertain. Chitale & Güven (1987) note that natroalunite may form if Na^+ substitutes for K^+ , and it is possible that it could form by cation exchange on pre-existing alunite, or by direct precipitation from solutions of appropriate composition.

Several other uncertainties exist and offer avenues for further exploration. The dominance of the opal-A and kaolinite over the alunite has not allowed the determination of the exact composition of the alunite or natroalunite within these stalactites, and has not permitted the calculation of the alunite unit-cell dimensions. Some slight differences are also seen between the properties of the XRD spectra of this alunite compared with the published characteristics of pure hydrothermal alunite. However, such variations are not uncommon (Keller et al., 1967), and they are not believed to cast doubt on the mineral identification. For example, the typically strong 2.29 Å and 1.92 Å peaks of pure alunite are attenuated on the stalactite XRD spectra, and seem to be shifted slightly. This has presumably resulted from the micro-crystalline alunite being mixed with large amounts of kaolinite and opal-A, slight variations in the chemistry of the different samples, or poor crystal ordering (perfection) delimiting crystal size as suggested by Keller et al. (1967).

CONCLUSIONS

A number of XRD and SEM-EDS spectra and element maps have provided evidence for the occurrence of authigenic alunite in small opal-A stalactites, produced during the normal silica stalactite-forming process. These spectra are the first known evidence for low temperature origin of alunite in silica speleothems, and only the second known instance of stalactitic alunite.

This low temperature co-production of alunite with speleothem opal-A seems to be an unusual geochemical process, but is consistent with observations of the authigenic formation of alunite and groundwater opal elsewhere. The presence of both alunite and kaolinite suggests that the geochemical conditions within these stalactites lie close to the opal-kaolinite-alunite stability boundary at moderately acidic pH. Reaction of sulphuric acid, generated from pyrite, with kaolinite is the probable mechanism of alunite genesis. Iron oxidation and ferrolysis, or unknown biologic-mediated mechanisms, might also lower pH sufficiently to contribute to alunite production.

It is also suspected that small amounts of natroalunite are present, but the XRD diffraction patterns are not sufficiently clear for positive identification.

To date, alunite-group minerals have not been discovered in any other Sydney region stalactites, but none have been analysed that have formed as close to pyrite-bearing estuarine/marine rocks as these. Further detailed field and laboratory investigations of other silica speleothems from this and other areas are therefore warranted.

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