Halloysite formation in Cenozoic sediments marginal to the Eucla Basin, South Australia

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The Eucla Basin in southern Australia is one of the world's largest onshore areas of Cenozoic marine deposits with a 2,000 km long coastal margin that extends up to 370 km inland of the present-day coastline (Fig. 1). The central basin is occupied by cool-water marine carbonates of Wilson Bluff Limestone, Abrakurrie and Nullarbor Limestone, up to 300 m thick, deposited during marine transgressions during Early Eocene to Miocene times. With the onset of marine transgression the flow in major rivers to the basin slowed and sand and organic matter accumulated as valley fills. This was particularly so along the northeastern basin margin where the formation of extensive coastal barrier dunes was accompanied by backshore lagoons and swamps. Sediments accumulated here under reducing conditions provide a huge store of organic and sulfidic materials. Subsequent marine regression, uplift and lowering of the water table have resulted in ongoing oxidation of Cenozoic sediments and acidification of groundwater, particularly within confined aquifers of the palaeovalley network. Under present-day arid conditions, sites of acid groundwater leakage and evaporation are marked by salts and mineral precipitates that include alunite and halloysite. Similar conditions have existed since Miocene times and there is potential for significant accumulation of these minerals.

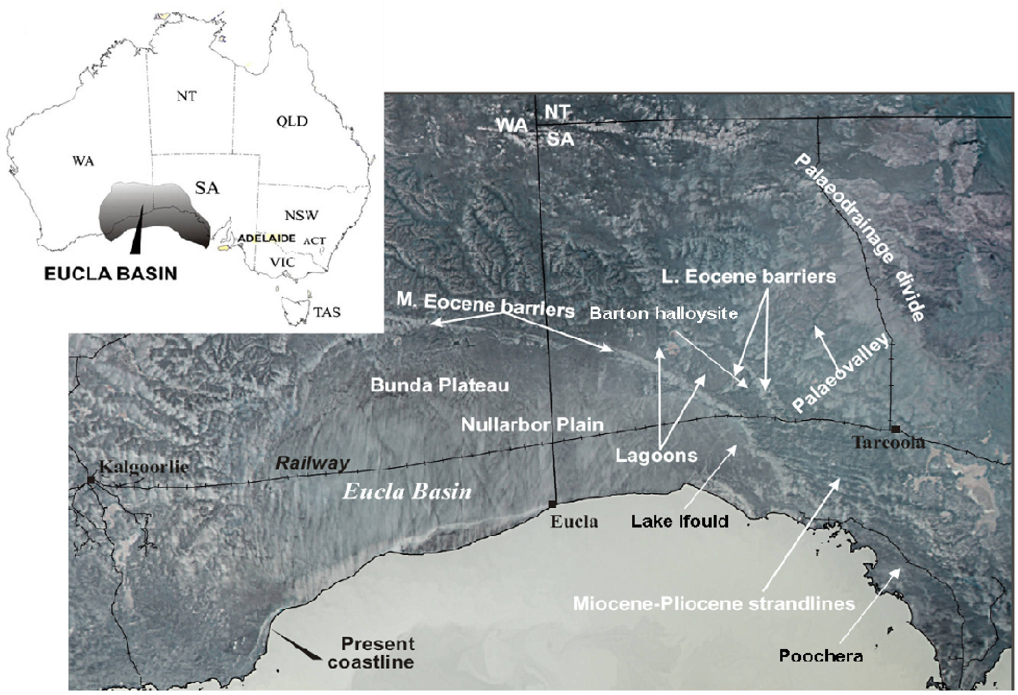

Fig. 1. Location Eucla Basin (inset) with palaeo-landscape and localities shown on NOAA-AVHRR night-time thermal image (modified from Hou et al., 2008)

Alunite and jarosite, associated with microcrystalline kaolin, were identified by Lock (1988) as a major mineral component in sediments of 22 playa lakes on northern Eyre Peninsula. Maximum thickness of chemical sediments was 2.3 m at Lake Wannamanna. Acidity of lake water ranged from pH 2.8 to 3.7. Similar low pH values, with high levels of dissolved aluminium, iron, potassium and silica were reported for saline groundwater sampled from bores drilled into Cenozoic valley fill at Oak Valley in the northern Eucla Basin (Table 1). At the Poochera kaolin deposit, 0.8 m of mixed halloysite and alunite was intersected in Cenozoic sedimentary cover on deeply kaolinised granitic bedrock (Ferris and Keeling, 1996). King (1952) reported intersecting 12 m of alunite-rich clays during drilling at Lake Ifould. Halloysite is present in these samples. An estimated 250,000 tonnes of alunitic clay was outlined. In 1976, CRA Exploration intersected 4 m of halloysite in hole RCH 7 (Fig. 2) while searching for lignite deposits in Eocene sands, northwest of Barton rail siding (Whitby, 1976). The same halloysite was present at the surface in a small playa lake, 250 m northeast of the drill site. The lake occurrence, Camel Lake site, was investigated in 1996 with three shallow auger holes and bulk samples were taken for mineralogical analysis (Keeling et al., 2002).

Table 1. Oak Valley groundwater chemistry - site 36036C (Tewkesbury and Dodds, 1996).

pH	2.8
Dissolved solids	38,000 mg/L
Calcium	195 mg/L
Magnesium	1,780 mg/L
Potassium	533 mg/L
Sulphate	7,140 mg/L
Chloride	10,100 mg/L
Silica (reactive)	94 mg/L
Aluminium	352 mg/L
Iron	228 mg/L

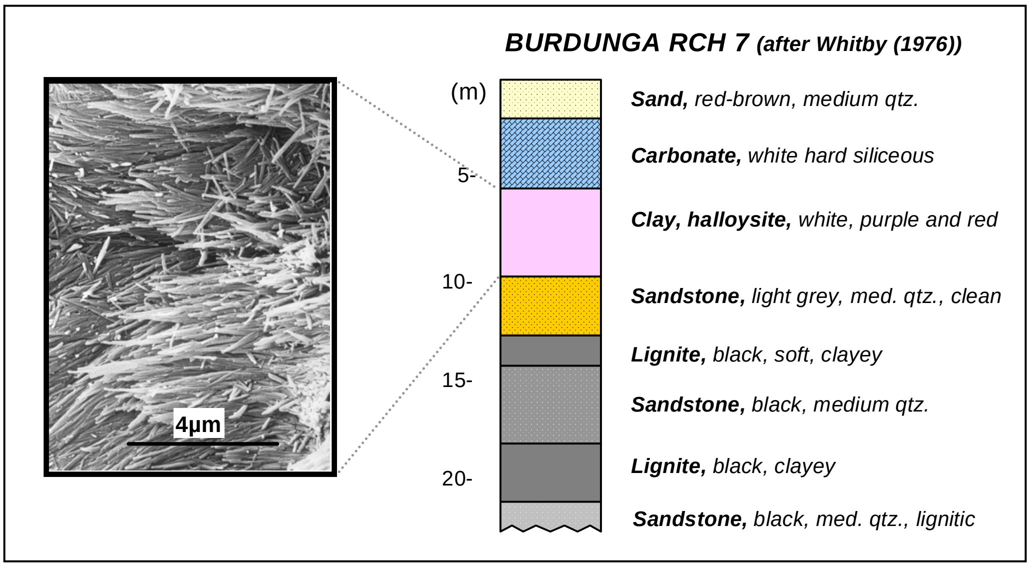

Fig. 2. Summary log of the upper portion of drill hole RCH 7 (after Whitby, 1976) with SEM image of halloysite taken of cuttings from the interval 6-8 m.

At Camel Lake, dehydrated halloysite (7.4Å) makes up between 9 to 72% of the sediment (Table 2) and forms as regular tubes, 0.5-4.0 microns in length and 0.05-0.08 microns diameter. Scanning electron microscopy of raw samples show the halloysite crystallizes with a high degree of alignment (Fig. 2). Other minerals present include halite, gypsum, alunite, quartz and hematite (Table 2).

Table 2. Quantitative mineralogy of auger samples (by rational analysis using XRD and XRF results).

Sample (Depth m)	Halloysite %	Quartz %	Alunite %	Halite %	Gypsum %	Magnesium phase (unidentified)	Hematite %	Anatase %	TOTAL
CLA1									
0.03-0.4	72	6	4	14	0.2	2.2	0.6	0.0	99.0
0.4-0.6	52	21	11	8	0.1	1.3	4.6	0.3	98.3
0.6 0.9	35	56	4	5	0.1	0.7	0.8	0.1	101.7
CLA2									
0.05-0.25	38	22	13	18	0.4	5.4	0.8	0.1	97.7
0.25-0.55	41	17	15	13	8.0	4.1	0.9	0.0	99.0
0.55-0.7	34	44	7	10	1.1	2.3	1.5	0.1	100.0
0.7-0.8	18	70	5	5	2.1	1.0	0.9	0.1	102.1
CLA3									
0.03-0.6	9	29	54	4	0.2	0.9	2.6	0.3	100.0
0.6-0.9	20	51	25	3	0.2	0.6	1.2	0.3	101.3

Assumptions: All Fe_2O_3 as hematite. All TiO_2 as anatase. All Na as halite. All K_2O as alunite. Remaining Al_2O_3 as halloysite. Remaining SiO_2 as quartz. Mg phase not identified in XRD analysis, assumed to be present as dehydrated poorly crystalline salts of $MgSO_4$ (based on remaining SO_3) and $MgCl_2$.

Playa lakes in the region reflect low lying sites in the landscape and are commonly aligned along older fluvial channels and lakes. This is the case with the Camel Lake playa where lacustrine carbonates overlie Eocene channel sands and confirm the area as a site of deposition throughout the Cenozoic. Halloysite content relative to alunite increases from east to west across the dry lake bed (see Fig. 3 for sample locations). Alunite was not recorded in the sample examined from RCH 7. Regional groundwater flow is from east to west. At times of groundwater recharge, a rise in the water table in channel sediments would bring acid groundwater to the surface of the playa. Evaporation of groundwater with a composition comparable to that within the Oak Valley channel (Table 1) would favour precipitation of alunite, with resulting decrease in pH. Halloysite precipitation would require pH >2.8, a significant reduction in sulphate ions and ideally an increase in reactive silica in solution. Critical factors at the Camel Lake site may include the overlying carbonate unit to buffer groundwater acidity and remove sulphate through precipitation of gypsum. The carbonate might also supply reactive silica, although amorphous silica is potentially available from silcrete layers in the sandstone (Fig. 3). Accommodation space required for thick accumulation of halloysite could result either from replacement of a pre-existing clay lense, silica dissolution, or more likely, dissolution along the base the overlying carbonate unit.

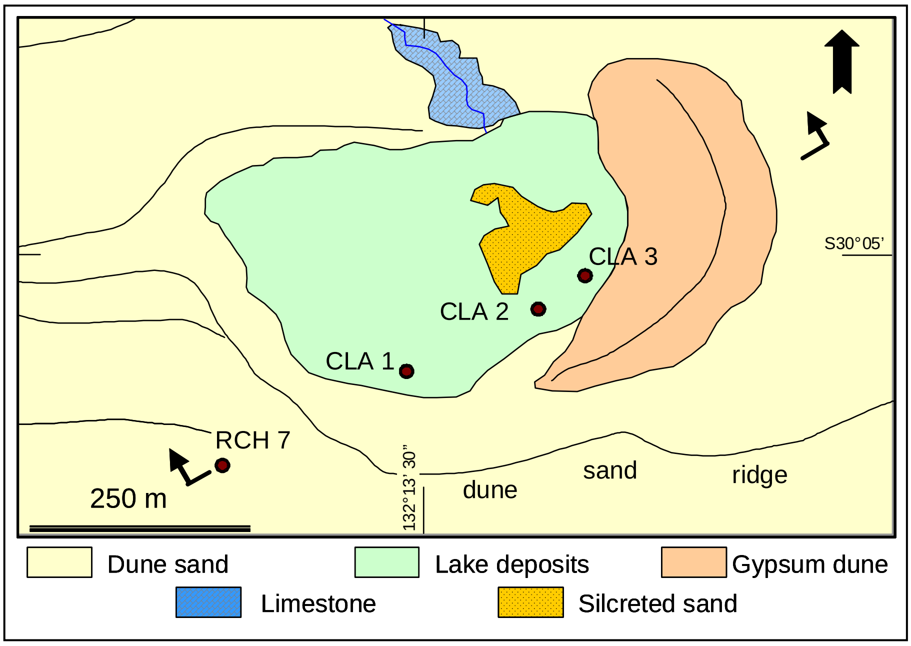

Fig. 3. Geological sketch of the Camel Lake playa showing drill hole and section location.

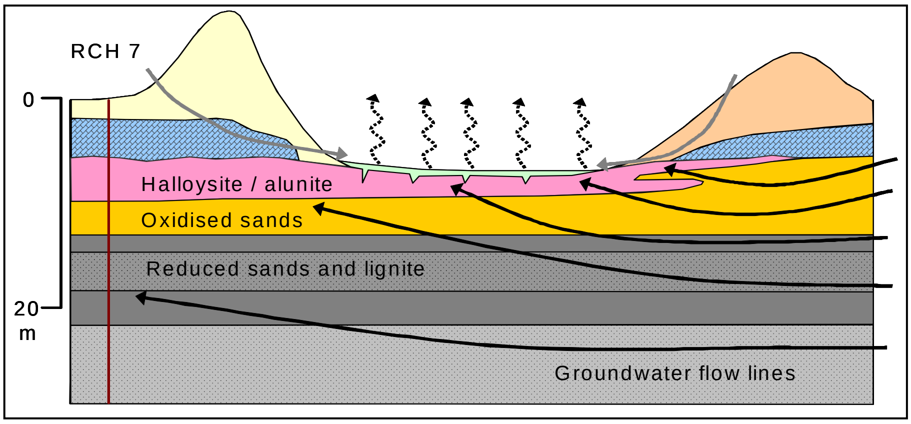

Fig. 4. Section through Camel Lake showing interpreted surface and groundwater flow lines.

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