

Salty Matters

John Warren - Thursday July 23, 2015

Saline clays

When discussing evaporites we typically focus on the formation and alteration of the various evaporite salts and their diagenetic evolution, but the same evolving saline hydrologies can also drive the formation and alteration of clays (Table 1). Many authigenic clay minerals formed in hypersaline settings are enriched in magnesium (Fisher, 1988), but authigenic clays do not make up the greater volumes of clay in modern or ancient salt lakes. Most of the clays in salt lakes and playas are detrital and reflect compositions of older argillaceous formations in the palaeodrainage areas. Illite, kaolinite, chlorite, dioctahedral smectite and a number of mixed-layers clays are commonplace detrital clay minerals in saline formations (Figure 1; Calvo et al., 1999). Widespread flocculation of clays is an effective sedimenter of suspended clay wherever freshwater runoff and streams flood an area of standing saline water. Thus the composition of initial clay sediments in a playa largely reflects that of the minerals carried as suspended load into the lacustrine depression.

The magnitude of detrital clastic input is thought to be a significant factor in the relative volume of authigenic clay. Regions with rapid deposition of clays, tied to high detrital inputs, tend to be areas where the authigenic clay component is swamped by the high detrital input. Clay authigenesis in evaporitic basins is favoured in marginal playa areas where rates of detrital clay input are low (Figure 1). This encompasses interdunal depressions, peripheral sandflats and muddy carbonate flats. In these low sedimentation areas the transformation of precursor clays is more effective, driven by episode surface inflow and groundwater discharge (Calvo et al., 1999). Highly

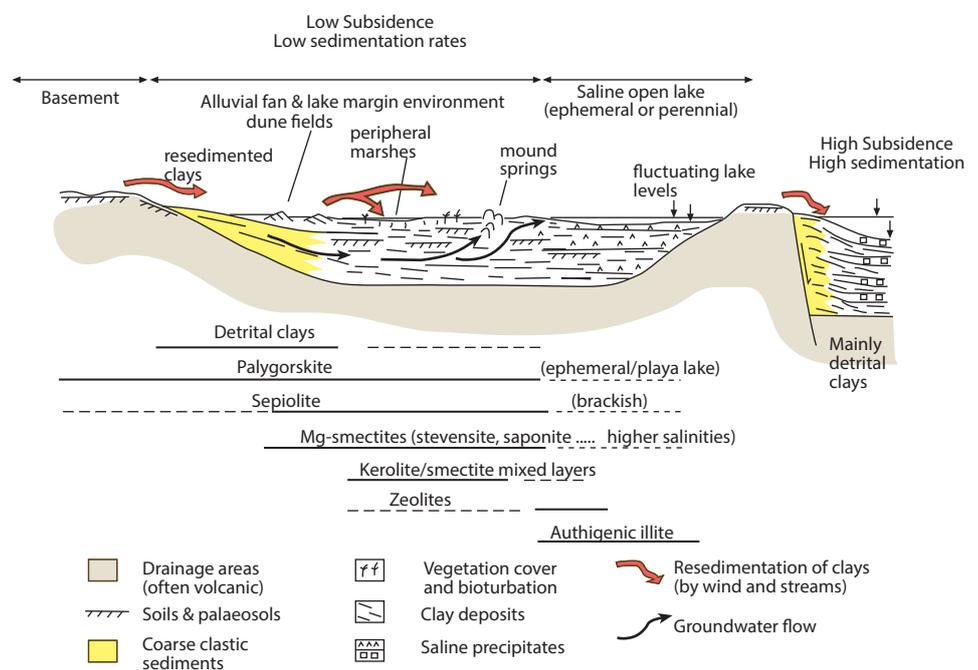


Figure 1. Distribution of authigenic clays in saline continental environments, emphasising the differences between basins undergoing slow versus rapid subsidence. Authigenic clays form mostly in saline lake-margin environments. Formation of authigenic clays in open-lake environments is dependent on the degree of schizohalinity.

reactive nearsurface and surface conditions are favoured by inherently large variations in pore water salinity, pH and $p\text{CO}_2$ levels.

Clay authigenesis in many saline depressions is driven by pedogenesis, especially in the marginal areas where sedimentation rates are low and subaerial exposure dominates at the sedimentation surface. Below the surface episodic wet-dry cycles means neoformed clays are the byproduct of complex reactions between

	Structural Formula	Mg/Si	Al/Si
Saponite	$(\text{Ca, Na})_{0.3}(\text{Mg, Fe})_3(\text{Si, Al})_4\text{O}_{10}(\text{OH})_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	0.76-0.87	0.07-0.18
Kerolite	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot \text{H}_2\text{O}$	0.75	0.0
Stevensite	$\text{Na}_{0.15}\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_4$	0.75	0.0
Hectorite	$\text{Na}_{0.3}(\text{Mg, Li})_3\text{Si}_4\text{O}_{10}(\text{F, OH})_2$	0.67	0.0
Sepiolite	$\text{Mg}_3\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$	0.67	0.0
Palygorskite	$(\text{Mg, Al})_2\text{Si}_4\text{O}_{10}(\text{OH}) \cdot 4\text{H}_2\text{O}$	0.17-0.49	0.02-0.31

Table 1. Main authigenic clay minerals occurring in continental evaporitic environments.

Clays in evaporitic environments are mostly detrital (wind and water carried), authigenic saline clays are most obvious in evaporitic regions with lesser detrital clay input.

Na and Mg-rich interstitial brines and detrital silicates. Pedogenic processes account for the formation of widespread lake margin palygorskite and sepiolite, typically in association with the creation of calcretes, dolocretes and silcretes. In cases where palygorskite dominates the soil profile, they are sometimes described as palycretes. Zeolites can also form from saline groundwaters in saline lake-margin pedogenic settings (Figure 2). Artesian and phreatic groundwater discharge through springs into the lake margin areas also plays a significant role in the formation of other authigenic clays, as in saline lakes at the foot of Mt Kilimanjaro, in Tanzania and Kenya (Hay et al., 1995).

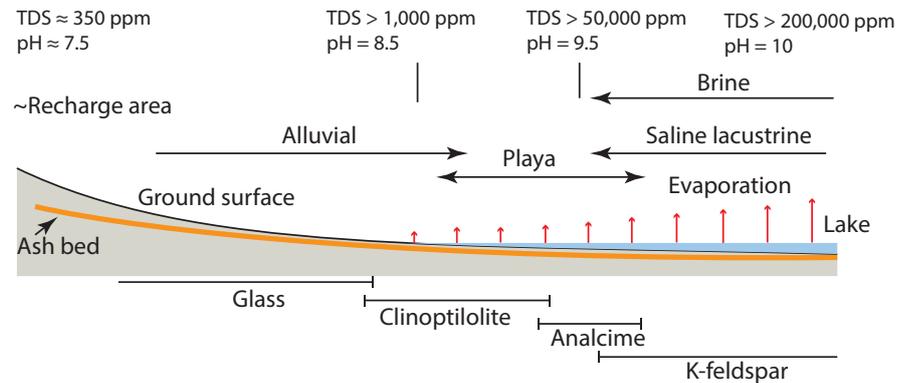


Figure 2. Zeolite distribution in relation to the pore brines in a saline lacustrine system that are driving the alteration of the volcanic glass. TDS = total dissolve solids. (after Deer et al., 2004)

Hypersaline brines in modern, marine-edge evaporite basins can also enhance clay authigenesis even in settings where thermal and saline stresses keep both organic and inorganic carbon concentrations in the sediments unusually low relative to coastal marine environments with lower salinities (Martini et al., 2002). This is the case in Salina Ometepec where sediment pore waters exhibit little microbial sulphate reduction, and dissolved inorganic C contents are also very low. Instead of carbonate alteration (dolomitisation) in the Mg brine, authigenic K-rich Mg-smectite (saponite) formation is occurring, driven by the concurrent processes of brine concentration, selective dissolution of K- and Mg-bearing salts, and dissolution of detrital aluminosilicates. Salina Ometepec pore waters at a depth of 1 m have $87\text{Sr}/86\text{Sr}$ ratios that require input of Sr that is less radiogenic than that of Gulf of California seawater. This Sr is likely derived from weathering and leaching of detrital aluminosilicates from nearby volcanoclastic sources. Although rare in Holocene successions, similar Mg-rich authigenic clay assemblages are well documented in Palaeozoic evaporite basins (Bodine, 1983; Janks et al., 1992; Andreason, 1992).

Once precipitated in an evaporite basin, authigenic clays can be retransported further out into the saline depression and in more humid climatic stages may even end up on the floor of freshwater lakes (Figure 1). This situation is seen in lacustrine sequences from the Miocene formations of the Madrid Basin (Bellanca et al., 1992) where significant amounts of palygorskite and sepiolite occur as either mud chips or clay aggregates in the basal part of a fresher water lacustrine unit. Eolian transport of saltating clay pellets or dust suspensions may also contribute to the transport of authigenic clays from marginal to more central areas. This sometimes leads to problems of interpretation of detrital versus authigenic in ancient lacustrine successions subject to oscillations in climate, especially when detrital clays are partially or fully inherited from arid soils.

Sepiolite, interstratified Mg-Smectite and palygorskite form authigenic phases in the Quaternary sediments of the Double Lakes Formation, Texas (Webster and Jones, 1994). The dominance of each of these minerals in separate horizons represents evaporative shifts in salinity at the time they precipitated. Sepiolite is thought to indicate a brackish lake, while Mg-smectite indicates more saline conditions. Palygorskite is interpreted as a saline pore water precipitate in the arid soils of the playa stage. Likewise Jones (1986) interpreted authigenic Mg-smectites (e.g. stevensite) as requiring higher salinity than sepiolite. Mg-silicates also define saline lake clays in Great Salt Lake (Spencer, 1983) and some Bolivian salars (Badaut and Risacher, 1983). In Bolivia, the authigenic Mg-smectite replaces the biogenic silica in diatom frustules and requires a pH in excess of 8.2. Authigenic stevensite occurs in unconsolidated

Sepiolite, interstratified Mg-Smectite and palygorskite and zeolites are significant authigenic saline clays

In alkaline settings authigenic clays can replace diatom frustules, and stevensite ooids can form.

muds underlying saline crusts in the interdunal depressions of northern Lake Chad and as small aragonite-associated oolites on the lake floor (Gac 1980, Darragi and Tardy, 1987). Similar stevensite oolites have been found in the Eocene Green River lacustrine basin. Stevensite is also an early authigenic phase in the modern carbonate thrombolites in the hyposaline Lake Clifton, Australia (Burne et al., 2014). Authigenic sepiolite associated with calcite, gypsum and dolomite occurs about the margin of Saline Valley Playa, California and the edges of saline pans in the Kalahari of southern Africa (Hardie, 1968; Kautz and Porada, 1976). Palygorskite, sepiolite and authigenic smectite are commonplace precipitates in calcretes of groundwater discharge playas in inland Australia (Arakel et al., 1990).

Clearly, palygorskite and sepiolite (both two-chain structure fibrous clays) occur worldwide as authigenic phases in the soils and palaeosols of arid and semi-arid regions, but the mode of precipitation is still not well understood (Singer, 1979). Both minerals are common in environments with elevated levels of magnesium and silica. Hence they form in alkaline lakes and caliche, as well as in deep sea sediments and Hydrothermal alteration products; Folk and Rasbury (2007) argue there may also be a microbial association to their formation, at least in some Texan caliches. Jones (1986) concluded sepiolite in the calcic soils of southwest Nevada required percolation of high salinity groundwaters. Magnesium and silica solutes were supplied by the weathering of nearby pyroclastics and carbonates. Sepiolite has replaced magnesite pebbles, from the edges in, during freshened highstand intervals in Miocene Lake Eskisehir in Turkey (Ece, 1998). Palygorskite in calcic soils is thought to be the result of incongruent dissolution of pre-existing clays (Jones and Galán, 1988). Fibrous clays degrade when climate becomes more humid and alter to smectite. Paquet and Millot (1972) conclude that the transformation takes place when mean rainfall exceeds 300 mm and Calvo et al. (1999) suggested the transformation can be used as a palaeoclimatic indicator.

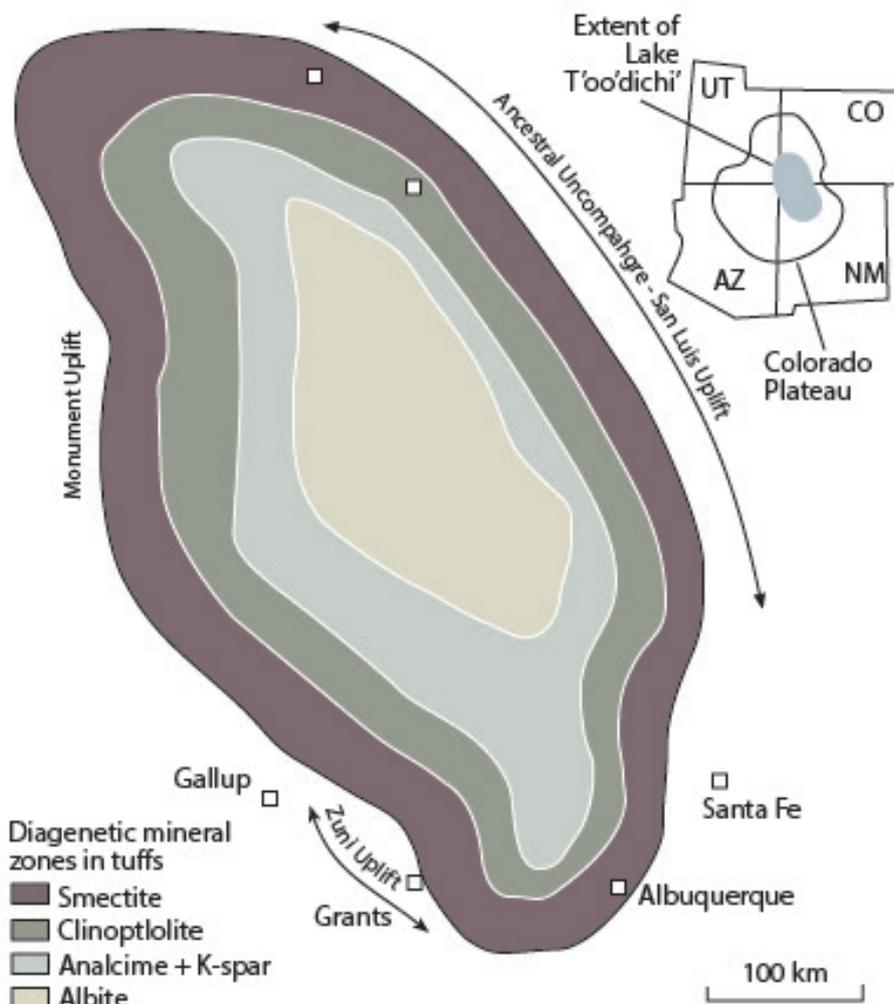


Figure 3. Basinward progression of concentric alteration haloes in the tuff lithofacies in the lacustrine Brushy Basin Member of Jurassic Lake T'oo'dichi' (after Turner and Fishman, 1991) This ancient alkaline lake occupied the combined San Juan-Paradox Basin area and was bound by structurally active uplift areas (related to an active volcanic arc that lay to the west).

Alunite, a potash clay and possible future potash ore is a authigenic clay in acid arid settings

It is a common product where precursor clays are present in saline zones of sulphate reduction

Alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) is a common clay product in acid saline lacustrine settings, but can also form diagenetically in regions where sulphate reduction is occurring. It is thought to be derived by the reaction of clay minerals with sulphuric acid created by oxidation of sulphides or H_2S at a redox boundary. It is a common product where clays are present in zones of sulphate reduction and examples have been documented in the Middle Miocene gypsums of the Gulf of Suez (Rouchy et al., 1995) and the Upper Miocene gypsums of the Lorca Basin in Spain (Rouchy et al., 1998).

Even the smectite to illite transformation, which is used as an indicator of diagenetic intensity and clay transformations occurring at higher temperatures may be influenced by salinity. This makes illite crystallinity a less reliable indicator of diagenetic stage in environments with saline pore fluids (Honty et al., 2004). Turner and Fishman (1991) found illite-smectite mixed layer clays having a range of expandabilities in altered tuff beds in a Jurassic lake in the Morrison Formation (Eastern Colorado Plateau, USA). The observed clays did not experience deep burial, and did not undergo hydrothermal alteration. The illite content generally increases from the lake margin (100–70% smectite) to the lake centre (30–0% smectite) and follows a lateral hydrogeochemical gradient, which was characterized by increasing salinity and alkalinity (Figure 3). It seems that in a saline depositional setting, solution chemistry is a principal factor controlling the smectite to illite proportion. Illite-smectite can form from smectite at low temperatures in several ways (see Honty et al., 2004), but forms best in saline environments subject to wetting and drying cycles, which is a hydrology exemplified in salt lakes and playas. In the presence of K^+ ions, alternating wetting and drying leads to irreversible fixation of K and the formation of illite layers. Illite-smectite clays forming at elevated pH may not even require wetting and drying cycles.

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John Warren, Chief Technical Director
SaltWork Consultants Pte Ltd (ACN 068 889 127)
Kingston Park, Adelaide, South Australia 5049

www.saltworkconsultants.com