

A GLIMPSE AT THE GEOCHEMISTRY OF ALKALINE SALT-AFFECTED SOILS

Michael S. Smith

CRC LEME, Department of Earth & Marine Sciences, Australian National University, Canberra, ACT, 0200

INTRODUCTION

Alkaline salt-affected soils are typically formed by the accumulation of sodium carbonate and bicarbonate. These ions are generally thought to be supplied by the discharge of shallow Na-HCO₃-rich groundwaters, especially in young volcanic areas that have very high rates of evapotranspiration (Kovda & Samoilova 1969, Szabolcs 1989). The specific geochemical evolution of alkaline salt-affected soils is unclear, but may be comparable with that of an open body of alkaline water. The concentration of ions in an evaporating open water body with a positive residual alkalinity (RA = carbonate alkalinity – 2[Ca²⁺] – 2[Mg²⁺], in eq/L) causes the precipitation of calcite with a concomitant increase in the Mg/Ca and Na/Ca ratios of the residual solution. Thus, the Mg/Ca ratio of subsequently precipitated carbonate will increase until thermodynamic and kinetic conditions in the waters enable the formation of dolomite or Mg-silicate (Eugster & Jones 1979) and perhaps, in turn, amorphous silica (Chernet *et al.* 2001). Smectite is typically the dominant clay mineral present (Kovda & Samoilova 1969, Szabolcs 1989) and silica commonly accumulates in considerable amounts (Kelley & Brown 1939, Szabolcs & Darab 1958) in alkaline salt-affected soils. Thus, as a cursory model, the evaporation of an open water body seems to fit the formation of alkaline salt-affected soils.

The evaporation model, however, neglects the possible influence of other discharge-site mechanisms that can supply bases to increase soil alkalinity. Such mechanisms include silicate and carbonate mineral weathering (Evans *et al.* 1986, Ohte *et al.* 1995), ion exchange (Mashhady & Rowell 1978), de-gassing, redox reactions (Whittig & Janitzky 1963) and the common-ion effect (Kelley 1951; Miller *et al.* 1989). The relative significance of these processes is unknown (Kelley 1951, Kovda & Samoilova 1969). Additionally, the soil system may be complicated by the interaction of selectively dissolved efflorescences (Drever & Smith 1978). Furthermore, the specific geochemical processes of calcium-carbonate precipitation in soils, both saline and non-saline, from groundwater sources have not been well defined (Fitzpatrick & Merry 1999) and the role of amorphous silica in the formation of alkaline salt-affected soils has not been thoroughly studied. The influence of bases such as borate may be significant even where the soil anions are dominated by carbonate and bicarbonate ions (Szabolcs 1989). Hence, further work is required to evaluate these aspects of alkaline soils.

Alkaline salt-affected vertosols are particularly common at the margins of Miocene basalt in northern New South Wales. Preliminary findings on the geochemistry of one scald and a non-alkaline soil about 300 m laterally adjacent to the scald are presented below. These results were obtained by X-Ray Diffraction (XRD), Energy-Dispersive X-Ray Analysis (EDXA) and the analysis of soil pore waters.

RESULTS

Mineralogy of soil salinisation

The saline soil under investigation is a salic, crusty, black vertosol. It is encrusted with pale, finely laminated and weakly consolidated sandstone generally less than 10 mm thick. This crust comprises clasts of predominately quartz, but also contains very minor pelletal carbonate. The sandstone is irregularly cemented with chalcedony and many of the quartz clasts have sutured boundaries with diffuse extinction in cross-polarised light. The soil also had a sporadic surface of puffy, powdery dark clay, but this texture has been destroyed by several years (2002-2005) of compaction by cattle. Silcrete fragments are common on the soil surface. For comparison, the non-alkaline, non-waterlogged soil adjacent to the scald is described. This soil is an epicalcareous, epipedal, black vertosol and contains a gypsic subsoil horizon between depths of 74-105 cm.

Highly soluble salts were not found in the scalded soil although similar puffy soil at a mud volcano contains halite. Calcite and dolomite exist in the scalded soil as microscopically disseminated crystals in the matrix and as mottles and, from a minimum depth of about 240 cm, nodules. In the adjacent soil, the matrix does not effervesce in dilute HCl whereas calcite nodules are present throughout the profile apart from the topsoil. At depths greater than about 1.8 m the mineral carbonate content in the profiles of both the scalded and adjacent soils is high and spatially highly variable (Figure 1a) due to the presence of calcareous segregations.

However, in about the uppermost 1 m of each profile, the calcite abundance systematically increases and then decreases toward the surface whereas the dolomite content at the scald decreases. Carbonates in the scalded soil profile range widely in their molar MgCO_3 content (Figure 1b) and comprise high-Ca dolomite and high-Mg calcite (> 4 mole percentage MgCO_3), except at the greatest depth sampled where at least some nodular stoichiometric dolomite (based on EDXA) exists. The MgCO_3 mol % of calcite in the shallowest 1 m of both profiles follows a trend similar to those of the weight percentages of calcite. From depth up to about 2 m in the scalded soil, the MgCO_3 mol % of calcite generally increases and the MgCO_3 content of two distinctly different dolomite populations converge. Above that depth, the dolomite with the higher MgCO_3 content disappears and above a depth of 1.2–1.4 m the MgCO_3 content increases toward the surface where it attains about 46 mol %. The soil profile adjacent to the scald contains mostly low-Mg calcite that, at depth, has a consistent MgCO_3 mol %. This percentage increases from the same depth that the MgCO_3 content of the scald's dolomite does. Dolomite, present only in the gypsic horizon, has a MgCO_3 content of 47 mol % and is, hence, also high-Ca dolomite.

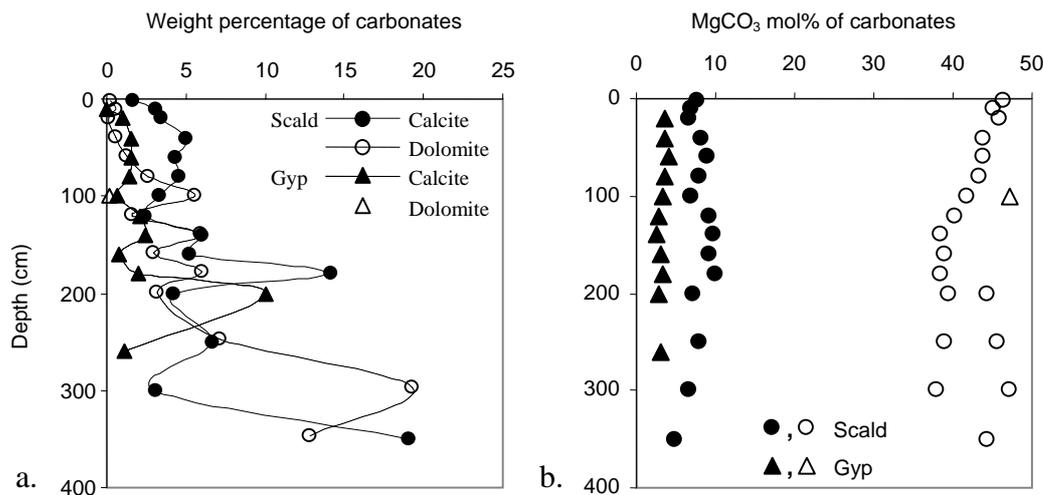


Figure 1: Abundance and Mg content of carbonates in the scalded (Scald) and adjacent (Gyp) soil profiles. **a (left):** Weight percentage of calcite and dolomite as determined by Rietveld analysis (Siroquant™). **b (right):** Mole percentage of MgCO_3 in calcite and dolomite as determined from their unit-cell dimensions by XRD.

Spherulitic silcrete, occurring as pebble- to cobble-size irregular to lobate nodules and internally laminated slabby fragments, exists across the entire scald and downslope to the edge of the modern alluvium. Downslope of the scald, the silcrete occupies an area substantially broader than the width of the scald. The silcrete commonly has surfaces with leaf moulds or reticulated sphaeresis cracks or comprises silicified wood. Structures that are reminiscent of soft-sediment deformation, especially contorted laminae, slickensides and the lobate habit, are common. Rarely, the silcrete hosts silicified pedotubules (infilled tubular macropores). These features suggest a shallow depth of the regolith prior to silicification. Some silcrete comprises fine (up to 2 mm) spherulites that are generally sutured together apart from pores that are filled with opaque Fe-oxyhydroxide, Ca-phosphate or, more rarely, sparry/microsparry calcite. Other silcrete contains spherulites in a matrix of blocky quartz or as sheaf-like mammillary linings of voids in microcrystalline quartz. The spherulites are composed of: (1) megaquartz with quartzine; or, (2) chalcidone. Quartzine is commonly found elsewhere in association with gypsum and anhydrite in evaporitic sequences (Folk & Pittman 1971). In addition, silcrete commonly replaces calccrete and limestone (Smale 1973).

Quartzine-megaquartz spherulites have a core and thin core-halo of high-Mg calcite and/or baryte (Figure 2a). Rare sylvite was found crystallised after thin-section preparation, suggesting either sample contamination or that salts present in the sample had been locally remobilised during preparation. Rounded nodules of calcite and dolomite averaging 3.0 and 45.3 mol % MgCO_3 (determined by EDXA), respectively, are abundant within one silcrete sample. Numerous examples of replacement structures in silcrete suggest the former presence of evaporite minerals within the regolith. Rhombic crystals of quartz occupy the cores of some spherulites (Figure 2b). Whilst most masses of megaquartz are spherulitic, some are distinctly rhombic or prismatic. Fractures within a silicified goethitic ferricrete are lined with skeletal relics of a mineral that have been replaced by goethite. The presence of relics as a fracture lining indicates their secondary nature with respect to ferricrete formation. These relics typically also exist floating within the silica fracture-filling cement. Goethitic relics after a rhombic mineral have also been preserved within microcrystalline quartz in

vughs of the scalded soil's laminated crust. The features of the silcrete are characteristic of Magadi-type chert (Sheppard & Gude 1986).

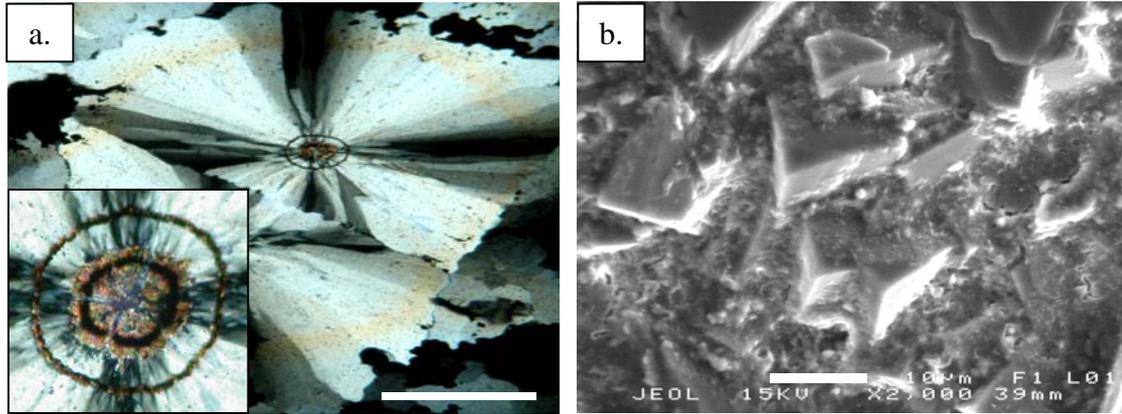


Figure 2: Spherulitic silcrete associated with alkaline salt-affected soils at Bellata. **a (left):** Spherulites of quartzine which grades radially into megaquartz. The cores typically contain high-Mg calcite (shown in inset) and baryte with minor Fe oxyhydroxide (xpl; scale bar is 1 mm). **b (right):** SEM image of a spherulite core comprising quartz pseudomorphs after a rhombic mineral (scale bar is 10 μ m).

Basic chemistry

The scalded soil's (Scald) profile of electrolytic conductivity (EC_w ; Figure 3) suggests that, if due solely to evapotranspiration, only a very minor increase in the solute concentration of the marginally saline groundwater (Tb) is necessary to precipitate carbonate minerals throughout the profile. In contrast, the EC_w of the adjacent non-alkaline soil (Gyp) is very high at depth, but decreases dramatically toward the gypic horizon and rises in the shallow subsoil. The scalded soil profile has a positive residual alkalinity (RA) and a sodium adsorption ratio (SAR) that increases toward the surface whereas the RA and SAR of the non-scalded soil, respectively, is generally very negative and decreases toward the surface (Figure 4). Thus, two very distinct processes of soil salinisation are taking place side by side and which cannot be a mere consequence of evapotranspiration of the same type of groundwater.

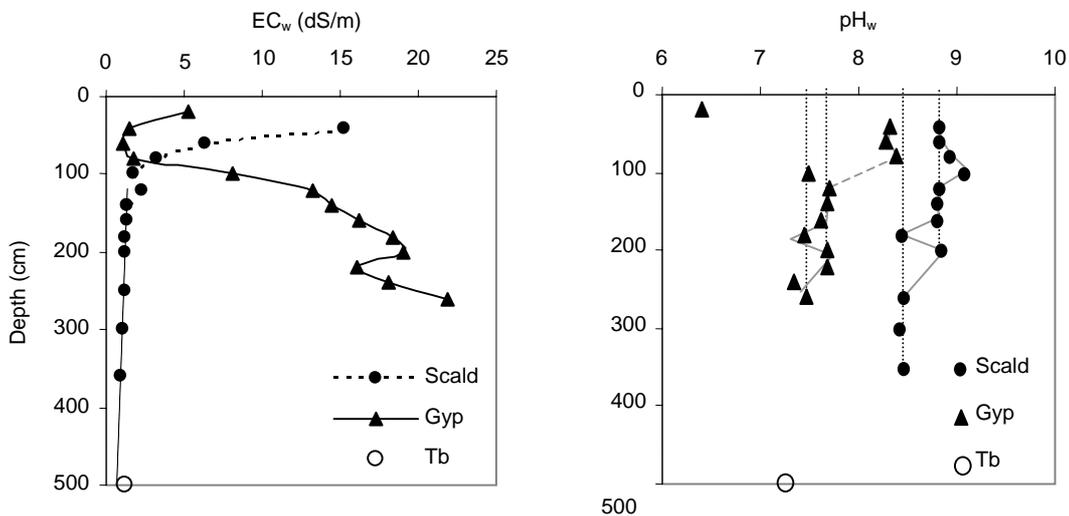


Figure 3. Depth profiles of soil-water electrical conductivity (EC_w) and pH (pH_w).

The $pH_{1.5}$ and pH_{CaCl_2} at the scald are greater than 8.5, which indicates the presence of: (1) borate; and/or, more likely, (2) sodium carbonates and bicarbonates, and a high exchangeable sodium percentage (Vorob'yova & Pankova 1996). Discrete changes in pore-water pH (pH_w) with profile depth are not apparent in the $pH_{1.5}$ or pH_{CaCl_2} data. The pH_w (Figure 3) is consistently about 8.45 at depth and 8.8 up to a depth of 80-100 cm where the pH_w increases sharply to about 9.1. The pH_w then gradually decreases back to about 8.8 in shallow soil. With increased EC_w the range in pH_w of the scald narrows toward 8.8. The pH of ca. 8.4 is, perhaps through no coincidence, the value above which carbonate ions form and calcite precipitates whereas the significance of pH 8.8 is currently uncertain. Although the pH_w of the adjacent soil profile is substantially

lower, with values of typically 7.4 or 7.7, it shows remarkably similar trends at depth to that of the scald except at about 80-100 cm depth where, rather than increasing, it decreases to 7.4 in the gypsic horizon. Hence, a mechanism common to the deeper portions of both profiles is controlling pH variability. Above the gypsic horizon, however, the pH_w locally reaches 8.4, but then decreases sharply into the shallowest subsoil.

A roughly linear relationship between alkalinity and pH_w suggests that the scalded soil approximates a system open to the upward flux of CO_2 from the discharging groundwater. However, minor discrepancies from this relationship that indicate changes in CO_2 partial pressure (PCO_2) do occur, particularly in the shallower soil (Figure 5a). The non-linear variability of alkalinity with pH_w in a deep part of the adjacent soil profile suggests that this part of the profile behaves as a closed system with respect to CO_2 while the shallowest metre of soil exhibits large differences in PCO_2 probably due to biotic and atmospheric influences as well as transient water content.

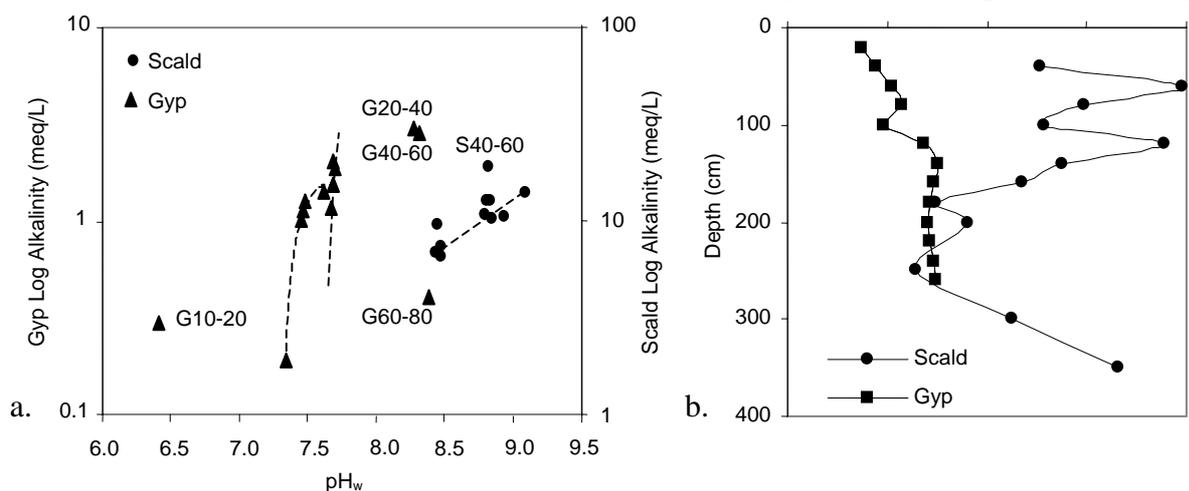


Figure 5a (left): Alkalinity- pH_w relationships. **b (right):** Mg/Ca ratios in pore waters of the scalded (Scald) and non-scalded (Gyp) soils.

The scald's pore water Mg/Ca ratio (Figure 5b) is relatively high in the deepest part and upper half of the profile, which contain, respectively, some stoichiometric dolomite and dolomite with a $MgCO_3$ mol % that increases toward the surface at a rate that declines as salinity increases. Hence, as highlighted by Folk & Land (1975), the Mg/Ca ionic ratio and salinity appear to be important controls on dolomite formation. The irregular change in Mg/Ca ionic ratio with depth and with dolomite's $MgCO_3$ content indicates that factors other than a constant flux of evapoconcentration and carbonate precipitation are taking place.

Further work is being undertaken on soil pore-water and mineral chemistry as well as isotope chemistry to elucidate the geochemical evolution of the alkaline salt-affected soil.

REFERENCES

- CHERNET T., TRAVI Y. & VALLES V. 2001. Mechanism of degradation of the quality of natural water in the Lakes Region of the Ethiopian Rift Valley. *Water Research* **35**, 2819-2832.
- DREVER J.I. & SMITH C.L. 1978. Cyclic wetting and drying of the soil zone as an influence of the chemistry of ground water in arid terrains. *American Journal of Science* **278**, 1448-1454.
- EUGSTER H.P. & JONES B.F. 1979. Behavior of major solutes during closed-basin brine evolution. *American*

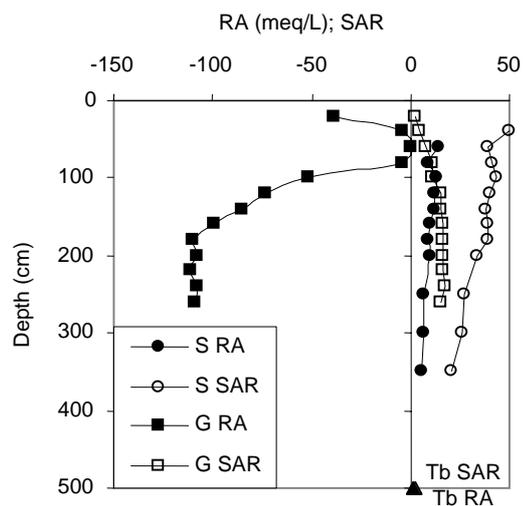
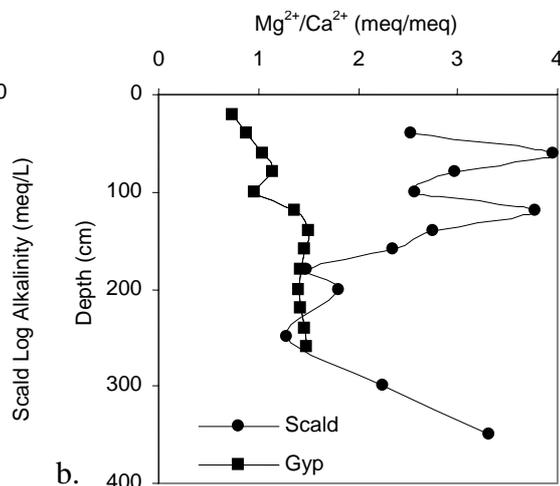


Figure 4. Residual alkalinity (RA) values and sodium adsorption ratios (SAR) of the scalded (S) and non-scalded (G) soil profiles. The values of the shallow groundwater in the underlying basalt (Tb) are also shown.



- Journal of Science* **279**, 609-631.
- EVANS W.C., PRESSER T.S. & BARNES I. 1986. Selected soda springs of Colorado and their origins. *Water Supply Papers* **2310**, US Geological Survey, Reston, Virginia, 45-52.
- FITZPATRICK R.W. & MERRY R.H. 1999. Pedogenic carbonate pools and climate change in Australia. In: LAL R., KIMBLE J. & STEWART B.A. eds. *Global Climate Change and Pedogenic Carbonates*. CRC Lewis Publishers, Boca Raton, pp. 105-119.
- FOLK R.L. & LAND L.S. 1975. Mg/Ca ratio and salinity: two controls over crystallization of dolomite. *The American Association of Petroleum Geologists Bulletin* **59**, 60-68.
- FOLK R.L. & PITTMAN J.S. 1971. Length-slow chalcedony: a new testament for vanished evaporites. *Journal of Sedimentary Petrology* **41**, 1045-1058.
- KELLEY W.P. & BROWN S.M. 1939. An unusual alkali soil. *Journal of the American Society of Agronomy* **31**, 41-43.
- KELLEY W.P. 1951. *Alkali soils: their formation, properties and reclamation*. Reinhold Publishing Corporation, New York, USA, 176 p.
- KOVDA V.A. & SAMOILOVA E.M. 1969. Some problems of soda salinity. *Agrokemia es Talajtan* **18**, 21-36.
- MASHHADY A.S. & ROWELL D.L. 1978. Soil alkalinity. II. The effects of Na₂CO₃ on iron and manganese supply to tomatoes. *Journal of Soil Science* **29**, 367-372.
- MILLER J.J., PAWLUK S. & BEKE G.J. 1989. Evaporite mineralogy, and soil solution and groundwater chemistry of a saline seep from southern Alberta. *Canadian Journal of Soil Science* **69**, 273-286.
- OHTÉ N. & TOKUCHI N. 1995. Biogeochemical influences on the determination of water chemistry in a temperate forest basin: factors determining the pH value. *Water Resources Research* **31**, 2823-2834.
- SHEPPARD R.A. & GUDE A.J. 1986. Magadi-type chert: a distinctive diagenetic variety from lacustrine deposits. *U.S. Geological Survey Bulletin* **1578**, 335-345.
- SMALE D. 1973. Silcretes and associated silica diagenesis in southern Africa and Australia. *Journal of Sedimentary Petrology* **43**, 1077-1089.
- SZABOLCS I. 1989. *Salt-affected soils*. CRC Press, Boca Raton, Florida, 274 p.
- SZABOLCS I. & DARAB K. 1958. Accumulation and dynamism of silicic acid in irrigated alkali ("szik") soils. *Acta Agronomy, Academy of Sciences, Hungary* **8**, 213-235.
- VOROB'YOVA L.A. & PANKOVA YE.I. 1996. Nature of alkalinity and diagnostics of alkaline soils in arid and semiarid territories. *Eurasian Soil Science* **28**, 23-33.
- WHITTIG L.D. & JANITZKY P. 1963. Mechanisms of formation of sodium carbonate in soils. I. Manifestations of biological conversion. *Journal of Soil Science* **14**, 322-333.