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Errors and omissions:
The photograph on p.34 is of De Courcy Island as stated, but it is Valdes Island that faces northeast out over the strait. Both islands have extensive honeycombing only on their southwest sides, as do also Link and Mudge Islands, and to a lesser extent Gabriola Island. Galiano Island is curiously not honeycombed, at least at its northern end.

References:

http://www.nickdoe.ca/pdfs/Webp26c.pdf
http://www.nickdoe.ca/pdfs/Webp58c.pdf
http://www.nickdoe.ca/pdfs/Webp217c.pdf

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Salt-weathering of sandstone off the southwest side of De Courcy Island.

Although such weathering is often attributed to the "wind and waves", there is nothing like it on the opposite side of the island, even though that side looks out northeast over the open water of the Strait of Georgia. Such geographic asymmetry is common and can be seen, for example, in Taylor Bay on Gabriola, which is quite sheltered. There, sandstone along the north side of the bay facing the sun is honeycombed, but sandstone along the south side of the bay is not.

The weathering is actually due to salt left behind as wet rock dries out on in the sun. Some of the evaporating salt water does come from wave splash, but some is wicked up by capillary action, and some comes from immersion at high tide, but the evidence is that most is seepages of "rockwater"—rain mixed with droplets of seawater carried by the wind that has soaked into the rock and moved, exactly as groundwater does, through fractures and interstices in the sandstone. That the salty water is being drawn out of the rock by the sun explains why erosion is often most severe on the inside of honeycomb holes, and on the back walls and under the roofs of galleries—surfaces that are not especially exposed to wind or waves.

Exactly how salt weathers sandstone is not clear and explanations for it are controversial.

Salt-weathering of upper Nanaimo Group sandstone

by Nick Doe

Introduction

Sedimentary rock weathers in all sorts of wonderful ways, and this is particularly true of the sandstone of the upper Nanaimo Group formations.[1] These late-Cretaceous rocks were formed from mud, sand, and silt swept rapidly down mountain slopes into a warm, stagnant, marine basin,[2] leaving little chance for them to mature physically—as they would during a prolonged stay on a beach or river bed—or chemically—as they would by prolonged exposure to the atmosphere. Now that the sandstone is being exposed to the elements more than 65-million years later, weathering and erosion are very active.[3]

Honeycombing, cavernous weathering, fretting, alveolization, and *tafoni*, are the most striking erosion patterns in the sandstone of the Gulf Islands, and I wrote about them at length in an earlier *SHALE* article.[4] Honeycombing and cavernous weathering is often said to be due to "the wind and the waves" despite the complete lack of evidence that wave- and windswept places are where honeycombing mostly occurs. Most such weathering on cliff faces is actually caused by salt left behind by evaporating water drawn to the surface from *inside* the rock by the heat of the sun.

In this article, I want to describe some experiments made to help discover exactly what the salt does. Apart from being an interesting aspect of honeycombing, salt-weathering of sandstone is important when it comes to the question as to why Gabriola's petroglyphs are being eroded so rapidly.[5] We need to know what kinds of salt (assuming that's what the problem is) are doing the damage.[6]

Previous studies

Salt-weathering has attracted a great deal of attention, particularly in Europe where it causes deterioration of heritage buildings and statues. The vast amount of literature on the topic attests to the complexity of the

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[1] See *SHALE* 7 for articles on the basic geology of Gabriola and the Gulf Islands.

[2] The late-Cretaceous atmosphere was richer in carbon dioxide than it is now, and hence the climate everywhere was warmer due to the greenhouse effect. Without polar ice-caps, the flow of cold, oxygen-rich water to the lower latitudes was weak. An added factor reducing ocean currents locally was the absence of the Juan de Fuca Strait, which only developed later. Micro-organisms feeding on organic debris on the floor of the basin also used up oxygen.

[3] Chemical immaturity shows up as a relatively low concentration of quartz and an abundance of feldspars. Iron-bearing minerals in the sand and mud have not yet been fully oxidized to the trivalent iron oxides and hydroxides (rust) that give sand its "sandy" colour. Sulphides, rather than sulphates, are also present. Gabriola's sand and anaerobic beach mud are often black for these reasons.

[4] *What makes holes in sandstone*, *SHALE* 9, pp.12–40, August 2004. The patterns may be an example of Turing patterns.

[5] *Petroglyphs—discovery and demise*, *SHALE 13*, pp.2–6, June 2006.

[6] A "salt" is any crystalline ionic compound with positive metal ions (cations) in place of the positive hydrogen ions (protons) of an acid. Table salt, sodium chloride, ($NaCl$), for example, is a salt of hydrochloric acid, (HCl).

The Carnegie Community Centre building in Vancouver's downtown eastside is a testament to the durability of Gabriola Formation sandstone away from the sea. It was built in 1903 from rock quarried on Gabriola Island. The stone has a rosy-buff tinge to it now compared to its original blue-grey, but it has weathered well without the slightest sign of honeycombing.

phenomenon.[7] The source of at least part of this complexity is easy to identify. There are different kinds of sandstone; there are different kinds of salt (an infinite number if you include mixes); and there are different kinds of physical weathering environments, some not easy to replicate in the laboratory. It is evident that there is no single, simple explanation of the phenomenon.[8]

Sandstone properties

Composition

To understand why sandstone weathers the way it does, we first have to know what it's made of. The grains (clasts) of the sandstone are mainly *quartz* and various kinds of *feldspar*.[9] There are also some

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[7] A. Elena Charola, *Salts in the deterioration of porous materials—an overview*, Journal of the American Inst. for Conservation, 39, 3, article 2 (online), 2000. Environmental Geology, *Special issue on salt decay*, 52, 2, March 2007.

[8] As an example, on a recent visit to New Mexico (Bandelier National Monument), we observed cavernous weathering similar to that seen in the Gulf Islands, yet the rock was far from the sea and was tuff (cemented volcanic ash), not sandstone. The

explanation for the weathering given by Park Guides was that it was due to the wind; the Pueblo Indians that lived in the caverns evidently didn't mind drafts. The tuff had a pinkish rind, making chemical weathering a more intriguing explanation.

[9] *Quartz* has a glassy appearance with uneven fractures. The *feldspars* are mainly Na-Ca *plagioclase* but with some K *orthoclase*. The sodium (Na) and calcium (Ca) rich *feldspars* are milky-white, while the potassium (K) rich form is pink or orange.
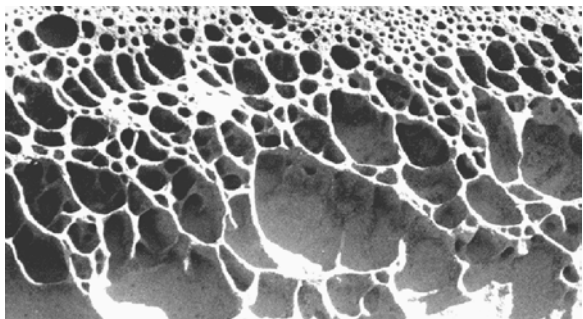
Above: Honeycombing (cavernous weathering) in medium to fine sandstone.

Below: The sandstone on the insides of the cavities commonly breaks away in flakes about 1-mm thick. The implication is that the saltwater causing the weathering does not percolate between individual grains of sand but rather flows through networks of microscopic cracks that crumble into flakes. It also suggests precipitation occurs slightly below the evaporation surface.

darker, iron-rich minerals, such as *biotite*, and *amphibole* (probably *hornblende*).[10] "Also rans" include *magnetite*, *pyrite*, *zircon* (rare), and rock fragments of all kinds (volcanic, intrusive, and sedimentary).[11]

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[10] *Biotite* is a colourless to black mica with highly reflective flat faces. *Hornblende* is a dull dark green, almost black, and lamellar.

[11] If you are unsure of the difference between a *rock* and a *mineral*, think of rock as a mixture of minerals; rock is, as it were, "the soup" and minerals are the ingredients, "the carrots, tomatoes…etc.".

Cement

Perhaps surprisingly, you cannot make sandstone from sand by simply compressing the sand, no matter how hard you squeeze. You always need some sort of cement. This can be a mineral such as *quartz*, *calcite*, limonite, *marcasite*, *zeolite*, or a bag of something you bought at the lumberyard.

The clasts of the upper Nanaimo Group sandstone[12] touch and interlock to some degree, and this provides a measure of structural support for the rock, but not enough to hold it all together; however, none of the minerals just listed are present as cement. Instead, the spaces between the clasts (the interstices) are packed with a "grout" composed of silt, very fine-grained micas (*sericite*), *chlorite* (a mica-like mineral), and clay. This "matrix" comprises about 10-15% of the rock, and it is the clay within it that appears to be acting as cement.

That different cements cause different weathering patterns is evident on Gabriola when you look at the honeycombing of concretions. These have a *calcite* cement, and the sizes and densities of the honeycomb holes in concretions are commonly different from those of the host, which contains relatively little *calcite*.

You can see salt-stained deposits of clay on the roofs of galleries, like the Malaspina Galleries. If you take some honeycomb debris and put it in a glass of water and shake it up, you'll notice that although the sand particles very quickly settle to the bottom of the glass, the water remains cloudy for some time. This cloudiness is due to the presence of clay.

While one might reasonably imagine that the very smallest particles in rocks were simply

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[12] (Sample 7, Gabriola I., Gabriola Fm.) and (Sample 8, Gabriola I., Geoffrey Fm.). Technically a "dirty" sandstone known as feldspathic wacke.

tiny fragments of the bigger grains, this is not true. The smallest particles are clay minerals and these have a complex mineralogy all of their own. The physical properties of aggregates of clay particles are the result of weak electrostatic forces and the plate-like structure of the microscopic crystals rather than the strong ionic bonding that occurs in minerals that form far larger, three-dimensional, crystals.[13]

Porosity and other properties

The intergranular porosity of the upper Nanaimo Group sandstone is low, but may have formerly been higher, the pores having been filled with the matrix. Under the microscope, old microfractures are seen both around the margins, and cutting through some of the grains. These are now packed with *sericite*,[14] a weathering product of feldspar, presumably put there by ancient groundwater flows.[15]

Other properties of the sandstone that likely influence weathering of sandstones are grain size, pore size, and permeability (the degree to which pores are interconnected).

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[13] A *mineral* has a crystalline structure and a chemical composition that is fixed or varies only within specific limits. A mineral crystal is essentially a macromolecule in that all of the atoms within it are chemically bonded. Although at least 4000 minerals are known, only 30–50 are common. Water has no crystalline structure and so is not a mineral, but ice is.

[14] (Sample 03, Gabriola I., ?Gabriola Fm.). For a petrographic analysis, see *Great balls of stone— concretions*, *SHALE* 9, p.10, August 2004. *Sericite* is a generic term for fine-grained micas that can be all or partly *muscovite*, *illite*, or *paragonite*.

[15] Fractures in the sandstone, both large and small, sometimes have *zeolite* associated with them, indicating that ground water temperatures and pressures in them were once high, possibly momentarily during a major seismic event.

Salt properties

The cations (positively charged metal or semi-metal ions) most often associated with salt weathering (in order of their abundance in seawater) are:

sodium (Na^+), magnesium (Mg^+), calcium (Ca^{2+}), and potassium (K^+);

and the anions (negatively charged non-metals) are:

chloride (Cl^-), sulphate (SO_4^{2-}), carbonate (CO_3^{2-}), and nitrate (NO_3^-).[16]

The solubility of the anhydrous salts in kilograms per cubic metre ($kg.m^{-3}$), or in older units, grams per cubic centimetre:

kg/m^3	Cl^-	SO_4^{2-}	CO_3^{2-}	NO_3^-
Na^+	360	50	70	920
Mg^{2+}	540	200	0.4	1250
Ca^{2+}	750	2	0.01	1210
K^+	350	120	1120	130

You can see from the table that the salts most likely to be precipitated as evaporites are calcium carbonate (*calcite*) with a solubility of only 0.01 $kg.m^{-3}$, followed by magnesium carbonate (*magnesite*) at 0.4 $kg.m^{-3}$, and calcium sulphate (*gypsum*) at 2 $kg.m^{-3}$. These solubilities will however be different in mixed-salt solutions.

All these salts, except the nitrates, are undoubtedly present in the rockwater responsible for honeycombing. They are also likely present, although in different proportions, in rainwater runoff in the forested interior of the island;[17] however, there, we should add to the list, ions that

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[16] "Carbonate" in water is mostly HCO_3^-, but it usually forms carbonates rather than bicarbonates: $2M^+ + HCO_3^- + OH^- \Rightarrow M_2CO_3 + H_2O$

[17] Potassium and nitrates are likely to be scarce because of their high nutritional value to plants.

have a biological origin including complex organic anions like humate (from humic acid) and fulvate (from fulvic acid). Organic salts are rarely mentioned in the technical literature on salt-weathering, one reason being that they appear to play no role in the weathering of buildings in urban environments, which is where the focus of many studies lies.

All of the physical properties of the various combinations of cations and anions are of some interest, but the particular ones concerning salt-weathering are solubility, crystallization pressure, valency, coordination number (whether the ion is simple, complex, or a chelate), and the different kinds of hydrate each salt can have and their properties—sodium sulphate, for example, exists in nature as *thenardite* (Na_2SO_4) and *mirabilite* ($Na_2SO_4.10H_2O$). There's also a heptahydrate ($Na_2SO_4.7H_2O$).

Environment

General environment

Readers who live on Gabriola will be well acquainted with the island's climate but for the benefit of those who don't, I've included a "boxed" summary.

At Gabriola's latitude, if every day of the year were cloudless, horizontal surfaces would receive 77% of the sun's annual radiant energy in the summer half of the year. Given that winter days are often overcast, the actual disproportionality between summer and winter sunshine must be even greater than this. It would be my contention that the local sandstone absorbs water in winter (not a lot but some) and loses it to evaporation in the summer, and this plays a significant role in its weathering.

Gabriola's climate

We have what's called a cool Mediterranean climate—summers are dry and warm (August daily mean 18°C); winters are wet and cool (January daily mean 4°C). Prevailing winds are from the northwest in summer, and from the southeast in winter. The average sea-surface temperature is about 11°C and the water is usually only a few degrees warmer in summer, and a few degrees colder in winter, though patches with temperatures outside this range are not uncommon. The sea never freezes, though we know that in earlier centuries it did. Although freeze-thaw weathering (and fracturing) of rocks is sometimes cited as being significant on Gabriola, it seems unlikely to me that this is so, there being no observed relation between weathering and frequency or intensity of frost.

About 75% of our precipitation falls between October and March. Most of the winter rain is associated with the passage of warm fronts, and the rain is often accompanied by very strong southeast winds that blow over the island from the Strait of Georgia and Pylades Channel. This weather pattern is known locally as the "Pineapple Express" because the mild, moist air originates out in the Pacific Ocean in the general direction of Hawaii.

Salt-weathering environment

From the perspective of weathering, there are two different environments on the island. Honeycombing is mostly confined to the coastal fringe, which only rarely extends more than a kilometre inland. In the interior, where most petroglyphs are, perhaps because there is less sea-spray in the rain, or the vegetation (mainly Douglas-fir forest) removes salt, the weathering is far less spectacular.

Rock surface environment

The "best" honeycombing always occurs on surfaces that are fully exposed to the sun and face southeast to southwest. So far as I am aware, no study has been made of the surface temperature of the local rocks, but summer-time temperatures of nearly 80°C have been measured in deserts. On Gabriola, rock surfaces often feel hot to the touch in the sun, especially if the surface is coated with black lichen, and in the evening the air inside rock cavities feels warmer than the outside air; however, this is usually not considered to be enough to induce hydrothermal reactions among the minerals present on the sandstone surfaces.

Sandstone surfaces rapidly soak up moisture due to capillary forces and then tend to retain the moisture. In theory, coarse-grained sandstone should be able to lift water about 500mm, but my own experiments show that, if it indeed it can, it takes a long time. Usually water is wicked up over the surface about 100mm, but over the next few days, it appears to make little further progress. Honeycombing is observed much higher than this above the high-tide mark.

Honeycombing is absent on surfaces that are kept constantly moist by groundwater seepage. This is entirely consistent with the idea that salt crystallization is the cause.

The petroglyphs are commonly carved on flat horizontal sandstone surfaces, although some are on vertical surfaces. There is often a certain amount of exposure to the sun because the sandstone "pavement" hinders the development of trees and the petroglyph sites are consequently in natural glades in the forest. Petroglyphs on vertical surfaces may be suffering less than those on horizontal surfaces, but this casual observation needs to be checked.

Sandstone weathering

General

Unweathered sandstone in the upper-Nanaimo Group formations is bright grey with a bluish tinge. On exposure to the elements, the grey sandstone develops a "surface zone" of weathering that has a characteristic sandy colour.[18]

The surface zone is more resistant to weathering than fresh rock—the sandstone has become "case-hardened". Case-hardening forms the visors of galleries; the shells of "cannon-ball" concretions; the shells of hollowed-out boulders; the "thick-lips" of fractures; and many other interesting weathered-sandstone features commonly seen on Gabriola's shoreline.

The surface zone is subject to internal compression stress due to the (frustrated) expansion of the zone as the minerals oxidize. So long as the zone remains intact, the compression gives it great strength and it becomes very resistant to further weathering as evidenced by the visor of the Malaspina Gallery, which appears in century-old photographs exactly as it does today.

Most of these observations can be related to the weathering of iron-rich minerals in the sandstone. The iron in the minerals exists mainly in its ferrous state (Fe^{2+}). Weathering disrupts the balance of electrical charges in the crystals by oxidizing this iron to its ferric state (Fe^{3+}). Iron is then distributed between the grains of the sandstone and precipitated as oxides and hydroxides (*magnetite*, *limonite, hematite*). These compounds form rust-like coatings that cement grains of sandstone at their points of contact, and give the rock its strength.

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[18] A more detailed note is to be found in *SHALE* 17, pp.51–3.

Many of the changes in colour observed in the surface zone are attributable to changes in the nature of the iron oxides present as the zone moves towards thermodynamic stability. There are about six oxides and hydrous oxides of iron (including nonstoichiometric forms)[19] all differently coloured; and manganese, which also colours weathered mudrock accompanying Nanaimo Group sandstone, has even more.

The role of iron in the case-hardened surface zone of weathered sandstone from near the coast can easily be demonstrated by soaking a sample in oxalic acid. The case-hardened sandstone disintegrates, while leaving unweathered sandstone intact. This is because oxalic acid dissolves iron by forming a chelate.

Salt-weathering

Salt-weathering disintegrates the sandstone leaving a residue of sand, silt, and clay particles. This is different from freeze-thaw weathering, which tends to chip the sandstone. Although freeze-thaw weathering is sometimes said to cause honeycombing, shaded locations exposed to the north are not eroded in this way.

Presumably, salt-weathering is responsible for the erosion of the petroglyphs, especially those that are horizontal. If you gently rub your finger on near-by surfaces you can sometimes feel some grit. Similar weathering of gravestones is very apparent in the island's cemetery, which is right by the sea.[20]

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[19] Compounds in which the ratio of iron to oxygen is not an exact whole number.

[20] *Petroglyph studies in the cemetery*, *SHALE* 17, pp.56–60.

Salt-weathering theories[21]

The most popular theory as to how exactly salt disintegrates sandstone is that crystallization pressure is responsible. If a supersaturated solution of a salt increases in volume when it suddenly changes from a solution to a mix of crystals and water, then undergoing the same change within the confines of a pore will generate pressure. Most common salts generate crystallization pressure.

Another, less popular idea, is that crystals expand when they hydrate, creating hydration pressure within a pore. Whatever the merits of this idea however, it seems unlikely that this could cause honeycombing as the walls of the honeycomb are losing water by evaporation, not gaining it.

Other ideas include the possibility that salt crystals adhering to the rock may generate stress due to volume changes with temperature and humidity. Another suggestion is that supersaturated solutions within a pore may absorb ions from the rock leading to a greater than normal volume of crystals when they precipitate. None of these "minor" theories however seem very convincing in the Gabriola context.

Microscope analysis

One obviously good idea for trying to figure out why salt weathers sandstone is to take a look at some salt-weathered rock with a microscope and compare it with unweathered rock. Geologists do this sort of analysis all the time. A sample of rock is prepared for examination by grinding down a slice until it is so thin that light can pass through it. The slices are called "thin sections".

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[21] A. Elena Charola, *ibid*.
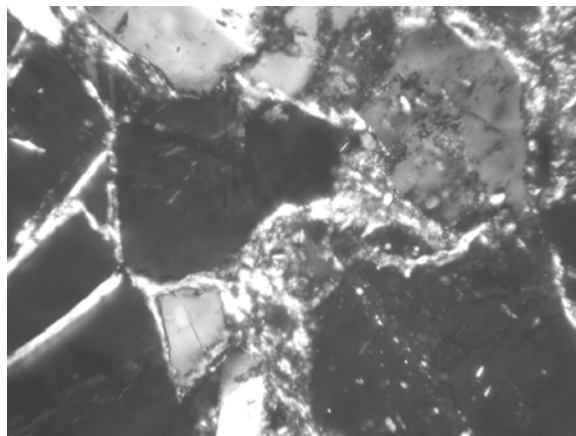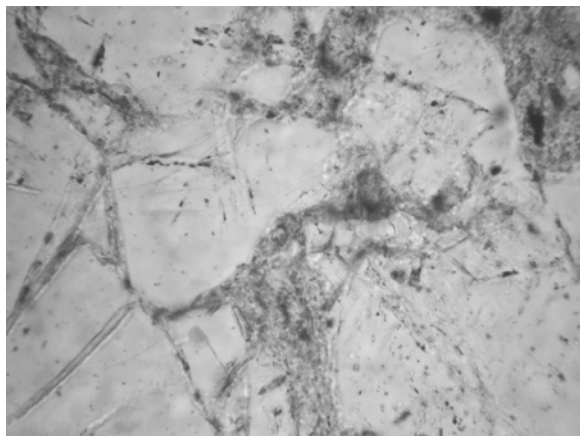
Unweathered sandstone (Sample 3) in plane-polarized light (PPL) *left* and cross-polarized liight (XP) *right*. The field of view (FOV) is about 0.25mm across. All of the large grains, seen in light grey in PPL *left* and any shade of grey from white to black in XP *right*, are *quartz* or *feldspar*. What is of interest in the photographs is how well the spaces between the grains are filled. There are no empty spaces anywhere in this photograph and almost none in the whole slide. Open voids, if present, would be white on the *left* (PPL) and black on the *right* (XP). The bright halos around the large grains in XP are gaps filled mainly with fine-grained micas while the voids contain a mix of small particles, *chlorite*, and clay. Tiny particles that are black in both photographs are clay or opaque minerals such as *magnetite*.
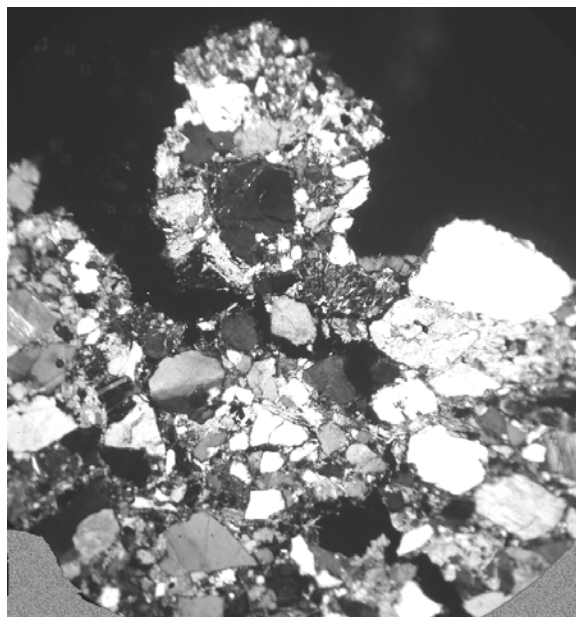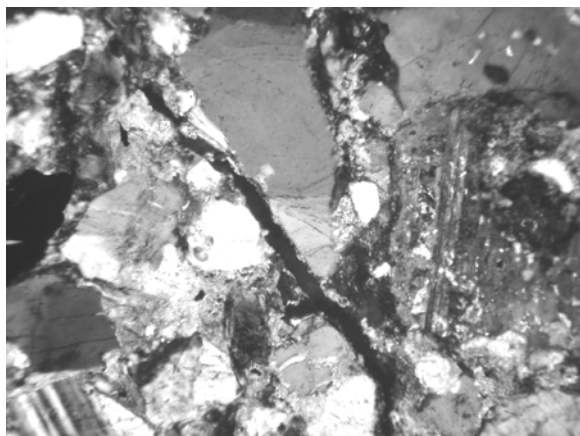
Sandstone from a honeycomb showing microfractures (Sample 9). Both pictures are XP light and show a variety of types of grains. FOV on the *left* is about 1 mm and a microfracture shows up as a long black line (top to bottom sloping \ ) extending well beyond the edges of the picture. FOV on the *right* is about 2 mm. A flake is about to break free from the surface. Although hard to see, microfractures lead into the "bays" on both sides of the flake, appearing like rivers. Although some fractures in this sample appear to have been created and widened by displacement, others meander through the sample around and through grains, giving the appearance of being old fractures from which the fill has been recently flushed. The fractures are generally no more than 40 μm wide and often less. Another sample (Sample 12) taken from a back wall showed no sign of open fractures, only what appeared to be advanced weathering of the *feldspar* and *biotite*.

Unfortunately, the standard thin-sectioning process removes any soluble salts that are present; one can only look for the damage they might have done.

Two samples from the back walls of large honeycombs were examined.

One was broken off by hand and was very friable. It turned out on examination to be partially concreted with *calcite*, which casts some doubt on its value as a representative sample.[22] What is well worth recording however is that some of the microfractures of the type that were described in an unweathered sample earlier were, in this sample, open. This would account for the loss of competency of the sandstone. Why the microfractures were open is not clear. One, plausible, explanation is that the carbonate that forms, or has replaced, some of the matrix has also displaced the *sericite* in the fractures and then subsequently been lost. There was however no evidence of this. None of the open microfractures examined contained any carbonate along their lengths. There thus remains the distinct possibility that the loss of matrix from the microfractures is unrelated to the concreting and is rather salt-weathering. That this thin-section remains intact might then be thanks solely to the patches of carbonate cement.

A second sample for thin-sectioning was obtained by drilling into the back wall of a honeycomb.[23] The most significant feature of this more robust sample was the presence of abundant *hydrobiotite* in the matrix, and apparently replacing some of the clasts. *Hydrobiotite* can also be seen with a hand lens in salt-weathering debris where its golden, glistening flakes attract attention in the same way that they commonly do in

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[22] (Sample 9, De Courcy I., De Courcy Fm.)

[23] (Sample 12, Gabriola I., Spray Fm.)

granite.[24] Locally, there was also a lot more *chlorite* and *sericite* than usual in the thin-section. Some of this was *limonite* (rust)-stained, but this was mainly where adjacent to *magnetite* particles.[25]

In sharp contrast to the first sample, no open microfractures were noted anywhere. Possibly the weathering surface had been destroyed in drilling the sample and preparing the thin section—the weathering surface is a delicate "crust" only a few gains thick—but we can't be sure that that is what happened.

In short, the only evidence that the two thin-sections provided is that whatever the salt-weathering process is, it is subtle, very localized, and not likely to be directly observable with an optical microscope because it operates on too small a scale. We are looking for a failure of the matrix to hold the sandstone together rather than a disruptive force creating new microfractures.

X-ray diffraction analyses

X-ray diffraction analyses give some idea as to what the clay might be. The first sample tested was clay extruded during

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[24] "Hydrobiotite" is a not-well-defined mineral and some mineralogists avoid using the term. It comprises mixed-layers of *biotite* and of *vermiculite*, which is a clay that, as gardeners know, readily absorbs water and swells. *Hydrobiotite* has however not been related to salt-weathering.

[25] It is difficult to know what to make of the apparent increased "hydrothermal" weathering of this second sample. Both *hydrobiotite* and *chlorite* are common weathering (oxidation) products of the iron-rich mica *biotite*. Field evidence however suggests that iron does not play a significant role in the weathering; honeycomb surfaces are commonly clean looking with no sign of staining by "rust". Any salt stains are usually white. Perhaps the weathering is a consequence of an increase in porosity and access to water as the matrix of the sandstone in the honeycomb is lost.

drilling into sandstone (Sample 23, Geoffrey Fm. GDL: V04-0042R). It showed: *montmorillonite*, *albite* (Na-feldspar), *quartz*, and very minor *kaolinite*. The second sample, clay gathered from the roof of a gallery (Sample 18, Gabriola Fm. GDL: V03-0666R), showed: *quartz*, *albite* (Na-feldspar), *muscovite-illite* [likely the *sericite* seen optically], *gypsum* (calcium sulphate), *kaolinite*, probably *montmorillonite*, and minor *chlorite*.[26]

In a study of the mudrocks (shales) on Gabriola, John Packard found *kaolinite*, "mica" [likely *muscovite-illite* in *sericite*], and some *chlorite* (5 samples Northumberland Fm.); and *kaolinite*, a smectite [probably *montmorillonite*], and again, "mica" (6 samples Spray Fm.).[27]

Some, or most, of these names are not familiar names, but there are no surprises, except perhaps calcium sulphate. *Kaolinite*,[28] *illite*,[29] and *montmorillonite* [30] are all common clay minerals.

My tentative conclusion is that the "ancient" clay minerals in the sandstone are *kaolinite* plus members of the "mica" weathering sequence *muscovite* /*sericite* /*illite*. *Montmorillonite* is likely a recent product of weathering; it is often present at the start of the wet-dry weathering of feldspar-rich sedimentary rock that contains ferromagnesian minerals, particularly *hornblende*. In tropical climates especially, *montmorillonite* slowly weathers to the more simply structured *kaolinite*. *Chlorite* is a common weathering product of *biotite* and *hornblende*.[31, 32]

Montmorillonite and the *vermiculite* in the *hydrobiotite* are the only observed clays that absorb water and swell at the most basic (intra-crystal) level, but these are such ubiquitous minerals that it would be difficult to argue that they cause salt-weathering. One also has to consider that the other "non-swelling" clay minerals actually do swell too but at (using the terminology of soil scientists) the inter-crystal and inter-domain levels of their structural hierarchy.

Calcium sulphate often appears "on the scene of the crime", but nobody seems to be able to pin anything on it. One suggestion is that when microfractures open and close as the water-content of the clay varies, calcium sulphate may precipitate in the microfractures and, being relatively insoluble, wedge them open, thereby allowing the ingress of more salt. My own experimental evidence however shows no support for this idea. My suspicion is that

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[26] *Chlorite* was rated "doubtful" in the X-ray diffraction analysis but is seen with the microscope.

[27] J.A. Packard, *Paleoenvironments of the Cretaceous Rocks, Gabriola Island, BC*, Oregon State University, 1972.

[28] *Kaolite* has a two-sheet per layer structure. Interlayers are thin and don't readily absorb water or other molecules.

[29] *Illite* has a three-sheet per layer structure. The interlayer cations are K^+, which bind the layers tightly because K^+ is an excellent geometric fit. *Illite* doesn't readily absorb water or other molecules.

[30] *Montmorillonite* also has a three-sheet per layer structure. The interlayer cations are Na^+ and Ca^{2+}. *Montmorillonite* is one of the clays that does absorb water and other molecules.

[31] X-ray diffraction analyses of samples of Holocene mud obtained from the Fraser delta have shown the dominant clay mineral to be *chlorite* with secondary *illite* and minor smectite. C.E. Dunn, *Geochemistry of seafloor sediments from the Strait of Georgia, British Columbia*, GSC Bulletin 525, p.262, 1998.

[32] *Biotite* has a very similar structure to *illite*, the main difference being the substitution of some Fe^{2+} and Mg^{2+} for Al^{3+} in the gibbsite sheet. *Chlorite* is similar to *biotite* but with more Fe^{3+}, which displaces Al^{3+}, and interlayers, more structured than usual, containing $MgOH^+$ (*brucite*) rather than K^+. *Hydrobiotite* contains *vermiculite*, which has a structure like *chlorite*, but the interlayers are occupied by a structured arrangement of water molecules rather than $MgOH^+$.

precipitation of calcium sulphate removes Ca^{2+} ions, leaving behind more damaging sodium and magnesium salts.[33] Either that or precipitated calcium sulphate only partially fills pores allowing more soluble salts to generate more force in the remaining voids with the same pressure.[34]
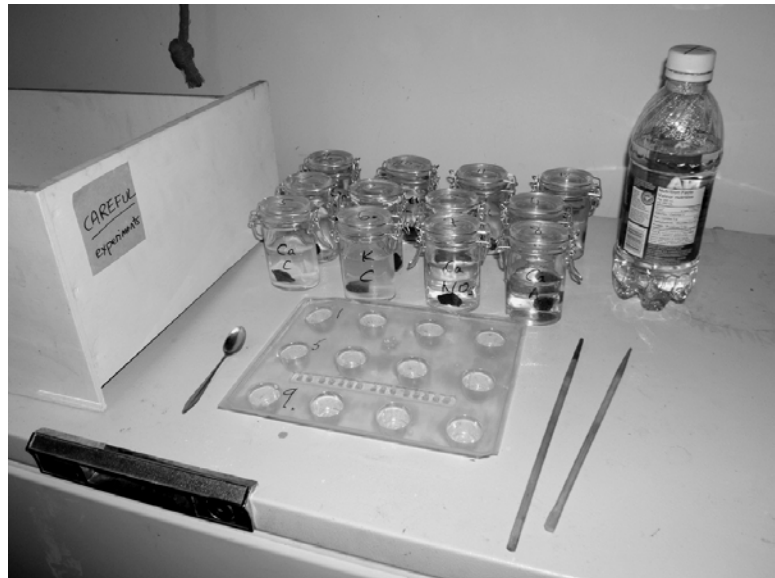
Soak-dry cycling— the initial tests

The next step in the investigation was to try some more soak-dry experiments, as described in the earlier article.[35] Seven experiments were made. The principle of each was the same: soak a sample in a salt solution for a while, and then remove it and let it dry, and then return it to the solution. Whenever possible, the samples were dried in bright sunshine.[36] This procedure gradually de-cements the sample in a way that appears to closely resemble what happens in nature.

Pieces of sandstone being soaked in salt solutions in jars at the back. Periodically, the samples were removed from the jars and put in the tray in front to dry. Once dry, the samples were returned to the jars for more soaking. Doing this with pure water does nothing to the rock, but with salt added, the sandstone very slowly disintegrates in a way that appears to mimic quite closely what goes on in honeycomb holes. Different kinds of salt weather the rock at different rates.

All of the samples used in all of the experiments except Test 2 were taken from the same block of unweathered sandstone.

Test 1

Procedure

Three samples were used weighing roughly 50 grams each. The solutions used for the test were contained in two 250 mL jam-jars with bottoms about 50×50 mm square. The solutions contained:

sodium chloride; and **sodium sulphate**.

Both solutions were saturated, though presumably in the honeycombing environment, the initial concentrations of the salts are not important as they will greatly

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[33] Calcium sulphate is less soluble in a solution of sulphates because of the common-ion effect.

[34] A. Micallef, *Capillary migration of anions in porous rocks: Laboratory simulations and implications for weathering sandstones*, Geophysical Research Abstracts, 8, 1607-7962/gra/EGU06-A-01950, 2006.

[35] *What makes holes in sandstone*, SHALE 9, p.22–3, August 2004.

[36] Experiments have shown that radiative heating is more damaging than convective heating because radiation heats faster. Miguel Gomez-Heras & Rafael Fort, *Patterns of halite* (NaCl) *crystallization in building stone conditioned by laboratory heating regimes*, Environmental Geology, 52, pp.259–267, 2007.

increase anyway during the drying-out process. The third sample was treated with **water** alone.

The procedure was to immerse the sample in the solution for 24 hours, and then remove it and allow it to dry for another 24 hours. This cycle was then repeated again and again. These particular tests were all made at normal room temperatures.

Results

After a week, signs of de-cementation were apparent in both of the salt-immersed samples. The solutions initially went cloudy, but the particles responsible were too small to see with the naked eye. Later, fine particles of sand began accumulating in the bottom of the jars.

The experiment was terminated after about six months (roughly 100 complete cycles of 48 hours each). At this point, the bottoms of the jars were completely covered with fine sediment several millimetres thick.

There was no obvious difference between the amounts of sediment in the two solutions. Measurements after the sediment had settled however indicated that the volume of sediment in the chloride was actually greater. Compensating for surface area (see table below) showed again that there was little difference between the samples.

	sample dry weight g	sediment volume $10^{-6}m^3$	sediment volume per surface area $10^{-3}m$
NaCl	46	6.5	0.80
Na_2SO_4	45	4.9	0.72
H_2O		0.0	0.00

The measured erosion rates (a little under a millimetre for 100 cycles) are about the same as those observed in nature. The erosion rate of the back wall of the

Malaspina Gallery, for example, is somewhere between 0.5–3 mm per year (less than 365 cycles depending on the daily weather).

The colour of the sample tested with water changed slightly from grey to buff, but the water remained perfectly clear and there was no sign of de-cementation.

Discussion

The results of this experiment would appear on the face of it to put paid to the crystallization pressure idea. Sodium sulphate is as good as sodium chloride at de-cementing the sandstone, yet, in a widely cited table by Winkler,[37] the crystallization pressure of sodium sulphate is given as only 72 (atm) while that of sodium chloride is over seven times higher at 554 (atm). Moreover, measurements of the pressure in a pore have suggested that sodium sulphate may not actually exert any pressure at all.[38]

However, and it is a big "however", it could well be that expecting the damage done to be directly proportional to the crystallization pressure is too simplistic a hypothesis. The de-cementation may depend on the mobility of the concentrated salt solution in the sandstone, and where, in relation to the surface, the crystals form as the sample dries out. Perhaps too, the crystallization pressure in the actual environment of the pores is, for some reason, different than that in Winkler's table. Crystallization pressure is very difficult to measure.

[37] E.M. Winkler & P.C. Singer, *Crystallization pressure of salts in stone and concrete*, Geological Society of America Bulletin, 83, pp.3509–14, 1972, cited in Will Bland & David Rolls, *Weathering—An introduction to the scientific principles*, pp.97–9, Arnold, 1998.

[38] L.A. Rijniers, H.P. Huinink, L. Pel, K. Kopinga, *Salt crystallization in porous materials and its implications for stone decay*, EUROMAT 2003, Symposium P2, Lausanne.

Test 2

The next step in the investigation was to try to make sure that there was nothing unusual about the particular block of sandstone chosen for the experiments.

Procedure

The procedure was as for Test 1. Only **sodium sulphate** was used. Three samples of sandstone were tested, namely:

- unweathered sandstone (grey)

- "case-hardened" sandstone from a large honeycomb hole visor (buff)

- a chip of weathered sandstone from an inland petroglyph site (dark grey/buff).

Results

All three samples were de-cemented.

Unweathered sandstone: bottom of jar about 75% covered with a very fine grey sediment.

Case-hardened sandstone: thick brown sediment covering the bottom of the jar.

Petroglyph site: sediment, grainier than the unweathered sample, and brown. About 50% of the bottom of the jar covered.

Discussion

Although differences between the samples merit thinking about, the main conclusion was that indeed sodium sulphate does de-cement sandstone and this is not due to any peculiarity of the sample used for testing.

A "new" theory

At this point in the research, the idea arose that the ability to de-cement the sandstone might not have anything to do with crystallization pressure, but might instead be linked to the charge on the cations in the salt solution. This would account for the performance of the two sodium salts being roughly the same. The suspicion behind this idea is that de-cementation is due to the adverse effect of salt on the clay that is holding this particular type of sandstone together.

Soil and plant nutrition specialists have long studied the effect of different cations on soil and soil texture, and it is well known that excess sodium in the soil (sodicity) is responsible for soil degradation and the collapse of its structure into hardpan.

The basis of soil instability (to over-simplify) when saturated with sodium seems to be the added instability of the clay domains. The attractive force between crystals in near-contact is weaker with monovalent sodium ions (Na^+) than it is with divalent calcium cations (Ca^{2+}). Domains have been reported to much larger in Ca-saturated *illite* than in Na-saturated *illite*.[39] The well-known solution to excess sodicity in soil is to add calcium.
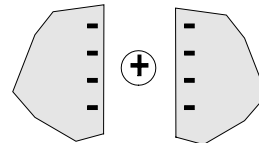
Clay minerals have negative surface charges. Freely moving cations position themselves between the faces thereby providing intermediary attractive forces holding the crystals together, albeit rather weakly compared with other types of bond. The greater the charge on the cations, the more effective the bond, which is why calcium (Ca^{2+}) and magnesium (Mg^{2+}) cations bind more effectively than do sodium (Na^+) and potassium (K^+) cations.

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[39] James P. Quirk, *Interparticle forces as a basis for the interpretation of soil physical behaviour*, pp.121–183, Advances in Agronomy, 1994.

The "new" theory on the salt-weathering would go like this. On weathering surfaces, there is an exchange of sodium ions for calcium ions in the clay in the matrix with the consequence that the clay loses its cohesiveness. This allows the matrix to be washed out of the pores and old microfractures, and the sandstone then falls apart. Cycling between wet and dry is an essential part of the process.

Besides washing out loose matrix, the wet phase of the process brings new exchangeable ions to the surface of the clay. The water diffusing into formerly dry areas of the sandstone brings with it the more soluble salts, which, in general, are the salts of sodium, not calcium. The drying phase of the process greatly increases the concentration of ions in any water around the clay, thereby influencing the exchange process. Immersed sandstone does not weather because the water-saturated clay remains swollen, the concentration of salt is low, and there is no flow of water through the rock to flush out the matrix.

Not only does this explanation fit the field and microscopic observations of honeycombing, it might too explain why hollows in the sandstone on the beach fed by runoff from the forest are far more deeply eroded on the outflow side than the inflow side.[40]

Soak-dry cycling—the follow-up tests

Test 3

Procedure

This was a repeat of Test 1 except that the three solutions used were:

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sodium chloride; potassium chloride; and **calcium sulphate**.

One change in procedure was to use two samples per solution. While one sample was drying the other was soaking, thereby effectively doubling the sample size.

Regardless of whether the clay in the sandstone is K-rich *illite* or Na-rich *montmorillonite*, one would expect a different reaction to the sodium and potassium salts if interaction with the clay during salt-weathering is a significant factor. On the other hand, these two salts have similar physical and chemical properties, and so if interaction with the clay is not a significant factor, then one might expect the reactions to the two salts to be similar.

Results

The results were similar to those reported in Test 1. The de-cementation was slightly, but observably, more with the sodium chloride than with the potassium chloride, but the difference was small.

The calcium sulphate did not de-cement the sample at all—the appearance of the sample remained unchanged and the solution remained perfectly clear.

	sample dry weight g	sediment volume $10^{-6}m^3$	sediment volume per surface area $10^{-3}m$ *
NaCl			0.80
KCl			0.64
CaSO$_4$			0.00

* the amount of sediment was not measured, only the ratios. The figures have been normalized to the absolute figure for NaCl obtained in Test 1.

Discussion

The result gives support to the idea that any chemical affinity for the salt and sandstone

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[40] *More about…runnels*, *SHALE* 10, p.37–44, January 2005.

is less significant than the salts' physical properties and perhaps the charge on the cations.

The inertness of the calcium sulphate is a bit of a puzzle because *gypsum* is often cited in the literature on salt-weathering as being the *cause* of the weathering. It seems more likely in our case that its presence just indicates that sulphate anions are present. The more soluble sulphates are probably the real culprits. In an environment where water is being lost to evaporation, the precipitation of calcium sulphate is irreversible, so the sulphate anions are, so long as their supply lasts, removing calcium from the sandstone and preventing it from being re-adsorbed.

Test 4 (a)

Procedure

A hunt was made to locate two equally soluble salts, one of monovalent sodium and one of divalent calcium. Many soluble calcium compounds are hygroscopic making them unsuitable for the soak-drying experiment. Two likely candidates would be sodium thiosulphate and calcium thiosulphate; however, no source for calcium thiosulphate could be found (unless bought by the tonne) even though it is used as a fertilizer and soil conditioner. In the end, **sodium acetate** and **calcium acetate** were used. Acetates were chosen because, unlike many other salts of organic acids, they are sufficiently simple chemically not to form organometallic complexes. The acetate ion is

$$CH_3COO^-$$

The solubilities of the acetates, chlorides (for reference), and the citrates (which were used in a subsequent experiment) are:

kg/m^3	acetate	citrate	Cl^-
Na^+	1190	720	360
Ca^{2+}	374	0.85	750
Mg^{2+}	1200	200	540
K^+	2920	1670	350

Six samples were used weighing on average 9 grams each. The roughly estimated average surface area of the samples was 2.1×10^{-3} m^2 each.

The solutions used for the test were contained in small 150 mL jars with glass lids and bottoms about 40 mm in diameter.

The procedure was as before except that because the samples were smaller a cycle was completed in 24 hours (instead of 48) and testing lasted only three months.

The solutions used were: **sodium chloride; sodium sulphate; potassium chloride; sodium acetate; calcium acetate**; and **water**.

Results

	sediment volume $10^{-6}m^3$	sediment volume per surface area $10^{-6}m$	normalized sediment volume per surface area $10^{-3}m$ *
Na_2SO_4	6.3	3230	1.14
NaCl	4.4	2260	0.80
Na{acetate}	2.2	1500	0.53
KCl	4.4	1490	0.53
Ca{acetate}$_2$ **	0.63	390	0.14
H_2O	0.0	0	0.00

* these are figures normalized to the absolute figure for NaCl obtained in Test 1.

** sample broke in two.

Discussion

The ability to de-cement sandstone does seem that it might be linked to the charge on the cations. Not only did calcium acetate produce less sediment than the sodium and potassium salts, but the calcium solution remained bright and clear. A preponderance of monovalent cations (Na^+ or K^+) appears to encourage the de-cementation process. We should note however that even though the de-cementation was slow with the calcium acetate, it nevertheless did happen. Also, we should note that the sodium sulphate was twice as damaging as sodium acetate, an observation that the "new" theory does not explain—salts with the same cations ought to act in similar ways.

Test 4 (b)

Procedure

This test was carried on at the same time as Test 4 (a). One of the two samples was tested with a 50:50 mix (by volume) of:

sodium chloride and **calcium acetate;**

and second was soaked alternately in:

sodium acetate; and then **calcium acetate**.

Results

	sediment volume $10^{-6}m^3$	sediment volume per surface area $10^{-6}m$	normalized sediment volume per surface area $10^{-3}m$ *
NaCl + Ca{acetate}$_2$	0.31	140	0.05
Na{acetate} + Ca{acetate}$_2$ **	0.19	70	0.02
* these are figures normalized to the absolute figure for NaCl obtained in Test 1. ** sample alternately soaked in sodium and calcium acetate.			

These rather extraordinary results showed that the mix, and alternate soaking, with the calcium acetate actually produced *less* sediment than any of the salts, sodium or calcium, did alone.

In the first sample, given that sodium acetate is the most soluble of the combinations of cations and anions, one might expect a result far closer to that of sodium acetate alone (0.53 mm), not an order of magnitude less (0.05 mm). The implication of the result is that if a mix of sodium and calcium ions is available, the clay prefers to adsorb calcium, thereby maintaining its stability. Before pondering this result however, see the result of Test 5(b), second sample.

The result for the second sample, which showed virtually no weathering when the solutions were alternated between being sodium- and calcium-rich, suggests that a single wet-dry cycle is not sufficient to cause any damage. One can imagine a partial adsorption by the clay surfaces of Na^+ at the expense of Ca^{2+} during the sodium-rich cycle, followed in the next calcium-rich cycle by the re-instatement of the previously lost Ca^{2+}, thereby not allowing any salt-weathering to progress.

Test 5 (a)

Procedure

The basic procedure was the same as before except that a new method of assessing the volume of tiny amounts of sediment was used. A measured amount of honeycomb debris was added to the same amount of water as was used for soaking the samples and in an identical container. The sediment in the sample jar was then compared visually with the sediment in the calibration jar. If the amount of sediment in the calibration jar was judged to be greater than in the sample jar, the calibration jar was vigorously shaken and the sediment

suspension divided into two. One half was discarded, and the other topped up with plain water to the original level. After the sediment had settled, the comparison was then made again. This was repeated as often as necessary. The whole procedure was repeated three times to check that the results were consistent, which they were in spite of the subjective nature of the visual comparisons.[41]

All of the samples were carefully cut to be the same weight, 5 grams, and as near as possible the same cubic shape, though this was difficult and surface areas were measured separately for each sample. Salt solutions were about 2 mL of salt (a little under 0.5 tsp.) in 70 mL of de-ionized water. Calcium citrate had to be filtered, as it is not very soluble. The samples were dried out at room temperature for not less than 6 hours, usually 12, but whenever the opportunity arose they were left out in the sun, which has a remarkably drying effect, reducing the drying time to less than half an hour. They were soaked for not less than 6 hours, and usually 12 hours.

The salts tested were:

magnesium sulphate, $MgSO_4$
sodium sulphate, Na_2SO_4

calcium nitrate, $Ca(NO_3)_2$
potassium nitrate, KNO_3

calcium chloride, $CaCl_2$
sodium chloride, $NaCl$

calcium acetate $Ca(CH_3CO_2)_2$
sodium acetate $NaCH_3CO_2$

calcium citrate $Ca_3((CH_2)_2COH(CO_2)_3)_2$
potassium citrate, $K_3(CH_2)_2COH(CO_2)_3$
sodium citrate, $Na_3(CH_2)_2COH(CO_2)_3$.

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[41] The only reservation I have about the method is that in might give undue significance to the clay, which is quite visible, yet minute in volume.

The measured pHs of the salt solutions were in the range 7.5−8.8.

Citrates were added to the test as easily-obtainable representatives of salts of more complex and larger organic acids. Humic acid, for example, is $C_{187}H_{186}O_{89}N_9S$, and fulvic acid is $C_{135}H_{182}O_{95}N_5S_2$, yet despite their complexity, the functional group is carboxylic acid:

$$R\text{-}COOH \Leftrightarrow R\text{-}COO^- + H^+$$
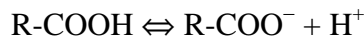
The citrate ion (from hydroxytricarballylic acid) is:

$$\begin{array}{l} CH_2COO^- \\ | \\ HO-C-COO^- \\ | \\ CH_2COO^- \end{array}$$
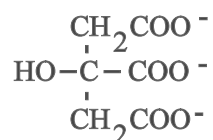
The test was halted after 41 cycles when the magnesium sulphate and sodium sulphate samples began to disintegrate.

The potassium and calcium citrates solutions developed a slight filmy, white cloudiness that seemed organic in nature. It was easily cleared with a little acid.

Results
The results are shown in the table on the next page.

The most vigorous de-cementers were the sulphates, particularly magnesium sulphate. The large numbers, 14.0 and 7.02 mm, however are a little misleading in that, as noted in the table, the samples were on the verge of disintegration. Had the experiment been stopped a few cycles earlier, the amount of sediment would have been substantially reduced. The sulphates were nevertheless clearly the most effective de-cementers throughout the test.

	molecular weight	sediment volume $10^{-6}m^3$	sediment volume per surface area $10^{-6}m$	normalized sediment volume per surface area $10^{-3}m$ *	previous tests	nature of sediment
MgSO$_4$**	120	1.25	1835	14.0		grey, not cloudy
Na$_2$SO$_4$***	142	1.10	922	7.02	0.72 1.14	grey, not cloudy
KNO$_3$	101	0.11	160	1.22		grey, not cloudy
NaCl	58	0.11	105	0.80	0.80 0.80 0.80	mixed
KCl	75				0.64 0.53	
Na$_3${citrate}	258	0.056	55	0.42		buff, cloudy
Ca(NO$_3$)$_2$	164	0.056	54	0.41		grey, not cloudy
CaCl$_2$	111	0.044	41	0.31		grey, not cloudy
K$_3${citrate}	306	0.021	20	0.15		grey, not cloudy
Na{acetate}	82	0.018	18	0.14	0.53	buff, cloudy
Ca{acetate}$_2$	158	0.015	15	0.11	0.14	grey, not cloudy
Ca$_3${citrate}$_2$	498	0.013	12	0.09		grey, not cloudy
CaSO$_4$	136				0.00	
H$_2$O					0.00	

* these figures normalized to the absolute figure for NaCl obtained in Test 1.

** sample broke in two. On the verge of complete disintegration, so the number is too high.

*** approaching disintegration near the end of the test, so the number is too high.

Although most of the salts with monovalent cations did de-cement well, there were significant exceptions. Neither sodium acetate nor potassium citrate de-cemented strongly; however, the sodium acetate result is low compared with a previous test result.

Similarly, although most of the calcium salts did not de-cement well, calcium nitrate and possibly calcium chloride were exceptions. It is evidently not true that the ability of a salt to de-cement the sandstone depends entirely on the nature of its cations.

In general, the organic salts (acetates and citrates) de-cemented less than any of the inorganic salts, but sodium citrate and possibly sodium acetate (based on an earlier test) were exceptions.

Discussion

The first observation to be addressed is that divalent magnesium ions (Mg^{2+}) clearly behave quite differently from divalent calcium ions (Ca^{2+}). This knocks a hole in the theory that the charge on the cation is the only critical factor. As always, there are possible explanations for this; it may simply be that magnesium ions form large hydrates $[Mg(H_2O)_6]^{2+}$ in aqueous solutions and the size of these diminishes the effect of the
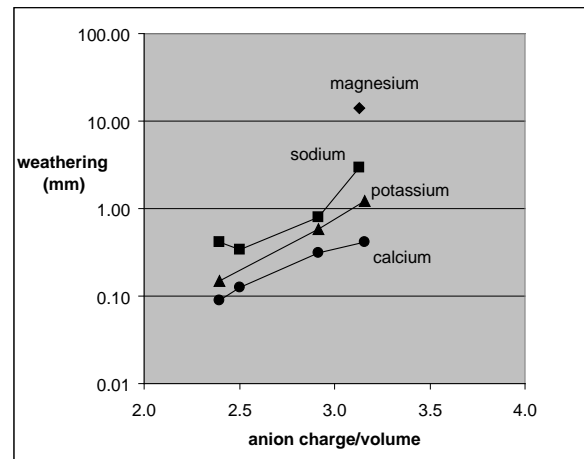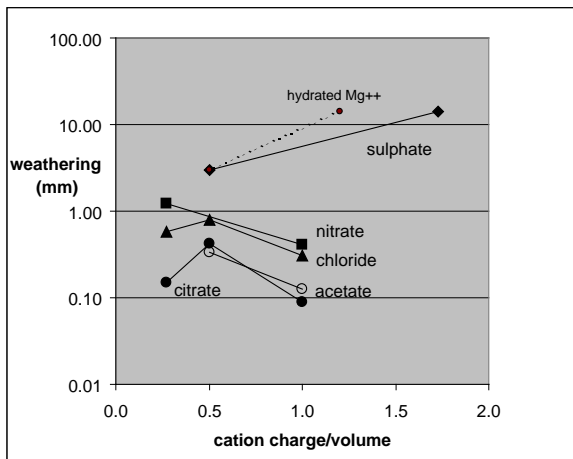
Left: There is a suggestion in the data that the higher the positive cation charge, and the smaller its volume, the *less* it weathers the sandstone. However, magnesium sulphate (the data point top right) with its high charge/volume ratio and high weathering ability clearly does not conform to any such trend even when the cation is taken to be $[Mg(H_2O)_6]^{2+}$.

Right: In contrast, the higher the negative anion charge, and the smaller its volume, the *more* it weathers the sandstone. That anion charge densities play a role is not something that the theory that the salt is interacting with the clay would predict.

Volumes are approximate and have been calculated by adding together the volumes of the individual atoms in the ion. The charge/volume ratios have all been normalized to the ratio for a divalent calcium ion.
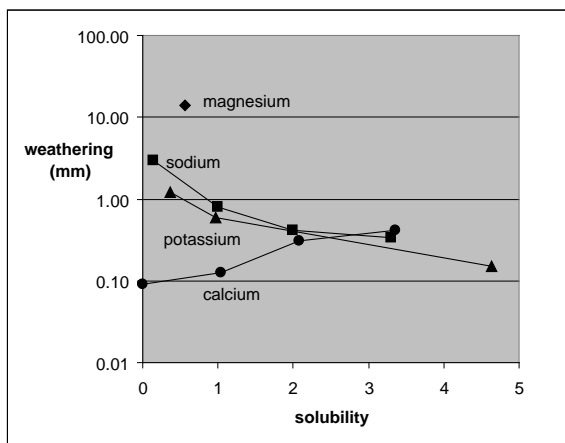
The salts of sodium and potassium weather less the more soluble they are, but the reverse is true for calcium. Why is not understood.

solubility is relative to sodium chloride

ions' double charge; or perhaps under supersaturation magnesium forms ion-pairs such as $MgOH^+$. That magnesium tends to behave less like calcium and more like

sodium has been observed in studies of the properties of soils, and of the negative effects of using *dolomite*, $CaMg(CO_3)_2$ as a source of calcium for the treatment of saline and sodic soils by farmers.[42]

Calcium citrate, like calcium sulphate, is not very soluble, so based on the idea that sulphate ions remove calcium and hence encourage de-cementation by more soluble sulphates, one might expect citrate ions to do the same. This was true of sodium citrate (0.42 mm), but not potassium citrate (0.15 mm). Why the two citrate salts should differ so strongly, while the two chloride ones do not, is a puzzle.

A second puzzle is why calcium nitrate (0.41 mm) and calcium chloride (0.31 mm) were so relatively more effective at de-

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[42] Katerina Dontsova & L. Darrell Norton, *Effects of Exchangeable Ca:Mg Ratio on Soil Flocculation, Infiltration and Erosion*, in Stott, Mohtar, Steinhardt (eds.), *Sustaining the Global Farm*, 2001.

cementation than calcium acetate (0.11 mm) or calcium citrate (0.09 mm).

One possible solution to the first of these puzzles is that salt-weathering cannot be explained at the clay-crystal level in the structural hierarchy of the clay alone. Clay behaviour at the sub-microscopic level is usually considered to be dominated by interactions between the negatively-charged silica surfaces and the external positively-charged cations attracted to them. Anions play only a minor role and are frequently ignored in theoretical analyses. If the nature of the anions is important, then perhaps this is because, through osmosis, electroosmosis, molecular size, or metal-ion-clay (*smectite*) chemistry they regulate the flow of cations and salt through the sandstone. Molecular size is related to surface tension. It is also related to viscosity, although in a complicated way.

A possible solution to the second puzzle is that considering calcium to be a divalent ion might in some circumstances be a mistake. In a recently published article, it was reported that calcium in seawater forms a monovalent ion pair, $CaCl^+$, and this is preferentially adsorbed by *montmorillonite*.[43] Perhaps there is also a monovalent ion pair, $CaNO_3^+$, but not one containing an acetate or citrate ion. The dominant anion in groundwater is neither chloride nor nitrate, so this effect would not normally be seen in nature.

Test 5 (b)

Procedure
This test was carried on at the same time as Test 5 (a), the only differences being that

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[43] Laurent Charlet & Christophe Tournassat, *Fe(II)-Na(I)-Ca(II) Cation Exchange on Montmorillonite in Chloride Medium—Evidence for Preferential Clay Adsorption of Chloride-Metal Ion Pairs in Seawater*, Aquatic Geochemistry, 11, pp.115–137, 2005.

one of the two samples was tested with 50:50 mixes (by volume) of:

sodium chloride and **sodium acetate;** **sodium chloride** and **calcium acetate**; and **sodium chloride** and **calcium citrate**.

Results
The results shown opposite again demonstrate that mixes sometimes produce *less* sediment than one might expect. The first test (sodium chloride with sodium acetate) produced a result, 0.75 mm, practically the same as that of sodium chloride alone, 0.8 mm, while sodium acetate alone produced only 0.14 mm of weathering.

The second test (sodium chloride with calcium acetate) produced a result, 0.59 mm, a little less than that of sodium chloride alone, 0.8 mm, while calcium acetate alone produced only 0.11 mm of weathering. This result contrasts strongly with that obtained in Test 4(b) in which the mixed salts produced only 0.05 mm of weathering. I have no idea as to the reason for this difference, nor any reason to suspect there was a procedural error in the tests.

The third test (sodium chloride with calcium citrate) produced a result, 0.22 mm, significantly less than that of sodium chloride alone, 0.8 mm, while calcium citrate alone produced only 0.09 mm of weathering.

Discussion
It is difficult to comment on these results in detail without an understanding of the movement of mixes of salt in a drying porous medium.

	sediment volume $10^{-6}m^3$	sediment volume per surface area $10^{-6}m$	normalized sediment volume per surface area $10^{-3}m$ *	previous tests	nature of sediment
NaCl + Na{acetate}	0.10	98	0.75		buff, cloudy
NaCl + Ca{acetate}$_2$	0.081	77	0.59	0.05	buff, cloudy
NaCl + Ca$_3${citrate}$_2$**	0.043	29	0.22		grey, not cloudy
Na{acetate} + Ca{acetate}$_2$				0.02	
* these are figures normalized to the absolute figure for NaCl obtained in Test 1.					
** sample broke in two.					

However, there does seem to be a common theme that mixes of sodium and calcium salts appear to be less destructive than might be foreseen. In every case, the weathering by common salt (sodium chloride) was reduced by the presence of a calcium salt.

Conclusions

Two explanations for what salt does to the sandstone have been proposed. The first is that the de-cementation is a result of pressure exerted by salts as they crystallize. The second is that concentrated solutions of salts weaken the adhesive properties of the clay that cements the sandstone together. Either or both processes likely facilitate the removal of the silt-clay "grout" from ancient microfractures rather than opening up new ones. It is possible that the increased permeability of the surface layers as a pre-cursor of micro-spalling changes the weathering pattern of the sandstone by encouraging the weathering of *biotite* to *hydrobiotite* and perhaps also the formation of *montmorillonite*, a clay that swells.

That salt-weathering is due to crystallization pressure is much discussed in the technical literature and many papers have been published supporting this idea. The results reported here however do not confirm that this is what is happening locally. If anything, there appears to be a negative correlation between pressure, according to the published data, and the weathering.

The results also do not support the theory that salt-clay interaction is the cause. If it were so, the nature of the anions on the salts would be of no import, contrary to what is observed. It also has to be noted that salt-weathering is not confined to sandstones cemented by clay, even on Gabriola, where calcareous-cemented concretions are frequently seen to be weathered in a similar fashion to the host rock.

The reason that neither theory *appears* to fit the facts is most likely that the simplest interpretations ignore the processes that lead to the deposition of salt where it can do the most damage, which is just below the surface (subflorescence). The evidence is

that this can be influenced by a number of factors including the properties of supersaturated solutions such as surface tension and viscosity, the geometry of the interstices, and the physical environment in which evaporation is taking place.

What the results do show is that the cations and anions that do the most damage in order of severity are:

$Mg^{2+} > (Na^+ = K^+) > Ca^{2+}$

$SO_4^{2-} > NO_3^- > Cl^- > organics.$

That divalent magnesium cations cause more damage than divalent calcium cations may be because magnesium cations form monovalent cations such as $MgOH^+$. Alternatively, it has been pointed out in the literature that the viscosity of saturated magnesium sulphate solutions is very high and this affects where crystallization occurs and in what kinds of pores.[44]

A cross-correlation analysis of the results indicates, quite consistently, that big anions with small negative charges do relatively little damage. Although not proven, this suggests that the less the surface tension of the supersaturated solution, the less is the weathering. This might be because the lower the surface tension, the lower is the capillary force pulling the liquid into the pores of the sandstone; or it might be because crystallization pressure is related to surface tension. The first of these possibilities raises the suspicion that the kind of wet-dry cycling used in the experiments might not mimic exactly what goes on in nature and for this reason no further testing along these lines is envisaged.

It is thus not possible to come to firm conclusions as to the causes of the

weathering of the sandstone, but most workers in the field believe that it is crystallization pressure and I see no reason to doubt this. The mobility of salts within the rock must also play a role.[45] Less soluble salts may partially fill pores and thereby contribute to the damage pressure does by changing pore geometry, and the location of precipitation below the surface may influence the thickness of spalls.

With regard to the surfaces on which the petroglyphs are carved, I would say this. The petroglyphs on Gabriola are weathering because of the effect of sodium in salt left behind as rainwater dries out. This process is greatly accelerated by removal of moss and forest litter covering for the following reasons. Exposure to sun and wind produces a wet-dry cycling environment more conducive to salt-weathering than would exist beneath the cover. This is probably the single most important reason. Also, the acidification of rainwater by bryophytes releases calcium from the minor amounts of *calcite* in the sandstone and this helps the clay cement in the sandstone retain its (beneficial) calcium.

The formation of organometallic complexes and large-molecular-weight organic salts in the moss and litter may hinder the mobility of simple ions in the sandstone and thereby restrict the damage they do. The experiments have shown that, in general, even sodium salts of organic acids are less damaging to the sandstone than inorganic salts and it would not be a surprise if this were to be an important aspect of salt-weathering in the forest. ◊

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[44] E. Ruiz-Agudo, F. Mees, P. Jacobs, & C. Rodriguez-Narvarro, *The role of saline solution properties on porous limestone salt weathering by magnesium and sodium sulfates*, Environmental Geology, 52, pp.269–281, 2007.

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[45] Aaron Micallef, Heather A. Viles, Andrew S. Goudie, & Carlos Sancho, *ibid*.