Context:

Geology, weathering, Nanaimo Group, sandstone, mudrock.

Citation:

Doe, N.A., Non-marine weathering of sandstone and mudrock, *SHALE* 25, pp.31–48, March 2011. {printed version}

Doe, N.A., Non-marine weathering of sandstone and mudrock, *SHALE* 25, pp.31–49, March 2011. {website version}

Note: The website version has an extra page, p.49. This is not in the published printed version because illustrations in the journal *SHALE* are black-and-white only and there was no point in including pictures for which colour is essential.

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Errors and omissions:

N/A

Later references:

N/A

Date posted:

February 23, 2011.

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Non-marine weathering of sandstone and mudrock

by Nick Doe

[NOTE: by "non-marine", I mean weathering other than by salt, though salt-weathering—*tafoni*, honeycombing, cavernus weathering—does sometimes occur away from the sea]

Sandstone composition—Gabriola Formation

The common minerals in Nanaimo-Group, Gabriola-Formation, late-Cretaceous, Maastrichtian-age sandstone on Gabriola Island are *Na/Ca-feldspar* (*plagioclase*, which is mostly *albite*)[1] and *quartz* with lesser amounts of *K-feldspar* (mostly *orthoclase*).[2] Together these constitute roughly 75–80% of its content in a matrix of about 10–15%. The remaining 5–15% is made up of the ferromagnesian (mafic) minerals *biotite-phlogopite* and *amphibole* (mostly *hornblende*). There are also lesser amounts of white mica (*muscovite*), plus other trace minerals[3] and lithic fragments that are mainly volcanic.

About half the matrix is finely comminuted grains of the major constituents. The most common clay minerals in the matrix, based on only a small number of samples, are *kaolinite* and *montmorillonite*, together with traces of white micas (*sericite*), *chlorite* (associated with weathered *biotite*), and possibly *illite* as fine-grained *sericite*.

The interstices and microfractures in unweathered samples are tightly packed—voids in thin-sections are rarely seen. The only cement appears to be the clay in the matrix.

Zeolite, possibly *heulandite* or *laumonite*, is mostly confined to fracture faces and veinlets where it occurs with *calcite* and traces of other evaporite minerals. *Calcite* occurs in locally-abundant concretions and associated veinlets and microfractures, but is generally absent.

Because of its high feldspar content and a matrix close to or exceeding 15%, I sometimes describe Gabriola Formation "sandstone" from Gabriola Island as "feldspathic wacke". Other researchers on other islands however have almost invariably found a more significant lithic component (volcanic with lesser chert and minor sedimentary fragments) and so descriptions vary.

Thin-section composition

A sample of the sandstone was carefully analysed by area in thin section, mineral clasts (grains) only, ignoring minor components and matrix, as:

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[1] XRD analyses of Nanaimo Group samples on Gabriola invariably show *albite* (An_{0-10}). Also sometimes seen is *oligoclase* (An_{10-30}), but nothing more calcium-rich than this. The feldspar does not dissolve in HCl.

[2] None of the hand specimens from Gabriola I have looked at have stained for K-feldspar.

[3] Including *magnetite, pyrite (?marcasite), limonite (?hematite*), *leucoxene*, *rutile*, and *epidote*. Some hand specimens are distinctly magnetic. Katnick (see fn.4.) also reports traces of *pyroxene* .

plagioclase 50%, *quartz* 28%, *hornblende* 6%, *biotite* 6%, *K-feldspar* 10%.[4]

Sandstone origin

The composition of the sandstone is consistent with the conjecture that the sediments forming the Gabriola Formation are mostly from the Coast Mountains of southwest BC.[5] The comparable composition of plutonic rocks in the southern Coast Mountain complex is (by area in thin section, 24 samples):

plagioclase 62±8%, *quartz* 21±5%, *hornblende* 7±3%, *biotite* 6±3%, *K-feldspar* 4±2%.[6]

These numbers indicate plagioclase-rich plutons with the IUGS rock types of the 24 samples being *quartz diorite* (9); *tonalite* (6); *granodiorite* (5); *granite* (2); *diorite* (1); and *quartz-rich granitoid* (1).[7]

All of these rock types are to be found among the pebbles on beaches on Gabriola and were brought here by glaciers from the Coast Mountains during the ice-age.

Whole-rock composition of sandstone

Whole-rock analyses are not always useful in assessing weathering processes because often changes in mineral composition are not reflected in changes in elemental composition. The most significant detectable changes are due to leaching and cation exchange when the weathering products have become elements of the soil. Whole-rock analysis is however fairly cheap and is not labour intensive, and it can give useful supplementary information such as the overall sodium to calcium ratio of feldspars in the *plagioclase* series.

Whole-rock analysis of two unweathered samples of Gabriola Formation sandstone gave the following results.[8] Included are averaged results for 25 samples of plutonic and volcanic southern Coast Mountain rock.[9] These have been normalized to have the same silicon content as the sandstone. Normalizing to 100% would be misleading, as it would encourage

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[4] Sample 3, Lockwood Drive, Gabriola. Analysis by Craig Leitch, Saltspring Island, Sept. 2003. Sampling and thin-section analyses by Vancouver Island University students showed similar results, with not so much *plagioclase* and more *quartz* in general (Steve Earle, personal communication). D.C. Katnick recorded for the Gabriola Formation on Hornby Island (3 samples, not including 5-10% matrix), total *feldspar* 27%, *quartz* 35%, other 15%, lithic fragments, mainly volcanic with minor sedimentary chert, 23%. The Gabriola Formation on Hornby is, in contrast to Gabriola, rich in conglomerate. D.C. Katnick, *Sedimentology, Stratigraphy and Provenance of the Upper Cretaceous Nanaimo Group, Denman and Hornby Islands, BC*, SFU M.Sc. thesis, March.2001. P.S. Mustard (see fn.5, p.51&53) cites for the Gabriola Formation in the southern Gulf Islands (29 samples) *plagioclase* 42%, *quartz* 34%, *K-feldspar* 10%, lithic fragments, mainly volcanic but with chert 14%.

[5] P.S. Mustard, *The Upper Cretaceous Nanaimo Group*, GSC Bulletin 481, p.90, 1994.

[6] Calculated from data in Yao Cui, *Geochemistry of Igneous Rocks from the Southern Coast Belt Plutonic Complex, Southwestern British Columbia*, UBC M.Sc. thesis, Oct. 1993. The range is the standard deviation.

[7] This assumes arbitrarily that 10% of the *plagioclase* is "pure" *albite* (Ab_{95-100}). There is no pink (K-feldspar) in most of the rock from this region. Katnick (see fn.4), describes volcanic fragments as being predominantly *andesite*, the volcanic equivalent of *quartz diorite*, and basalt, the volcanic equivalent of *diorite.*

[8] Sample 13, Dole Road, ACME File:A305008; and Sample 32, 707CP, ALS Chemex File:VA09134790. Carbon and sulphur not included.

[9] Yao Cui, *ibid*.

comparisons on the assumption that there has been no net gain or loss of elements in the transition from parent material to sediment. The table thus conjectures that only silicon is not lost or gained.[10]

Columns are by weight (shaded) and number of atoms (unshaded) of the element.

	sandstone	plutonic	sandstone	plutonic	sandstone	volcanic	sandstone	volcanic
	wt.	wt.	no.	no.	wt.	wt	no.	no.
Si	64.3	64.3	66	66	64.3	64.3	66	66
Al	14.8	20.0	16	22	14.8	24.2	16	26
Na	5.1	9.5	6	12	5.1	8.7	6	11
Ca	4.0	7.2	3	5	4.0	9.4	3	7
K	3.8	2.6	3	2	3.8	1.6	3	1
Fe	5.3	14.9	3	8	5.3	32.4	3	17
Mg	1.5	3.5	2	4	1.5	9.3	2	11
Mn	0.1	0.2	0.1	0.1	0.1	0.3	0.1	0.2
other	1.1	1.2	1	1	1.1	1.8	1	1
TOTAL	100.0	123.4	100	120	100.0	152.0	100	140

The whole-rock composition suggests that, no matter what type of Coast Mountain rock was the parent, the sandstone is depleted in all elements except potassium relative to silicon. With the exception of potassium, this is what one might expect if the sand had been weathered before being lithified.

Some interesting, but unproven, conjectures are: the relative losses of calcium (1.8/2.3), sodium (1.9/1.7), and potassium (0.7/0.4) suggest *anorthite* and then *albite* weathers faster than *orthoclase*; and the relative losses of magnesium (2.3/6.2) and iron (2.8/6.2) are in line with the assertion that *biotite* and *hornblende* weather faster than feldspars. The losses for aluminium were (1.4/1.6).[11] These relationships are given some support by the relative mineral solubilities:[12]
anorthite (Ca-feldspar) 10^{-3}> *hornblende* 10^{-4}> *biotite* 10^{-7}> *albite* (Na-feldspar)10^{-7}> *sanidine* (K-feldspar)10^{-7}> *muscovite* 10^{-9}> *microcline* (K-feldspar) 10^{-9}> *quartz* 10^{-10}.

The apparent acquisition of potassium is potentially interesting, but might just be a statistical aberration. The distribution of K-feldspar in the igneous rock varies from trace to 25%. Another possibility is that potassium is being captured by the formation of *muscovite*, which is comparatively insoluble and resistant to further weathering.

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[10] Some geologists prefer to keep the aluminium content constant, it being the least mobile of the major elements because of the very low solubility of Al_2O_3; however keeping silicon constant for the weathered Nanaimo Group rocks seems to produce numbers that make more sense. My conjecture is that this is because the rock is only relatively lightly weathered as evidenced by the absence of *gibbsite* and *bauxite*.

[11] The numbers in parentheses are the ratios of the number of atoms of the element in a sample of the conjectured parent rock (plutonic/volcanic) to the number of atoms of the same element in a sample of sandstone, both samples containing the same number of atoms of silicon. The higher the number, the more quartz-like the arenite has become compared with the parent rock.

[12] K.M. Scott and C.F. Pain, *Regolith Science*, p.65, Springer, 2008.

Whole-rock mineral composition of unweathered sandstone

The whole-rock analysis of two sandstone samples (fn.8), giving the elemental composition, was used to predict the composition by weight of conjectured minerals present. Several similar solutions are possible involving different combinations of the ferromagnesian minerals. One representative result was:

albite 31%, *anorthite* 16%, *quartz* 34%, *hornblende* 0%, Fe-*biotite* 8%, Mg-*biotite* 2%, *K-feldspar* 9%.

The equivalent composition by volume is:

plagioclase 48%, *quartz* 35%, *ferromagnesian* 9%, *K-feldspar* 8%.

This agrees comfortably with the thin-section analysis.

Physical weathering of sandstone

The first stage of the weathering of sandstone is the break-up of the rock to expose a surface to oxygen and water. The most important physical weathering mechanisms are seismic and paleotectonic fracturing (Eocene and Neogene) and frost wedging (freeze-thaw). Frost wedging would obviously have been more severe during the Pleistocene than at present.

Trees also break up the bedrock, but forests were not abundant on the Gulf Islands until four-thousand years ago. Lichens may play a role, likely very minor, in weathering boulders.

Chemical weathering of sandstone

Once the sandstone has been broken up to expose its surface, chemical weathering becomes the most important weathering agent. It takes place on and just under the surface of the rock fragments. This weathering creates a crust that subsequently exfoliates because of expansion of the ferricrete layer (the weathering products have more volume), exposing yet more surface to be chemically weathered.[13]

Colourful iron oxides and hydroxides (red-brown *limonite*) are the most readily observed weathering products. Over time, these darken, likely as the result of the replacement of the *hematite* component by *goethite*. The boundary between the weathered surface layer and unweathered rock below is extremely sharp (a fraction of a millimetre), which is consistent with it being caused by meteoric water being drawn into the rock by capillary action.

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[13] An alternative explanation is that the weathered crust is more competent than the underlying rock and thus better able to transmit and concentrate stress. The expansion theory is based on the observation that the fracture patterns somewhat resemble those seen when tempered glass is shattered. This is discussed at length in N.A. Doe, *Alligatoring on the beach*, *SHALE* 12, pp.7–29, November 2005.

Left: Unweathered blue-grey sandstone with sandy-coloured surface crust of weathering. This crust is cemented with iron oxide (case-hardened) making it mechanically strong and rigid compared to the host rock.

Right: Thick-lip weathering. Water and air penetrate fractures in the sandstone and weather the fracture faces by oxidizing the ferromagnesian minerals—mainly *biotite* and *hornblende*. The weathering is not severe, but is enough to colour the sandstone with iron oxides (*limonite*) which cement the grains more firmly than in the host rock.

Thick-lip weathering often stands proud of the surrounding surface, and sometimes the weathering is sufficient to “heal” the fracture.

Disintegration of sandstone weathering crust. On Gabriola, such channery fragments are the parent material for Saturna soil, a mainly sandy loam DYSTRIC BRUNISOL that is the dominant soil in the upland areas.

Granodiorite and *quartz diorite* boulders from glacial drift occasionally have a similar varnish of weathering as shown below. It is evident however, that such weathering is very much slower than it is with sandstone.

Weathering rind on quartz diorite. Such rinds sometimes have an orange-rusty tinge. The pattern of cracks with sharp right-angles in the rind is similar to that seen in sandstone crusts. Field of view is about 10 inches.

The following equations are primarily the work of an accountant and should not be taken as being accurate or authorative representations of the chemistry.

The important “textbook” reactions are:

Acidification of rainwater (mainly carbonation)

$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$

Many reactions that are expressed in the form:

$XM + H^+ \Rightarrow XH + M^+$ likely occur as: $XM + CO_2 + H_2O \Rightarrow XH + M^+ + HCO_3^-$

Also possible, though less important in general is:

$XM + H^+ + \{\text{organic anion}\}^- \Rightarrow XH + \{\text{organo-metal complex } M\}$

Oxidation, for example:

$2Fe^{2+} + O + 2H^+ \Rightarrow 2Fe^{3+} + H_2O$ (low pH)

$2Fe^{2+} + O + 4OH^- \Rightarrow Fe_2O_3$ (*hematite*) $+ 2H_2O$ (high pH)

Oxidation of sulphides can produce a strong acid, but in the Nanaimo Group sulphides are only associated with fossils and are otherwise insignificant.[14]

Most of the iron in the plutonic rocks of the Coast Mountains is in the Fe^{2+} state and therefore susceptible to oxidation.

Hydrolysis (involving a change in water), for example:

Fe_2O_3 (*hematite*) $+ H_2O \Rightarrow 2FeO.OH$ (*goethite*)

Hydration (involving only adding water), for example:

Fe_2O_3 (*hematite*) $+ nH_2O \Rightarrow Fe_2O_3.nH_2O$ (*limonite component*)

Precipitation:dissolution, for example:

$SiO_2 + 2H_2O \Leftrightarrow H_3SiO_4^- + H^+$ (high pH)

Feldspars

In thin sections, *plagioclase* and *orthoclase* are weathering to a white mica (*sericite*), either *muscovite* or something similar such as *pyrophyllite*, but these likely eventually weather to *kaolinite*:

$3(Na,K)AlSi_3O_8$ (feldspar) $+ 2H^+ \Rightarrow$
$(Si_{1.5}Al^-_{0.5}O_5).Al_2(OH)_2.(Si_{1.5}Al^-_{0.5}O_5).(Na,K)$ (*white mica, muscovite* with K)
$+ 6SiO_2 + 2(Na,K)^+$

$2(Na,K)AlSi_3O_8$ (feldspar) $+ 2H^+ \Rightarrow$
$(Si_2O_5).Al_2(OH)_2.(Si_2O_5)$ (*pyrophyllite*) $+ 2(Na,K)^+ + 2SiO_2$

$2(Na,K)AlSi_3O_8$ (feldspar) $+ 2H^+ \Rightarrow$
$(Si_2O_5).Al_2(OH)_4)$ (*kaolinite*) $+ 2(Na,K)^+ + 4SiO_2$

Plagioclase clasts (grains) however can weather to *montmorillonite* in the presence of magnesium in an acidic environment. *Montmorillonite* gleysol is very common on the

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[14] $4FeS_2 + 10H_2O + 15O_2 \Rightarrow 4FeO.OH + 8H_2SO_4$. Sample 13 had 0.1% carbon and 0.02% sulphur by weight. In shale, which is more fossiliferous, Sample 14 (ACME File:A305008, Northumberld. Fm.) had 3.7% carbon and 0.6% sulphur, and Sample 15 (ACME File:A305008, Spray Fm.) had 1.0% carbon and 1.0% sulphur.

island. *Montmorillonite*, or a similar smectite, is also sometimes visible in the field as thin laminae in shale and lodgement till where it appears to be modern weathering by groundwater seepage. The weathering reactions in chemical terms are something like:

$2NaAlSi_3O_8$ (*albite*, Na-feldspar) + $\tfrac{1}{3}Mg^{2+} + X^{+}_{0.33} + 2H^{+} \Rightarrow$
$(Si_2O_5).Al_{1.66}Mg^{-}_{0.33}\,(OH)_2.(Si_2O_5).X^{+}_{0.33}$ (*montmorillonite*) + $2SiO_2 + 2Na^{+} + \tfrac{1}{3}Al^{3+}$

$4CaAl_2Si_2O_8$ (*anorthite*, Ca-feldspar) + $\tfrac{2}{3}Mg^{2+} + 2X^{+}_{0.33} + 20H^{+} \Rightarrow$
$2(Si_2O_5).Al_{1.66}Mg^{-}_{0.33}\,(OH)_2.(Si_2O_5).\,X^{+}_{0.33}$ (*montmorillonite*) + $4\tfrac{2}{3}Al^{3+} + 4Ca^{2+} + 8H_2O$

where the loosely-bound exchangeable cation X^{+} is usually $\tfrac{1}{2}Ca^{2+}$, $\tfrac{1}{2}Mg^{2+}$, or Na^{+}.

K-feldspar usually weathers to *muscovite* or its weathering product *illite* when the pH is neutral or high; however, if the environment is conducive to the leaching of potassium (K^{+}) in wet-dry cycles, and is acidic, *montmorillonite* will again be produced:

$2KAlSi_3O_8$ (*orthoclase*, K-feldspar) + $2y\,Al(OH)_4^{-} \Rightarrow$ (neutral to high pH)
$(Si_{2-y}Al^{-}_{y}O_5).Al_2(OH)_2.(Si_{2-y}Al^{-}_{y}O_5).K^{+}_{2y}$ (*illite*)
$+ (2+2y)SiO_2 + (2-2y)K^{+} + (4y-2)H_2O + 2OH^{-}$

$2KAlSi_3O_8$ (*orthoclase*, K-feldspar) + $\tfrac{1}{3}Mg^{2+} + 2H^{+} + \tfrac{1}{3}X^{+} \Rightarrow$ (low pH)
$(Si_2O_5).Al_{1.66}Mg^{-}_{0.33}\,(OH)_2.(Si_2O_5).X^{+}_{0.33}$ (*montmorillonite*) + $2SiO_2 + \tfrac{1}{3}Al^{3+} + 2K^{+}$

where X^{+} may be $\tfrac{1}{2}Ca^{2+}$, $\tfrac{1}{2}Mg^{2+}$, Na^{+}, H^{+} , or (less commonly) another metal ion, or an organic molecule. There may also be minor occasional substitution of Fe^{2+} or Mn for the magnesium.

Quartz

Quartz usually dissolves only slightly in water; however, if the pH approaches 9.7 as it does in mixtures of clay, such as *montmorillonite*, *calcite*, and sodium chloride, it dissolves much more readily, enough to form a siliceous gel of $SiO_2.nH_2O$ (*hydrous silica*) when the pH is subsequently lowered. A long-term resident on Gabriola once told me of a patch of clay several metres across that behaved like a waterbed when you jumped on it, remarkably more so than waterlogged sand or peat. Just possibly it contained such a gel.

$SiO_2 + 2H_2O \Leftrightarrow Si(OH)_4$ [or H_4SiO_4] (*silicic acid*) $\Leftrightarrow H_3SiO_4^{-} + H^{+}$ (at high pH only)

Dissolved silica from weathering is the likely source of silicon for the diatoms that formed the diatomaceous earth on Gabriola; it is not necessary to postulate an exotic source such as volcanic ash.

Biotites

Biotite weathers to *vermiculite* and mixes of oxides and hydroxides of iron.

Sometimes *hydrobiotite* or *chlorite* form as an intermediate step in the weathering of *biotite* with *hydrobiotite* being more common in weathered sandstone not immersed in the sea. Abundant *hydrobiotite* has been found in the back walls of salt-weathered galleries. *Chlorite* is a major clay-component of Holocene mud in the Fraser delta.

Hydrobiotite is mixed-layer *vermiculite*:*chlorite* or mixed-layer *vermiculite*:mica. Apart from as a component of *hydrobiotite*, *vermiculite* is rarely seen in X-ray diffraction analyses of clays derived from these sandstones, so presumably it rapidly weathers directly to *kaolinite* once the sandstone is broken down, although another possibility is that *vermiculite* is escaping detection because two of the three X-ray spectrum peaks needed for a positive identification are weak.

$(Si_{1.5}Al^{-}_{0.5}O_5).Fe_3(OH)_2.(Si_{1.5}Al^{-}_{0.5}O_5).K^+$ (*annite*, Fe-biotite)
$+ nH_2O - e^- \Rightarrow$
$(Si_{1.5}Al^{-}_{0.5}O_5). Fe_2Fe^{+}(OH)_2.(Si_{1.5}Al^{-}_{0.5}O_5).nH_2O$ (*vermiculite*) $+ K^+$

$(Si_{1.5}Al^{-}_{0.5}O_5).Mg_3(OH)_2.(Si_{1.5}Al^{-}_{0.5}O_5).K^+$ (*phlogopite,* Mg-biotite)
$+ nH_2O + Al^{3+} \Rightarrow$
$(Si_{1.5}Al^{-}_{0.5}O_5). Mg_2Al^{+}(OH)_2.(Si_{1.5}Al^{-}_{0.5}O_5).nH_2O$ (*vermiculite*) $+ K^+ + Mg^{2+}$
both with some substitution of Al^{3+} for Si^{4+}, balanced with interlayer $(Mg,Ca)^{2+}_{0.5}$.

Or, skipping the *vemiculite* stage:

$(Si_{1.5}Al^{-}_{0.5}O_5).(Fe,Mg)_3(OH)_2.(Si_{1.5}Al^{-}_{0.5}O_5).K^+$ (*annite* Fe-biotite, *phlogopite* Mg-biotite)
$+ Al^{3+} + 4H^+ \Rightarrow$
$(Si_2O_5).Al_2(OH)_4$ (*kaolinite*) $+ K^+ + SiO_2 + 3(Fe,Mg)^{2+} + H_2O$

Chlorite has a structure similar to micas and is usually rich in magnesium, with *brucite*, $Mg(OH)_2$, rather than *gibbsite*, $Al(OH)_3$, layers.

$2(Si_{1.5}Al^{-}_{0.5}O_5).(Fe, Mg)_3, (OH)_2.(Si_{1.5}Al^{-}_{0.5}O_5).K^+$ (*annite* Fe-biotite, *phlogopite* Mg-biotite)
$+ (1,2)H^+ + (3,2)H_2O \Rightarrow$
$(Si_{1.5}Al^{-}_{0.5}O_5. OH^-).(Fe,Mg)_5(OH)_6 (Fe,Al)^{3+}(Si_{1.5}Al^{-}_{0.5}O_5 OH^-)$ (*chlorite*) $+ 2K^+ + 3SiO_2 +$
$(Al(OH)_3,Mg(OH)_2) + (1,0)e^-$

Although the equation doesn't indicate it, small grains of *magnetite,* $Fe^{2+}Fe^{3+}_2O_4$, sometimes accompany *chlorite*.

Amphiboles

Hornblende is usually reckoned to weather faster than *biotite*, but this is not strikingly apparent in the local sandstone. The weathering rate of *hornblende* is quite sensitive to pH and falls as pH rises. *Hornblende* weathers to a number of clay-minerals, most of which are scarcely known by non-specialists. These in turn disintegrate into their constituent parts:

$(Si_7AlO_{22}).Al(OH)_2.Mg_4.Ca_2$ (Mg-*hornblende*) $+ 12H^+ \Rightarrow$
$7SiO_2 + 2Al(OH)_3 + 4Mg^{2+} + 2Ca^{2+} + 4H_2O$

$(Si_7AlO_{22}).Al(OH)_2.Fe_4.Ca_2$ (Fe-*hornblende*) $+ 4H^+ + O_2 \Rightarrow$
$7SiO_2 + 2Al(OH)_3 + 2Fe_2O_3 + 2Ca^{2+}$

Clays

Montmorillonite and *illite* eventually weather to *kaolinite* though this step is very slow in poor leaching conditions.

After a long time, *kaolinite* may then weather to *silica* and *gibbsite*, but there's little evidence of this in the Nanaimo-Group sandstones.

Calcium

Calcium in the form of *calcite* occurs only locally in concretions in the sandstone where it acts as cement. Otherwise *calcite* is only present in trace amounts, if at all. However, calcium is plentiful in Gabriola groundwater. Its source must be weathering of aluminosilicates in the *plagioclase* series other than the sodium end-member *albite*. Calcium cations easily outnumber magnesium cations both in sandy and organic soils, but the ratio is much closer in heavy clay. Calcium is actively re-cycled by plants.

Concretions in sandstone weather more slowly than the host rock on the beach where the pH of water is high, but the reverse is true in the forest where surface water is acidic. "Cannon-ball" concretions are thus abundant near the sea, but hemispherical hollows in the bedrock are all that exist in the forest.

Magnesium

Magnesium does not occur in feldspars and yet is present in Gabriola groundwater. It is actively re-cycled by plants, though in lower concentrations than calcium. As noted already, magnesium is most abundant relative to calcium in clay soils. Presumably the ferromagnesian minerals are the sources of magnesium. Coast Mountain plutonic rocks contain almost as much magnesium as calcium, and volcanic rocks slightly more.

An observation, if you are interested in the weathering of *plagioclase*/*biotite* to *montmorillonite*, is that biotite weathering may be facilitated by the presence of *montmorillonite*,[15] the implication being that *montmorillonite*, by catalyzing the release of magnesium from biotite, leads to further production of *montmorillonite* from *plagioclase*. I don't know that this happens, but it is, I guess, possible:

plagioclase + $\mathbf{Mg^{2+}}$ $\Rightarrow$ (Na^+, Mg^{2+})–*montmorillonite* + Na^+ + Al^{3+}
Mg-biotite + Al^{3+} $\Rightarrow$ $\mathbf{Mg^{2+}}$ + (Na^+, Mg^{2+})–*vermiculite* + K^+
in (Na^+, Mg^{2+})–*montmorillonite* solution

Iron and manganese

Iron in weathering products may appear as the mix known as *limonite* $FeO.OH.nH_2O$ yellow-orange-brown, which may include:

goethite, $\alpha FeO.OH$ dark-brown to almost black. It is the most stable of all Fe-oxides;
ferrihydrite, $5Fe_2O_3.9H_2O$ reddish-brown. It is favoured in the presence of organic material and silicates; and more rarely,
hematite, αFe_2O_3 red. Produced in warm and dry conditions, and fires. There is also a crystalline form with metallic lustre called *specularite*;
maghemite, γFe_2O_3 brown. Usual only in tropical soil, but also produced in fires;
lepidocrocite, $\gamma FeO.OH$ dull red to bright-orange in soils. Produced in wet, anaerobic conditions with low carbonate and CO_2. Possibly this is what you see in nodules in

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[15] I. Abdel-Aal and H.Bergseth, *Alteration of biotite by suspended montmorillonite*, Colloid & Polymer Sci. 253, 144–149, 1975.

shale formed around the remains of brachiopods that used phosphate rather than carbonate for their shells.

Magnetite, Fe_3O_4 black, is associated with weathering to *chlorite*. It is fairly resistant to further weathering. Most of the sandstone is weakly magnetic.

Whole-rock composition of weathered sandstone

A whole-rock analysis was made comparing the core of a sandstone boulder with its weathered crust with the following result.[16]

	sandstone crust	sandstone core	sandstone crust	sandstone core
	wt.	wt.	no.	no.
Si	65.3	65.3	67.6	67.6
Al	13.0	14.8	14.0	15.9
Na	4.5	4.7	5.7	5.9
Ca	2.8	3.8	2.0	2.8
K	3.7	3.9	2.7	2.9
Fe	3.3	5.0	1.7	2.6
Mg	0.7	1.5	0.8	1.7
Mn	1.0	0.2	0.5	0.1
other	0.7	0.8	0.4	0.5
TOTAL	95.0	100.0	95.4	100.0

The relative losses of elements calculated as for the previous table are calcium (1.4), sodium (1.03), potassium (1.1), magnesium (2.2), iron (1.5), manganese (0.2), and aluminium (1.1).[17]

All elements show depletion in the crust relative to silicon (a ratio greater than 1), including this time potassium, and excepting manganese. The acquisition of manganese is an ice-age weathering phenomenon discussed below.

Whole-rock analysis of weathering

One very crude method of indirectly checking the above equations is to see if the conjectured mineral-content changes match whole-rock analyses. The procedure I used was:

1. calculate from the whole-rock analysis results (% oxide by weight), the weight of element present (% element by weight)
2. calculate the relative numbers of atoms present (% element by number of atoms)
3. list possible minerals present and the number of atoms of each element in one molecule of each mineral
4. calculate the relative number of molecules of the minerals that would result in the same relative numbers of atoms as observed in the sample (% molecules by mineral)

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[16] Sample 32 & 33, 707CP, ALS Chemex File:VA09134790.

[17] The numbers are the ratio of the number of atoms of the element in the core to the number of atoms of the same element in the crust, both samples containing the same number of atoms of silicon.

5. from the computed relative number of molecules of the minerals, calculate the weight of each mineral present (% molecules by weight)
6. from the weights of the minerals, using their density, calculate the proportion of mineral present by volume (% molecules by volume).

The trickiest part of this procedure, as mathematicians will quickly recognize, is step 4. If the number of conjectured minerals is the same as the number of elements, there is only one solution. However, if the number of minerals exceeds the number of elements, then there are many solutions. Since I did use more minerals than elements, the following results are least-squared solutions that, while being mathematically correct, should be regarded with some healthy suspicion by geologists and taken only as a general guide.

% mineral volume from whole-rock analysis (conjectured only, and undoubtedly with errors)

	albite	*anorthite*	*quartz*	Mg-mafic	Fe-mafic	*orthoclase*	*Mg-montmorillonite*	other
plutonic	48	13	25	7	7	0	–	–
volcanic	36	10	24	12	18	0	–	–
sandstone	32	11	42	5	9	2	–	–
sandstone	27	11	45	5	8	4	–	–
silty-clay	26	14	39	4	12	0	6	0
silty-clay	25	14	25	–	–	6	28	3

NOTES:

1. Plutonic & volcanic (from Yao Cui *ibid*); sandstone (Sample 13 & 32, *ibid*); silty-clay is Sample 35, ALS Chemex File:VA09134790 and was taken from the B horizon of Cowichan soil on the Commons land on Gabriola. It is a sticky silty-clay gleysol.

2. A dash (–) indicates not included in the analysis.

3. The elements included were Si, Al, Na, K, Ca, Mg, and Fe.

4. The minerals included were *albite* ($NaAlSi_3O_8$), *anorthite* ($CaAl_2Si_2O_8$), *quartz* (SiO_2), and *orthoclase* ($KAlSi_3O_8$). It is doubtful that there is any significant amount of “pure” *anorthite* present, so the *anorthite* content should be taken as meaning the calcium component of *plagioclase*. The magnesium-rich mafic minerals were originally represented by *biotite* (*eastonite* $K_2Mg_4Al_2Si_4Al_4O_{20}(OH)_4$) and *magnesiohornblende* ($Ca_2Mg_4AlSi_7AlO_{22}(OH)_2$), and the iron-rich mafic minerals were originally represented by *biotite* (*siderophyllite* $K_2Fe_4Al_2Si_4Al_4O_{20}(OH)_4$) and *ferrohornblende* ($Ca_2Fe_4AlSi_7AlO_{22}(OH)_2$); however, it was found the the analysis procedure was incapable of distinguishing the biotites from the amphiboles, so only the two biotites were used. The “other” minerals in the upper row of the silty-clay sample were *kaolinite* ($Si_2O_5Al_2(OH)_4$) and two *montmorillonites* ($Al_{3.3}Mg_{0.7}Si_8O_{20}(OH)_4X_{0.7}$ where X was $Ca_{0.5}$ and Na). Only *montmorillonite* with X being $Mg_{0.5}$ gave a non-zero result. “Other” in the lower row of the silty-clay analysis is Fe_2O_3 only. The % oxide by weight were SiO_2 61.8%, Al_2O_3 15.1%, Fe_2O_3 5.4%, CaO 3.0%, MgO 1.5%, Na_2O 2.8%, K_2O 1.0%, TiO_2 0.9%, MnO 0.1%, P_2O_5 0.1%, BaO, 0.1%, water? 8.2%.

7. The analysis preferred to allocate the K to the *biotites* rather than *orthoclase*, which may have been numerically correct but is probably an error. The apparent affinity of sandstone for potassium is however reproduced in the soil analyses of sandy soil discussed later.

8. Silty-clay contains as much as 60% silt, so the analysis of the silty-clay sample is probably not numerically reliable. The usefulness of this technique is limited by an insufficiently large difference between the elemental composition of clays and their parent minerals.

In very general terms, there is a decrease in feldspar content and an increase in quartz content as the rock weathers. It may be that sodium-rich feldspar weathers more than calcium-rich feldspar, but also possible is that sodium is more readily leached. It does appear, in support of the field observations, that smectite is a more common weathering product than *kaolinite*.

Pleistocene weathering of sandstone

Spherical concretion in sandstone. The concretion was formed around organic material of some kind, probably a shell or small piece of wood. The concretion contains the same minerals as the host rock, the only difference being that in the concretion, the sandstone is cemented with *calcite* derived from the fossil. In this particular case, the concretion has been weathered by Pleistocene meltwater. The dark chocolate-coloured weathering contains iron and a high concentration of manganese.

Weathered sandstone boulders on Gabriola have fairly commonly acquired thick, chocolate-brown, surfaces, rich in oxides of iron and manganese. Most likely, this is the result of prolonged exposure to flowing acidic water containing iron and manganese over a calcareous concretion. The locally-high *calcite* concentration raises pH to greater than 8 and this precipitates the metal oxides, particularly *goethite* and possibly *manganite*, MnO.OH, or a *birnessite*, $(Na,Ca_{0.5},K)(Mn^{4+},Mn^{3+})_2O_4.nH_2O$. I've never seen any sign of *pyrolusite*, MnO_2, either in a hand specimen or thin section.

$CaCO_3 + H_2O \Rightarrow Ca^{2+} + HCO_3^- + OH^-$

$Fe^{2+} + OH^- + O \Rightarrow FeO.OH$ (*goethite*) $+ e^-$
$Mn^{2+} + OH^- + O \Rightarrow MnO.OH$ (*manganite*) $+ e^-$

The acid in the water has weathered the concreted sandstone by removing the *calcite* cement and it consequently disintegrates. As this supposition predicts, the surface layers of such weathered boulders are comparatively deficient in calcium (cement) and potassium (leached).[18] This type of weathering occurs both above and below late-Pleistocene sea level.

The most likely source of the manganese is the *biotite*, as it is in *manganophyllite*; however, there are only tiny traces of manganese in sandstone compared to shale where in some samples (Northumberland Formation) the Mn:Fe ratio (by number of atoms) is as high as 1:3.8.

This of course raises the interesting question, where did the manganese in the weathering of the Gabriola Formation sandstone come from, given that there is no shale formation above it? Either the meltwater from the Pleistocene glacier was rich in it, or groundwater at one stage of deglaciation and isostatic adjustment flowed upward. The average Mn:Fe ratio in plutonic rocks from the the southern Coast Mountain complex is (by number of atoms) is 1:39, and in volcanic rocks from the same region, 1:57.

A suggestion requiring further investigation is that the manganese may have been accumulated in anaerobic water beneath melting glaciers in contact with bedrock or loaded with rock flour. There are several articles in the literature reporting a manganese “spike” in sediments at the end of deglaciation due to rapid oxidation of bottom water by surface water during the melting of large bodies of stagnant ice.

Mn^{2+} is quite resistant to oxidization in neutral and acid aqueous solution, and manganese has a much greater solubility compared to iron when the pH ranges from about 6 to 8 and the redox potential (Eh) from about +0.4 to +0.6 v, conditions approximately what might be expected in aerated water with no biological growths to remove the manganese.

Soil

The end result of weathering is soil. On Gabriola, soil is a combination of bedrock that has been weathered during the Holocene and/or weathered glacial till. The common soil on the Gabriola Formation sandstone is Saturna soil, which is a mainly sandy loam DYSTRIC BRUNISOL. The parent materials are the sandstone together with glacial lag gravel.

One of the interesting features of this soil is pockets of clay (gleysol) that gather in depressions and support wetland in an otherwise very well drained landscape. It is not immediately obvious where this clay has come from. The similarity of the mineral composition of the bedrock sandstone and the glacial drift from the southern Coast Mountains makes it difficult to distinguish the two possible sources, but I strongly suspect that this *montmorillonite*-rich clay is the result of early-Holocene alteration of deposits of glacial flour accumulated as sludge during deglaciation and subsequently left to dry out.

Normally, arid conditions and wet-dry cycling favours production of *montmorillonite* in soils, and the early-Holocene climate was drier than at present. This explanation also accounts for the uniform lack of the organic material in the clay one would expect if the clay had accumulated slowly over the centuries. On the Commons land on Gabriola, radiocarbon

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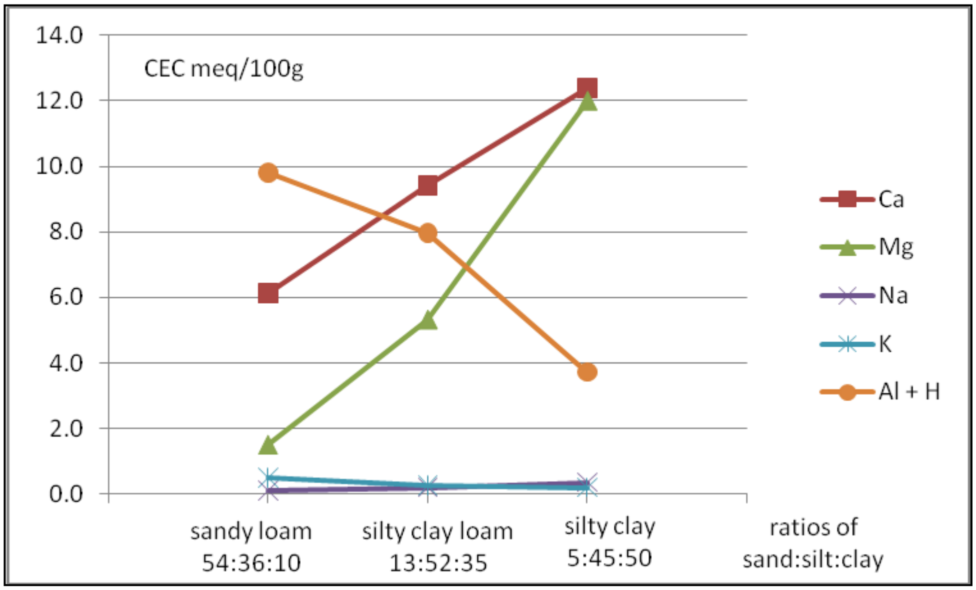
[18] N.A. Doe, *“Brown-stuff” weathering and manganese in your drinking water*, *SHALE* 14, pp.15–17, September 2006.



dating of peat layers overlying clay gave a mid-Holocene date for the earliest peat, which again supports the idea that the clay is basically an ice-age product and not a product of on-going weathering of the bedrock.[19]

The results of an analysis of the cation exchange capacity (CEC) of soils (B horizons) on Gabriola [Saturna (sandy loam Brunisol), Fairbridge (silty clay loam Brunisol with gleyed horizons); and Cowichan (silty clay Gleysol)] show most *montmorillonite* in depressions in the sandstone bedrock is calcium-*montmorillonite*, but with an additional magnesium-*montmorillonite* component that rises sharply with the clay content of the soil.[20] Sodium appears to be only a minor exchangeable cation.

Doing the algebra to separate out the sand, silt, and clay hosts of exchangeable cations gives the following results for CEC (meq/100g or 0.01 mol/kg):

	Ca	Mg	Na	K	Fe organic	Al organic
sand	6.6	0.0	0.0	0.7	0.2	0.2
silt	0.0	0.0	0.0	0.4	0.3	0.3
clay	24.5	21.0	0.7	0.0	0.0	0.0

Calcium-*montmorillonite* and magnesium-*montmorillonite* do not swell as much as sodium-*montmorillonite* when hydrated and this may be having as yet undiscovered and unsuspected effects on the characteristics of the Gabriola wetlands and fractured bedrock aquifers that sometimes rely on clay as an aquitard. The difference between potassium and sodium in weathering processes, and in mica and clay mineralogy, is again evident in this table.

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[19] N.A. Doe, *The geology of Gabriola Island's diatomaceous earth*, *SHALE* 24, pp.31–36, June 2010.

[20] Data for this analysis is from E.A. Kenny, L.J.P. van Vliet, A.J. Green, *Soils of the Gulf Islands of British Columbia*, vol. 4, *Soils of Gabriola and lesser islands*, Agriculture Canada Report 43, 1990.

Mudrock—Northumberland and Spray Formations

The Nanaimo-Group, Northumberland-Formation, late-Cretaceous, late-Campanian to early-Maastrichtian-age mudrock[21] on Gabriola Island is bluish-grey mud- and siltstone with some fine-sandstone interbeds.

The Spray-Formation is younger, early-Maastrichtian, but has a similar appearance. Most of the following remarks are based on observations of Northumberland Formation samples.

Calcite occurs in weakly-cemented locally-abundant concretions that are not always recognized as such. They lead to differential weathering often confused with spheroidal weathering.[22]

The mudrock also contains calcareous nodules[23] that are fossils including those of inoceramids and brachiopods. These nodules have attracted iron and manganese-rich deposits from groundwater as a consequence of their having a higher pH than the host rock. Some of the nodules also contain higher than usual amounts of phosphorus and, in the Spray Formation, *marcasite*. None of the following analyses include nodules, but it was impossible to completely eliminate weakly-cemented concretions.

Whole-rock composition of mudrock

Whole-rock analysis of two samples of mudrock gave the following results.[24] The table also includes previously presented results for sandstone. The two samples have to be described as "weathered" as they were obtained from the surface. "Unweathered" mudrock is only available by quarrying or drilling.

Columns are by weight (shaded) and number of atoms (unshaded) of the element.

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[21] Mudrock is commonly known as "shale" on Gabriola, even when the rock is not laminated.

[22] N.A. Doe, *Spheroidal weathering*, *SHALE* 13, pp.39–44, June 2006.

[23] There is much confusion in the literature as to the distinction between a concretion and a nodule. Concretions are clasts of the host rock that have been more firmly cemented than in the host. Although the cement in a concretion is commonly *calcite* derived from a fossil, the fossil itself makes up only a part, often only a tiny part, of the concretion. Nodules have a composition not related to the mineral composition of the host rock—they do not contain many host-rock clasts. They are commonly the soft parts of fossils that have been rendered unrecognizable as such by chemical activity.

[24] Sample 14, False Narrows (Northumberland), ACME File:A305008; and Sample 15, Easthom Rd. (Spray), ACME File:A305008. Carbon and sulphur are not included.

	mudrock North.	mudrock Spray	sandstone	mudrock North.	mudrock Spray	sandstone
	wt.	wt.	wt.	no.	no.	no.
Si	51.2	55.3	64.3	56	58	66
Al	19.6	18.4	14.8	22	20	16
Na	2.3	3.5	5.1	3	4	6
Ca	2.5	4.8	4.0	2	4	3
K	4.2	3.5	3.8	3	3	3
Fe	12.3	9.5	5.3	7	5	3
Mg	3.1	3.9	1.5	4	5	2
Mn	3.4	0.1	0.1	2	0.1	0.1
other	1.4	1.0	1.1	1	1	1
TOTAL	100.0	100.0	100.0	100	100	100

The whole-rock composition suggests as would be expected that the typical feldspar ratio of silicon to aluminium of 3:1 has moved in the mudrock closer to the 2:1 in micas and clays thereby moving the whole rock ratio from 4:1 to 2.7:1.

Weathering of mudrock

The weathering of Nanaimo-Group mudrock is mostly chemical, and proceeds very rapidly once the rock dries out and is exposed to the atmosphere. Within days, a boulder will have crumbled to pieces. Erosion of mudrock (shale) cliffs on Gabriola is often attributed to winter storms, but chemical weathering and dehydration in the sun causes most erosion.

Left: Core sample of Northumberland Formation mudrock obtained by diamond drilling. It shows few signs of micro-fracturing.

Right: Boulder of Northumberland Formation mudrock at the foot of a cliff showing very rapid disintegration on exposure to the atmosphere.

Boxwork

Honeycombing due to salt-weathering, which is common in sandstone, is never seen in mudrock unless it is in a very silty (coarse-grained) interlayer, and even then, it is quite rare. The surface of the mudrock does however sometimes show a pattern of erosion known as "boxwork"—what I have called in an earlier paper "crozzling".[25]

"Crozzling", or as it is more commonly called "boxwork", on the surface of mudrock. It is generally far easier to see in the summer when lichen and algae is dormant.

What appears to happen is that the surface of the shale develops compression stress as a result of weathering and so when the surface fractures, it does so in the same manner and for the same reason as tempered glass, a process known as "dicing fracturing". Subsequent "thick-lip" weathering of the surfaces of the microfractures, as described above for sandstone, form the basis of the boxwork and this is revealed when the shale between the fractures is eroded faster than the case-hardened faces of the microfractures.

Calcium

Calcium in the form of *calcite* occurs in calcareous nodules in the shale. Minute amounts of *calcite* are also found in the centre of very weakly-cemented concretions resembling spheroidal weathering.[22]

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[25] N.A. Doe, *Alligatoring on the beach*, *SHALE* 12, pp.7–29, November 2005.

Rapidly weathering mudrock showing concretions resembling spheroidal weathering

Pleistocene weathering of mudrock

Manganese-rich, steely-blue coatings possibly containing *specularite* can be seen on the fracture planes of shale. This sample is from the Northumberland Formation.

Coatings rich in iron and manganese occur in shale through which groundwater has been percolating, although "percolating" might not be the best word. These coatings appear on the surfaces of even very tight fractures that are scarcely visible until broken open. This suggests that the groundwater may have been under a great deal of hydraulic pressure. Manganese and iron are also found in abundance in calcareous nodules within the mudrock. Presumably, these coatings have the same history as the Pleistocene weathering of sandstone discussed earlier.[18] ◊