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What Gabriola is made of

by Nick Doe

Ever since way back when, there have been at least two ways of answering the question—what *is* this rock made of?

One way is basically a development of the techniques used by alchemists. You mix the powdered rock with various chemical reagents and observe what happens.

Geologists still are in the habit of putting tiny drops of hydrochloric acid on rocks to see if they fizz. That's a simple test to see if the minerals release carbon dioxide, which if they do, indicates that the rock contains carbonate, most likely *calcite* or calcium carbonate, the stuff shells, bones, and teeth are made of.

Another example of an alchemical technique is the simple trick of distinguishing between sodium and potassium by flicking a few sample grains into a flame. If it glows yellow, it contains sodium; if it glows violet,

it contains potassium.

However, while such procedures can be enormous fun—a great detective game—they are very slow, labour intensive, and qualitative rather than quantitative—they tell you what's there, but not how much.

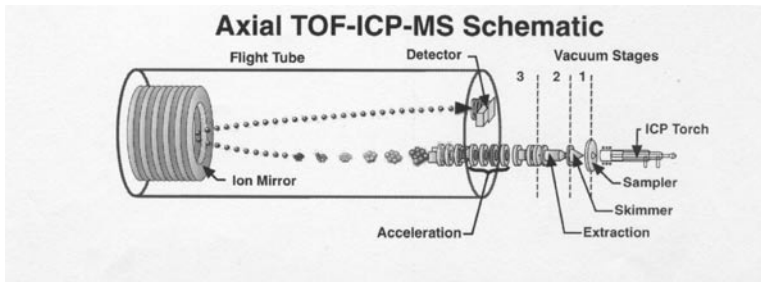
Nowadays, the standard method of testing for many elements simultaneously, is some form of spectral analysis. If you bombard a rock sample with a beam of high-energy electrons for example, X-rays will be emitted at various frequencies characteristic of the elements present. This is an especially powerful technique for analysing minute samples, because electron beams can be very tightly focussed.

Another spectroscopic technique is to use a mass spectrometer. The sample is torched at a very high temperature, and the resulting

ions are fed into a device that measures their mass to charge ratios, which again are characteristic of the elements present in the sample.

The second way of answering the question, what is this stuff, is the mineralogists' way.

The minerals in the rock are examined for a range of physical properties—colour, lustre, hardness, cleavage, magnetism, and so on, and based on the mineralogists' often-considerable experience, an assessment is made. This is the method used in the field by rockhounds, geologists, and prospectors. In the laboratory, samples of the



Analysis of rock samples the modern way. The sample is immersed in argon and heated with a high-power radio-frequency coil to a temperature of 2000–7500 K. This is the ICP (inductively-coupled-plasma) torch on the *right*. Ions from the plasma are then sent to a mass spectrometer (MS). In this case, the spectrometer measures the mass/charge ratio of each ion by measuring its time-of-flight (TOF) to the mirror on the *left* and back again. Hooked up to a computer, a device like this can measure the concentrations of up to 35 elements, at levels down to parts per trillion, in about 20 microseconds.

mineral bearing rocks are ground down into “thin sections”—thin enough to transmit light—and examined with a microscope, frequently using polarized lighting.

The most common element in rocks next to oxygen is silicon. In the analyses of common Gabriolan rocks described at the end of this article it was found that, in addition to the ubiquitous silicon, there is lots of aluminium, iron, calcium, sodium, potassium, and magnesium. Carbon is also plentiful locally as carbonate, and concentrations of manganese also occur.

Trace elements

Elements that are not abundant on the surface of the earth are found, either in very rare mineral deposits, or as trace elements. Trace elements in rocks are often to be found as substitutes for more common elements. The conditions for substitution include being similar in size and having the same ionic charge. The relatively rare metal cobalt, for example, exists in some minerals as Co^{2+} in place of iron, Fe^{2+} . This is possible because the radius of the ionic cobalt, 0.82 Å, is practically the same as that of the ionic iron 0.83 Å.

In the Nanaimo Group rocks, a very common trace element substitution is fluorine F^- , 1.33 Å, for the hydroxyl ion OH^- , 1.32 Å. About 0.6% of the *muscovite* micas (weathering products of potassium-rich feldspars) with the general formula:



contain a fluorine atom, thus becoming:

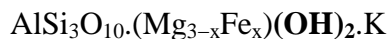


A *fluor-muscovite*, in which all four of the OH^- ions have been replaced with fluorine ions,



has even been synthesized in the laboratory.

Biotite, which is common in sandstone and mudrock,



also can carry fluorine ions in place of one or both of its hydroxyl ions.

Once the rock containing a trace element has been weathered, a different factor comes into play, namely, the aqueous chemistry of the trace element. All elements come in “families”, the members of which have a similar chemistry.

Examples of families are:

(lithium, sodium, potassium...)

(fluorine, chlorine, bromine, iodine...)

(magnesium, calcium, strontium, barium...)

(oxygen, sulphur, selenium...)

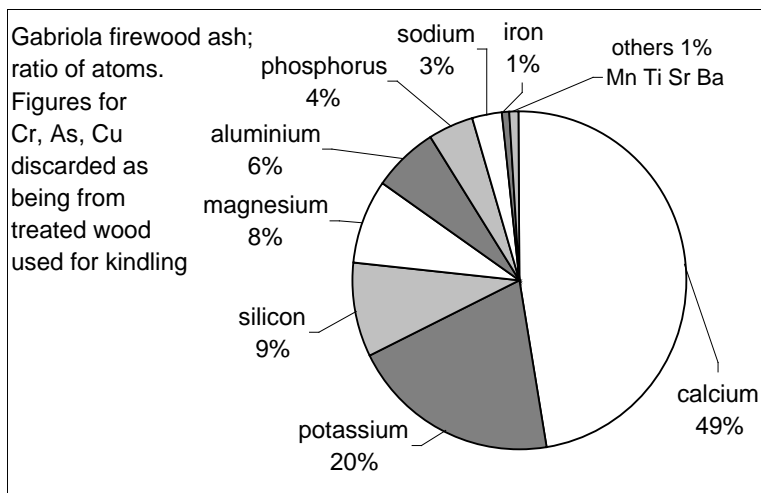
(silicon, titanium...)

(boron, aluminium....)

It was the similarity in the chemistry of calcium and strontium that played a large part in the banning of atmospheric atomic weapons testing in the 1960s—there was widespread concern at the time of the increasing amount of radioactive strontium finding its way into milk, which is, of course, a rich source of calcium. The strontium from the fallout was following the same chemical pathways as ordinary calcium.¹

Selenium, which belongs in the same family as sulphur, forms salts of selenic acid, H_2SeO_4 , which behave very similarly to the far more common sulphate- and bisulphate salts of sulphuric acid, H_2SO_4 . Like sulphur, selenium is often associated with volcanic material, which introduces these elements into the crustal environment.

¹ Both barium (Ba) and strontium (Sr)—hopefully the non-radioactive kind—are present in Gabriolan rocks in concentrations only slightly less than 1000 ppm.



appear in roughly equal amounts in the ash of mixed Gabriola firewood (*left*).

Some ten elements—apart from carbon, hydrogen, oxygen, and nitrogen—are necessary for the growth of plants. They are phosphorus, sulphur, potassium, calcium, magnesium, manganese, zinc, copper, molybdenum, boron, iron, and chlorine.

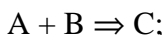
Titanium may be present as *rutile*, TiO_2 , which is often found as a trace element wherever there is *quartz*, SiO_2 .

Nutrients and toxins

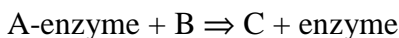
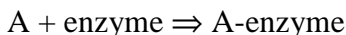
Although some trace elements appear to be neither beneficial nor harmful to plant and animal life, a surprising number are both.

Trace elements are often an essential element of *enzymes*—organic catalysts, which facilitate chemical reactions that would otherwise take place only slowly, if at all.

A difficult single-step reaction:



may become easier with an enzyme:



Enzymes, by definition, are not consumed in the process. A single enzyme molecule can be used again and again, which is why the elements in the enzyme are only required by the plant or animal in small quantities. Iron and manganese, for example, are essential components of the enzyme that help plants manufacture chlorophyll; yet, plant leaves do not contain high concentrations of either metal. Iron and manganese do however

Selenium is an essential micronutrient of animals, particularly ruminants, and is functionally related to vitamin E; yet concentrations of selenium in soil of less than one part per million may result in toxic vegetation.

Although boron, a semi-metal, may be a problem element in Gabriola's water, in some parts of the world the soil is boron-deficient and so boron has to be added as a fertilizer. Boron is lost from the soil in crops, and not quickly replaced because boron-containing minerals (aluminoborosilicates, *tourmalines*)² tend to be very resistant to weathering. The element is used by plants in processes involving cell growth, metabolism, and water usage. It is present in sea water.

The tightness of the limits between concentrations of trace elements that are beneficial and concentrations that are harmful arises because of the chemical activity of the element. In enzymes, their chemical reactivity is what makes the enzyme tick, but that same chemical reactivity can easily be harmful when the trace element starts taking part in reactions that it shouldn't.

² All *tourmalines* contain borate, BO_3^{3-} , and some contain fluorine.

Whole rock analyses

The following are the results of some analyses made of Gabriola's rocks, using the "hi-tech" method, the so-called "whole rock" analysis method. The analyses were done using an inductively coupled plasma (ICP) ion generator and mass spectrometer (MS), plus LECO analysis for carbon and sulphur. Results for cations (positive charged metals) after ignition were calculated from measurements by weight of Al₂O₃(aluminium), Fe₂O₃(iron), MgO(magnesium), CaO(calcium), Na₂O(sodium), K₂O(potassium), TiO₂(titanium), MnO(manganese), Cr₂O₃(chromium), Ba(barium), Ni(nickel), Sr(strontium), Zr(zirconium), Y(yttrium), Nb(niobium), and Sc(scandium).

Results for anions (negatively charged non-metals) were taken from LECO analysis for C(carbon) and S(sulphur), plus Si(silicon) calculated from the metals result for SiO₂, and P(phosphorus) calculated from the metals result for P₂O₅, assuming no loss of Si or P on ignition.

The measurements were made by ACME Analytical Laboratories, Vancouver BC.

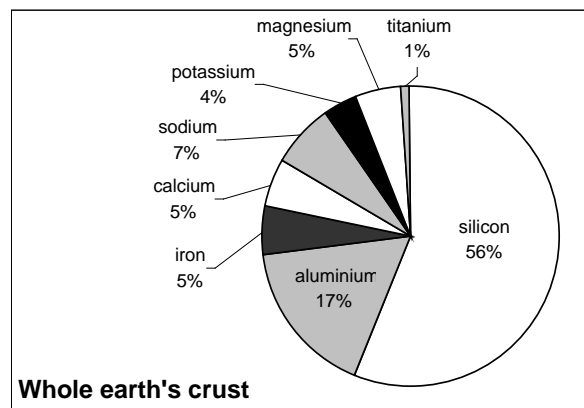
The "whole earth" sample is the averaged elemental composition of the whole of the earth's crust, igneous and sedimentary obtained from (Parker, 1997).

The "sandstone" sample was sandy-grey, homogeneous, fine-grained, freshly exposed on Dole Road (437750,5445500), away from the sea (Sample 13, Gabriola I., Gabriola Fm.). ACME File: A305008.

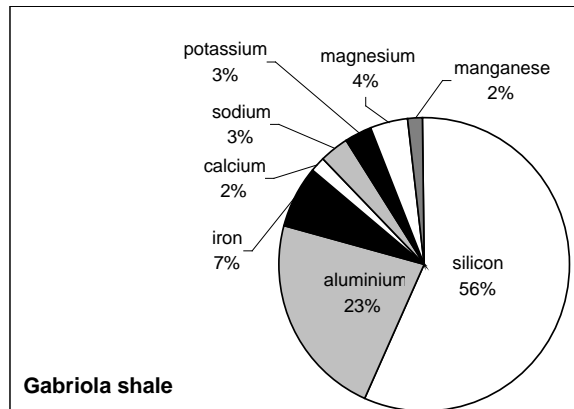
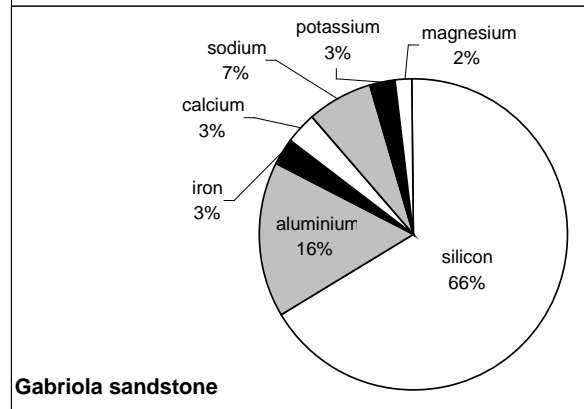
The "green shale" sample was khaki-green unweathered shale with blue rind (probably hematite plus manganese oxide), from beach cliffs on False Narrows (443450,5442400) (Sample 14, Gabriola I., Northumberland Fm.). ACME File: A305008.

The "blue shale" and "brown shale" samples are the results of tests reported for the Gabriola brickyard when it was operational (442500,5443500) (Mines, 1919).

No estimates of oxygen content were included in any of the calculations.



These charts are percentages by number of atoms



Cation (metal) weight [number of atoms] ratios.					
	whole earth	sandstone	green shale	blue shale	brown shale
aluminium	32 [39]	41 [47]	40 [51]	49 [60]	51 [63]
iron	20 [12]	15 [8]	25 [15]	32 [19]	32 [19]
calcium	14 [12]	11 [9]	5 [4]	0 [0]	0 [0]
sodium	11 [16]	15 [20]	5 [7]	*18 [19]	*16 [17]
potassium	<u>10</u> [9]	<u>10</u> [8]	<u>9</u> [7]	<u>-</u> [-]	<u>-</u> [-]
	87 %	92 %	84 %	99 %	99 %
magnesium	8 [11]	4 [5]	6 [9]	1 [1]	1 [1]
titanium	2 [2]	2 [1]	2 [1]	- [-]	- [-]
manganese	- [-]	0 [0]	7 [4]	- [-]	- [-]
strontium	<u>-</u> [-]	<u>1</u> [0]	<u>0</u> [0]	<u>-</u> [-]	<u>-</u> [-]
	97 %	99 %	99 %	100 %	100 %
others	<u>3</u>	** <u>1</u>	*** <u>1</u>	<u>-</u>	<u>-</u>
	100 %	100 %	100 %	100 %	100 %
silicon	52 [56]	63 [66]	51 [56]	55 [59]	56 [60]
non-silicon	<u>48</u> [44]	<u>37</u> [34]	<u>49</u> [44]	<u>45</u> [41]	<u>44</u> [40]
	100 %	100 %	100 %	100 %	100 %

* sodium and potassium combined (alkalies)

** Ba >Zr >Cr >Y >Ni=Sc >Nb

*** Ba >Ni=Zr >Cr >Y >Sc >Nb

C/P/S/Si weight [number of atoms] ratios					
	whole earth	sandstone	green shale	blue shale	brown shale
carbon	- [-]	0.2 [1]	7.0 [15]	- [-]	- [-]
silicon	- [-]	99.7 [99]	91.6 [84]	- [-]	- [-]
phosphorus	- [-]	0.1 [0]	0.2 [0]	- [-]	- [-]
sulphur	<u>-</u> [-]	<u>0.0</u> [0]	<u>1.2</u> [1]	<u>-</u> [-]	<u>-</u> [-]
	-	100 %	100 %	-	-
loss on ignition	-	3.7 %	12.2 %	9.0 %	9.4 %

Comment

Less sodium and calcium in shale than sandstone likely reflects the weathering of feldspars to clay. Aluminium is a major component of mud. Higher concentrations of iron and manganese in shale are a consequence of ice-age weathering. The solubility of these metals is very sensitive to both pH (proton availability) and redox potential (electron availability). During de-glaciation, the rock was immersed in meltwater, which was at times anaerobic, under pressure, and saturated with glacial flour. Whenever this water came in contact with relatively high-pH concretions containing calcite, it deposited a film of oxides. These are commonly steely-blue in shale and are rich in both iron and manganese. Similar surface weathering of concretions in sandstone is chocolate brown.

Black shale—whole rock analysis

Black shale is often black because it contains a lot of organic matter, so much so that the weathering of black shale by micro-organisms has recently been recognized as a hitherto neglected item in the earth's carbon cycle. This test was to see if Gabriola's "black" shale is carbonaceous, or whether the colour is due to metal oxides.

The "green shale" sample was khaki-green with blue rind, from beach cliffs on False Narrows (443450,5442400) (Sample 14, Gabriola I., Northumberland Fm.). ACME File: A305008.

The "black shale" sample was uniformly very-dark-grey, even when perfectly dry, from beach cliffs on Easthom Road (437250,5447000) (Sample 15, Gabriola I., Spray Fm.). ACME File: A305008.

Cation (metal) weight [atoms] ratios		
	green shale	black shale
aluminium	40 [51]	41 [49]
iron	25 [15]	21 [12]
calcium	5 [4]	11 [9]
sodium	5 [7]	8 [11]
potassium	<u>9</u> [7]	<u>8</u> [6]
	84 %	89 %
magnesium	6 [9]	9 [12]
titanium	2 [1]	2 [1]
manganese	7 [4]	0 [0]
strontium	<u>0</u> [0]	<u>0</u> [0]
	99 %	100 %
others	* <u>1</u> %	** <u>0</u> %
	100 %	100 %
silicon	51 [56]	55 [59]
non-silicon	<u>49</u> [44]	<u>45</u> [41]
	100 %	100 %
* Ba > Ni = Zr > Cr > Y > Sc > Nb		
** Ba > Zr > Cr > Ni > Y > Sc > Nb		
C/P/S/Si weight [atoms] ratios		
	green shale	black shale
carbon	7.0 [15]	1.8 [4]
silicon	91.6 [84]	96.2 [94]
phosphorus	0.2 [0]	0.1 [0]
sulphur	<u>1.2</u> [1]	<u>1.9</u> [2]
	100 %	100 %
loss on ignition	12.2 %	11.0 %

Comment

Black shale is often said to be carbon-rich, and this was a test to see if it is true in our rocks. The test failed; the black shale actually contained less carbon than the green shale. However, a complication not investigated is that some carbon may be present as carbonate, which wouldn't contribute to the dark colour, while organic carbon might. Even so, the amount would be small. This result is consistent with the fact that the Spray shale is not very fossiliferous.

References

Dorothy Carroll, *Trace elements in weathering*, in *Rock Weathering*, pp.145–168, Plenum Press, 1970.

Sybil P. Parker (ed.), *Dictionary of geology & mineralogy*, p.339, McGraw-Hill, 1997. ◇