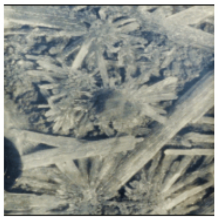
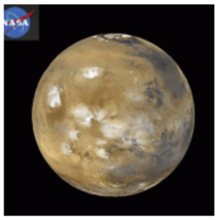
Geochemical News 141 | Oct 2009





In This Issue

Highest pH?
by Michael J. Mottl

The chemical composition of saline lakes of the Northern Great Plains, Western Canada
by William M Last and Fawn M. Ginn

Sample Analysis at Mars: Developing Analytical Tools to Search for a Habitable Environment on the Red Planet
by Paul Mahaffy

Book Review: Thermodynamics and Kinetics of Water-Rock Interaction
Review by William M. White

Interesting Freeware: Part II
by Geochemical News Staff

GNews 141 Staff

Stephen Komor, Ph.D. (Editor)
U.S. Geological Survey (retired)
sck15@cornell.edu

Seth Davis (Webmaster)
Geochemical Society
seth.davis@geochemsoc.org

The Geochemical Society · 5241 Broad Branch Rd, NW · Washington, DC 20015-1305

Highest pH?

by Michael J. Mottl
Dept. of Oceanography, University of Hawaii, 1000 Pope Road, Honolulu HI 96822 USA

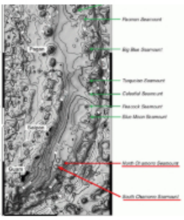


Figure 1

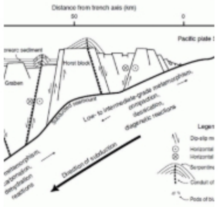


Figure 2

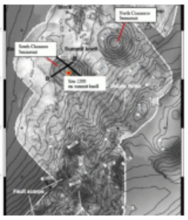


Figure 3

Probably the highest pH ever measured in the deep sea, and possibly in any natural setting, is that of pore water ascending through the serpentinite mud volcanoes in the Mariana forearc (Figure 1). These mud volcanoes were discovered by my colleague Dr. Patty Fryer in the mid-1970's, while completing field work with Don Hussong, then at the University of Hawaii, as part of her doctoral thesis. It was a great surprise to find what appeared to be volcanoes there, as these were supposed to belong properly in the arc, and not in the forearc. Further investigation over the past 30 years (Fryer and Salisbury, 2006) has demonstrated that these are mud volcanoes, similar structurally to conventional volcanoes except that they are cold, and are formed and fed by a rising column of serpentinized peridotite rather than by molten rock. The serpentinite is mobilized from the lithospheric mantle of the overriding Philippine plate, by water and other volatiles sweated off the westward subducting Pacific plate as it is pressurized and heated on its descent (Fryer et al., 1999; Figure 2). Because this mantle has been melted to yield crust apparently multiple times in its history, it is highly depleted in crustal components, so that the source rock of the serpentinite is depleted harzburgite. This is a rock comprised mainly of olivine and orthopyroxene, and is about as chemically simple an igneous rock as can be found on or in the seafloor.

The mud volcanoes produced by this process are big: the largest, Big Blue seamount, is 2 km high and 50 km across. There are dozens of these mud volcanoes in the Mariana forearc, all within the outer half, along a 600 km-swath from about 50 to 90 km behind the trench (e.g. Figure 3). They form when the low-density serpentinite rises buoyantly along intersecting fractures and extrudes at the seafloor, though a central conduit that is narrow relative to the diameter of the volcano. This conduit feeds flows of unconsolidated sedimentary serpentinite that cascade from the summit down the slopes of the building volcano to distances of 18 km. These flows comprise the bulk of the seamount and contain variably serpentinized clasts of harzburgite ranging in size from silt to boulders. The upwelling serpentinite brings up fragments of subducted ocean crust metamorphosed in the blueschist facies, the first ever found in a modern tectonic setting (Maekawa et al., 1993).

Beginning in 1989, when we first drilled one of these mud volcanoes on Ocean Drilling Program (ODP) Leg 125, we have sampled more than a dozen of them at depth below the seafloor, by drilling (again on ODP Leg 195), piston and gravity coring, and push coring from manned submersibles (both *Alvin* and *Shinkai-6500*) and from the ROV *Jason*. These precision tools allowed us to sample both at depth and at seafloor springs, for the waters responsible for serpentinization, derived by dehydration of the subducting Pacific plate, ascend through the rising column of serpentinite mud that feeds the volcano and exit as cold springs on its summit. These springs, in turn, form chimneys of chemical precipitate and support both chemosynthetic microfauna and macrofaunal assemblages at the springs (Mottl et al., 2003), analogous to those found at hot springs along the mid-ocean ridge axis.

The ascending waters, as sampled both within the seafloor and at the springs, are among the most unusual waters ever sampled in the deep sea. Because of the simplicity of their depleted-harzburgite matrix, the upwelling pore waters retain a clear chemical signal of their deep metamorphic origin (Mottl, 1992) in spite of their long ascent, which ranges from 15 to 28 km from the top of the subducting plate to the seafloor. Because the waters originate by dehydration of the subducting slab, they are nearly always fresher (chlorinity of 235 to 546 mmol/kg) than the ambient bottom seawater (542 mmol/kg). Their chemistry varies abruptly with distance across the forearc (Mottl et al., 2004), and hence with depth to the top of the subducting plate: near the trench, at 48-54 km, they have pH 10.7, much higher Ca and Sr than seawater and much lower alkalinity, sulfate, Na/Cl, K, Rb, and B. These proximal springs form chimneys of brucite, $Mg(OH)_2$. Farther from the trench, at 70 to 90 km, the waters have pH 12.5 and show the opposite trends relative to seawater for all of these species. These distal springs form chimneys and crusts of $CaCO_3$. Seamounts at intermediate distances from the trench have intermediate values. Sulfate, Na/Cl, K, Rb, Cs, and B all increase regularly with distance from the trench, leached from the subducting sediment and altered basalt in response to increasing temperature at depth from ~100-350°C.

The pH, alkalinity, and methane content of the springs increase abruptly with distance between 66 and 71 km from the trench, corresponding to depths of 21 to 22 km to the top of the subducting plate. As methane climbs from 44 mmol/kg, and alkalinity from 3 to 69 meq/kg, pH increases abruptly from 10.7 to 12.5, as measured at 25°C. We have measured pH in excess of 12 at three mud volcanoes farthest from the trench, in seven different ODP holes at two sites (780 and 1200), in one gravity core, one piston core, and one *Jason* push core, for a total of 54 pore water samples. Of these, 38 are in excess of 12.3. The deepest samples, most representative of the upwelling end-member water, have pH as high as 12.60.

How do these waters achieve such high pH? While it is well known that serpentinization produces high-pH waters, these values are exceptionally high even for this setting. Solutions involved in serpentinization evolve toward high pH primarily because peridotites contain so little Al and have a low ratio of Si to Mg. Weathering of silicate rocks in general consumes H^+, causing solutions to become more alkaline. The pH of the weathering solution rises until it becomes saturated with secondary aluminosilicates such as clay minerals, which buffer the pH at near neutrality. When Al and Si are scarce aluminosilicates do not form, and pH rises with dissolution of olivine and orthopyroxene until brucite saturation is reached. As modeled by Palandri and Reed (2004), this occurs at a pH of 10.3 at 25°C, in the simple system $MgO\text{-}SiO_2\text{-}H_2O\text{-}CO_2$, a value close to the 10.7 we measured in pore water ascending beneath the mud volcanoes closer to the trench. If CaO is added pH can rise as high as 12.0, but if FeO and Fe_2O_3 are added the maximum pH at 25°C drops again to 11.6. This compares with a range of values in natural waters from serpentinites of 10.7-11.8 (Palandri and Reed, 2004). The highest $pH_{25°C}$ measured at the ultramafic-hosted hydrothermal system at Lost City on the Mid-Atlantic Ridge is 11

GN141 Content

About Michael Mottl

Michael Mottl has spent 939 days at sea (about 2½ years). He has served on 29 research cruises, six as Chief Scientist, and has made 22 submersible dives. These activities are testaments to his stature in the marine geochemistry community. Mike is an expert in pore-water compositions and reactions in fine-grained sediments, serpentinite muds, and everything in between.

measured at the ultramafic-hosted hydrothermal system at Lost City on the Mid-Atlantic Ridge is 11 (Kelley et al., 2005).

We have consistently measured $\text{pH}_{25^\circ\text{C}}$ in the Mariana forearc pore waters well in excess of these values at the three distal seamounts, 70-90 km from the trench: Big Blue (pH 12.34; 9 samples >12.0), South Chamorro (pH 12.49; 39 samples >12.0), and Conical (pH 12.60; 6 samples >12.0). Springs at these distal seamounts have low Ca, in contrast to the high Ca at the proximal sites where pH is lower; this is exactly opposite to the prediction of Palandri and Reed (2004) that high Ca promotes high pH. The $\text{pH}_{25^\circ\text{C}}$ of 12.5 measured in the deep upwelling water at South Chamorro Seamount on ODP Leg 195 becomes 13.1 ± 0.1 at the in-situ temperature of 2.4ºC, calculated using PHREEQC (Parkhurst and Appelo, 1999)(and the $\text{pH}_{25^\circ\text{C}}$ of 10.7 measured at springs proximal to the trench becomes 11.1). These are the highest pH values ever measured in the deep sea, or in any other natural environment that I know of. They are equivalent to that maintained by a $Ca(OH)_2$ buffer. Whereas the pH of 10.7 at the proximal springs can readily be explained by serpentinization, the much higher pH of the distal springs clearly requires an additional explanation.

We hypothesize that the abrupt increases in pH, alkalinity, and methane that occur between 66 and 71 km from the trench have a common cause, namely, dissolution of carbonate minerals in the subducting plate (Mottl et al., 2008). Carbonate dissolution apparently commences at 21-22 km below the seafloor at an estimated temperature of 200-250°C, and joins dehydration as a major process that devolatilizes the subducting plate. Whereas CaCO3 minerals become less soluble with increasing temperature at low pressure, their solubility increases with temperature at pressures of 3 kbar and higher (Caciagli and Manning, 2003), equivalent to burial depths of 10 km and more. Dissolution of carbonate minerals increases the alkalinity of the ascending solutions.

Besides generating high pH, serpentinization is well known to generate large quantities of H2 by oxidation of Fe^{2+} in olivine and orthopyroxene to Fe^{3+} in magnetite. This H_2 will react with the dissolved carbonate now added to the ascending alkaline solutions and reduce it to methane via the reaction:

$$4H_2 + CO_3^{2-} = CH_4 + H_2O + 2OH^-$$

Note that total alkalinity, enhanced by carbonate dissolution, is conserved in this reaction, but that the original carbonate alkalinity is replaced by hydroxyl alkalinity, which increases pH. At the same time the carbonate-C is reduced to methane. This reaction neatly accounts stoichiometrically for the much higher pH of the distal springs and the fact that most of the ascending C is as methane rather than dissolved carbonate.

But why is the transition to carbonate dissolution so abrupt? The transition occurs ~70 km from the trench, where metabasites recovered from the serpentinite mud indicate the transition from lawsonite-blueschist to epidote-blueschist facies also occurs. Thermodynamic modeling indicates that replacement of lawsonite by epidote, which occurs at a temperature of ~223ºC for the chemically simple end-member epidote clinozoisite, causes an abrupt increase in the Na/Ca ratio in solution. As the major cation in solution Na cannot vary much, as its concentration is largely fixed by charge balance. The abrupt increase in Na/Ca is thus accomplished mainly by a drastic decrease in Ca^{2+}: the epidote effectively sucks most of the Ca out of solution. Because the solutions are saturated with $CaCO_3$, and appear to remain so throughout their long ascent, the drop in Ca^{2+} is accompanied by a large increase in carbonate ion, which can only be supplied by massive dissolution of $CaCO_3$ at the top of the subducting slab. We hypothesize, therefore, that the abrupt increase in dissolution of $CaCO_3$ is triggered by the transition with increasing depth from the lawsonite- to the epidote-blueschist facies, which in turn triggers the transition from a high $\text{pH}_{25^\circ\text{C}}$ of 10.7 to an extremely high $\text{pH}_{25^\circ\text{C}}$ of 12.5.

References

Caciagli, N.C., and C.E. Manning (2003) 'The solubility of calcite in water at 6-16 kbar and 500-800ºC. *Contrib. Mineral. Petrol.* **146**:275-285.

Fryer, P.B., and M.H. Salisbury (2006) Leg 195 Synthesis: Site 1200--Serpentine Seamounts of the Izu-Bonin/Mariana Convergent Plate Margin, ODP Leg 125 and 195 Drilling Results. *Proc. Ocean Drill. Program Sci. Results* **195**:1-30.

Fryer, P., C.G. Wheat, and M.J. Mottl (1999) Mariana blueschist mud volcanism: implications for conditions within the subduction zone. *Geology* **27**:103-106.

Maekawa, H., M. Shozui, T. Ishii, P. Fryer, and J.A. Pearce (1993) Blueschist metamorphism in an active subduction zone. *Nature* **364**:520-523.

Mottl, M.J. (1992) Pore waters from serpentinite seamounts in the Mariana and Izu-Bonin forearcs, Leg 125: evidence for volatiles from the subducting slab. *Proc. Ocean Drill. Program Sci. Results* **125**:373-385.

Mottl, M.J., S.C. Komor, P. Fryer, and C.L. Moyer (2003) Deep-slab fluids fuel extremophilic Archaea on a Mariana forearc serpentinite mud volcano: Ocean Drilling Program Leg 195. *Geochemistry, Geophysics, Geosystems* **4**(11):9009, doi:10.1029/2003GC000588, 14pp.

Mottl, M.J., C.G. Wheat, P. Fryer, J.Gharib, and J.B. Martin (2004) Chemistry of springs across the Mariana forearc shows progressive devolatilization of the subducting plate. *Geochim. Cosmochim. Acta* **68**:4915-4933.

Mottl, M.J., T.M. McCollom, C.G. Wheat, and P. Fryer (2008) Decarbonation of the Subducting Pacific Plate Triggered by the Lawsonite-to-Epidote Transition Beneath the Mariana Forearc Serpentinite Mud Volcanoes (abstract). American Geophysical Union Fall Meeting, U51C-03.

Salisbury, M.H., M. Shinohara, C. Richter, et al., (2002) *Proceedings of the Ocean Drilling Progarm, Initial Reports* Volume 195.

Figure Captions

Figure 1. Bathymetry of the southern Mariana arc and locations of selected serpentinite mud volcanoes (Salisbury et al., 2002). Figure 3 shows a detailed side-scan sonar image of the North and South Chammo Seamounts. The term 'seamount' is descriptive whereas 'mud volcano' is interpretive.

Figure 2. A conceptual sketch of how serpentinite mud volcanoes form in the forearc of the Marianas subduction complex. Fluids from heated and pressurized sediments on the underthrust plate flow up through faulted harzburgite in the overthrust mantle wedge. Slurries of serpentinized harzburgite erupt on the seafloor to form and enlarge serpentinite mud volcanoes. (Salisbury et al., 2002).

Figure 3. Sidescan sonar image of the North and South Chamorro seamounts. The water depth is about 2920 meters. Rock cores and pore fluids were sampled at depths down to 50.4m beneath the seafloor at Site 1200 on the South Chamorro seamount knoll. This work was accomplished on Leg 195 of the Ocean Drilling Program (Salisbury et al., 2002).

The chemical composition of saline lakes of the Northern Great Plains, Western Canada

by William M. Last and Fawn M. Ginn
Department of Geological Sciences, University of Manitoba, Winnipeg, Canada R3T 2N2

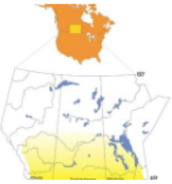
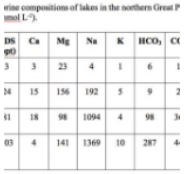


Figure 1



rine compositions of lakes in the northern Great P
mol L^{-1}).

DS pt)	Ca	Mg	Na	K	HCO_3	C
3	3	23	4	1	6	1
24	15	156	192	5	9	2
31	18	98	1094	4	98	3
03	4	141	1369	10	287	4

Table 1

Introduction

> *"We passed during the day many salt lakes, fringed round the edges with thick encrustations of salt, highly indicative of the rapid evaporation that takes place in these arid regions."* (Palliser, 1862)

As pointed out in this quote from one of the first scientific efforts in the northern Great Plains of western Canada, in much of the region ponded saline brines are the only natural surface waters present. In fact, this region contains an estimated 3.5 million lakes and another 6-8 million 'sloughs', most of which are saline or hypersaline (Last, 1988; 1989a). These lakes show a tremendous diversity in size, basin morphology, hydrology, hydrochemistry, and sedimentary and biological characteristics. In this water stressed region of North America, any changes in lake salinity or chemistry are of major concern to the environmental manager.

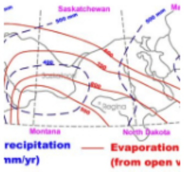


Figure 2

Salinity has a significant impact on the emergent vegetation of the lake's littoral zone and thus influences the value of the area as a waterfowl nesting and staging ground (Conly and van der Kamp, 2001). These lakes, collectively, act as a major breeding ground for over 80% of North America's ducks (Batt et al., 1989; Scott and Scott, 1986; Sorenson et al., 1998). In addition to the importance of this surface water within the realm of wildlife conservation, future industrial and agricultural development in the Great Plains will likely lead to conflicts and potential environmental problems associated with the lakes in the region (Cameron, 1986; Harrington et al., 1997). For example, historically western Canada has been the world's leading producer of natural sodium sulfate ('glauber's salt' or mirabilite: $Na_2SO_4 \cdot 10H_2O$), with sales of the product contributing over $50,000,000 annually to the Canadian prairie economy (Last, 1994; Last and Slezak, 1987). This valuable industrial mineral was extracted by solution and open pit mining of deposits in the saline lakes of the region. If the North American demand for Na_2SO_4 returns to levels of the late 20th century, more lakes will be leased and more mining operations initiated. Increased industrial development of this type will have a profound impact on the wetlands resource. In short, high priority must be given to the study and understanding of the salinity and chemistry of the lakes in this region and the factors that control their chemical variability.

Figure 3

Comments About Units And Nomenclature

Water salinity, while a very simple concept, is often confusing due to the large variety of methods used to measure this basic parameter (Williams and Sherwood, 1994) and a plethora of nomenclature applied. Biological limnologists and ecologists often use conductivity as a measure of salinity. Conductivity, or specific conductance, is a measure of the ease with which electrical current will pass through the water: in general, the greater the salinity, the greater the conductivity. This relationship, however, is not straightforward and is controlled by the specific ions present in the solution as well as the level of concentration of the ions. For example, a conductivity of 126 mS_{20} in a lake such as Bitter Lake in southwestern Saskatchewan, dominated by sodium and chloride ions, would be equivalent to about 100 parts per thousand (ppt or ‰) total dissolved solids (TDS), but this same conductivity value would be recorded in a brine having only about 75 ppt TDS that was dominated by magnesium and sulfate ions (Desai and Moore, 1969). Clearly, the use of conductivity to quantitatively evaluate salinity in lakes having diverse chemical compositions, such as these basins in western Canada, should be avoided.

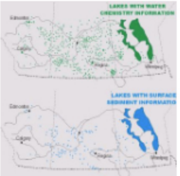


Figure 4

The quantity or abundance of individual ionic components in the water is usually reported as weight concentration of the ion in solution (i.e., the weight of the dissolved ion in g or mg per kg of solution). This is preferred to the use of weight per litre because of the large increase in density of the solution at high salinities. Care must be exercised in evaluating and comparing published reports using g L^{-1} units; unless density is taken into account by the analyst, the difference can be substantial at elevated salinities (>7 ppt TDS). For example, the bottom water of Freefight Lake, a deep, meromictic lake in Saskatchewan, is 275 ppt (weight/weight) or 340 g L^{-1}. It follows then that the total salinity (total dissolved solids) should be the sum of the measured ionic components.

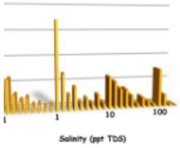


Figure 5

Terminology also varies widely for the various levels of salinity, as reviewed by Williams (1967), Carpenter (1978) and Hammer (1986). Most biological limnologists use the classification scheme of: fresh water (< 1‰), subsaline (1-3‰), hyposaline (3-20‰), mesosaline (20-50‰), and hypersaline (> 50‰). Groundwater researchers often refer to fresh water as < 1‰, brackish water as 1-10‰, saline water as 10-100‰, and brine as > 100‰. Finally, most geoscientific literature uses: fresh water (< 3‰), saline (3-35‰), and hypersaline (> 35 ‰).

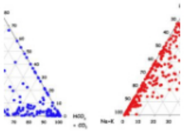


Figure 6

The Northern Great Plains: A Regional

GN141 Content

About William Last

William Last has authored and co-authored dozens of papers about the geochemistry of present-day and ancient non marine evaporites and carbonates in central and western Canada, Australia, north-central U.S., and Spain. He wrote about correlations between El Nino events and the fractal dimensions of finely laminated sediments from the Galapagos Islands. He has been an associate editor or editorial board member of several journals.

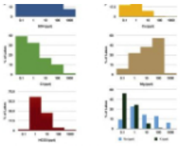


Figure 7

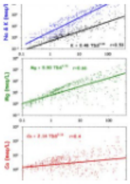


Figure 8 (A)

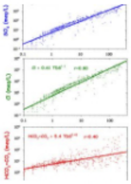


Figure 8 (B)

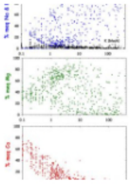


Figure 9 (A)

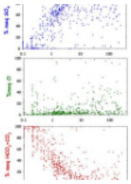


Figure 9 (B)

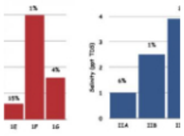


Figure 10 (A)

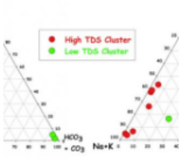


Figure 10 (B)

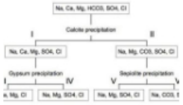


Figure 11

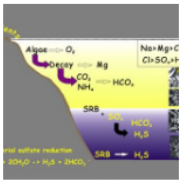


Figure 12

The Northern Great Plains: A Regional Picture

The northern Great Plains (NGP) geomorphic province of western Canada is a vast region of North America comprising over 350,000 km^2. Stretching from the Precambrian Shield near Winnipeg, Manitoba, westward for over 1600 km to the foothills of the Rocky Mountains (Figure 1), the region is the agricultural heartland of Canada and also contains most of the population of western Canada. The NGP is characterized by flat to gently rolling topography and experiences a cold, semi-arid climate. Pleistocene continental glaciation has resulted in a thick sequence of unconsolidated glacial, glaciofluvial, and glaciolacustrine sediment mantling the generally flat-lying Cretaceous and Tertiary sedimentary bedrock.

From the standpoint of salt lake geochemistry, the two most important physical features of the region are the high evaporation to precipitation ratios, and the presence of large areas of endorheic drainage. Although the mean annual temperature of ~3°C would imply relatively low evaporation rates, the high winds, low humidity, and warm summer temperatures create evaporation/precipitation values of generally between 3 and 10 (Figure 2). The average annual moisture deficit over the region is about 350 mm. These climatic features combined with the poorly integrated drainage, in which nearly 45% of southern Saskatchewan and eastern Alberta is topographically closed (Figure 3), result in a large number of saline lakes of diverse morphologies and geochemical characteristics. In contrast to many other areas of the world in which there is an abundance of salt lakes (e.g., see summaries in Jones and Bowser, 1978; Jones and Deocampo, 2003), the northern Great Plains region is tectonically very stable, does not exhibit striking topographic relief, nor is there dramatic lithologic diversity of either the glacial deposits nor the bedrock on a local or regional scale.

Compiling A Regional Database: 80 Years Of Lacustrine Hydrochemistry

The saline nature of the surface waters and associated lake deposits of the northern Great Plains was well known to local aboriginal groups at the time of European expansion and settlement in the region during the mid-19th century. Although the first chemical analyses of salt lake waters from this region were published in the 1890's, it was not until nearly half a century later that the full extent and degree of diversity of the salt lakes were recognized. For over thirty years after the 1890's, the only scientific efforts and data on these lakes came from economic geologists interested in exploitable reserves of initially nitrate salts and later sodium and magnesium salts in the lakes. Indeed, the results of a regional survey of these economic deposits undertaken by the Canadian government in the early 1920's (Cole, 1926) still ranks as one of the best and most extensive summaries of the salt lake hydrogeochemistry.

Although still not as advanced as in some other parts of North America, our knowledge of the chemistry of the surface waters in the Canadian Great Plains has progressed somewhat from these early geological/geochemical reconnaissance efforts. In one of the first systematic limnological surveys in the region, Rawson and Moore (1944) reported the water chemistry of 53 lakes from southern Saskatchewan. Rutherford (1970) compiled the composition data for several hundred lakes in Saskatchewan (including both fresh and saline basins). Hammer (1978) reported the water chemistry for 60 mainly perennial saline lakes in southern Saskatchewan. The results of much of this early regional work have been summarized by Northcote and Larkin (1963), Hammer (1986) and Last (1989a).

Other important contributions covering smaller geographic areas of the Great Plains include: Govett (1958) Bierhuizen and Prepas (1985), Derry et al. (2003), and Evans and Prepas (1996) in central and eastern Alberta; Hartland-Rowe (1966) in southeastern Alberta; Rozkowski (1967) and Roskowska and Roskowski (1969) in the Moose Mountain area of southern Saskatchewan; Lieffers and Shay (1983) and Driver and Peden (1977) in central Saskatchewan; and Driver (1965) and Barica (1975; 1977) in western Manitoba. More recently, reports by Pham et al. (2008; 2009), Kelly and Holmden (2001), and Lemmen and Vance (1999) included water chemistry data of ~65 saline lakes in western and central Saskatchewan.

We now have brine chemistry data from about 800 of the salt lakes in the northern Great Plains of Canada (Figure 4). Although most of these data represent analyses of single samples, some are averages of numerous samples collected over a period of months, years, or decades. In general, the larger lakes (e.g., Lakes Manitoba, Quill, Manito, etc.) have the longest temporal records, in some cases dating back to the early twentieth century. However, no lake in the Canadian prairies has a continuous monitoring record of more than four decades in duration. Of the lakes for which there are data, 10% are located in Manitoba, 72% in Saskatchewan, and 18% in Alberta.

What Do We Know About The Chemistry Of These Salt Lakes?

Even though most of the lakes in the Great Plains of western Canada have similar overall origins, nonetheless, the waters show consider diversity in terms ionic composition and concentration. The early investigators (mainly economic geologists concentrating on the most concentrated saline brines), emphasized a strong predominance of Na and SO_4 in the lakes (e.g., Cole, 1926; Tomkins, 1954a, b). Rutherford (1970) and Hammer (1978) similarly stressed the importance of sodium, magnesium and sulfate components in the perennial lakes of Saskatchewan, but also recognized a broad spectrum of water types on the basis of ionic ratios. Rutherford (1970) was able to relate spatial variation in water types to climatic gradients within the province and to shallow groundwater composition. We now realize that not only is there a complete spectrum of salinities from relatively dilute water (0.1 ppt TDS) to brines more than an order of magnitude greater than sea water (Figure 5), but also virtually every water chemistry type is represented in lakes of the region (Figure 6). Although it is obviously misleading to generalize by quoting means and averages, the 'average' lake water has about 30 ppt TDS and shows (in meq%): $Na \approx Mg > Ca > K$ and $SO_4 > HCO_3 > Cl > CO_3$.

It is hardly surprising that the lake waters of the northern Great Plains show such a considerable range in ionic composition and concentration, considering the enormous geographic area and the varying hydrologic, geomorphic, and climatic settings. With such a vast range of salinities, it follows that the concentrations of the individual ionic components also vary greatly. The frequency distributions of Mg, Na, Cl, and SO_4 concentrations in the lake waters tend to be multimodal as opposed to the Ca and HCO_3 ions which show a much narrower distribution pattern (Figure 7). Sulfate and carbonate-rich lakes clearly dominate the Great Plains, comprising over 95% of the total lakes. This paucity of Cl-rich lakes makes the region unusual compared with many other areas of the world (e.g., Australia, western USA; Eugster and Hardie, 1978; Williams, 1981). The cation ratios are much more diverse, with the abundance of all three major types showing approximately subequal proportions.

As would be expected, most of the solutes in the lake waters increase in concentration with increasing total salinity (Figure 8). Sulfate, chloride, and sodium ions show the most statistically significant correlations with TDS, whereas calcium and carbonate concentrations are less directly related to salinity. The proportions of some of the solutes also show a systematic change with salinity (Figure 9). Sulfate increases in relative ionic proportion from less than 30% equivalents in dilute lakes to generally more than 70% in lakes with more than 10 ppt TDS. Calcium and bicarbonate + carbonate proportions show an inverse relationship with salinity, decreasing from over 70% equivalents in the dilute waters to nearly 5% in lakes with more than 25 ppt TDS.

The relatively uniform distribution of lakes in the northern Great Plains for which water chemistry data allows us to examine of the ionic contents on a spatial basis. Last and Schweyen (1983) and Last (1988; 1989a) discuss these regional trends and present isohaline maps for the saline lakes of Saskatchewan, Alberta, North Dakota, and Montana (see Table 1). Lakes with highest Na, Mg, and SO_4 *concentrations* generally occur in the east central Alberta, west central and southern Saskatchewan area, whereas lakes with high alkalinity and Cl contents are found in central Alberta and western Saskatchewan. Lakes with relatively low *proportions* of Ca and Mg occur in the northern and central parts of the Plains.

A Statistical Analysis Approach: Insight Into Water Composition Controlling Factors

The major ion composition and concentration of these lakes is the result of: (i) a complex interaction between unconsolidated glacial sediments, bedrock, and precipitation/meltwater in the drainage basin, (ii) the composition and amount of groundwater recharge (and discharge) and streamflow in each basin, and (iii) a wide variety of other physical, chemical, and biological processes operating within the water column itself. In general, several types of geochemical approaches have been taken to help understand the major factors controlling surface water chemistry. These include mass balance calculations, thermodynamic equilibrium considerations, and statistical evaluations (see overview in Drever, 1988). In western Canada, both mass balance and thermodynamic calculations have proved valuable in deciphering many of the intrinsic (within-drainage basin) processes important in water composition on a local scale (e.g., Roskowski, 1965; Wallick and Krouse, 1977; Wallick, 1981; Last, 1984). In contrast, on a regional scale, various statistical techniques have been successfully applied to help understand the relationships between the water chemistry and extrinsic environmental factors such as climate, bedrock, geomorphology, and till composition (e.g., Dean and Gorham, 1976; Last, 1992; Winter, 1977). However, these statistical approaches lack the ability to resolve the often important local conditions and processes, however they are essential to our overall understanding of the lacustrine geochemical setting of the region as a whole.

One of the most straightforward ways to analyze the interrelationships within a data set is to examine the simple linear correlations that exist among the various parameters. The concentrations of Na, Ca and Mg in the brines of these lakes are all significantly positively correlated, as are SO_4 and Cl. In addition, the ion pairs of Mg-SO_4, Mg-Cl, and Na-Cl tend to strongly covary. Importantly, the concentrations of Na and SO_4 do not show statistically significant linear correlation, suggesting different suites of processes affect the abundance of each of these ions. The proportions of Ca and HCO_3 exhibit significant positive covariation, whereas the proportions of Mg and Na, and HCO_3 and SO_4 are inversely related.

Using a Q-mode cluster analysis (associations among lakes) Last (1992) subdivided the lakes into two major categories: a group of high salinity (> 20 ppt TDS) lakes and a group characterized by relatively lower TDS values. Each of these major clusters was further divided into smaller groups of lakes as related to their major ion composition (Figure 10).

By combining a variety of morphological (basin area, maximum depth), geological (bedrock type, depth to bedrock, till type), hydrological (drainage basin area, number of streams entering lake, elevation, groundwater composition), and climatic (mean annual precipitation, evaporation, temperature) variables with a lake water chemistry database, Last (1988, 1992) used R-mode factor analysis to identify a set of seven statistical factors that explained over 90% of the variance in the data. These statistical factors can be interpreted in terms of the most important intrinsic and extrinsic controls of water composition and concentration on a regional basis as follows: (i) Over a third of the total variance in the data is explained by the composition of inflowing groundwater. (ii) The evaporation to precipitation ratio of the basin accounted for about 20% of the variance, followed by (iii) the elevation or position of the lake within the drainage basin. Variables related to bedrock type, glacial drift composition, fluvial input, and lake morphology are statistically less important.

Source Of Salts

It is generally well accepted that groundwater plays a very important role not only in the overall hydrology of saline lakes, but also in dictating their hydrochemistry. However, with a few notable exceptions (e.g., Birks and Remenda, 1999; Freeze, 1969; Kelley and Holmden, 2001; Van der Kamp and Hayashi, 1998; Wallick, 1981), groundwater interaction processes with individual salt lake basins in the northern Great Plains are still poorly understood. In contrast, *regional* subsurface water composition, variation, and hydrodynamics are reasonably well known. As summarized elsewhere (see overviews in Betcher et al. (1995), Brown (1967), Lennox et al. (1988), Pupp et al. (1981), Remenda and Birks (1999), Rutherford (1967)), subsurface water compositions in the region are of several main types. Most of the groundwater in unconsolidated surficial deposits is of low to moderate salinity (< 3 ppt TDS) and dominated by Ca, Mg, and HCO_3 ions. In the areas of lowest precipitation (southwestern Saskatchewan and southeastern Alberta), shallow drift groundwater is usually dominated by the SO_4 ion rather than HCO_3. The shallow bedrock aquifers (Upper Cretaceous and younger rocks) are mainly sodium-bicarbonate in southern Alberta, calcium-magnesium-sodium-sulfate in Saskatchewan, and calcium-magnesium-sodium-bicarbonate in western Manitoba. The deeper Paleozoic and Cenozoic bedrock contains much higher salinity water (up to 300 ppt TDS) that is usually dominated by Na and Cl.

While there is little disagreement that groundwater is an important factor in the hydrology of the salt lakes, the specific origin and ultimate source of the ions in the lakes of the northern Great Plains have been topics of considerable discussion. Some of the early work suggested that the deeply-buried Paleozoic evaporites which occur in the subsurface could be a possible source for the salts in the lakes. Grossman (1968) showed that there is a correlation between the occurrence of sodium sulfate deposits in lakes at the surface and the presence and trends of various salt units in the Devonian Prairie Formation in the region. In contrast, shallow Cretaceous and Tertiary bedrock, as opposed to the deep Paleozoic sequence, has been implicated as the source of at least some of the dissolved components in the lakes (Cole, 1926; Sahinen, 1948; Wallick and Krouse, 1997).

Finally, rather than invoking bedrock sources, there is considerable support for the source of the ions being the Quaternary deposits within which the lakes are immediately situated (Kelley and Holmden, 2001; Rozkowski, 1967; Rutherford, 1970). A variety of physiochemical and biochemical reactions, including cation exchange, dissolution of feldspars, and precipitation of authigenic sulfate, carbonate, and silicate phases in the tills can be documented which support this latter hypothesis. Furthermore, many researchers (e.g., Freeze, 1969; Last, 1984b; Rueffel, 1968a; Rueffel, 1968b; Witkind, 1952) have stressed the close association of the more saline lacustrine brines with buried preglacial and glacial valleys, and have concluded that these buried valleys act as conduits for groundwater supplying dissolved material to the lakes.

Other Important Considerations

Short-term Temporal Variation: A major complicating factor in characterizing the chemistry of the salt lakes of the NGP is that many of the lakes exhibit playa characteristics, filling with water during the spring and early summer and drying completely by late summer or fall. Last and Ginn (2005) estimate that 85% of the salt lakes in this region are influenced by this type of seasonal hydrologic cycle. This strong seasonality of water levels gives rise to dramatic changes in both ion concentrations and ratios, as demonstrated by numerous studies. For example, Ceylon Lake, a salt-dominated playa in southern Saskatchewan, annually undergoes changes in concentration from about 30 ppt TDS to greater than 300 ppt (Last, 1990). This lake also exhibits dramatic fluctuations in ionic ratios on a seasonal basis from a Ma-(Mg)-SO_4-HCO_3 type in early spring to a Mg-(Na)-Cl-SO_4 composition by fall (Last, 1989b). Hammer (1978, 1986) and Last (1984a) summarize the short-term temporal changes in salinity and chemistry of several other saline lakes in the region. Unfortunately, only a few basins in the northern Great Plains have undergone periodic detailed sampling over a period of years.

Brine Evolution: The composition of any closed basin lacustrine brine is ultimately determined by two main factors: (i) the solutes are acquired by dilute inflow waters through weathering processes and by atmospheric fallout, and (ii) subsequent evaporation and concentration of ions leads to precipitation of minerals, which further affects the final brine composition. This latter change in lake water composition is referred to as brine evolution and has been the subject of considerable scientific interest (e.g., Jones, 1966; Jones and van Denburgh, 1966). Working with natural waters of the Sierra Nevada region in western United States, Garrels and McKenzie (1967) first pointed out that mineral precipitation, triggered by evaporative concentration, is the primary control of brine evolution. Hardie and Eugster (1970) subsequently generalized the evolutionary scheme and concluded that are three main brine evolutionary pathways resulting in five dominant brine types in evaporitic lacustrine basins (Figure 11).

Although there have been many modifications of the basic Hardie-Eugster evolutionary scheme, the most important contribution of the model is that of the chemical divide. A chemical divide is a point in the evolution sequence of a brine in which precipitation of a mineral depletes the water in certain cations or anions and further evaporation moves the solution along a distinct pathway. The result of this process is that small differences in ionic ratios in the dilute starting composition of the lake are amplified as the lake water evolves and produce brines of different and diverse composition.

Because of their relatively low solubility, the calcium carbonates (calcite, aragonite) are usually the first to precipitate; these comprise the first divide for most continental brines (Figure 11). The proportions of Mg, Ca, and HCO_3 in the dilute parent solution then determine the subsequent evaporation pathway and the Mg/Ca ratio determines which specific carbonate mineral will precipitate. If calcium is enriched relative to carbonate alkalinity, then the brine will follow pathway I after the initial $CaCO_3$ precipitate divide. Further evaporation of this type of brine will lead to a second divide: the precipitation of gypsum. After this, further evolution will be controlled by the relative proportions of Ca and SO_4 (i.e., pathways III and IV in Figure 11).

If, however, HCO_3 is enriched compared to Ca in the dilute inflow solution, then the brine evolution will follow pathway II after the initial divide. In this path, calcium will ultimately be depleted leaving an excess of HCO_3, which, in turn, may combine with Mg and Na to produce a variety of complex Na-Mg-carbonate-sulfate evaporites. A second divide in this evolution pathway is that of sepiolite [$Mg_4Si_6O_{15}$ $6H_2O$]. Further brine evolution after this divide is controlled by the relative concentrations of Mg^{2+} versus HCO_3^-. If the magnesium concentration is greater than the remaining alkalinity, the brine will evolve to a sulfate or chloride end member (V in Figure 11). Conversely, the water will become an alkali carbonate brine (VI in Figure 11) if magnesium is less than HCO_3 alkalinity after sepiolite precipitation.

While this model works well in theory and the principles of chemical divides and evolutionary paths are valid, clearly the model is an oversimplification of a complex series of sedimentary and geochemical processes. Only relatively recently have we begun to understand this complexity (e.g., Drever, 1988; Herczeg et al., 2001; Jones and Deocampo, 2003). In fact, few continental brines actually follow any of the paths outlined in this model. For example, in path II, Mg-silicate (sepiolite) is rarely found as a primary mineral and thus does not seem like a reasonable divide. Also, the model implies that only a relatively small number of brine types will evolve from a typical dilute inflow; this clearly is not the case and there are many common brine types not represented. For example, the typical Na-Mg-SO_4-HCO_3 brine that is very common in the northern Great Plains is not represented.

However, because of the wide spectrum of water chemistry types exhibited by the lakes of the Great Plains, these lakes provide critical information to help better understand continental brine evolution. Since salt minerals are thermodynamically and kinetically responsive to even relatively minor changes in brine composition, the basins in the Great Plains having relatively thick, continuous sequences of Holocene evaporites provide a glimpse at a complex series of evolutionary sequences. Last (1995) used Markov chain analysis to identify four generalized anion sequences and five cation sequences in the Holocene evaporates of several dozen Great Plains lakes. The most commonly occurring cyclicity among the anions (occurring in ~50% of the lakes) is: $CO_3 \rightarrow CO_3\text{-}SO_4 \rightarrow SO_4$. This anion sequence was best represented in Ceylon Lake in south-central Saskatchewan and was thus termed the Ceylon type. The three other anion sequences, which occur less frequently, are:

Alsak type (~20%): $CO_3 \rightarrow Cl\text{-}SO_4 \rightarrow SO_4$
Metiskow type (~10%): $SO_4 \rightarrow CO_3\text{-}SO_4 \rightarrow CO_3$
Waldsea type (~10%): $SO_4 \rightarrow CO_3$

The cation evolutionary sequences present in the 24 study lakes were considerably more complex than the anion sequences and about 20% of the stratigraphic sections exhibited no statistically significant temporal compositional trends. The most common cation sequences present in about 60% of the lakes, are the Lydden type (33%): Ca → Ca-Mg → Na → Na-Mg-Ca and Ingebright type (28%): Na-Mg → Ca-Na-Mg → Na-Mg → Na
followed by:

Metiskow type (~15%): Ca → Na-Mg → Ca-Mg-Na → Na
Little Manitou type (~10%): Ca-Mg → Mg-Na → Mg
Freefight type (~5%): Ca → Mg-Ca → Mg-Na

Because of the complexity of the interplay between intrinsic processes (i.e., sedimentary, geochemical, hydrologic, and biological processes operating *within* the lake basin itself) and extrinsic processes (i.e., 'external' factors, such as climate change, drainage basin modification), identification of the causal mechanisms for these various evolutionary sequences is not straightforward. Clearly, much more quantitative data from the evaporites of these and other saline lakes in the region need to be collected in order to explain and properly model the observed composition trends.

Biological Processes Affecting Salt Lake Chemistry: Overall, the biological processes in salt lakes of western Canada are similar to those in fresh standing waters, notwithstanding their physical and chemical extremes. The biota, however, differ significantly between fresh and saline lakes (Hammer, 1986). At low salinities the species composition of salt lakes is comparable to that of their fresh water counterparts (Evans, 1993). As salinity increases, the diversity of species declines (Haynes and Hammer, 1978), and as salinities reach extremely high values, species diversity becomes very low. At these elevated salinities, the lake is usually dominated only by halotolerant organisms.

Saline and hypersaline lakes have some of the highest measured rates of organic productivity in the world (Warren, 1986). At moderate to high salinities (30-100 ppt TDS), the main contributors to this biomass are green algae and cyanobacteria. At more elevated salinities halophilic bacteria dominate the ecosystem.

Many biological processes can affect the chemistry of saline lakes (Figure 12). For example, photosynthesis by aquatic plants, ammonification, denitrification, sulfate reduction and anaerobic sulfide oxidation cause a rise in pH as carbon dioxide is utilized by the flora, and an increase in the concentration of HCO_3. Decay of organisms, in turn, can lead to a release of ions such as Mg and Ca, as well as elevated levels of HCO_3 creating favorable conditions for carbonate precipitation (Castanier, 1999; Riding, 2000; Visscher et al., 1992).

The organisms that can thrive at high salinities in a saline lake are greatly restricted. Life at high salt concentrations requires considerable energy to maintain the steep ion gradient across the membrane required for osmoregulation (Orhen, 2002). The specific type of metabolism also determines the limit of salt concentration that an organism can withstand. Thus, in most saline lake environments, as salinity increases, the diversity of organisms decreases.

Ionic composition also affects species diversity. Chloride, bicarbonate and sulfate are most important in controlling species composition of salt lakes (Herbst, 2001). The striking increase in proportion of SO_4 with increasing salinity in the lakes of the northern Great Plains (Figure 9b) means that sulfate reducing bacteria (SRB) are a dominant taxa. The reduction of sulfate by SRB leads to the production of bicarbonate ions and thus the generation of alkalinity according to:
$SO_4^{2-} + 2CH_2O \rightarrow HS^- + 2HCO_3^-$, where $2CH_2O$ represents organic matter. The direct effects that SRB have on the environment (i.e., reduction of sulfate and production of H_2S and alkalinity) can, in turn, directly affect the solubility and precipitation/dissolution of a wide variety of minerals, including carbonates, silicates, oxides, sulfides, and many evaporites Thus, bacterial sulfate reduction is an important mineralization process in the saline and hypersaline systems of western Canada.

When the end product of sulfate reduction, S^{2-}, is produced, the fate of the sulfide is key in determining whether or not certain minerals will precipitate (Castanier, 1999). If the generated sulfide degasses, the sulfate reduction process will result in an increase in pH in the aqueous environment, thereby encouraging carbonate mineral precipitation. Similarly, if the sulfide is taken up by sulfide-oxidizing microbes, pH will also increase and carbonate will precipitate. In contrast, if the sulfide is oxidized back to sulfate within the aqueous environment, a strong acid, H_2SO_4, may form, decreasing the pH and discouraging carbonate precipitation. Finally, if the sulfide remains in the environment, the pH will decrease and no carbonate will precipitate.

The role of these organisms in the saline lake ecosystems of the northern Great Plains are critical areas of investigation, especially with respect to their potentially important role in the formation and diagenesis of carbonate minerals. A better understanding of the biomineralization processes in these lakes provides important insight into the evolution of the brine systems and will allow for the development of critical proxies for changes in the environmental conditions. Furthermore, these biomineralizaton processes will help us better understand what to look for in the search for life in extraterrestrial environments.

References

Barica, J., 1975. Geochemistry and nutrient regime of saline eutrophic lakes in the Erickson-Elphinstone district of southwestern Manitoba. *Canadian Fisheries and Marine Services Research Development Technical Report* 511.

Barica, J., 1977. Variability in Ionic Composition and Phytoplankton Biomass of Saline Eutrophic Prairie Lakes within a Small Geographic Area. *Archiv Fur Hydrobiologie*, **81**(3): 304-326.

Batt, B.D., Anderson, M.G., Anderson, C.D. and Caswell, F.D., 1989. The use of prairie potholes by North American ducks. *Northern Prairie Wetlands*: 204 - 227.

Betcher, R., Grove, G. and Pupp, C., 1995. Groundwater in Manitoba: Hydrogeology, Quality Concerns, Management. *National Hydrology Research Institute Contribution* No CS-93017.

Bierhuizen, J.F.H. and Prepas, E.E., 1985. Relationship between Nutrients, Dominant Ions, and Phytoplankton Standing Crop in Prairie Saline Lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, **42**(10): 1588-1594.

Birks, S.J. and Remenda, V.H., 1999. Groundwater inputs to a closed-basin saline lake, Chappice Lake, Alberta. Holocene Climate and Environmental Changes in the Palliser Triangle, Southern Canadian Prairies: *Geological Survey of Canada Bulletin* **534**: 23 - 55.

Brown, I.C., 1967. Groundwater in Canada. *Economic Geology Report* Number **24**, 228 pp.

Cameron, D.R., 1986. Saline waters: agricultural uses. Evaluating Saline Waters in a Plains Environment. *Canadian Plains Proceedings*, **17**: 75 - 100.

Carpenter, 1978. Origin and chemical evolution of brines in sedimentary basins. *Oklahoma Geological Survey* Circular **79**: 60-77.

Castanier, S., 1999. Ca-carbonates precipitation and limestone genesis-the microbiogeologist point of view. *Sedimentary Geology*, **126**(1): 9-23.

Cole, L.H., 1926. Sodium sulfate of western Canada. Occurrence, uses and technology. *Canadian Department of Mines Publication* Number **646**, 155 pp.

Conly, F. and van der Kamp, G., 2001. Monitoring the hydrology of Canadian prairie wetlands to detect the effects of climate change and land use changes. *Environmental Monitoring and Assessment*, **67**(1): 195-215.

Dean, W.E. and Gorham, E., 1976. Major chemical and mineral components of profundal surface sediments n Minnesota Lakes. *Limnol Ocean*, **21**: 259 - 284.

Derry, A.M., Prepas, E.E. and Hebert, P.D.N., 2003. A comparison of zooplankton communities in saline lakewater with variable anion composition. *Hydrobiologia*, **505**(1-3): 199-215.

Desai, K. and Moore, E.J., 1969. Equivalent NaCl determination from ionic concentrations. *Log Analyst*, **10**: 12-21.

Drever, J.I., 1988. *The Geochemistry of Natural Waters*. Prentice Hall, Inc., Englewood Cliffs, New Jersey, 437 pp.

Driver, 1965. Limnological aspects of some saline lakes in west-central Manitoba. *Journal of Fisheries Research Board of Canada*, **22**: 1165-1173.

Driver, E.A. and Pedden, D.G., 1977. The chemistry of surface water in the prairie ponds. *Hydrobiologia*, **53**: 33 - 48.

Eugster, H.P. and Hardie, L.A., 1978. *Saline lakes, Lakes, Chemistry, Geology, Physics*. Springer, New York, pp. 237-293.

Evans, J., 1993. Paleolimnological studies of saline lakes. *Journal of Paleolimnology*, **8**(2): 97-101.

Evans, J. and Prepas, 1996. Potential effects of climate change on ion chemistry and phytoplankton communities in prairie saline lakes. *Limnology and Oceanography*: 1063-1076.

Freeze, R.A., 1969. *Regional groundwater flow - Old Wives Lake drainage basin, Saskatchewan*. Scientific Series No 5. Canadian Inland Waters Directorate, Burlington, Ontario, 234 pp.

Garrels, R.M. and Mackenzie, F.T., 1967. Origin of the chemical compositions of some springs and lakes. Equilibrium Concepts in Natural Water Systems. *Am. Chem. Soc. Adv. Chem.* Ser, **67**: 222-242.

Govett, G.J.S., 1958. Sodium sulfate deposits in Alberta. *Alberta Research Council Preliminary Report* 58-5.

Grossman, I.G., 1968. Origin of sodium sulfate deposits of the Northern Great Plains of Canada and the United States. *United States Geological Survey Professional Paper* **600-B**, 104-109 pp.

Hammer, U.T., 1978. Saline Lakes of Saskatchewan .3. Chemical Characterization. *Internationale Revue der Gesamten Hydrobiologie*, **63**(3): 311-335.

Hammer, U.T., 1986. *Saline Lake Ecosystems of the World*. Dr W. Junk Publishers Dordrecht, The Netherlands 616 pp.

Hardie, L.A. and Eugster, H.P., 1970. The evolution of closed-basin brines. *Mineral. Soc. Am. Spec. Publ*, **3**: 273-290.

Harrington, R., Johnson, B. and Hunter, F., 1997. *Responding to Global Climate Change in the Prairies*, Volume III of the Canada Country Study: Climate Impacts and Adaptation. Environment Canada, Prairie and Northern Region.

Hartland-Rowe, R., 1966. The fauna and ecology of temporary pools in western Canada. *Verh. Internat. Verein. Limnol.*, **16**: 577-584.

Haynes, R.C. and Hammer, U.T., 1978. Saline Lakes of Saskatchewan .4. Primary Production by Phytoplankton in Selected Saline Ecosystems. *Internationale Revue der Gesamten Hydrobiologie*, **63**(3): 337-351.

Herbst, D.B., 2001. Gradients of salinity stress, environmental stability and water chemistry as a templet for defining habitat types and physiological strategies in inland salt waters. *Hydrobiologia*, **466**: 209 - 219.

Herczeg, A.L., Dogramaci, S.S. and Leaney, F.W.J., 2001. Origin of dissolved salts in a large, semi-arid groundwater system: Murray Basin, Australia. *Marine & Freshwater Research*, **52**(1): 41-52.

Jones, B.F., 1966. Geochemical evolution of closed basin water in the western Great Basin., *Proceedings of the Second Symposium on Salt*. Northern Ohio Geological Society, pp. 181-200.

Jones, B.F. and Bowser, C.J., 1978. *The mineralogy and related chemistry of lake sediments. Lakes: Chemistry, Geology, Physics*. Springer-Verlag, New York, **323**: 179-235.

Jones, B.F. and Deocampo, D.M., 2003. Chapter 13: Geochemistry of Saline Lakes. In: J.I. Drever (Editor), *Treatise on Geochemistry*. Elsevier Scientific Publishers.

Jones, B.F. and van Denburgh, A.S., 1966. Geochemical influences on the chemical character of closed lakes. Symposium of Garda, Hydrology of Lakes and Reservoirs, *Proceedings of the International Association for Scientific Hydrology*, Publication **70**: 438 - 446.

Kelley, L. and Holmden, C., 2001. Reconnaissance hydrogeochemistry of economic deposits of sodium sulfate (mirabilite) in saline lakes, Saskatchewan, Canada. *Hydrobiologia*, **466**(1): 279-289.

Last, W.M., 1984a. Modern Sedimentology and Hydrology of Lake Manitoba, Canada. *Environmental Geology*, **5**(4): 177-190.

Last, W.M., 1984b. Sedimentology of playa lakes of the northern Great Plains. *Canadian Journal of Earth Sciences*, **21**(1): 107-125.

Last, W.M., 1988. Salt lakes of western Canada: a spatial and temporal geochemical perspective. *Proceedings of Symposium on Water Management Affecting the Wet-to-Dry Transition*: 99-113.

Last, W.M., 1989a. Continental brines and evaporites of the northern Great Plains of Canada. *Sedimentary Geology*, **64**: 207-221.

Last, W.M., 1989b. Sedimentology of a saline playa in the northern Great Plains, Canada. *Sedimentology*, **36**(1): 109-123.

Last, W.M., 1990. Paleochemistry and paleohydrology of Ceylon Lake, a salt-dominated playa basin in the northern Great Plains, Canada. *Journal of Paleolimnology*, **4**(3): 219-238.

Last, W.M., 1992. Chemical composition of saline and subsaline lakes of the northern Great Plains, western Canada. *International Journal of Salt Lake Research*, **1**: 47 - 76.

Last, W.M., 1994. Paleohydrology of playas in the northern Great Plains: perspectives from Palliser's Triangle. Paleoclimate and Basin Evolution of Playa Systems. *Geological Society of America, Special Paper* **289**: 69 - 80.

Last, W.M., 1995. Evolution of saline lakes in western Canada. In: I.D. Campbell, C. Campbell, D. Lemmen and B. Vance (Editors), *Climate, Landscape, and Vegetation Change in the Canadian Prairie Provinces*, Edmonton, pp. 55-64.

Last, W.M. and Ginn, F.M., 2005. Saline systems of the Great Plains of western Canada: an overview of the limnogeology and paleolimnology. *Saline Systems*, **1**(1): 10.

Last, W.M. and Schweyen, T.H., 1983. Sedimentology and geochemistry of saline lakes of the northern Great Plains. *Hydrobiologia*, **105**: 245-263.

Last, W.M. and Slezak, L.A., 1987. Sodium sulfate deposits of western Canada. Economic Minerals of Saskatchewan. *Saskatchewan Geological Society Special Publication*, **8**: 197 - 205.

Lemmen, D.S. and Vance, R.E., 1999. Holocene Climate and Environmental Changes in the Palliser Triangle, Southern Canadian Prairies. Geological Survey of Canada Bulletin 534. *Geological Survey of Canada Bulletin* **534**, 295 pp.

Lennox, D.H., Maathuis, H. and Pederson, D., 1988. *Region 13, Western glaciated plains*. The Geology of North America, volume O-2, Hydrogeology.

Lieffers, V.J. and Shay, J.M., 1983. Ephemeral Saline Lakes on the Canadian Prairies - Their Classification and Management for Emergent Macrophyte Growth. *Hydrobiologia*, **105**(SEP): 85-94.

Northcote, T.G. and Larkin, P.A., 1963. Chapter 16: Western Canada. In: D.G. Frey (Editor), *Limnology in North America*. University of Wisconsin Press, Madison, Wisconson, pp. 451-485.

Orhen, A., 2002. *Halophilic Microorganisms and Their Environments*. Kluwer, Dordrecht, 575 pp.

Palliser, J., 1862. *Journals, detailed reports and observations relative to the exploration by Captain Palliser of a portion of British North America, London*, 325 pp.

Pham, S.V., Leavitt, P.R., McGowan, S. and Peres-Neto, P., 2008. Spatial variability of climate and land-use effects on lakes of the northern Great Plains. *Limnology And Oceanography*, **53**(2): 728-742.

Pham, S.V., Leavitt, P.R., McGowan, S., Wissel, B. and Wassenaar, L., 2009. Spatial and temporal variability of prairie lake hydrology as revealed using stable isotopes of hydrogen and oxygen. *Limnol. Oceanogr*, **54**(1): 101-118.

Pupp, C., Maathuis, H. and Grove, G., 1981. Groundwater Quality in Saskatchewan: Hydrogeology, Quality Concerns, Management. *National Hydrology Research Institute Contribution* No CS-91028.

Rawson, D.S. and Moore, G.E., 1944. The saline lakes of Saskatchewan. *Canadian Journal of Research* (Series D), **22**: 141 - 201.

Remenda, V.H. and Birks, S.J., 1999. Groundwater in the Palliser Triangle: an overview of its vulnerability and potential to archive climate information. Holocene Climate and Environmental Changes in the Palliser Triangle, Southern Canadian Prairies: *Geological Survey of Canada Bulletin* **534**: 23 - 55.

Riding, R., 2000. Microbial carbonates: the geological record of calcified bacterial-algal mats and biofilms. *Sedimentology*, **47**(s 1): 179-214.

Rozkowska, A.D. and Roskowski, A., 1969. Seasonal changes of slough and lake water chemistry in southern Saskatchewan, Canada. *Journal of Hydrology*, **7**: 1 - 13.

Rozkowski, A., 1967. The origin of hydrochemical patterns in hummocky morain. *Canadian Journal of Earth Sciences*, **4**: 1065 - 1092.

Rueffel, P.G., 1968a. Development of the largest sodium sulfate deposit in Canada. *Canadian Mining and Metallurgical Bulletin*, **61**: 1217-1228.

Rueffel, P.G., 1968b. *Natural sodium sulfate in North America*, Third Symposium on Salt, Northern Ohio Geological Society, pp. 429-451.

Rutherford, A.A., 1967. *Water Quality Survey of Saskatchewan Groundwaters*. Saskatoon: Saskatchewan Research Council, Report C-66-1, 267 pp.

Rutherford, A.A., 1970. *Water quality survey of Saskatchewan surface waters*, C-66-1. Saskatchewan Research Council, Saskatoon, 133 pp.

Sahinen, U.M., 1948. *Preliminary report on sodium sulfate in Montana*. Bureau of Mines and Geology, Montana School of Mines Report, 9 pp.

Scott, M.D. and Scott, S.A., 1986. Saline lake management for waterfowl resources in western North America: a review of concepts. Evaluating Saline Waters in a Plains Environment. *Canadian Plains Proceedings*, **17**: 23 - 38.

Sorenson, L.G., Goldberg, R., Root, T.L. and Anderson, M.G., 1998. Potential Effects of Global Warming on Waterfowl Populations Breeding in the Northern Great Plains. *Climatic Change*, **40**(2): 343-369.

Tomkins, R.V., 1954a. Magnesium in Saskatchewan. *Saskatchewan Department of Mineral Resources Report* No **11**, 23 pp.

Tomkins, R.V., 1954b. Natural sodium sulfate in Saskatchewan. *Saskatchewan Department of Mineral Resources Report* No **6**, 71 pp.

Van der Kamp, G. and Hayashi, M., 1998. The groundwater recharge function of small wetlands in the semi-arid northern prairies. *Great Plains Research*, **8**(1): 39-56.

Visscher, P.T., Prins, R.A. and van Gemerden, H., 1992. Rates of sulfate reduction and thiosulfate consumption in a marine microbial mat. FEMS Microbiol. *Ecol*, **86**: 283-294.

Wallick, E.I., 1981. Chemical evolution of groundwater in a drainage basin of Holocene age, east-central Alberta, Canada. *Journal of Hydrology*, **54**: 245 - 283.

Wallick, E.I. and Krouse, H.R., 1997. Sulfur isotope geochemistry of a groundwater-generated Na2SO4/Na2CO3 deposit and the associated drainage basin of Horseshoe Lake, Metiskow, east central Alberta, Canada. Strasbourg, France: *2nd International Symposium on Water-rock Interaction*: II56 - II64.

Warren, J.K., 1986. Source rock potential of shallow-water evaporitic settings. *American Association of Petroleum Geologists Bulletin*, **70**(5): 442-454.

Williams, W., 1981. Inland Salt Lakes - an Introduction. *Hydrobiologia*, **81**(2): 1-14.

Williams, W.D., 1967. The chemical characteristics of lentic surface waters in Australia. In: A.H. Weatherley (Editor), *Australian Inland Waters and Their Fauna*. The Australian National University Press, Canberra, pp. 18-77.

Williams, W.D. and Sherwood, J.E., 1994. Definition and measurement of salinity in salt lakes. *International Journal of Salt Lake Research*, **3**: 53 - 63.

Winter, T.C., 1977. Classification of the hydrologic settings of lakes in the North Central United States. *Water Resources Res*, **13**: 753 - 767.

Witkind, I.J., 1952. The localization of sodium sulfate deposits in northeastern Montana and northwestern North Dakota. *American Journal of Science*, **250**: 667-676.

Figure Captions

Figure 1. Map showing the location of the northern Great Plains of western Canada (yellow) in North America.

Figure 2. Sketch map of the northern Great Plains of western Canada showing major drainage systems and areas of internal drainage (red).

Figure 3. Sketch map of the northern Great Plains of western Canada showing major drainage systems and areas of internal drainage (red).

Figure 4. Maps showing the distribution of saline lakes in the northern Great Plains for which water chemistry (top) and modern sediment composition (bottom) data have been compiled.

Figure 5. Bar graph showing the frequency distribution of salinities (ppt TDS) of the lakes of the northern Great Plains.

Figure 6. Trilinear diagrams (meq%) showing the range of ionic compositions of saline lakes of the northern Great Plains. Each dot represents one lake.

Figure 7. Bar graphs showing the frequency distributions of the major cations (A) and anions (B) relative to salinity in the lakes of the northern Great Plains.

Figure 8. Scatter plots of cation (A) and anion (B) concentration versus salinity. Note that both axes are logarithmic. Best-fit trend lines are significant at the 0.01 confidence level.

Figure 9. Scatter plots of cation (A) and anion (B) proportions (%meq) versus salinity.

Figure 10. Q-mode cluster analysis of water chemistry data from the Northern Great Plains showing (A) the subdivision of lakes into two major groups: Cluster I (high salinity) and Cluster II (low salinity) and (B) the mean composition of each subcluster. Percentage figures on the bars of the histogram are the proportion of lakes in each subgroup.

Figure 11. Summary of the Hardie-Eugster model for evolution of non-marine waters by evaporative concentration (modified from Drever, 1988).

Figure 12. Summary diagram showing some of the major biological processes affecting water composition in a typical perennial stratified saline lake in the northern Great Plains.

Sample Analysis at Mars: Developing Analytical Tools to Search for a Habitable Environment on the Red Planet

by Paul Mahaffy
NASA Goddard Space Flight Center, Greenbelt, MD 20771

Mars provides one of the most accessible locations in our solar system outside Earth into geological and geochemical windows through which to view planetary evolution from billions of years in the past until the present. Successful missions in the past decade to both study Mars from orbit and to land on its surface have dramatically advanced our understanding of our neighboring cold but volatile-rich planet. Taking advantage of nearly every recent launch window that presents itself every 2.135 years the 'follow the water' theme has been vigorously pursued as a first exploration step most relevant to the driving question of the possibility of past or present microbial life on Mars. With this exploration directive, the global distribution of near surface water ice and hydrated minerals was mapped from orbit by NASA's Odyssey spacecraft (Boynton et al., 2002) using measurements of the energy distribution of cosmic ray generated neutrons produced from the near surface. High latitude regions were inferred to be typically composed of more than 50% water ice in the top tens of centimeters of soil. Hard on the heels of this discovery, the Mars Exploration Rovers Spirit and Opportunity found convincing evidence at mid latitudes but on opposite sides of the planet of aqueous alteration by liquid water (Squyres et al., 2004 and 2008). This evidence came in the form of minerals (jarosite, goethite, and opaline silica) formed by aqueous transformation and also in the form of signatures of water flow revealed in returned images of cross-bedding in sedimentary layers from the rover cameras. The Phoenix high latitude lander mission (Smith et al., 2009) trenched down through surface soil to an icy layer and provided ground verification of the Odyssey measurement. More recent observations from high resolution orbiting telescopes and imaging spectrometers (Murchie et al., 2009) have resulted in a better understanding of the surface transformations over the history of Mars by water, giant impacts, volcanoes, winds, and the large scale movement of surface ice caused by the periodic variations in the planet's axial tilt (its obliquity). Rich assemblages of phyllosilicates (clays) and hydrated mineral layers continue to be revealed in many locations by imaging spectrometers on both the European Mars Express Mission and NASA's Mars Reconnaissance Orbiter. An emerging paradigm now paints a picture of an early wetter Mars that enabled clay formation in a more neutral chemical environment than the following more acidic sulfur dominated surface environment produced by immense volcanic activity (Bibring et al., 2006). Exposure of ancient terrains and the lack of plate tectonics for much of the history of Mars suggest that geochemical windows into the distant past may be preserved in the near-surface so that future surface landers and rovers may be able to explore the environmental conditions necessary for life in ancient sites.

The Mars Science Laboratory (MSL) now planned to be sent on its way to Mars in the 2011 launch opportunity is designed to explore habitability with a large heavily instrumented rover. After landing, MSL will be able to traverse 10's of kilometers over the 2-year mission lifetime (one Mars year) and access specific sites that have been identified from orbit by imaging and spectroscopy measurements. The MSL primary science goals are (1) to assess the past or present biological potential at the targeted site, (2) to characterize the site's geology at various spatial scales, and (3) to investigate other planetary processes that influence habitability. The MSL mission moving beyond the 'follow the water' theme seeks an even more detailed understanding of the history of the Mars environment (Grotzinger, 2009) and how significant transitions in this environment might have impacted potential habitats for even the simplest microorganisms or even their chemical precursors.


Figure 1


Figure 2

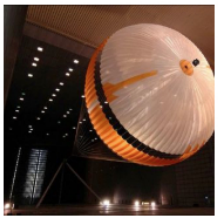


Figure 3

Dust storms on Mars are predicted to enhance the abundance of hydrogen peroxide in the atmosphere to the point where it accumulates on the surface (Atreya et al., 2006). A first order question for MSL is whether organic compounds produced by early or current biological processes, by abiotic processes, or even delivered from space by meteoritic infall can be preserved in what is likely to be this oxidizing surface environment. MSL will not only search for these organic compounds but will also inventory other chemical building blocks of life containing carbon, hydrogen, nitrogen, oxygen, phosphorus, and sulfur compounds. Regardless of the fate of ancient or recent reduced carbon compounds in the Martian soils and rocks the chemical processes that might destroy or preserve organic compounds must be understood and so MSL intends to study the geology and chemistry in detail to interpret processes that have formed and transformed rocks and regolith. Planetary process that impact habitability such as climate change and loss of a portion of the atmosphere over time will be explored by MSL by signatures of these processes in isotopic composition, particularly in the inert noble gases in the atmosphere. MSL will be launched in late 2011 on an Atlas V 541 rocket. Its entry, descent, and landing (EDL) through the thin atmosphere of Mars in the late summer or fall of 2012 will utilize first a heat shield to slow down the entry vehicle during a guided descent, then deployment of a large supersonic parachute followed by a powered descent, and finally tethered release of the MSL rover directly onto its wheels from the descent stage hovering several meters above the surface. This final sky crane touchdown system is intended to enable a soft landing for the ~900 kg rover since airbag technology of the type used to protect the MER landers after their release from their parachute is not suitable for this size vehicle. The nominal mission duration is one Mars year (2 Earth years) although an additional exploration period may be realized in an extended MSL mission. Figure 1 shows an artist's conception of MSL on the surface of Mars and Figure 2 a picture of the MSL spacecraft and aeroshell being prepared for tests in a thermal vacuum chamber. Figure 3 is a picture of the massive parachute being tested in a large wind tunnel.

The MSL science payload summarized in Table 1 enables four different types of scientific investigation. Using the high resolution mast camera (Mastcam) and a laserinduced breakdown spectrometer (LIBS or ChemCam) the geology and a rapid survey of chemical differences in targeted rocks in the immediate vicinity of the rover can be established.

GN141 Content

About Paul Mahaffy

Paul Mahaffy is the Principal Investigator and Team Leader of the Sample Analysis at Mars (SAM) instrument Package. The Lab is now called *Curiosity*, which was suggested by a 12-year-old girl who won a NASA-sponsored contest to assign a more prosaic name to the rover. Paul has held several important posts in NASA's robotic exploration program. He is the Chief of the Atmospheric Experiments Laboratory in the Solar System Exploration Division at NASA, Goddard. Previously, he was: the manager of the Planetary Instrument Definition and Development Program; Theme leader for GSFC Astrobiology Node - Evolution of Organics in Planetary Systems; and in charge of the Galileo spacecraft's measurements of the Jovian atmosphere's isotopic and major-element compositions.

In September, 2009, Paul gave a lucid lecture about the SAM package to the Press Corps. He established a firm historical framework for present-day Mars missions. This perspective is very illuminating. The hyperlink leads to the first of a five-part lecture.

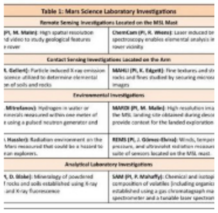


Table 1: Mars Science Laboratory Investigations	
Remote Sensing Investigations Located on the MSL Mast	
(PI, M. Malin): High spatial resolution d video to study geological features rover	ChemCam (PI, R. Wiens): Laser induced br spectroscopy enables elemental analysis in rover vicinity
Contact Sensing Investigations Located on the Arm	
Gellert): Particle induced X-ray emission scence utilized to determine elemental on of soils and rocks	MAHLI (PI, K. Edgett): Fine textures and st rocks and fines studied by securing microsc images
Environmental Investigations	
Mitrofanov): Hydrogen in water or minerals measured within one meter of e using a pulsed neutron generator and	MARDI (PI, M. Malin): High resolution ima the MSL landing site obtained during desce provide context for the landed exploration
Hassler): Radiation environment on the Mars measured that could be a hazard to nan explorers.	REMS (PI, J. Gómez-Elvira): Winds, temper pressure, and ultraviolet radiation measur suite of sensors located on the MSL mast.
Analytical Laboratory Investigations	
PI, D. Blake): Mineralogy of powdered f rocks and soils established using X-ray and X-ray fluorescence	SAM (PI, P. Mahaffy): Chemical and isotopi composition of volatiles (including organic established using a gas chromatograph ma spectrometer and a tunable laser spectrom

Table 1

At the same time the neutron detector (DAN) provides information on the near subsurface abundance of water containing minerals. Once these tools identify an interesting site and specific rocks or soils the MSL arm is extended to allow a more detailed examination by a microscope (MAHLI) and an alpha particle X-ray spectrometer (APXS) that can establish elemental composition. Finally, samples of greatest interest are processed into powder by a rotary percussive drill/sieve system and delivered to two instruments in the interior of the rover. In these instruments the mineralogy of the sample can be established by an X-ray diffraction/X-ray fluorescence instrument (ChemMin) and the search for organics, inorganic volatiles, and the measurement of various isotopes will be carried out by a suite of instruments (SAM). The SAM science investigation, its instruments, and supporting technology is described in more detail below. Finally, atmospheric winds, temperatures, pressures, and ultra violet radiation are measured by an additional instrument in the mast (REMS), the energetic radiation environment of the type that could be hazardous to future human explorers is measured with the RAD instrument, and the geological context of the landing site is obtained by the descent camera MARDI.

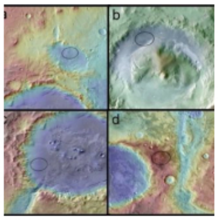


Figure 4

The diversity of geology and mineralogy revealed by ongoing orbital tools provides an excellent set of tools to select a MSL landing site that can best address the mission's scientific goals. Several dozen proposed landing sites have been presently narrowed down to four through a series of open workshops that brought Mars scientists and MSL engineers together to discuss the relative merits of each site. In parallel with the development of the scientific motivation for landing at particular site, the practical issue of avoiding rocky terrains and extreme slopes was addressed and the altitude and winds at the landing site considered. Landing more than 1 km above the mean Mars altitude, for example, might not give the MSL entry system enough time in the atmosphere to robustly exercise its multiple deceleration modes so lower altitude sites are preferred. Fortunately, the four sites that were judged to be of extraordinary scientific interest appear to also provide the required safety factors for the MSL entry, descent, and landing (EDL) systems. Listed from North to South these are Mawrth Vallis, Gale Crater, Eberswalde Crater, and Holden Crater. Orbital images of these sites superimposed on a color coded map of altitude from the Mars Orbiter Laser Altimeter are shown in Figure 4 together with candidate landing ellipses that avoid much of the rocky or highly slopped terrain.

Figure 5

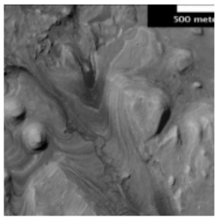


Figure 6

Two of the landing sites show clear evidence of the past presence of flowing water (Malin and Edgett, 2003). A well-defined delta (Figure 5) is present inside the Eberswalde Crater that could be reached through a rover traverse. Likewise, a reasonable explanation for features observed at the Holden Crater candidate-landing site is that ancient sedimentary deposits from a lake that formed in the crater were later exposed by a river that spilled over the walls of the crater from the south. The sediments in both these locations are compelling locations for the exploration of habitability with the MSL. Compelling spectroscopic features are among the factors that provide strong motivation for the in situ exploration of the Gale Crater and Mawrth Vallis candidate landing sites. A rich sequence of layered terrain with diverse spectroscopic signatures includes both clays and sulfates in the central mound of Gale crater (Figure 6). Slopes are gentle enough in some locations that these sites can be reached by an extended traverse from the smoother landing site. Mawrth Vallis shows some of the strongest and most diverse phyllosilicate signatures seen anywhere on the planet. This site is evidently from the early Noachian period of Mars with the spectral features more recently exposed by erosion processes. An attractive feature of the Mawrth Vallis site is that features of interest are found in the landing ellipse and can be accessed without a long traverse.

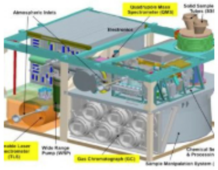


Figure 7

A 3 dimensional representation of the SAM suite of instruments and associated supporting subsystems is shown in Figure 7. The three instruments that measure either atmospheric gas or gas extracted from solid samples are a quadrupole mass spectrometer (QMS), a tunable laser spectrometer (TLS), and a gas chromatograph (GC). The six column GC not only has its own detectors, but also can operate together with the QMS as a gas chromatograph mass spectrometer (GCMS). The supporting systems are a Chemical Separation and Processing Laboratory (CSPL) and sample manipulation system (SMS). The manipulation of solid sample and the processing of gaseous samples in SAM is schematically illustrated in the block diagram of Figure 8. The SAM suite has been tested in an environmental chamber designed specifically for this instrument (Figure 9) where the temperatures and pressures encountered by the instrument can be set to those expected inside the rover on the surface of Mars.

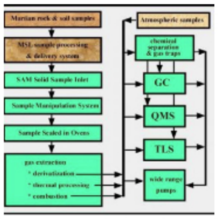


Figure 8

The Mars atmosphere is sampled by SAM micro-valve operations that introduce a small volume of atmospheric gas through an inlet tube to the SAM instruments. This manifold gas volume is either introduced into the QMS through a capillary leak or directed to the TLS. Finely sieved solid phase materials delivered from the MSL rotary percussive drill to a SAM inlet funnel that delivers sample down a tube to one of 74 SAM sample cups. The funnel is vibrated during sample delivery to insure complete transfer to the cup. The cup is then inserted into a SAM oven and thermally processed to release volatiles. The gas processing manifold includes high conductance and micro valves, chemical and mechanical pumps, carrier gas reservoirs and pressure regulators, pressure monitors, the pyrolysis ovens, the chemical scrubbers and getters, and all the associated heaters and temperature sensors.

Figure 9

The quadrupole mass spectrometer can operate in static or dynamic mode with a mass range of 2-550 m/z. Its ion detector dynamic range $>10^{10}$ with both a channeltron pulse counting electron multiplier and a Faraday Cup. The crosstalk between adjacent peaks is greater than one million which enables isotopes of interest to be accurately measured. The gas chromatograph utilizes on of six columns to separate a complex mixtures of organic compounds into its molecular components which are detected both by the mass spectrometer and the thermal conductivity detectors on 5 of the 6 columns. The GCMS detection limit exceeds the part per billion mission requirement for organic detection. The TLS is a two channel Herriott cell design spectrometer that provides detection of CH_4, H_2O, and CO_2 and the isotope ratios $^{13}C/^{12}C$, $^{18}O/^{16}O$, and $^{17}O/^{16}O$ in carbon dioxide, D/H in water, and $^{13}C/^{12}C$ in methane. The TLS sensitivity for atmospheric gas is < 1 ppb and the detection limit can be substantially reduced by methane enrichment in SAM's CSPL.

A mixture of several calibration gases is brought to Mars in SAM to be used at regular intervals during the mission. The calibration gas cell includes N_2, CO_2, Ar, and a Xe mix that is heavily spiked with ^{129}X to clearly distinguish it from terrestrial or martian xenon. Three fluorocarbon compounds are included in this cell to evaluate the performance of the GCMS before launch and over the course of the mission. An organic check material that processes the same fluorocarbons adsorbed on an inert silica glass matrix through the entire sample processing chain provides both a check on the performance of the SAM organics detection and the cleanliness of the sample transfer chain.

The first steps by the SAM suite to search for organics will be to heat a powdered sample of rock and analyze the evolved gas. This analysis is first implemented with rapid mass spectrometer scans as the sample is heated and a portion of the gas stream introduced through capillary leaks into the QMS. Subsequently a GCMS analysis of gas trapped from the evolved gas stream is carried out to enable a complex mix of organics, if present, to be separated into their individual constituents. The study of the source of organics will rely first of all on an examination of patterns such as molecular weight distribution, linearity or branched characteristics of hydrocarbons, and odd/even enhancements in chain length. Terrestrial biology leaves what are often such distinct patterns while extraction of carbon compounds from meteorites shows us that hydrocarbons produced and processed by abiotic processes in space exhibit more extensive branching and more randomized chemical structures. A second tool available to SAM for organics analysis will be carbon isotopic analysis. Refractory organics can be combusted to CO_2 and their carbon and oxygen isotopes measured by the TLS. Comparisons of $^{13}C/^{12}C$, for example, can then be made with these ratios in meteoritic carbon and with the isotopic composition of the oxidized carbon in the atmosphere.

Finally if a site rich in organics is identified samples can be analyzed in SAM utilizing one of the several chemical derivatization cells. In this experiment the foil sealing a metal cup is punctured and sample introduced to a liquid consisting of a mixture of the solvent DMF (dimethylformanide) and a derivatization agent MTBSTFA (N,N-Methyl-tert,-butl(dimethylsily)trifluoroacetamide). The silylation reaction that ensues turns polar molecules such as carboxylic acids and amino acids into non-polar volatile compounds that readily make their way through the GC column into the QMS. This extraction method has been utilized in our laboratory to analyze organics from samples of the highly oxidized, organic-poor soil from the driest part of the Atacama desert. This wet extraction method avoids the potential issues associated with the transformation by oxdation of these organic compounds during pyrolysis.

Localized methane has recently been identified by spectroscopy in the atmosphere of Mars (Formisano et al., 2004; Krasnopolsky et al., 2005; Mumma et al., 2009). What is just as exciting as the discovery itself is the observation of its rapid disappearance over a period of weeks or months (Mumma et al., 2009). The lifetime of methane in the Mars atmosphere is predicted to be more than 300 years and there is evidently a destruction mechanism that operates on a much faster timescale (Lefevre and Forget, 2009). The SAM TLS undertakes a sensitive search for atmospheric methane and its ^{13}C isotope. Methane will also be enriched for the TLS measurements in the SAM gas processing system to improve the precision of the isotope measurement. Regular measurements over the course of the two-year landed mission will provide better temporal resolution than the presently sparse ground-based measurements. As extensive terrestrial field work has illustrated (Sherwood Lollar et al., 2006), a broad range of measurements will ultimately be required to definitively prove if the source of methane on Mars is biotic or produced abiotically by processes such as serpentization. Related experiments carried out by SAM that we expect will contribute to the study of the source of the methane are measurements of the mixing ratio of other trace hydrocarbons and isotope ratios such as D/H in water. These measurements will include atmospheric samples and gases released from surface rock and soil samples.

Regardless of outcome of the MSL/SAM search for organics, the SAM suite is expected to provide a wealth of data on the chemical and isotopic composition of the atmosphere and of volatiles in solid samples. Measurements of the SNC (Martian) meteorites combined with the 1976 Viking lander data indicate that D/H, $^{15}N/^{14}N$, and $^{38}Ar/^{36}Ar$ are all fractionated and enriched in the heavier isotopes. A precise measurement of the major Xe isotopes could solidify the widely held belief that Mars is really the origin of the SNC meteorites. Assuming this is found to be the case, a better precision SAM measurement of atmospheric isotope ratios of the other noble gases and $^{15}N/^{14}N$ in nitrogen could help determine what portion of the SNC gas was trapped from the atmosphere during the impact melt event or represents components present in the solid when these fragments were ejected into space. Although the present Mars atmosphere is being removed by processes such as solar wind sputtering, photo dissociation, and dissociative recombination of species such as N_2^+ with electrons it is not yet clear what the Mars composition and atmospheric pressure was more than 3.5 billion years ago when liquid water was probably much more prevalent and left its mark in the features seen in Eberswalde and Holden craters. Better measurements of carbon, nitrogen, hydrogen, oxygen, and noble gas isotopes with SAM will provide improved constraints on models of atmospheric loss over the history of the planet. If MSL lands on ancient terrain a comparison of these light isotopes in ancient rocks compared with the present atmosphere will give additional constrains on these models of atmospheric evolution.

MSL has the range of analytical tools to search for windows that could preserve evidence of the nature of ancient environments. Exploration at the MSL landing site is not limited to the search for organic compounds, but is planned as a systematic in situ examination of geomorphology, microscopy, mineralogy, chemistry, and isotopes over an extended area on the surface of Mars where hypotheses regarding habitability and geological processes can be tested with multiple experiments in diverse locations. The in situ studies will be well supported by orbital imaging and spectroscopic data. We anticipate that the MSL investigations will provide a significant step forward in exploring the processes that have shaped Mars and in our understanding of the present or past biological potential of the selected landing environment.

References

Atreya, S.A. et al., (2006), Oxidant Enhancement in Martian Dust Devils and Storms: Implications for Life and Habitability, *Astrobiology* **6**, 439-450.

Bibring, J.-P., et al. (2006), Global mineralogical and aqueous Mars history derived from OMEGA/Mars Express data, *Science*, **312**, 400 - 404, doi:10.1126/science.1122659.

Boynton, W.V. et al. (2002), Distribution of Hydrogen in the Near-Surface of Mars: Evidence for Subsurface Ice Deposits, *Science Express* **10.1126**, 1073722.

Formisano V. et al. (2004), Detection of methane in the atmosphere of Mars, *Science* **306**, 1758-1761.

Grotzinger, J. (2009), Beyond water on Mars, *Nature Geoscience* **2**, 1-3.

Krasnopolsky V. A., et al., (2005) Detection of methane in the martian atmosphere: Evidence for life?; *Icarus*, **172**, 537-547.

Lefevre, F. and Forget, F. (2009), Observed variations of methane on Mars unexplained by known atmospheric chemistry and physics, *Nature* **460**, 720-723.

Malin, M.C. and Edgett, K.S. (2003), Evidence for persistent flow and aqueous sedimentation on early Mars, *Science*, **302**, 1931-1934.

Mumma M. J. et al. (2009), Strong release of methane on Mars in northern summer 2003, *Science*, **323**, 1041-1045.

Murchie, S.L. et al. (2009), A synthesis of Martian aqueous mineralogy after 1 Mars year of observations from the Mars Reconnaissance Orbiter, *Journal of Geophysical Research*, **114**, E00D06.

from the Mars Reconnaissance Orbiter, *Journal of Geophysical Research*, 114, E00D06, doi:10.1029/2009JE003342.

Sherwood Lollar, B. (2006), Unravelling abiogenic and biogenic sources of methane in the Earth's deep subsurface, *Chemical Geology* **226**, 328-339.

Smith, P. (2009), H2O at the Phoenix landing site, *Science* **325**, 58-61.

Squyres, S.W. et al. (2008) Detection of silica-rich deposits on Mars. *Science* **320**, 1063-1067.

Squyres, S.W. and 49 CoAuthors (2004), The Opportunity Rover's Athena Science Investigation at Meridiani Planum, Mars, *Science* **306**, 1698-1703.

Figure Captions

Figure 1. An artist's conception of the MSL rover on the surface of Mars. MSL is able to carry a much more substantial payload to the surface of Mars than any other previous Mars lander.

Figure 2. The aeroshell that will protect the MSL lander during the first stages of the entry into the Mars atmosphere is shown in an environmental test chamber.

Figure 3. The parachute design that will be utilized during the descent is tested in a large wind tunnel.

Figure 4. The 4 prime candidate MSL landing sites are shown with the color in these orbital images showing elevation. The sites are (a) Eberswalde Crater, (b) Gale Crater, (c) Holden Crater, and (d) Mawrth Valles. Landing ellipses of approximately 20 km are shown that avoid areas of high slopes or areas cluttered with large rocks.

Figure 5. The Eberswalde delta features are clearly evident in this image from space (Image: Malin Space Sciences/NASA/JPL).

Figure 6. Gale crater shows multiple layers in this high resolution image from the Mars Reconnaissance Orbiter (Image: NASA/JPL/University of Arizona).

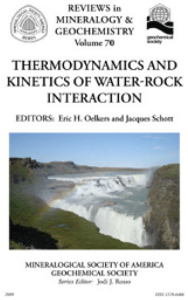
Figure 7. A three dimensional model of SAM shows the instruments and major subsystems.

Figure 8. The SAM sample processing flow is illustrated for both transfer of solid and gaseous samples.

Figure 9. The SAM suite is here being prepared for tests in its environmental chamber that span the range of temperatures and pressures that SAM will encounter on the surface of Mars.

Thermodynamics and Kinetics of Water-Rock Interaction

Book review by William M. White, Cornell University, Ithaca NY



REVIEWS in
MINERALOGY &
GEOCHEMISTRY
Volume 70

THERMODYNAMICS AND
KINETICS OF WATER-ROCK
INTERACTION

EDITORS: Eric H. Oelkers and Jacques Schott

MINERALOGICAL SOCIETY OF AMERICA
GEOCHEMICAL SOCIETY
Series Editor: Jodi J. Rosso

Thermodynamics and Kinetics of Water-Rock Interaction, edited by Eric Oekers and Jacques Schott, is the latest volume in the very valuable series, *Reviews in Mineralogy and Geochemistry*, published by the Mineralogical Society of America and the Geochemical Society. This 35 year-old series began with an exclusive focus on mineralogy but expanded to geochemistry a few years later with the 1981 publication of volume 8 of the series: *Kinetics of Geochemical Processes*. That volume is one the most well-thumbed book on my bookshelf; I have relied on it heavily in teaching geochemistry. It had a heavy focus water-rock interaction, so I was expecting this new volume to be, in part, an update and extension of that volume, as well as some the classic, but now aging, texts, such as *Principles and Applications of Aquatic Chemistry* by Morel and Hering (1993). It succeeds in this respect, but it is also more. The book is based on a short course held prior to the 2009 Goldschmidt meeting in Davos, but according to the preface its real origins date to summer courses for graduate students held over the previous decade. From this, one might reasonably assume that the target audience is graduate students. While some chapters do provide brief introductions to basic thermodynamics and kinetics, the book is written at a high level and is appropriate mainly for advanced students and those already familiar with the field. As is generally the case with multi-authored treatises, readers will likely be interested only in reading selected chapters rather than reading it cover to cover.

The first chapter, *Thermodynamic Databases for Water Rock Interaction*, provides a brief but useful overview of thermodynamic concepts and variables and background as to how fundamental thermodynamic data have been determined. But it mainly serves as a warning to those who rely on nominally sophisticated thermodynamic computer models such as PHREEQC. This is because the fundamental thermodynamic data, upon which these models depend, would seem to be in sorry shape. The authors point out the estimates of the equilibrium constant for fluoro-apatite dissolution range over 10 orders of magnitude. Table 2 of that chapter provides a selection of thermodynamic databases (datasets might be a better word - these are not organized, searchable databases in the modern sense), the most recent of which is from 1998 and the most extensive remains that of Helgeson et al. (1978). The authors' certainly succeed in making their point that 'it is best to consider the current state of thermodynamic databases as a work in progress rather than a completed task.' One can only hope that the chapter will lead to a community effort to address the situation.

The next few chapters provide an overview of the current understanding of modeling water-rock interaction in detail. I found them all useful and they enhanced my understanding of the subject and will impact my teaching. There is some duplication here, but that may be just as well as some authors' approaches will resonate with some readers, while other approaches will resonate with others. I found Manual Prieto's chapter on *Thermodynamics of Solid-Solution Aqueous Solution Systems* and David Sherman's chapter on *Surface Complexation Modeling: Mineral-Fluid Equilibria at the Molecular Scale* to be particularly useful. I also found the chapter by Schott, Pokrosky, and Oelkers entitled *The Link Between Mineral Dissolution/Precipitation Kinetics and Solution Chemistry* particularly useful because it did an excellent job of linking theory with experimental observation.

The longest chapter, over 100 pages, is entitled *Organics in Water-Rock Interaction*, but it may have been the chapter from which I took away the least. Organic compounds are, of course, ubiquitous in natural waters and the number of different organic compounds potentially present in water is overwhelming - the chapter contains a 5-page table just listing this compounds and their role in water-rock interaction. So it is certainly a broad topic. Consequently, the uninitiated, such as me, will be looking for simplifying and unifying concepts but won't find them in this chapter. That may be, of course, because there are none.

The chapter entitled *Mineral Precipitation Kinetics* begins with a useful review of the fundamental kinetic considerations in nucleation and crystal growth, and appendices usefully extend these concepts from the simply spherical case to more realistic geometries. Much of the chapter, however, describes the NANOKIN code developed by the authors and it applications. What is missing from this is any attempt to compare predictions of the code to observational data. One is thus left wondering how useful this code actually is.

The last few chapters take an integrative approach applying thermodynamics to the outcrop, watershed, and global scales. The first of these is a chapter entitled *Towards an Integrated Model of Weathering, Climate, and Biospheric Processes*. The chapter succinctly reviews efforts of the authors over the last few years to advance global models relating water-rock interaction to climate. This is of course, an important area of inquiry and one that attracted wide attention since the BLAG (Berner, Lasaga and Garrels) model was introduced 25 years ago. One comes away with the impression that the science has indeed advanced greatly since BLAG, for reasons that include a greater willingness to tackle the complexity of the issue, greater computer power, and greater understanding of underlying thermodynamics and kinetics. I also liked the 3 subsequent chapters because they tied theory to observation, demonstrated both present capabilities and limitations.

In describing the background history of the book in the preface, the editors relate that they 'received numerous demands from our students requesting a book to help them follow the subject as they...got rapidly lost among the equations, symbols, and conventions, and standard states.' In this respect, the editors could have served students better. To begin with, one would hope that in the 21st century geochemistry would finally get around to using SI units exclusively. The first chapter, however, insists on using calories rather than joules as the unit of energy and one subsequent chapter uses both (!). There is little that is more daunting in geochemistry than the great number of parameters involved and this becomes all the more confusing when different symbols are used for the same parameters. Some of this may be unavoidable as convention has evolved so that some symbols represent more than one common parameter. For example, Q is commonly used to represent heat, mineral surface charge, the reaction quotient, and diffusive or advective flux. Readers would have been better served, however, had the editors made some effort to mitigate this problem and enforce a uniform system of symbols throughout the book. For example, ρ and I are used in the conventional way in several chapters to represent density and ionic strength, respectively, but are used, unconventionally, to represent radius and the

GN141 Content

Highest pH?
by Michael J. Mottl

The chemical composition of saline lakes of the Northern Great Plains, Western Canada
by William M Last and Fawn M. Ginn

Sample Analysis at Mars: Developing Analytical Tools to Search for a Habitable Environment on the Red Planet
by Paul Mahaffy

Book Review: Thermodynamics and Kinetics of Water-Rock Interaction
Review by William M. White

Interesting Freeware: Part II
by Geochemical News Staff

ratio of reaction quotient to equilibrium constant, respectively, in the *Mineral Precipitation Kinetics* chapter. That ratio is elsewhere represented by *Ω*; why not use *Ω* throughout? Brantley and White go so far as to warn the reader in the introduction to their chapter on *Approaches to Modeling Weathered Regolith* that 'symbol definitions differ' throughout the chapter! At the very least, perhaps a list of symbol definitions at the start of each chapter would have helped.

Notwithstanding these complaints, the volume represents an up-to-date overview of water-rock interaction by the leaders in this field. It will be a useful addition to the bookshelves of those of us who teach geochemistry and to graduate students and others with an interest in this topic.

References

Helgeson, H. C., J. Delaney, H. W. Nesbitt and D. K. Bird (1978) Summary and critique of the thermodynamic properties of rock-forming minerals, *Am. J. Sci.*, **278A**:1-229.

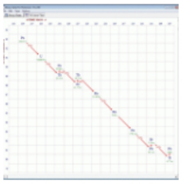
Morel, F. M. M. and J. G. Hering (1993) *Principles and Applications of Aquatic Chemistry*, John Wiley and Sons, New York, 588pp.

Lasaga, A. C. and R. J. Kirkpatrick, eds. (1981), *Kinetics of Geochemical Processes, Reviews in Mineralogy and Geochemistry, vol. 8*, Mineral. Soc. Am., Washington 398pp.

Interesting Freeware: Part II

x4FFF; (Part I, Geochemical freeware, was published in GN139).

Rad Decay - Figure 1a



Rad Decay - Figure 1b

Rad Decay This periodic table is distinguished by its plots of nuclide decay paths. The accompanying text lists the particles, x-rays, and energy emitted at each decay step. Shown here is the decay of ^{239}Pu to ^{207}Pb. Fast breeder reactors contain a core of ^{239}Pu surrounded by a shell of ^{238}U. Neutrons[1] from decaying ^{239}Pu strike the ^{238}U, which changes into ^{239}Pu by two beta decays. The reactions stop when the ^{238}U shell is used up. This is a valuable and intelligent program.

[1] A neutron walks into a bar. It says to the bartender 'I'll have a beer'. The bartender gets the beer. The neutron says 'What do I owe you?' The bartender says 'For you, no charge'.

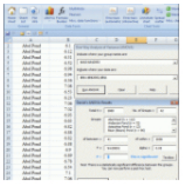
Ground-Zero II - Figure 2a

Ground-Zero II - Figure 2b

Ground-Zero II - Figure 2c

Ground-Zero II - Figure 2d

Ground-Zero II Programs can be useful or useless, user-friendly or user-vicious, stable or crash-prone. Here is a *sad* program. Have you ever been to Madison, Wisconsin? This great small city is the home of the Oscar Meyer Weiner-Mobile, Cows on the Concourse, Lakes Monona, Mendota and Wingra, and cheese-head hats. It is the birthplace of American Girl dolls. Madison has a preeminent university with a geochemistry group second to none.Suppose an American TB61 340 kiloton nuclear weapon detonated over Madison. The plots speak for themselves.



XL-Toolbox v2.57 - Figure 3

Statistics is a dangerous discipline[2]. Computer programs can make any statistical test you want, but naïve users may misinterpret the results. We include ourselves in this group, so we stick to simple tests. Our favorite statistical routines are Excel add-ins because they work in a familiar spreadsheet format. Many add-ins and stand-alone statistics programs are listed at Free Statistics. The add-in used in the example is XL-Toolbox v. 2.57.

The example shows the results of a one-way ANOVA test of pH values of lakes in Maine. The sample set includes 2080 pH measurements from 42 lakes.

Our hypothesis is that average pH values differ among the lakes. The null hypothesis is that the average pH values are not different. The numbers of measurements per lake are variable so the test is not valid. The example illustrates the utility of this Excel add-in; it does not prove any scientific point.

The ANOVA find a 95% probability that the pH values *do* differ among the lakes. Now we have to figure out why. That can be done with additional water chemistry in the database of Maine limnology.

[2] A well-known witticism about statistics is: 'There are lies, damn lies, and statistics.' Precedence for this phrase goes to Benjamin Disraeli, British Prime Minister, although many mistakenly attribute it to American author Mark Twain.

GN141 Content

Highest pH?
by Michael J. Mottl

The chemical composition of saline lakes of the Northern Great Plains, Western Canada
by William M Last and Fawn M. Ginn

Sample Analysis at Mars: Developing Analytical Tools to Search for a Habitable Environment on the Red Planet
by Paul Mahaffy

Book Review: Thermodynamics and Kinetics of Water-Rock Interaction
Review by William M. White

Interesting Freeware: Part II
by Geochemical News Staff