

THE LITHOLOGICAL INFLUENCE UPON LAKE CHEMISTRY
IN THE CROOKED LAKE REGION
OF NORTHERN MINNESOTA AND SOUTHERN ONTARIO

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The field area for this study includes a section of wilderness terrain along the U.S./Canadian border, roughly 325 square kilometers in area and heavily populated with lakes. The region of study is enclosed by latitudes 48°02' N. and 48°15' N. and longitudes 91°36' W. and 91°54' W. The area's resistant rocks of the Canadian Shield were scoured by Pleistocene glaciers, scraping away softer overlying material and leaving much of the bedrock exposed at the surface. The multitude of lakes reflects the immature drainage system that was left behind. These relatively shallow, bedrock-perched lakes thus typically do not have strong groundwater influences. In general, human impacts are minimal as there is no local industry or sewage. Atmospheric inputs should be equal for all lakes in the study area. Therefore, if differences in lake chemistry are to be found, the remaining sources are bedrock and organics.

Through past geologic field mapping of the area, a large difference in the color of the surface waters draining the region was noticed. Waters draining the Vermilion Batholith seemed to be much lighter in color than those draining metamorphic units further south. The underlying objective of this past summer's research was to determine if this difference is real, and if so, to what it can be attributed. Because the major lithologic contact is nearly coincident with the international boundary in this area, lakes were sampled in both the Boundary Waters Canoe Area Wilderness of northern Minnesota and the Quetico Provincial Park of southern Ontario.

Field data measurements were taken at three different depths per site. A lack of vertical mixing during the summer months produces a sharp thermocline in sites over 10m deep. Measurements were thus taken at 0.5m from the bottom, 0.5m from the top, and at the midpoint of the column. Due to field limitations, samples for further analysis were collected only at the midpoint in the hope that this would represent a rough average chemistry for each site. For each site, one sample was filtered (at 0.45 microns) and acidified to a pH below 2 while another sample was left "raw." At five sites, samples were collected every one to two meters to give a more detailed picture of chemical changes with depth. The middle value does in fact give a reasonable average (see Table 1), usually occurring easily within one standard deviation of the average for all samples of the profile. Thus, for all calculations the data from the midpoint is used to represent each site.

After filtering (at 0.45 microns) the "raw" version of these samples, various ion, DOC, and SiO₂ were measured by ion chromatography under the direction of Dr. David Dethier at Williams College. The 0.45 micron filter size was used to remove any particulate matter, and thus theoretically leave behind only dissolved constituents to be analyzed. In using "raw" samples there was concern that leaving the water unacidified would cause metals, such as Ca⁺² and Mg⁺², to adsorb on the container walls of the sample bottles and thus become underrepresented in solution [Hem, 1985]. By not immediately filtering samples, bacteria may influence ionic concentrations as well. Since calcium and magnesium hardness determinations were made in the field, one can estimate the validity of the lab techniques by comparing the two measurements.

First the data must be converted to a common unit. The ion form was chosen due to a majority of the data occurring in that form. When plotted, the lab data vs. the field data for calcium matches up very well (see Figure 1). There is nearly a one to one correlation (1.08 slope), the y-intercept is nearly zero, and the correlation $r^2 = .804$. The magnesium data (see Figure 2) does not match up quite as well, but the field titrations used so little titrant due to low concentrations that the error would be expected to be high. As is apparent from the slope, the error in the field measurements typically underrepresented the real magnesium concentration.

Given the above data, apparently adsorption in the containers is not a significant process for the concentrations of calcium and magnesium found in these waters. Excepting NO₃⁻, other ion concentrations are on the same order of magnitude and they should behave similarly. In addition, significant bacterial influence seems unlikely as bacteria cannot increase the concentration of magnesium or any other ion and the calcium concentrations did not appear to change from the field to the lab.

In general, sites were chosen in which the bedrock surrounding the lake could be confidently determined to represent only one lithology. The two major lithologies considered were "Batholithic,"

consisting of the Vermilion Batholith, and "Metamorphic" which includes a complex of metasediment and metavolcanic units, many of which have been migmatized. A third major grouping was considered, consisting of sites in the bays of Crooked Lake which receive waters draining both the batholithic and metamorphic lithologies. The term "Mixed" is used for these waters. It was hypothesized that these waters, through mixing, might represent an intermediate chemistry between the two lithologies if distinct chemistries represent each lake type.

Compiling the chemical averages and standard deviations for each lake type does reveal three distinct chemistries (see Table 2). Perhaps the most dramatic trend is that produced from the measurement of color. Batholithic lakes average 13 platinum-cobalt units (PCU) of color while the metamorphic average is 68 PCU. The mixed bays fall in the middle at 49 PCU. The color difference noticed in previous field seasons is real. Turbidity, as measured by secchi disk, also reflects this trend, yielding values of 4.6m (batholith), 3.2m (mixed), and 2.4m (metamorphic).

The color differences, significant in themselves, also occur with differences in chemistry. As one moves from the batholithic to metamorphic lakes, the concentrations of Mg^{+2} , Ca^{+2} , and K^{+} all increase, as does the overall conductivity. There appears to be a greater dissolved mineral content in the metamorphic lakes. Calcium, magnesium, and especially potassium are essential elements for nearly all forms of life. Increased concentrations of these elements would be expected to yield a greater abundance of life in these lakes. Casual observations were made that noted algae and lily pads seemed much more prevalent in the metamorphic lakes. In fact, no recollection of lily pads in any of the batholithic lakes could be made. These observations are backed with the hard evidence of the dissolved organic carbon (DOC) measurements which show metamorphic lakes on average have nearly twice the DOC content of batholithic lakes.

With these two distinct lake chemistries, one might expect Crooked Lake, draining both metamorphic and batholithic terrains, to show an intermediate chemistry. It clearly does not as some ion concentrations are two to three times greater than the batholithic or metamorphic values. In fact concentrations for all ions measured, excepting nitrate which only appears in trace amounts, are the greatest in the mixed waters of Crooked Lake.

There are two phenomena which might explain this observation. First, if the residence time of Crooked Lake is long, especially relative to the lakes feeding it, evaporation may be playing a significant role in the vast open water bays of Crooked Lake. Prolonged evaporation could continually concentrate the dissolved substances until some equilibrium is reached between the outflow and inflow of waters into the system. It should be remembered that the summer was an abnormally hot and dry one. The data from "Leech Lake" (unnamed lake east of Thursday Bay at $48^{\circ}07'45''$ N., $91^{\circ}44'20''$ W.) gives at least some credence to this evaporation theory. Leech Lake does not fit into a strict category since its waters are exposed to both batholithic and metamorphic units. It is also a very shallow body, reaching 4m at its deepest point and has no outlet, thus making evaporation an important process. Though not reaching the concentrations found in mixed waters, values for Ca^{+2} , Mg^{+2} , SiO_2 , and alkalinity are significantly greater than batholithic or metamorphic lake values by 20-40 percent.

Another logical hypothesis is that the increased ion concentrations are due to some other source. Such a potential source does exist to the southeast in the form of greenstones. If these greenstones are weathering at a faster rate and releasing more ions into the water, this could explain waters of higher ionic concentrations. Waters contiguous with the greenstones include Basswood Lake which drains by way of the Basswood River. It is this river which in turn feeds Crooked Lake. Four sites were sampled on the Basswood River. For silica and the major ions, the concentrations are relatively high, approaching the figures of Crooked Lake. The exception is potassium which is low, only slightly higher than the batholithic value. Since the Vermilion Batholith is the other major unit exposed in Basswood Lake, the data may be suggesting the other rock units (including the greenstones) do not contribute a significant amount of K^{+} to the waters. One should also note that since Basswood Lake is fed from the east through Prairie Portage there may be additional ionic sources from other rock units.

In attempting to explain the Crooked Lake concentrations, evaporation and influence from other geologic units probably both play a part. The evaporation model is given further credence as the concentrations of silica and all measured ions (excepting sulfate) increase in going from the Basswood River to Crooked Lake. Waters emptying into the Basswood River at this point include only the less concentrated batholithic and metamorphic waters.

Several lakes, in addition to those already cited, did not fit the major lake designations and should be noted. Kett Lake displays a wide range of chemical tendencies, spanning concentrations typical of both batholithic and metamorphic lakes. Not surprisingly Kett is transected by at least four geologic units, including the Vermilion Batholith, two migmatites, and a hornblende adamellite. "Lake Python" (unnamed lake southeast of Robinson Lake at $48^{\circ}10'40''$ N., $91^{\circ}39'30''$ W.) is another lake which yields data that does

not conform to an easily understood pattern. Geologic maps place the lake within the batholith, but the color is a dark 45 PCU and the DOC a high 7.4 mg/l. Both field parties involved with the lake suggested it may have multiple influences. Rani Arbo noted the presence of a metamorphic unit under the cliffs of nearby Gardner Mountain and questioned if the same unit might not be under Lake Python. Another party sampled rocks along the shoreline and found many loose metamorphic specimens. Here then is a case where the water chemistry suggests the bedrock may be more complicated than originally thought and calls attention to an area that is probably worth closer study.

The duo of Sandpit and Tin Can Mike Lakes is odd, especially with respect to Horse Lake which appears to be a normal metamorphic influenced body of water. All three lakes are located in a faulted region of metamorphic rocks. the relationship between color, conductivity, and most ions does not follow any logical pattern. A splay fault from the Burntside Lake Fault zone runs through the trio of lakes, apparently the controlling factor for their location. One hypothesis is that the fault runs deep enough that groundwater is influencing chemistry. Differential infiltration of relatively mineral rich groundwater may be causing the unusual patterns. In any case Sandpit and Tin Can Mike have little use as "typical" lakes.

In conclusion, waters draining the batholith and metamorphic units differ markedly in color, turbidity, and chemistry. Waters of the batholith are lighter, clearer, and have lower concentrations of dissolved constituents than their metamorphic counterparts. The organic content of the lakes seems to be largely dependent on the dissolved nutrients available. The data thus strongly suggests the bedrock in the Crooked Lake region exerts a very large control on the chemistry of the surface waters. Because this relationship is expressed visually by the water's color, a quick check on bedrock mapping of an area can be accomplished. Discrepancies may be effectively used to target areas where more detailed mapping should be done, suggesting the presence of geologic units previously overlooked.

REFERENCE CITED

Hem, John D., 1985, Study and interpretation of the chemical characteristics of natural water: U.S. Geological Survey Water Supply Paper 2254, 263 p.

Table 1 Water quality measurements from four profiles in the Crooked Lake region. Data from the midpoint of the column appears first, then the average value for the column with the standard deviation in parentheses.

	DAN 002		DAN 003		DAN 004		DAN 005	
	Midpt.	Average	Midpt.	Average	Midpt.	Average	Midpt.	Average
Color (PCU*)	12	13 (5)	74	76 (11)	69	74 (13)	75	79 (15)
pH	6.46	6.58 (.82)	6.68	6.60 (.22)	6.69	6.73 (.31)	6.74	6.73 (.28)
Conductivity**	20	22 (7)	28	26 (6)	21	22 (2)	30	28 (7)
DOC*** (mg/l)	2.6	3.1 (1.0)	9.5	9.4 (.5)	8.4	8.0 (.8)	6.6	8.0 (.8)
Ca ⁺² (mg/l)	1.92	2.02 (.28)	2.50	2.48 (.20)	2.58	2.52 (.14)	2.48	2.75 (.49)
Ca ⁺² (from hardness)	2.08	2.13 (.14)	2.56	2.27 (.49)	2.72	2.88 (.46)	2.40	2.70 (.31)
Ca Hardness****	5.2	5.3 (.4)	6.4	5.7 (1.2)	6.8	7.2 (1.2)	6.0	6.7 (.8)
Mg ⁺² (mg/l)	.63	.69 (.08)	1.04	.93 (.09)	.93	.90 (.04)	.91	.99 (.16)
Mg ⁺² (from hardness)	.39	.51 (.31)	.39	.91 (.60)	.49	.60 (.29)	.87	.76 (.37)
Mg Hardness****	1.6	2.1 (1.3)	1.6	3.8 (2.5)	2.0	2.5 (1.2)	3.6	3.1 (1.5)
Na ⁺ (mg/l)	.99	1.03 (.31)	.90	.86 (.07)	.82	.84 (.05)	.95	1.01 (.25)
K ⁺ (mg/l)	.63	.58 (.11)	.63	.67 (.03)	.67	.68 (.02)	.67	.74 (.11)
SiO ₂ (mg/l)	.05	.54 (.71)	1.05	1.18 (.49)	.70	.89 (.36)	.80	1.17 (.91)
Total Hardness****	6.8	7.4 (1.2)	8.0	9.4 (1.4)	8.8	9.7 (.7)	9.6	9.9 (1.9)
Alkalinity****	7.8	8.3 (3.1)	7.4	7.0 (1.2)	5.8	6.8 (.9)	6.0	6.7 (1.8)
HCO ₃ ⁻ (mg/l)	9.5	10.2 (3.7)	9.0	8.5 (1.4)	7.1	8.2 (1.0)	7.3	8.1 (2.2)
SO ₄ ⁻² (mg/l)	2.53	2.53 (.23)	2.59	2.49 (.13)	2.58	2.60 (.06)	2.69	2.50 (.25)
Cl ⁻ (mg/l)	.67	.67 (.47)	1.36	.84 (.36)	.82	.75 (.13)	1.04	.92 (.16)
NO ₃ ⁻ (mg/l)	.05	.06 (.03)	.02	.04 (.04)	.02	.01 (.01)	-----	-----

*Platinum-Cobalt Units
**microMHOS/cm @ 25°C

***Dissolved Organic Carbon
****as mg/l CaCO₃

Calcium Ion Lab Data vs. Field Data

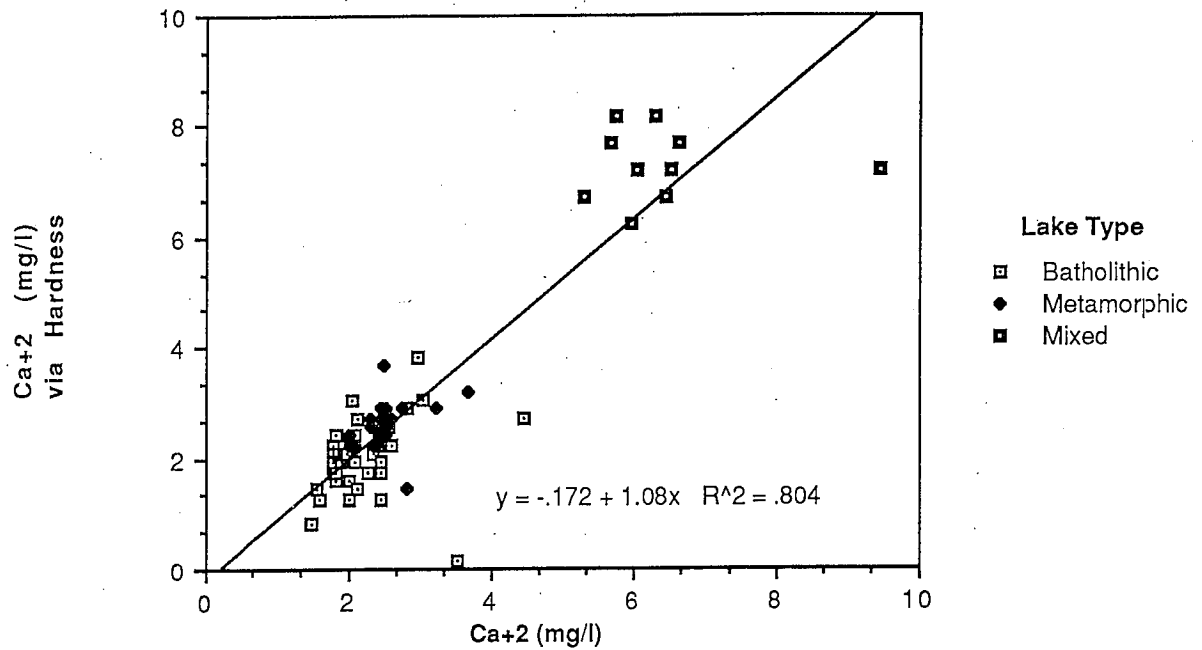


Figure 1

Comparison between lab data and field data for the calcium ion in lakes of the Crooked Lake region.

Magnesium Ion Lab Data vs. Field Data

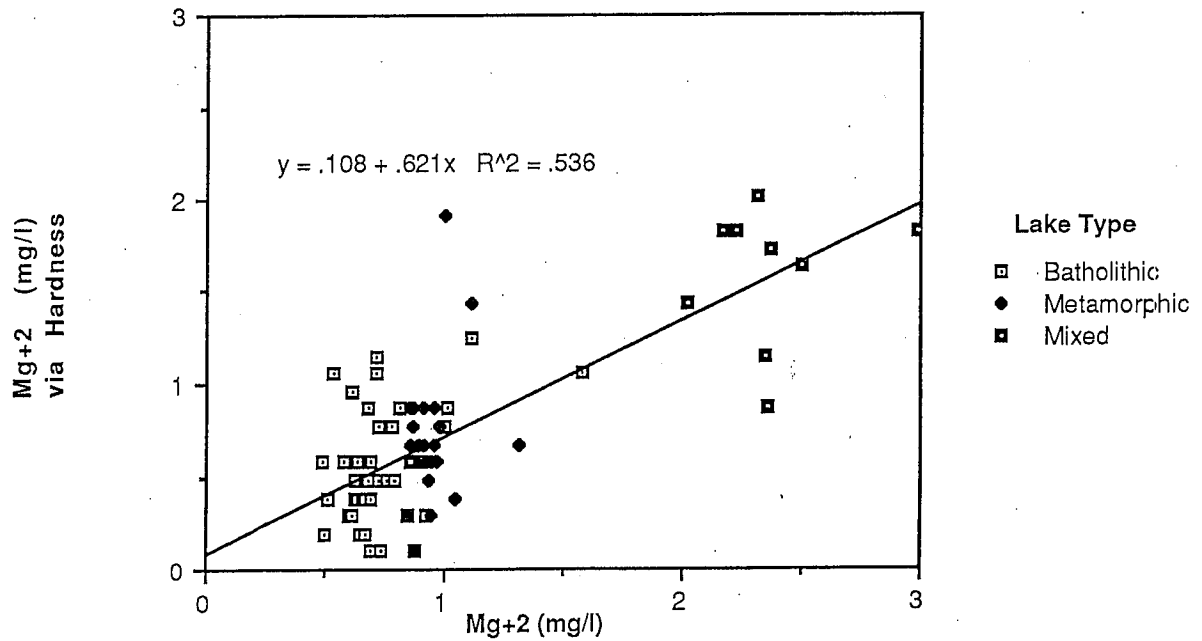


Figure 2

Comparison between lab data and field data for the magnesium ion in lakes of the Crooked Lake region.

Table 2 Water quality measurements from the Crooked Lake region's three major lake types. Data is reported as averages with the standard deviation in parentheses.

	Batholithic	Metamorphic	Mixed
Secchi Depth (m)	4.6 (.9)	2.4 (.5)	3.2 (.9)
Color (PCU*)	13 (7)	68 (16)	49 (5)
pH	7.35 (.72)	6.87 (.39)	7.64 (.46)
Conductivity**	26 (7)	31 (12)	55 (4)
DOC*** (mg/l)	4.2 (1.3)	8.1 (1.1)	8.2 (.6)
Ca ⁺² (mg/l)	2.16 (.55)	2.58 (.43)	6.40 (1.15)
Ca ⁺² (from hardness)	1.99 (.66)	2.59 (.43)	7.30 (.63)
Ca Hardness****	5.0 (1.6)	6.1 (1.8)	22.8 (2.8)
Mg ⁺² (mg/l)	.73 (.19)	.97 (.11)	2.21 (.54)
Mg ⁺² (from hardness)	.55 (.31)	.71 (.37)	1.49 (.48)
Mg Hardness****	2.3 (1.3)	2.8 (1.7)	6.2 (2.0)
Na ⁺ (mg/l)	.94 (.18)	.97 (.25)	1.48 (.13)
K ⁺ (mg/l)	.51 (.15)	.74 (.12)	.77 (.34)
SiO ₂ (mg/l)	.71 (.59)	.88 (.64)	4.54 (.89)
Total Hardness****	7.3 (2.3)	8.8 (2.6)	24.4 (1.6)
Alkalinity****	7.7 (2.7)	7.9 (2.4)	22.0 (2.8)
HCO ₃ ⁻ (mg/l)	9.4 (3.3)	9.2 (2.6)	26.8 (3.4)
SO ₄ ⁻² (mg/l)	3.05 (.71)	2.36 (.32)	3.81 (.31)
Cl ⁻ (mg/l)	.99 (.71)	.96 (.65)	1.10 (.37)
NO ₃ ⁻ (mg/l)	.10	.01	.01

*Platinum-Cobalt Units

**microMHOS/cm @ 25°C

***Dissolved Organic Carbon

****as mg/l CaCO₃