

EVIDENCE OF CONCEALED GEOTHERMAL ACTIVITY NEAR THE NAZKO VOLCANIC CONE, BRITISH COLUMBIA, CANADA, FROM AN INTERPRETATION OF GROUND AND SURFACE WATER GEOCHEMICAL DATA.

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Introduction

Water-rock and water-mineral interactions, aquifer geology, solution residence times, environmental factors and reaction rates are all factors affecting ground and surface water geochemistry. Where there is geothermal activity the water chemistry will also be influenced by increased rock weathering and changes in mineral solubility at higher (> 30°C) subsurface temperatures and by the mixing of hot and cold ground water.

For example, Pasvanoğlu (2013) interpreted high dissolved CO₂, Si, Li, As, Hg and B concentrations in the thermal waters from wells in Eastern Turkey to be the result of reactions between hot water and silica-rich volcanic rocks and by the mixing of hot and cold water during the ascent of solutions from depth to the surface. Hence, the relative solubility of different minerals in the near-surface water may be an indication of temperature variation on water reactions in a confined aquifer. This paper describes simulations of mineral solubility in ground and surface water

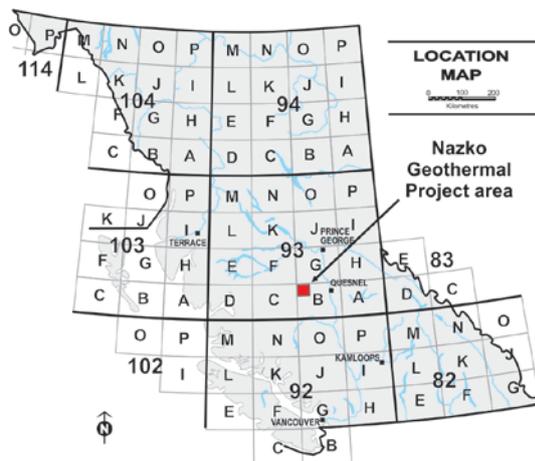


Figure 1. Nazko geothermal project location.

using the PHREEQC software (Parkhurst and Appelo, 2013) applied to data generated from the analysis of water samples collected in two wetlands, the North and South Bogs, near the Nazko volcanic cone, British Columbia, Canada. The simulations were designed to detect evidence of sub-surface geothermal activity from the water geochemistry.

In their study of the North and South Bog water geochemistry (Figure 1), Lett and Jackaman (2014) describe the Nazko Cone as the most easterly of several Pleistocene-Holocene volcanoes in the east-trending Anahim volcanic belt that crosses west-central British Columbia. Souther et al. (1987) determined that pyroclastic ash, lapilli and volcanic bombs ejected periodically after the Fraser Glaciation (29,000 to 9,000 years BP) formed the Nazko Cone. An ash layer deposited between 7100 and 7200 years BP covers much of the area around the cone including the bogs (Souther et al. 1987). Older rocks are the Eocene Ootsa Lake Group, Miocene Endako Group and Pleistocene-Holocene volcanic rocks and clastic sedimentary rocks of the Cretaceous Taylor Creek formation (Talinga and Calvert, 2014). Bedrock is largely concealed beneath Pleistocene deposits including till and glacio-fluvial sediments. An earthquake swarm near the Nazko cone in 2007 (Cassidy et al. 2011) and an interpretation of seismic data by Kim et al. 2014 suggested that magma, a possible geothermal heat source, has accumulated in the lower crust. There are also scattered travertine deposits on the surface of the North and South bogs and many carbon dioxide gas seepages including a vigorous gas flow from a small travertine cone on the edge of the North Bog (Figure 2). While there is anecdotal surface evidence of a buried heat source beneath the bogs, the highest water temperature measured is 23°C.

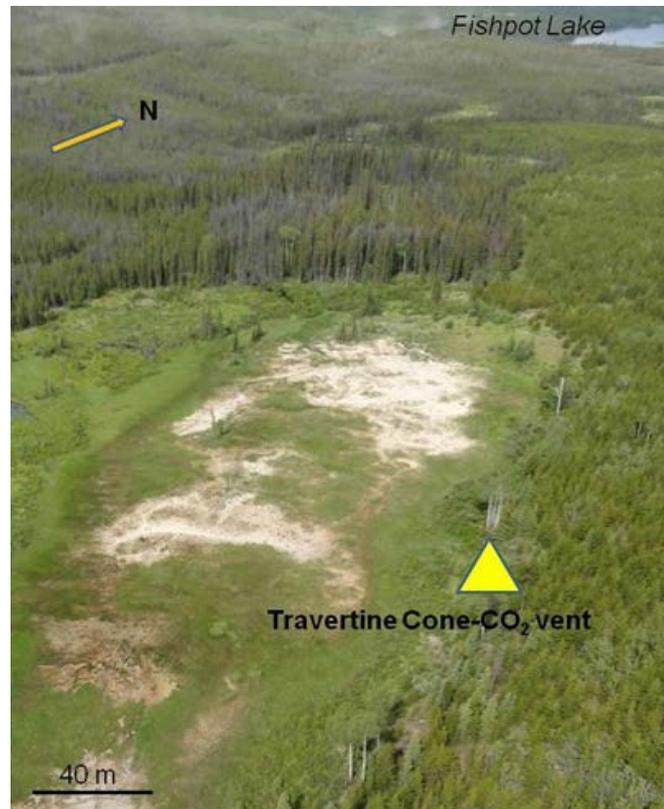


Figure 2. View towards Fishpot Lake across the North Bog. The white coloured surface area is carbonate mud. Carbon dioxide seeps are common through surface water pools and there is a vigorous gas flow in the travertine cone - CO₂ vent.

Methodology

Sampling

In 2013 and 2014 17 ground and 23 surface water samples were collected by Lett and Jackaman (2014) in the North and South Bogs from pits, pools and stream sites. At each site one sample was filtered (0.45 micron) and acidified (HNO₃) for

trace metal analysis, a second, unfiltered sample for laboratory anion and alkalinity analysis, a third sample for field determined dissolved CO₂ and alkalinity measurement and (at selected sites) a filtered, acidified (HCl) sample for dissolved Hg analysis. Water pH, conductivity, total dissolved solids and salinity was measured and site characteristics recorded. Figure 3 shows the distribution of the water samples. Filtered, deionized water blank samples were also prepared in the field to detect contamination during filtering. The water accumulating at the base of the small travertine cone was sampled twice in 2013 and, again, in 2014 to monitor possible temporal and seasonal changes in the ground water chemistry.

Sample Analysis

All of the water samples were analysed by ALS Environmental, Vancouver, BC, Canada. Filtered, acidified water samples, water blanks and the NRCC standard SLRS 3 were analysed for ALS Environmental for Ag, Al, As, Ag, Ba, Be, Bi, B, Cd, Ca, Cs, Cr, Co, Cu, Ga, Fe, Pb, Li, Mn, Mo, Ni, Na, P, K, Re, Rb, Sb, Se, Si, Sr, Sn, Te, Tl, Ti, U, V, Y, Zn and Zr by high resolution mass spectrometry (ICPMS). Unfiltered water samples were also analysed by ALS Environmental for hardness, total alkalinity by titration and for F⁻, Cl⁻, Br⁻, NO₃²⁻, NO₂⁻ and SO₄²⁻ by ion chromatography. Selected water samples were analysed for dissolved Hg by cold vapour-ICPMS. Instrument detection limits for trace elements (e.g. Cu, Li, Zn) ranged from 0.05 to 1 ppb and for minor elements (e.g. Ca, Mg, Na, K, Br⁻) from 1 to 0.5 ppm. Only Ca, Li and Sr were detected in water blank samples. However, their concentrations were less than twice the detection limit. Water sampling, sample analytical techniques, data analysis and an interpretation of the water and soil geochemistry are described in more detail by Lett and Jackaman (2014).

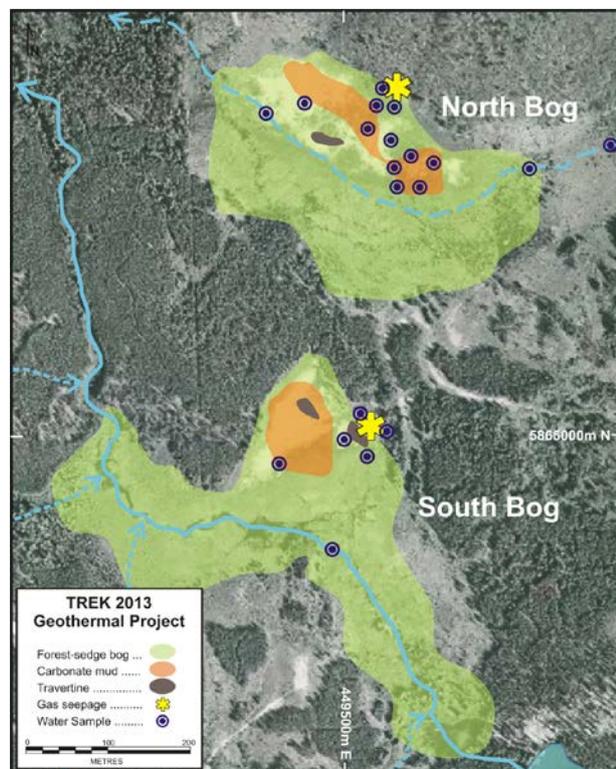


Figure 3. Water sample location in the North and South Bog.

Results

Lithium B, As, Rb, Sr and Hg are known as geochemical pathfinders for geothermal activity. In thermal water concentration of these elements may reach several hundred parts per million. For example, wells in Eastern Turkey, sampled by Pasvanoğlu (2013) have a temperature that reaches 78°C and concentrations of up to 762 ppm Ca, 104 ppm Mg, 138 ppm Si, 2.7 ppm Li, 37 ppm B, 2820 ppm Sr, 5070 ppb As and 0.3 ppb Hg in the water. Table 1 reveals that the Nazko bog waters only have up to 637 ppb B (ground water); 547 ppb Li (surface water); 2.6 ppb As (ground water); 56.1 ppb Rb and 15.9 ppm Sr (surface water). In addition, the water has up to 383 ppm dissolved Ca (ground water); 850 ppm dissolved CO₂ (surface water) and up to 18.7 ppm Si. The highest Ni (44 ppb), As (2.4 ppb) and Fe (3920 ppb) concentrations measured in the water are from the bottom of the small travertine cone surrounding an active CO₂ vent on the edge of the North Bog (Figure 2). No mercury was detected in this water and the highest temperature measured is 5.9°C. The travertine cone - CO₂ vent water was sampled several times in 2013 and again in 2014 to monitor seasonal changes in the water geochemistry. Results of the sample analysis indicate that water temperature, pH, and most element concentrations are similar from year to year and from month to month, but there is a 3,910 ppb difference in the Fe concentration between June and August, 2014.

Several of the elements in the water have a sympathetic association. For example, there is a positive correlation between Ca and Sr (correlation coefficient + 0.89) and between Li and Ce (correlation coefficient + 0.88). Figure 4 shows the distribution of Li versus Cs in bog surface, bog ground and stream-lake water samples. Most bog ground water samples with higher element concentrations cluster together along the common Li-Cs trend whereas bog surface and stream waters are more scattered.

Table 2 lists pH, temperature, bicarbonate alkalinity, sulphate and element concentrations in the water sampled at six locations in the North Bog (Figure 5). The sample sites are from the stream flowing through the bog, the travertine cone - CO₂ vent, a typical bog surface pool and ground water sampled in two pits adjacent to the travertine cone - CO₂ vent. Typical minerals that could be expected to precipitate or dissolve in the water and their saturation indices calculated from the water data with a PHREEQC simulation are also listed in Table 2. There is a marked increase in the pH, and in concentrations of Ca, Mg, B, Li, Fe, Ni, HCO₃⁻ and SO₄ measured in the ground water upslope from the bog (142003) to the levels detected in the travertine cone - CO₂ vent water (142004) and in the ground and surface pool water toward the interior of the bog (14002, 13009). The water pH decreases as the stream flows through the bog, but most element concentrations increase (14007, 142006).

The positive saturation indices predict that aragonite, calcite, magnesite and dolomite should precipitate from the North Bog surface and the travertine cone-CO₂ vent ground water, but not in the stream water and in the ground water upslope from

the bog. Conversely, the saturation indices predict that chalcedony and illite precipitate from the stream water and in the upslope ground water reflecting higher dissolved silica. Oversaturation of $\text{Fe}(\text{OH})_3$ in several of the water samples explains visible iron oxide deposits around several of the seeps.

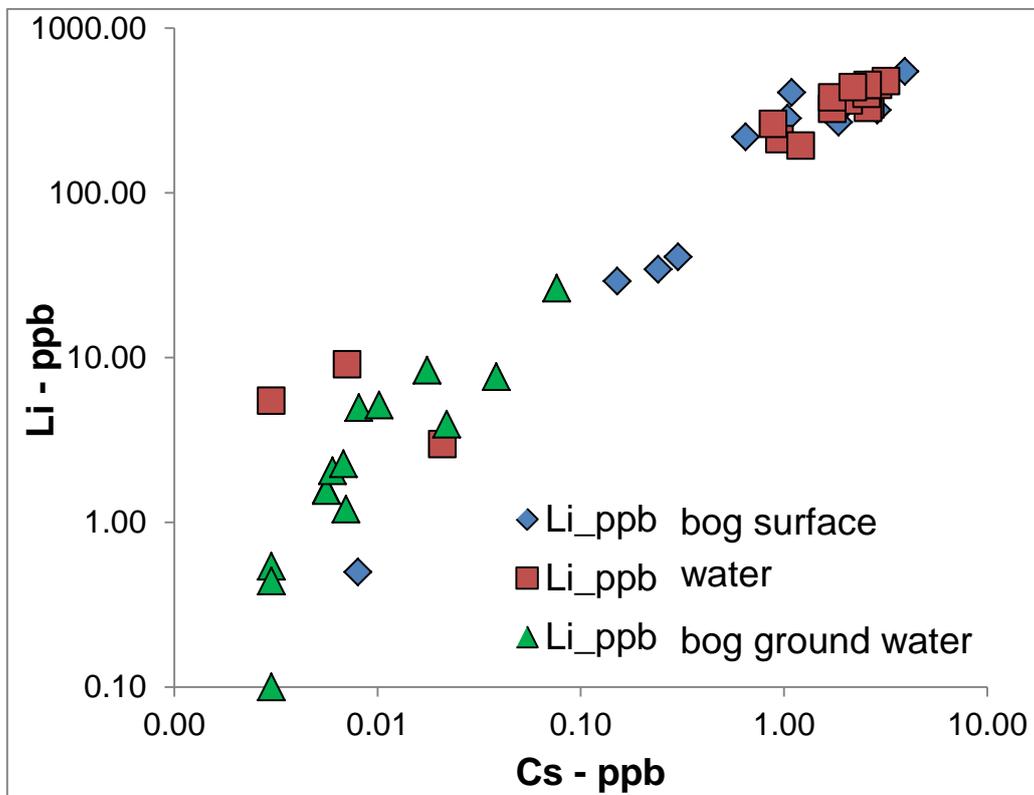


Figure 4. Scatter plot for Li and Cs in bog, stream and lake waters.

Discussion

Variations in the Nazko ground and surface water chemistry could reflect (1) cold water flowing into the bogs from the surrounding uplands (2) thermal water upwelling from bedrock (3) mixing of hot and cold water in bedrock and overburden aquifers. The low temperature of the water in the travertine cone- CO_2 vent on the edge of the North Bog compared to surface and other ground water temperatures would suggest that hot water is absent. However, the net enthalpy for the formation of carbonic acid from carbon dioxide and water is $+ 1.76 \text{ kcal mol}^{-1}$ (Faure, 1995) and the reaction is endothermic. Consequently, bubbling CO_2 through the water could absorb heat and lower the water temperature. Alternatively, water upwelling from depth could dissipate heat to cooler aquifer rocks along the flow path to the surface. While Li, B and Sr concentrations measured in the Nazko bog ground water are lower than levels reported by Pasvanoğlu (2013) they are higher than those detected in stream water. The elevated Li, Sr, Cs and Si may therefore be the soluble products of volcanic rock - ground water and/or overburden - ground water reactions whereas higher B levels could be the results on diluting more concentrated B in upwelling thermal water.

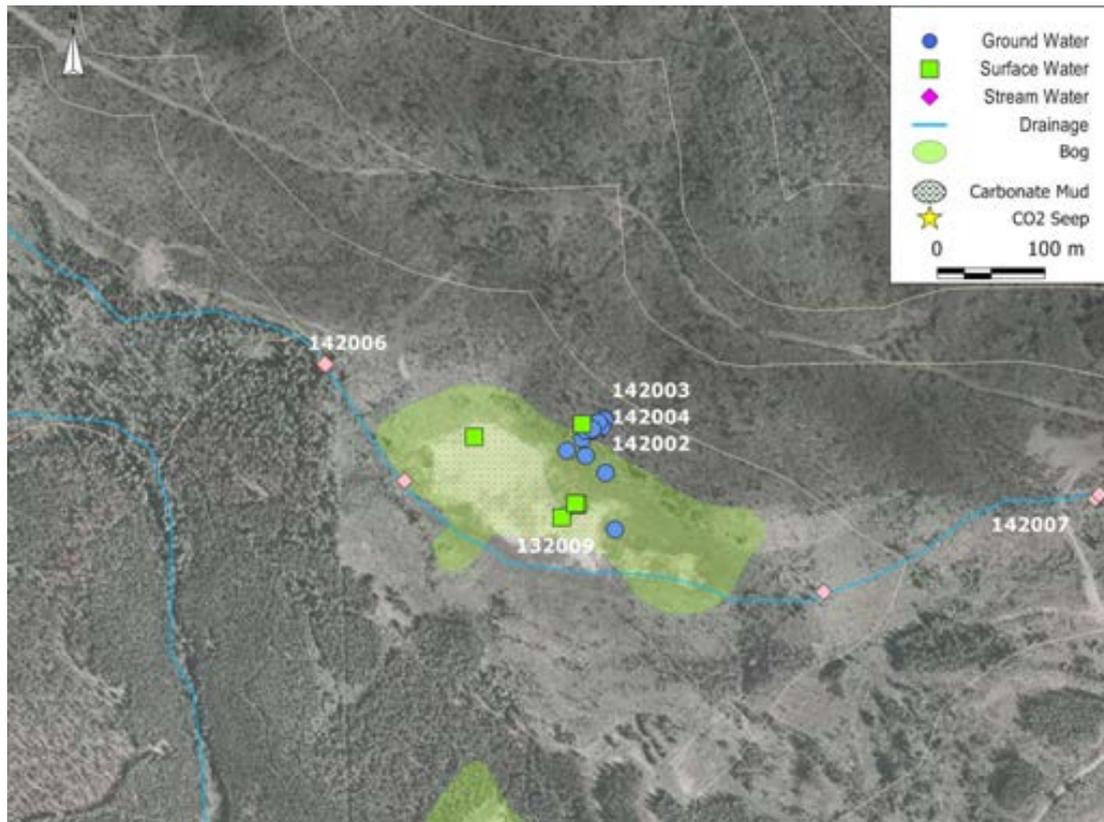


Figure 5. Water samples in the North Bog used for mineral solubility simulations.

Mineral solubility predictions are useful, but results need to be interpreted cautiously because computer thermodynamic modelling can oversimplify complex natural water systems (Leybourne and Cameron, 2007). The abundant mineral carbonate mud and travertine in the North Bog are clearly predicted by the oversaturation of calcite and aragonite carbonate most likely when the CO₂ seeping from beneath the bog reacts with higher dissolved Ca and Mg concentrations in the ground and surface pool water. While saturation indices suggest calcite forms in preference to aragonite, an X-ray diffraction analysis of rock from the wall of the travertine cone determined that the mineral is predominately aragonite (> 80 percent). A higher temperature and a faster carbonate precipitation rate favour formation of aragonite rather than calcite (Railsback, 2010). Water temperature can also be predicted from silica saturation assuming that SiO₂ is in equilibrium with the water. Based on the North Bog saturation indices chalcedony is a probable SiO₂ mineral and the equation proposed by Pasvanoğlu (2013) for predicting temperature from chalcedony equilibrium is:

$$\text{Log SiO}_2 = 4.69 - (1.32/t^{\circ}\text{C} + 273.15)$$

The SiO₂ geo-thermometer temperatures listed in Table 2 are clearly much higher than those actually measured in the water and are likely unrealistic since only trace amounts of quartz were detected in travertine samples by x-ray diffraction analysis. However, the predominance of aragonite in the travertine and the higher Si

content of the water suggest that higher water temperatures may have existed in the past.

One possible source for the Ca and Mg may be calcium carbonate in vesicular basalt outcropping near streams draining into the bog. Higher Ni and Fe in the travertine cone-CO₂ vent and nearby ground water could also be a reflection of weathered basalt bedrock or glacial sediment. A geochemical survey by Jackaman and Sacco, 2014 found that the till north west of the North Bog has a higher Ni background.

Conclusions

Higher Li, B, Sr in bog waters and existence of CO₂ seeps may be geochemical indicators for deeper geothermal activity although trace element concentrations are lower than normal for thermal springs. The detected element concentrations may reflect aquifer rock-water reactions and mixing of cool and warm waters. Travertine and calcium carbonate organic mud deposits form where high concentrations of dissolved Ca and Mg in bog waters reacts with CO₂. The travertine in the Nazko bogs is predominantly aragonite suggesting that the carbonate was deposited from warm water. A source for the elevated Ca, Mg, Fe and Ni in bog ground water may be weathered basalt bedrock and/or till. A SiO₂ geo-thermometer based on chalcedony solubility suggests that in the past bog water temperatures could be higher.

Table 1. Median & range for analytes in ground water (GW) and surface water (SW) samples from the North and South Bogs and surrounding area.

Analyte	Median GW	Median SW	Range GW	Range SW
pH	6.53	7.76	5.85 - 7.03	6.58 - 9.06
Temp °C	13.5	14.5	5.9 - 15.3	7.2 - 23.0
Alk. ppm	2200	140	55 - 3000	60 - 3000
TDS	2490	205	285 - 3380	2 - 3080
CO ₂ ppm	300	40	150 - 750	3 - 850
Al ppb	1.00	3.00	0.5 - 14.2	0.5 - 49.3
As ppb	0.25	0.49	0.05 - 2.56	0.05 - 0.85
B ppb	343	13	12 - 637	5.4 - 430
Ca ppm	218	34	43 - 383	6 - 358
Co ppb	0.134	0.07	0.05 - 6.73	0.05 - 0.44
Fe ppb	106	65	30 - 5240	30 - 1290
Li ppb	327	7.7	3 - 475	0.2 - 547
Mg ppm	239	18	23 - 393	5 - 390
Na ppm	250	10.4	6 - 412	6.2 - 311
Ni ppb	0.8	0.3	0.4 - 44.0	0.24 - 6.73
Rb ppb	39.6	4.2	2.8 - 52.4	1.4 - 56.1
Si ppm	13.7	13.4	6.89 - 18.7	6.58 - 18.5
Sr ppm	7.53	0.41	0.24 - 15	0.05 - 15.9

Table 2. Chemistry and mineral saturation indices for ground, surface pool and stream water sites in the North Bog. Ground* indicate the chemistry of the travertine cone-CO₂ vent water. HCO₃⁻ ppm = ppm CaCO₃. Temp. °C is calculated for chalcedony equilibrium by $\text{Log SiO}_2 = 4.69 - (1.32/t^{\circ}\text{C} + 273.15)$ (Pasvanoğlu, 2013)**

Analyte	13009	14006	14007	142002	142004	142003
Type	Pool	Stream	Stream	Ground	Ground*	Ground
pH	7.8	7.14	8.12	6.5	6.37	5.76
Temp. °C	19.3	14.3	11.2	5.8	5.9	11.26
Temp. °C**	35.2	67.6	47.6	30.6	27.5	66.9
HCO ₃ ⁻ ppm	1590	375	123	2670	2410	249
Al ppb	0.5	8.5	2.12	1.1	0.5	30.7
Ca ppm	90.8	65.1	25.2	231	235	47.1
Mg ppm	213	42.6	11.9	306	239	26.3
Fe ppb	65	6390	15	1750	3920	15
Ni ppb	0.34	2.62	0.26	37.3	44.0	12
B ppb	234	44	21	429	343	34
Li ppb	283	26.4	2.27	450	323	9
Si ppm	10.4	21.6	14.0	9.26	9.63	21.3
Sr ppm	3.6	1.05	0.149	8.05	9.37	0.278
SO ₄ ppm	1.0	1.00	4.0	19.0	18.0	10.3
<i>Aragonite</i>	1.02	-0.27	-0.15	0.42	0.04	-1.97
<i>Calcite</i>	1.17	-0.12	0.01	0.57	0.18	-1.82
<i>Chalcedony</i>	-0.14	0.24	0.08	-0.12	-0.04	0.27
<i>Dolomite</i>	2.99	-0.23	-0.17	1.19	0.49	-0.45
<i>Fe(OH)₃</i>	2.0	4.1	1.91	3.04	3.93	0.52
<i>Illite</i>	-2.05	2.85	0.02	0.06	3.23	1.58
<i>Magnesite</i>	1.26	-0.65	-0.71	0.08	-0.19	-2.46

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