

Stable Isotope and Chemical Composition of Groundwater Associated with Sodium Sulphate Deposits, Southern Saskatchewan

L.I. Kelley, J.J. Smith¹, and C. Holmden¹

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The origin of Saskatchewan's sodium sulphate deposits is not well understood. Most authors ascribe a genetic role to the springs and seeps that are ubiquitous on the periphery or in the bed of most of the alkaline lakes associated with economic or potentially economic resources of sodium sulphate. Although water from the springs and seeps is generally considered potable, it typically contains 1000 to 5000 parts per million (ppm) of total dissolved solids (TDS). Na⁺ and SO₄⁻ are typically the most abundant dissolved ions. Potential sources for the springs include: recent meteoritic water or Pleistocene glacial meltwater traveling through surficial (glacial) aquifers; connate water or deeply circulating water in Cretaceous or deeper formations, possibly modified during ascent; and overland flow of meteoric water and surface leaching of the surrounding terrain.

The focus of this season's field work was to assess the nature of the groundwater that carries ions into these systems by using major ion chemistry and hydrogen and oxygen isotopes. This work is seen as a preliminary step in a multi-year project aimed at developing a model for the genesis of sodium sulphate deposits in southern Saskatchewan.

Springs and seeps at six locations with known sodium sulphate reserves were sampled. Preliminary hydrogen and oxygen isotope results indicate that the groundwater that emanates from the springs is from shallow aquifers that are not hydrologically connected to Paleozoic strata. The data don't discriminate as to whether the groundwater is from Recent meteoric waters, Pleistocene glacial meltwater, or Cretaceous connate water. Major ion chemistry suggests that the groundwater that discharges sodium sulphate deposits is from pre-Wisconsinan or Cretaceous aquifers.

1. Geologic Setting

Natural sodium sulphate deposits occur in many shallow alkaline lakes in southern Saskatchewan, northwestern North Dakota, northeastern Montana, and east-central Alberta. The deposits are generally recognized to be post-glacial accumulations in internally drained basins (Tomkins, 1954; Last and Schweyen, 1983; Broughton, 1984; Last and Slezak, 1987).

Southern Saskatchewan and adjacent parts of Montana, North Dakota, and Alberta are underlain by a thick (in excess of 5000 m) sequence of nearly-horizontal sedimentary rock. The Paleozoic section consists predominantly of carbonates and evaporites, whereas the Mesozoic and Cenozoic rocks are dominantly clastic sedimentary rocks. The unconsolidated glacial, glaciofluvial, and glaciolacustrine sediment that mantles the bedrock is over 300 m thick in places, and averages about 100 m thick in southern Saskatchewan (Simpson, 1997). During deglaciation, meltwater carved numerous channels and spillways in the glacial sediment.

Collapse structures caused by the dissolution of Paleozoic evaporites, most notably from the Devonian Prairie Evaporite Formation, have disrupted the horizontal structure over much of southern Saskatchewan (Christiansen, 1967a; Broughton, 1988). Furthermore, the bedrock surface was strongly modified by erosion that took place prior to the onset of Wisconsinan glaciation (Christiansen, 1967b). Witkind (1952), Grossman (1968), and Rueffel (1970) noted that alkali lakes often occupy surface depressions that overlie pre-glacial valleys.

2. Economic Geology

Natural sodium sulphate has been produced from saline lakes and lake bed deposits in Saskatchewan since 1918. More than 20 companies have produced sodium sulphate from at least 10 different deposits (Tomkins, 1954). Currently, three companies produce commercial sodium sulphate from four deposits. Two other Saskatchewan companies produce sodium sulphate as a raw material for the production of potassium sulphate. Sodium sulphate is used in laundry powders, carpet fresheners, glass-making, kraft paper production, and textile manufacturing.

Sodium sulphate accumulations are of three types:

- 1) In solution as lake brine.
- 2) As beds of intermittent crystal, deposited from the brine in autumn as the ambient temperature cools. Intermittent crystal may re-dissolve the following

¹ Department of Geological Sciences, University of Saskatchewan, 114 Science Place, Saskatoon, SK S7N 5E2.

spring, or be covered by clastic material carried by spring runoff, and protected from re-dissolving.

- 3) As permanent beds of mirabilite mixed with other salts, clastics, and organic sediment. The permanent crystal beds are typically 1 to 5 m thick, but exceed 30 m in a few deposits.

Most of the active Saskatchewan operations pump brine into crystallization ponds, where the brine is concentrated by evaporation over the summer. In the fall, as the ambient temperature cools, Glauber's salt (the commercial name for mirabilite) crystallizes and accumulates on the pond liner. The pond is then drained of any remaining liquid, and the Glauber's salt is harvested from the pond. At some locations, intermittent and permanent crystal is harvested using a dredge-mounted excavator. Solution mining has been tried in the past, but is not currently being used. Figure 1 schematically illustrates the three types of sodium sulphate accumulations and the three mining methods.

Value-added processing of sodium sulphate has increased interest in the resource base in the last few years. Two Saskatchewan firms (Big Quill Resources and Potassium Sulphate Company Alsask, Inc.) combine sodium sulphate with potash to produce potassium sulphate, mainly for use as fertilizer for chloride sensitive crops. Both firms also produce high purity potassium sulphate, which has a wide variety of industrial uses. Airborne Technologies, the parent company of Saskatchewan sodium sulphate producer Ormiston Mining and Smelting, recently announced plans to produce sodium bicarbonate using sodium sulphate as a feedstock.

3. Previous Work

a) Saskatchewan Deposits

Cole (1926) and Tomkins (1954) prepared the most comprehensive studies of Saskatchewan's sodium sulphate resource base. These two papers are standard references for the industry. They document drill testing of deposits and estimation of ore reserves. Various papers by Last and colleagues (Last and Schweyen, 1983; Last, 1984; Last and Slezak, 1987) contain important ideas regarding deposit genesis.

b) Origin of Sodium Sulphate Deposits

McIlveen and Cheek (1994) summarized the controversial and far-ranging mechanisms for genesis of these deposits. At issue are the ultimate source of Na^+ and SO_4^{2-} ions and the nature of the solutions that carry these ions into the internally drained post-glacial basins that the deposits occupy. Potential sources of ions include:

- 1) till containing abundant smectite with exchangeable sodium,
- 2) Cretaceous or older rocks containing bentonite with exchangeable sodium,
- 3) connate water from marine rocks, and
- 4) Paleozoic evaporites.

Potential agents for transport of ions include:

- 1) meteoric waters flowing on the surface,
- 2) shallow circulating groundwater of Recent (meteoric) or Pleistocene (glacial) origin which discharges into the basins via springs and seeps, and
- 3) deeply circulating groundwater or connate water which reaches surface via fractures and discharges in springs and seeps.

Ricketts (1888), in a study of Wyoming alkali lakes, noted a correlation between the presence of springs and accumulation of salts. He pointed out that basins without springs contained only a thin crust of alkali. Wells (1923) hypothesized that oxidation of pyrite to form sulphuric acid, which in turn broke down "basic oxides" (feldspar?) in granitic rocks (e.g. boulders in drift) accounted for the SO_4^{2-} and Na^+ , respectively.

Cole (1926) concluded the most likely source of sodium ions was bentonite. Bentonite is

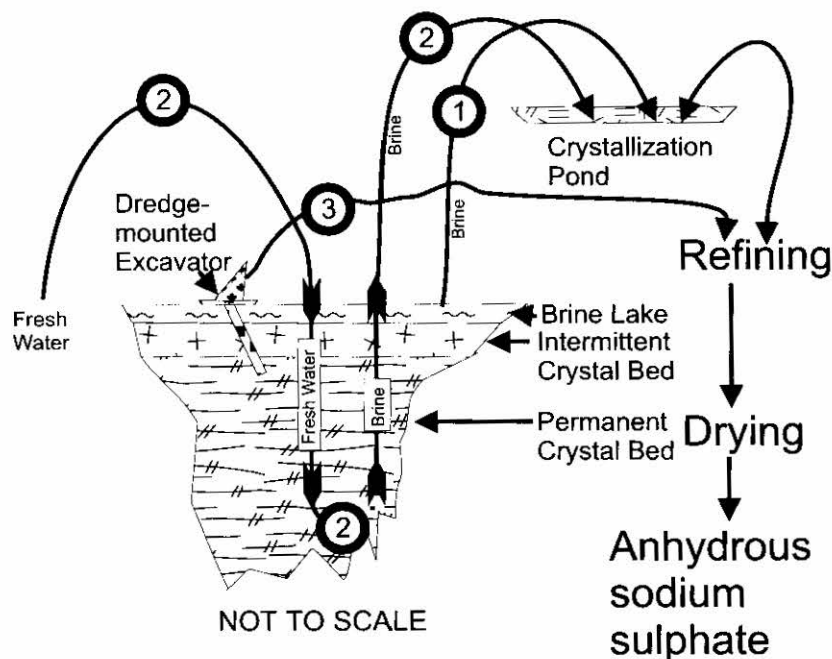


Figure 1 - Schematic cross-section of idealized Saskatchewan sodium sulphate deposit. Mining methods illustrated are: 1) Evaporative concentration of lake brine in crystallization pond, followed by precipitation of crystals of Glauber's salt (mirabilite) as the water cools in autumn; 2) Solution mining of thick crystal bed. The brine return is treated as in 1; and 3) Dredging of lake bottom crystal beds.

widespread in the Cretaceous and Tertiary strata of southern Saskatchewan and contains abundant exchangeable sodium. Cole (1926) believed that meteoric water would contain dissolved CaSO_4 , because gypsum (selenite) crystals are common in prairie drift. Cole (1926) observed that the matrix of locally derived tills would be bentonitic, reflecting their bedrock source. He demonstrated in a laboratory experiment that a CaSO_4 aqueous solution became enriched in Na^+ when in contact with swelling (sodium) bentonite, while distilled water did not gain appreciable sodium upon similar treatment.

Cole (1926) also mentioned connate water from deeply buried marine deposits as a hypothesis but he dismissed it because chloride would be expected to be the dominant ion in connate water, rather than sulphate.

Cole (1926) observed that many lake basins were fed by springs or seeps in or around the lake bed, but he rejected the idea that the springs were a causative agent. Witkind (1952) used evaporative concentration of salt-laden artesian (spring) water to explain the origin of sodium sulphate deposits of Montana and North Dakota. Tomkins (1954, p50) suggested a genetic link between the springs and the sodium sulphate deposits. He calculated that groundwater containing 1,000 ppm sodium sulphate flowing into a basin at 100 gallons per minute could produce a 3 million ton deposit in 12,000 years. Most subsequent workers in some way acknowledged a link between springs and deposit genesis, except for Rueffel (1970) who, with little convincing evidence, embraced an overland flow model.

Grossman (1968) demonstrated the coincident alignment of northern Great Plains sodium sulphate deposits with major structural features in the Devonian

Prairie Evaporite. He invoked deeply circulating water that entered the upturned flanks of aquifers in the Rockies, dissolving salt from the Prairie Evaporite on its way to discharge points where the sedimentary rocks onlap crystalline rocks at the western margin of the exposed Canadian Shield. Solution-collapse tectonics would provide leakage conduits for this water in locations west of the Shield margin. Freeze-separation of sodium sulphate crystals followed by periodic flushing was invoked to explain the purity of the deposits and relative absence of halite and other salts.

Last and colleagues (Last, 1984; Last and Schwyen, 1983) investigated the sedimentology and geochemistry of saline lakes in detail. They discussed the importance of groundwater in supplying salts to the basins but pointed out that the groundwater contribution had not been adequately documented (Last and Slezak, 1987). They also dismissed Paleozoic evaporites as a source of ions on the basis of incompatible brine chemistry.

4. Methods

A total of fourteen water samples were collected from springs, seeps or shallow flowing (artesian) wells near the shores of six alkali lakes (Figure 2) with measured sodium sulphate resources. Temperature, specific gravity, and pH were measured at each sample site. In several cases, a spring orifice could not be visually identified in marshy ground. Prospecting with a thermometer usually led to defining a discrete point of discharge.

Water samples for major dissolved ions were collected in two 250 ml Nalgene™ bottles and analysed in the laboratory of Big Quill Resources. Duplicates of two of the fourteen samples were analysed by another laboratory for verification. Water samples for δD and $\delta^{18}\text{O}$ analyses were also collected in 250 ml Nalgene bottles and analysed at the University of Saskatchewan Isotope Laboratory.

5. Results

a) Major Ion Chemistry

Table 1 presents major ion chemistry results for groundwater samples. The range of TDS concentrations was 900 to 5700 ppm with the dominant ion species in most of the water samples being Na^+ and SO_4^{2-} . Mg^{++} and HCO_3^- were slightly higher in a few samples.

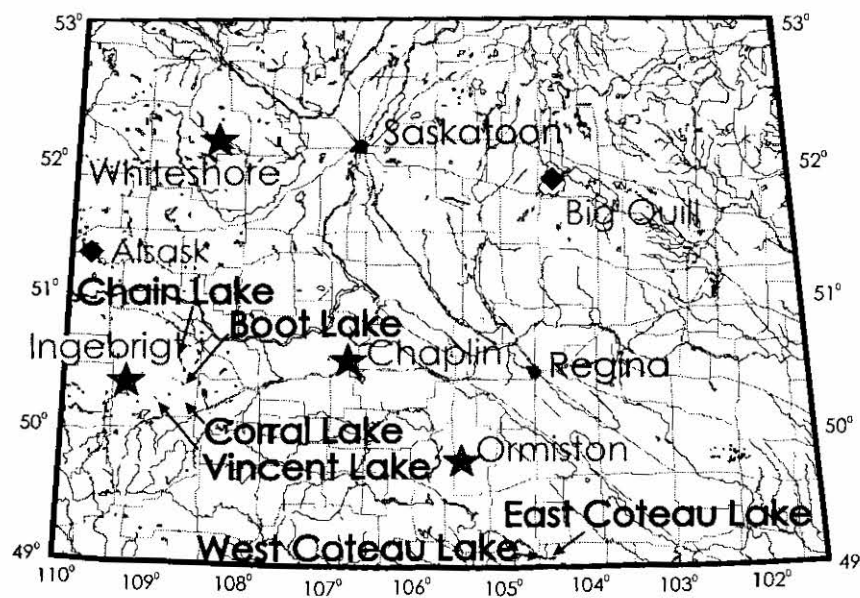


Figure 2 – Locations of sodium sulphate deposits sampled in this study are in bold text; ☆=sodium sulphate mine/plant; and ◇=potassium sulphate plant.

Table 1 - Major ion chemistry results; dup.=duplicate; and Tr=trace.

Sample No.	Deposit	Location	Latitude	Longitude	Major ions, expressed in parts per million									Field Measurements			
					Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	SO ₄ ⁻	Cl ⁻	HCO ₃ ⁻	CO ₃ ⁻	TDS	Lab pH	Field pH	Specific Gravity	Temperature
LK-98-006	Corral Lake	Corral-1	50,10,40N	108,38,08W	100	100	Tr	0	100	0	500	0	900	7.1	7.5	0.998	15.0
LK-98-009	Chain Lake	Chain-1	50,29,56N	108,40,31N	100	100	100	Tr	300	0	600	0	1200	7.5	7.5	0.992	7.5
LK-98-010	Chain Lake	Chain-2	50,31,10N	108,41,45W	100	100	400	0	800	0	600	0	2000	7.3	7.4	0.992	9.0
LK-98-012	Chain Lake	Chain-3	50,30,11N	108,41,27W	100	100	100	0	500	0	500	0	1300	7.2	7.6	1.000	7.0
LK-98-014	Chain Lake	Chain-3 (dup.)	50,30,11N	108,41,27W	79	120	92	5.1	487	15	508	<1	1310	7.6	7.6	1.000	7.0
LK-98-016	Boot Lake	Boot-1	50,17,29N	108,44,01W	100	100	100	Tr	600	100	600	0	1600	7.3	7.1	0.998	6.5
LK-98-018	Boot Lake	Boot-2	50,17,26N	108,44,29W	200	500	400	0	3600	200	800	0	5700	7.2	7.3	0.998	10.0
LK-98-021	Vincent Lake	Vincent-1	50,13,10N	108,55,42W	100	0	800	0	1500	300	1300	0	4000	7.7	7.6	1.000	8.0
LK-98-023	Vincent Lake	Vincent-2	50,13,05N	108,55,57W	100	0	700	0	1300	300	1300	0	3700	7.5	7.7	1.002	14.0
LK-98-025	Vincent Lake	Vincent-3	50,13,49N	108,55,51W	100	100	Tr	0	300	0	400	0	900	7.4	7.4	1.000	12.0
LK-98-026	Vincent Lake	Vincent-4	50,13,47N	108,57,23W	100	100	800	0	2400	200	1200	0	4800	7.3	7.4	1.000	8.0
LK-98-028	Vincent Lake	Vincent-4 (dup.)	50,13,47N	108,57,23W	108	42	1360	8	2140	199	1070	<1	4940	7.6	7.4	1.000	8.0
LK-98-030	West Coteau Lake	Coteau-1	49,03,27N	104,32,35W	100	100	100	0	200	Tr	600	0	1100	7.5	7.4	1.000	7.2
LK-98-034	West Coteau Lake	Coteau-2	49,03,09N	104,32,26W	100	Tr	400	0	300	Tr	800	0	1600	7.4	7.4	1.000	8.0
LK-98-036	East Coteau Lake	Coteau-3	49,02,30N	104,26,27W	100	100	400	0	1000	Tr	800	0	2000	7.2	7.0	1.000	6.0
LK-98-038	West Coteau Lake	Coteau-4	49,01,52N	104,31,27W	100	100	400	0	800	Tr	900	0	2500	7.5	7.4	1.000	8.0

b) Hydrogen and Oxygen Isotopes

Table 2 presents δD and δ¹⁸O results for groundwater samples. The data are plotted on Figure 3 and Figure 4 along with representative Saskatchewan data for lakes, meteoric water, shallow groundwater, and deep groundwater for comparison. The data from this study plot within the field of shallow Saskatchewan groundwater.

presented here do not shed light on whether the source of water that feeds the springs associated with the sodium sulphate deposits is Cretaceous connate water, trapped glacial meltwater, or Recent meteoric water.

Previous workers have noted fluctuations in major ion chemistry through seasonal changes and during periods of drought or high rainfall. Isotopic compositions may vary seasonally as well. Repeated sampling should be conducted to verify the quantity of seasonal fluctuations.

6. Discussion

The hydrogen and oxygen isotopic composition of meteoric water over the Williston Basin has remained relatively constant for the past 110 million years (Holmden *et al.*, 1997). Because of this, the data

The data presented here suggest that the groundwater that discharges through springs near alkaline lakes in southern Saskatchewan has no affinity to deep saline waters (e.g. dissolved salts from the Prairie Evaporite as described by Grossman, 1968).

Table 2 - Hydrogen and oxygen isotope results. Reproducibility of δD and δ¹⁸O is better than ±2.5 permil and ±0.2 permil (1σ) respectively.

Sample No.	Deposit	Location	Latitude	Longitude	δD	δ ¹⁸ O
LK-98-007	Corral Lake	Corral-1	50,10,40N	108,38,08W	-162	-21.4
LK-98-008	Chain Lake	Chain-1	50,29,56N	108,40,31N	-162	-21.4
LK-98-011	Chain Lake	Chain-2	50,31,10N	108,41,45W	-160	-21.3
LK-98-013	Chain Lake	Chain-3	50,30,11N	108,41,27W	-166	-20.6
LK-98-015	Boot Lake	Boot-1	50,17,29N	108,44,01W	-164	-20.9
LK-98-017	Boot Lake	Boot-2	50,17,26N	108,44,29W	-166	-20.2
LK-98-020	Vincent Lake	Vincent-1	50,13,10N	108,55,42W	-158	-18.6
LK-98-022	Vincent Lake	Vincent-2	50,13,05N	108,55,57W	-152	-18.0
LK-98-024	Vincent Lake	Vincent-3	50,13,49N	108,55,51W	-164	-20.5
LK-98-027	Vincent Lake	Vincent-4	50,13,47N	108,57,23W	-160	-19.5
LK-98-032	West Coteau Lake	Coteau-1	49,03,27N	104,32,35W	-139	-15.8
LK-98-033	West Coteau Lake	Coteau-2	49,03,09N	104,32,26W	-156	-17.9
LK-98-035	East Coteau Lake	Coteau-3	49,02,30N	104,26,27W	-156	-17.8
LK-98-039	West Coteau Lake	Coteau-4	49,01,52N	104,31,27W	-152	-17.2

McMonagle (1987) presented chemical and isotope data for Saskatchewan groundwater. She classified aquifers as follows:

- 1) surficial aquifers - generally 15 m deep or less;
- 2) intertill aquifers;
- 3) Empress Group aquifers; and
- 4) Bedrock aquifers, including:
 - a) undifferentiated Frenchman, Battle, Eastend, and Whitemud formations,
 - b) Judith River Formation,
 - c) Ribstone Creek member (Judith River Formation).

Figure 5 is a plot of Na⁺/Ca⁺⁺ vs. SO₄⁼/HCO₃⁻ for samples from this study and those for various shallow Saskatchewan aquifers. Our data show a similar

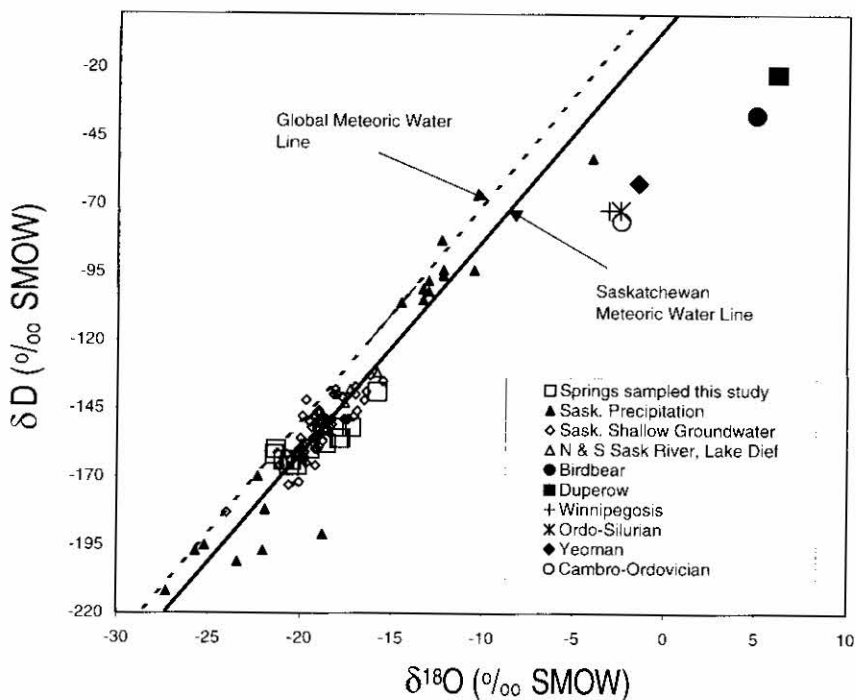


Figure 3 - δD vs. $\delta^{18}O$ for study data. Representative Saskatchewan data for comparison is from McMonagle (1987) and Rostron et al. (1998). The Saskatchewan Meteoric Water Line is from average isotopic compositions for precipitation.

distribution to the Ribstone Creek and Empress Group waters. The groundwater sampled in our study appears to be enriched in Na^+ relative to groundwater from the intertill aquifer, but is relatively less sodic than that from the Judith River aquifer. One interpretation is that the waters reported here formed from the mixing of deeper water, as represented by the Judith Creek data, with water from drift aquifers.

7. Conclusions

The stable isotope data presented here suggests that the spring systems that currently supply ions to alkali lakes in southern Saskatchewan are not hydraulically connected to deep (Paleozoic) saline aquifers.

Comparison of ion ratios for data from this study with data of McMonagle (1987) suggests that groundwater sampled from springs and seeps near sodium sulphate deposits may be at least partly from a pre-Wisconsinan source, perhaps mixed with shallower groundwater during ascent.

8. Acknowledgments

All of the private landowners who allowed us access for sampling were generous in sharing local knowledge. Carl Lambert and Peter Haugen of Big Quill Resources facilitated major ion chemical analyses. Kevin Treptau ably and cheerfully assisted the senior and second authors with fieldwork.

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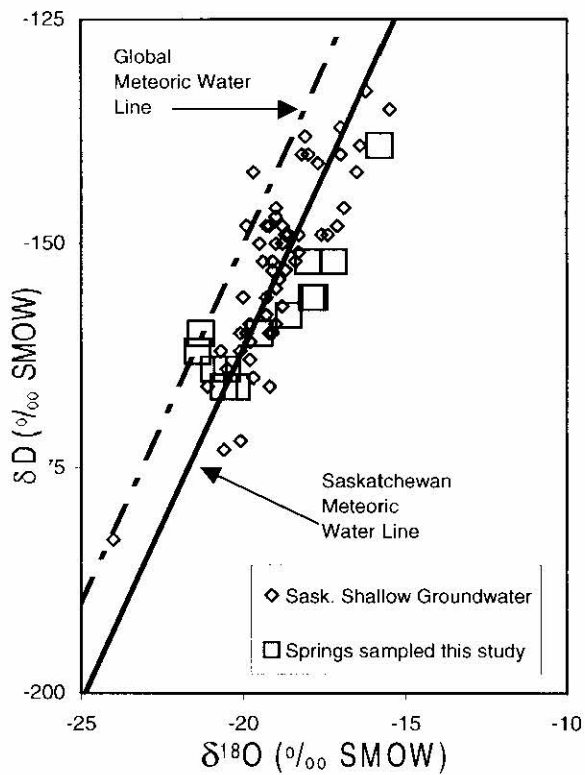


Figure 4 - Essentially an enlargement of Figure 3, this graph compares δD vs. $\delta^{18}O$ for study data with data compiled by McMonagle (1987) for Saskatchewan shallow (<200 m) groundwater.

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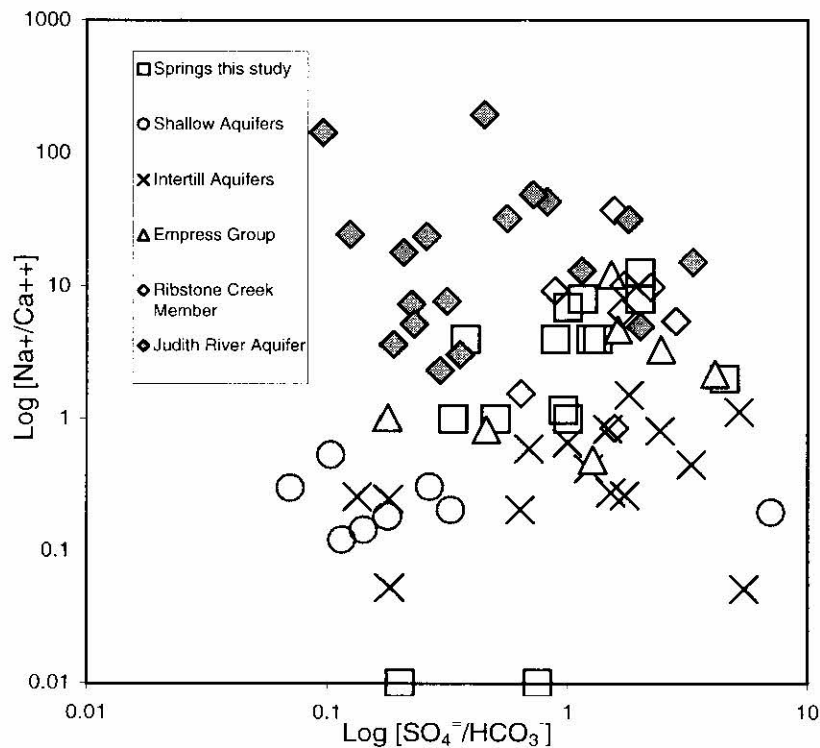


Figure 5 - Graph of Na^+/Ca^{++} vs. SO_4^{2-}/HCO_3^- for samples from this study and data for various shallow (<200 m) Saskatchewan aquifers from McMonagle (1987).

