

GEOCHEMISTRY AND SOURCE OF THE SARATOGA SPRINGS¹

by

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INTRODUCTION

The City of Saratoga Springs is situated in the lowlands southeast of the flanks of the southeastern Adirondack foothills. The crystalline rocks of the Adirondacks are in contact with the overlying Paleozoic sediments along an early Cambrian unconformity and along faults. The faults are mostly high angle, typically trending north-northeast, and normal, mostly down-dropped to the east. Faulting was probably associated with downwarping of the Laurentian continental margin during Late Ordovician collision with the Taconian volcanic arc, though this may have involved reactivation of earlier faults. The McGregor fault, and its southerly branch of interest that runs through downtown Saratoga Springs, hosts a remarkable collection of springs (actually now all drilled wells¹) that tap a carbonate aquifer in the Beekmantown Group at depths ranging from 75 to 300 m. All of the original springs and producing drilled wells are on the east side of the Saratoga Springs-McGregor fault where shale cap rock exists. To the west of the fault the Beekmantown Group carbonates are exposed at the surface, and no waters of the Saratoga type are found.

Saratoga Springs, New York is 300 km north of New York City and is situated on the western margin of the Hudson Valley. Streams within the drainage basin around Saratoga Springs generally flow towards the east and southeast, more or less parallel to the regional dip towards the Hudson River (Fish, 1881; Kemp, 1912). Subsurface water flow follows the dip of the strata, apparently paralleling overall surface water flow (Fish, 1881). Not surprisingly, Saratoga Springs experiences four distinct seasons throughout a year. Summer temperatures can reach 40°C in the summer and can drop below -30°C in the winter. Despite this large temperature range, early analyses of the springs indicated that the temperature and flow of the springs is practically constant over time (Fish, 1881), an observation that we can partially confirm.

The rising of the spring waters through natural fractures and drilled wells is driven principally by rise of CO₂ bubbles degassing from the rising water, though in some cases there is also a significant artesian head. Some wells, if turned off, apparently have to be primed to get them to start flowing again (e.g., the "water seal" of Kemp, 1912). CO₂ degassing causes the waters to become supersaturated with respect to calcite, and precipitation gradually seals off the water conduits. The fact that natural springs were present at least in the 1700's hints at recent fault movement opening new fractures.

HISTORY OF THE SARATOGA SPRINGS

The Iroquois Indians who lived in the Saratoga region drank water from the Big Medicine Spring to cure their ailments, and in 1767 introduced these springs to European settlers who further proclaimed the therapeutic effects of the spring water (Kemp, 1912). Many believed in and sought the curative powers of the spring waters, which doctors and others claimed to be useful in treating gastrointestinal, dermatological, and other problems (Fish, 1881; Siegel, 1996). The fame of the springs increased after the Revolutionary War, with visits from various generals and dignitaries including George Washington and Alexander Hamilton (Fish, 1881; Kemp, 1912; Davis and Davis, 1997). Many of the springs and wells that currently flow were identified and named between 1792 (Congress) and 1905 (Hathorn 3).

The first documented chemical analyses of the mineral waters occurred in 1809 by Valentine Seaman, who wrote his doctoral paper, *Dissertation upon the Mineral Waters of Saratoga*, on the possible origins of the springs (in Davis and Davis, 1997). Beginning in about 1912, the first formal studies of the health effects of the spring waters were done by Dr. Simon Baruch who focused on a program of cardiac therapy (Informational sign near the Geyser Mineral spring, Saratoga Springs, 1999). Dr. Baruch and his research were key players in the development of the spas (Saratoga Spa Park Administration brochure, 1999).

During the growth and development of the Saratoga region, Saratoga was nicknamed the Queen of Spas, (Informational sign near the Geyser Mineral spring, Saratoga Springs, 1999). Spas, bathhouses, drinking saloons, and various other establishments were erected to allow visitors and members of the community access to the spring

¹ The term "springs" will be used herein though all currently flowing Saratoga mineral waters are in fact drilled wells.

waters. Saratoga Springs mineral and fresh waters were bottled and sold widely to the public, which inevitably brought many of the visitors. Geysers, Hathorn 3, and Coesa mineral springs were bottled from 1935 to 1970, and State Seal spring was also bottled and sold as fresh, non-carbonated water (Saratoga Springs Park Administration brochure, 1999). Both carbonated and non-carbonated versions of Saratoga Springs waters are still bottled and found in stores today. Only one bottling plant and one bath house currently remain in Saratoga Springs.

During the early 1800's most of the natural springs were altered by the drilling of wells as deep as 300 m to increase flow (Kemp, 1912; Siegel, 1996; Davis and Davis, 1997). By 1880, over 200 mineral water wells had been drilled for carbon dioxide gas production alone (Saratoga Springs Park Administration brochure, 1999). Over 150 million gallons (570,000 m³) of mineral water were removed each year during the period of maximum expansion of the spas and for carbon dioxide production between 1892 and 1904. As a result the aquifer potentiometric surface dropped up to thirty meters (Siegel, 1996). Such severe exploitation of the springs during this time caused many of the springs to cease to flow (Davis and Davis, 1997). Since 1910, the spring waters have been protected by the State of New York as a natural resource; 163 springs and wells on one thousand acres of land were acquired by the State, and by 1912 New York State had closed all but 19 of the mineral water outlets (Davis and Davis, 1997).

THE PROJECT

Since 1996 faculty and students at Union College have been attempting to better characterize the chemical composition of the Saratoga Springs waters, to better understand the origin of the chemical characteristics of the water, and to speculate on the ultimate source of the mineral waters. This work has involved extensive sample collection and analytical programs using modern analytical instrumentation, and extensive geochemical modeling. Chemical analysis of the waters is difficult as chemical components of interest range in concentration from several parts per thousand down into the sub-parts per trillion range. Realistic modeling of the aquifer system is hampered by lack of detailed knowledge of the system and lack of the composition of the most saline mineral water end member. Nonetheless, a plausible conceptual and geochemical model has been developed and so is open to discussion.

GEOLOGY OF THE SARATOGA SPRINGS REGION

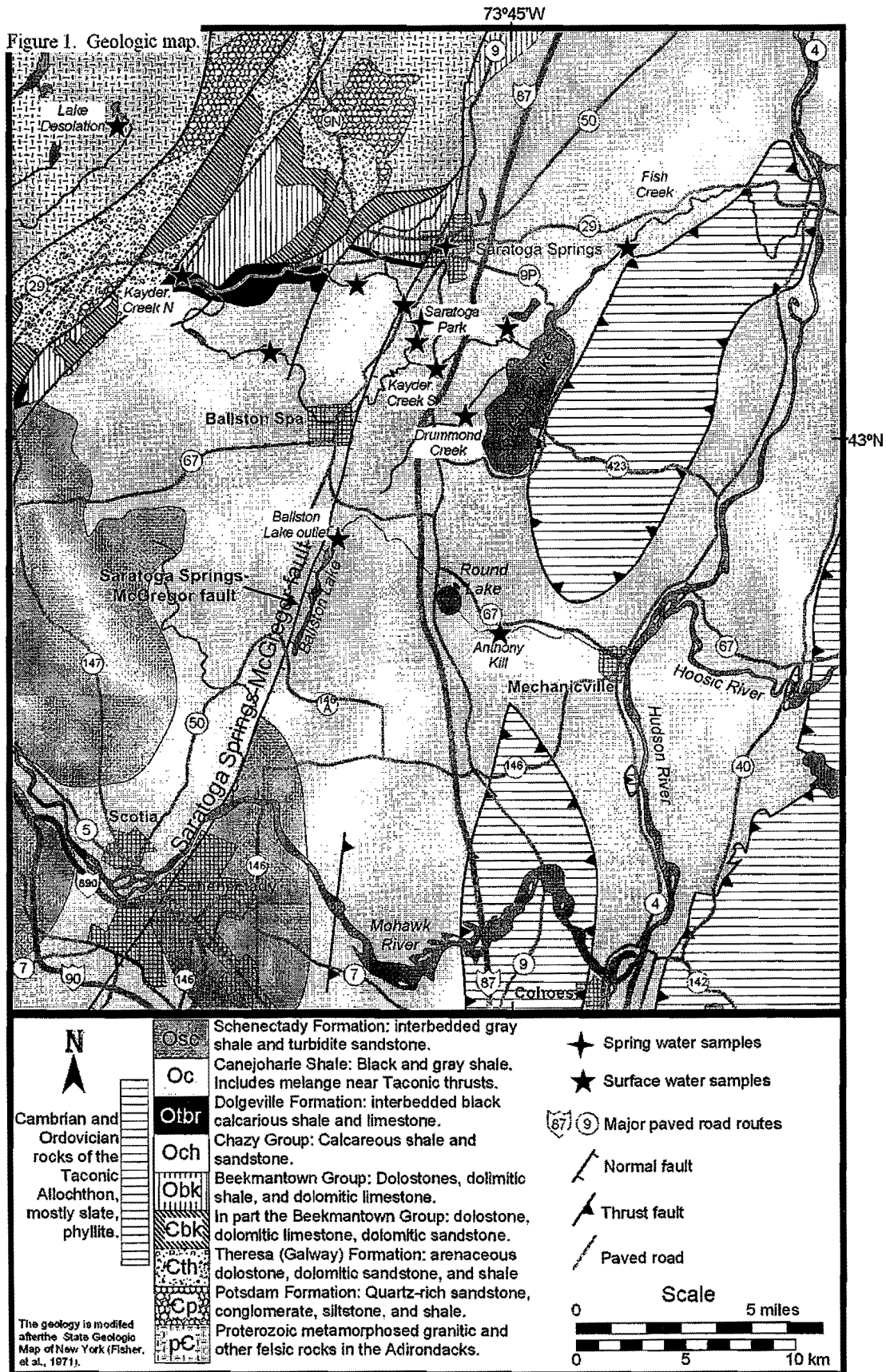
Crystalline basement rocks of the Adirondacks are exposed in the northwestern part of the map area (Figure 1). Overlying an early Cambrian unconformity are clastic rocks of the Potsdam and Theresa (Galway) Formations. These are overlain by late Cambrian and Ordovician limestones and dolomites that include the Beekmantown Group, thought to be the principal aquifer rock for the mineral spring waters. These carbonate-rich rocks are overlain by progressively more clastic-dominated rocks of the Chazy Group and Dolgeville Formations. Deepening of the sedimentary basin in the Middle and Late Ordovician (e.g., Hollocher et al., 2002) was caused by the approach of the continental margin to the Taconian volcanic arc subduction zone, with deposition of dark gray Utica (formerly Canajoharie) Shale and Schenectady Formation flysch. The Utica Shale in particular is the cap rock to the mineral water aquifer.

The city of Saratoga Springs lies along part of the Saratoga Springs-McGregor fault system, which runs from the eastern Adirondacks north of Saratoga Springs, south-southwest, sub-parallel to the Taconian deformation front. The Saratoga Springs-McGregor fault, extends from Saratoga Springs, through Ballston Spa, just to the west of Ballston Lake, and through the City of Schenectady. Its fate near the Helderberg Escarpment is unclear. It may die out (as shown in Fisher et al., 1971) or it may continue to the south beneath Silurian and Devonian sediments.

The aquifer rocks that hold the deep, carbonated spring water are the Middle Ordovician Beekmantown Group limestones and dolomites (Figure 2). These rocks crop out along the southeastern margin of the Adirondack foothills (Figure 2) and are between 30 and 200 meters below the surface in Saratoga Springs as indicated by well records, deepening to the south-southwest along the trace Saratoga Springs-McGregor fault. Kemp (1912) states that, on his survey of spring site distribution, nowhere do mineral water springs flow to the surface more than a "few hundred feet from the fault". Cushing and Ruedemann (1914) made it clear that no Saratoga-type mineral springs were found west of the fault. Putman et al. (1978), and Putman and Young (1985) stated that the carbonated spring waters are not known to occur east of Albany or in Paleozoic carbonate rocks elsewhere surrounding the Adirondack Mountains.

A 3-well pump and potentiometric surface test done in the early 1900s suggested that water in the Saratoga Springs-McGregor fault system was flowing to the north (no reference or other details provided; Putman et al., 1978). This observation, combined with the possible southern extent of the Saratoga Springs-McGregor fault system beneath Silurian and Devonian sedimentary cover, suggests a southerly source of the mineral waters.

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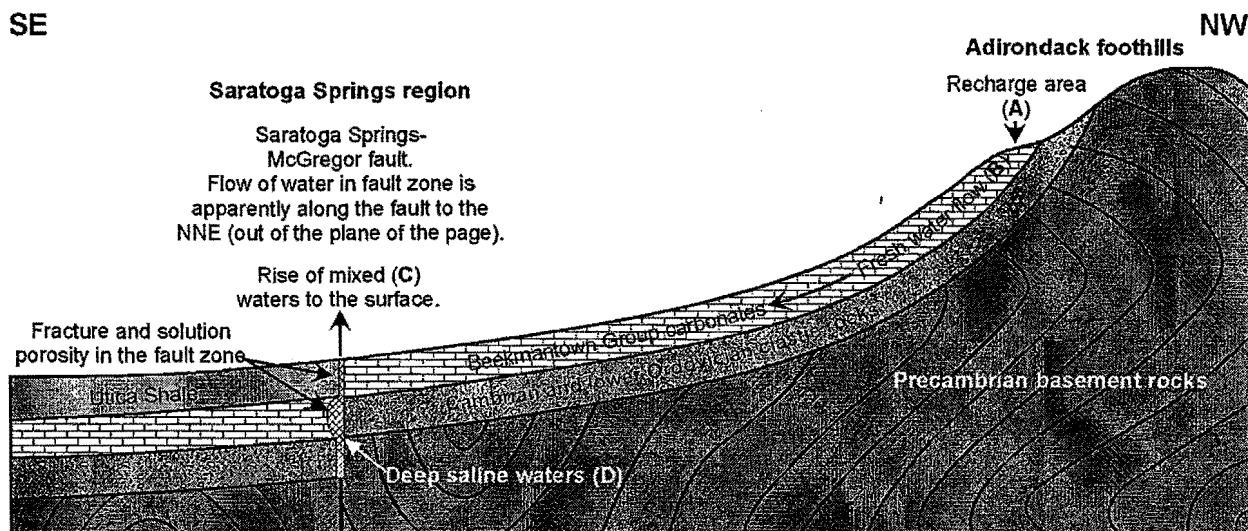


Figure 2. Schematic geologic model for the Saratoga Springs mixed waters. The most saline, carbonated, deep mineral water (model mixing end member **D**), equivalent to or more concentrated than the Hathorn spring, flows northward along solution and fracture porosity in the Saratoga Springs-McGreggor fault zone. Flow is principally in the Beekmantown Group carbonates. Surface precipitation (model mixing end member **A**) enters the aquifer with small quantities of dissolved CO_2 and flows downgradient toward Saratoga Springs. Carbonate rock dissolution and other water-rock interactions yield a hard Ca -, Mg -, and HCO_3^- -rich but K -, Na -, and Cl -poor fresh water (composition **B**). The saline and fresh waters mix to yield a density stratified system beneath Saratoga Springs in the fault zone (mixtures **C**). The mixtures are undersaturated with respect to carbonates and therefore dissolve carbonate rock and become more Ca -, Mg -, and HCO_3^- -rich. As the deep mineral water flows northward and up dip, it shallows and may start to degas. Rising CO_2 bubbles enter the overlying layer of fresher, CO_2 -undersaturated water and go back into solution. This yields a more acidic water that also dissolves adjacent carbonate rock.

Travertine deposits surround various springs, most notably in large mounds surrounding the Island Spouter and Orenda springs. Organic material on these mounds, such as leaves, twigs, and dead insects, can be quickly covered by layers of calcite. Flow of the springs tends to become constricted over time by subsurface deposition of calcite, which can cause the flow path to the surface to be permanently blocked. Periodic re-boring of wells is necessary to maintain flow.

WATER GEOCHEMISTRY

The composition of the average fresh waters sampled in this study, the average composition of three mineral spring waters, including the most saline spring, Hathorn 3, and sea water are given in Table 1. Water chemistry in general is vastly more complex than, say, the chemistry of all igneous rocks, and tables are difficult to comprehend directly. One way to get a grasp of the spring water composition is by normalizing to a familiar geological material such as seawater (Figure 3A). The mineral springs are quite different from seawater, making unlikely the old idea that the mineral springs are diluted, relatively unmodified connate sea water trapped eons ago in local rocks (Kemp, 1912). With the notable exception of Li , there seems to be a pattern of enrichment of large alkali, alkaline earth, and halogen ions compared to small ions in the spring waters compared to sea water. Interestingly, all of the chemical components in Figure 3A, except Ca , Mg , and HCO_3^- , are undersaturated with respect to all phases calculated in modeling. The tremendously high enrichment in Ba in the spring waters over ocean water is permitted by the very low sulfate content of the springs, inhibiting saturation with respect to barite.

Three of the intermediate concentration mineral spring waters have high sulfate, ~ 27 ppm, in contrast to ~ 0.2 ppm in the other intermediate springs and in all of the most saline springs (Figure 3B). The strong odor of hydrogen sulfide, the measured presence of NH_4^+ , and the relatively high concentrations of Mn^{2+} (0.1 ppm) and Fe^{2+} (~ 5 ppm) in all of the mineral spring waters indicate that they are all reducing (calculated Eh approximately -200 mV). Note that the mineral waters do not contain a concentrated, fast redox couple, so direct measurement of the water redox potential is difficult. A possible explanation of the three anomalous high sulfate mineral springs is that low sulfate mineral waters mix with sulfate-rich fresh waters soon before reaching the surface, before inorganic or bacteria-mediated reduction of sulfate can occur.

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Table 1. Average composition of fresh water and Hathorn 3 spring water. Concentrations in ppm.

	Average fresh water	Old Red	Ferndell	Hathorn 3	Average sea water
pH	7.9	6.4	6.2	6.5	8.0
T°C	16.0	14.0	11.9	10.4	5
Cond. mS	0.37	2.8	5.1	22.7	33.4
O ₂	7.4	0.1	0.23*	0.75*	8
HCO ₃ ⁻	137	1221	1926	4969	140
Li	0.007	1.0	2.4	14.8	0.17
B	0.03	0.5	1.1	4.3	4.5
NO ₂ ⁻	<0.001	<0.001	<0.001	<0.001	~0
NO ₃ ⁻	6.3	<0.01	<0.01	<0.01	38
NH ₄ ⁺	<0.001	1.4	3.2	27	~0
F	0.13	0.46	0.58	0.23	1.3
Na	22	363	718	4339	10805
Mg	9	61	106	450	1288
Al	0.02	0.02	0.02	0.17	0.0008
SiO ₂	8	52	19	14	6.0
PO ₄ ³⁻	0.01	<0.01	<0.01	<0.01	0.22
SO ₄ ²⁻	25	0.02	0.28	0.19	2690
Cl	41	454	1188	7178	19499
K	1.3	25	86	374	399
Ca	40	191	334	938	413
V	0.0006	0.002	-	0.001	0.0012
Cr	0.0002	0.0001	-	0.0002	0.0002
Mn	0.04	0.14	0.08	0.09	0.0003
Fe	0.5	5.9	2.9	5.9	0.00006
Co	0.0002	0.0004	0.0006	0.0010	0.000002
Ni	0.001	0.003	-	0.014	0.0005
Cu	0.003	0.001	0.001	0.002	0.0003
Zn	0.007	0.005	0.001	0.004	0.0004
As	0.003	0.003	0.004	0.038	0.002
Se	0.004	0.02	0.04	0.22	0.0001
Br	0.04	4.1	11.6	68	67
Rb	0.0009	0.022	0.08	0.31	0.12
Sr	0.16	3.4	3.4	19.8	7.6
Mo	0.0004	0.00060	0.00002	0.00010	0.011
Cd	0.000009	0.000016	0.000040	0.000370	0.00008
Sn	0.000015	0.000002	-	0.000018	0.0000005
Sb	0.00006	0.00001	-	0.00008	0.00015
Cs	0.000003	0.0008	0.0027	0.0095	0.0003
Ba	0.03	2.9	4.7	28.1	0.014
W	0.000006	0.00002	-	0.00005	0.0001
Tl	0.000003	0.000000	-	0.000004	0.00001
Pb	0.0002	0.00006	0.00004	0.00006	0.000002
U	0.0003	0.000004	0.0028	0.0008	0.0031

*May be contaminated with surface air.

segments that intersect at point **C**. The important point is that **C** is not in fact along a straight mixing line between hard fresh groundwater **B** and saline end member **D**, but rather has a Ca concentration higher than that predicted by a straight mixing line. Since Ca, Mg, and HCO₃⁻ all follow this same pattern, this suggests that mixed waters can dissolve dolomite and calcite even though ground water **B** and saline end member **D** are probably in equilibrium with these minerals.

Most previous workers have described the compositional variations among the Saratoga Springs mineral waters as simple mixtures between fresh ground water and a deep saline water end member that may or may not be more saline than that tapped by the Hathorn 3 Spring. In general the mixing concept seems to be correct, but in detail the situation is a little more complicated. Figure 4 shows Ca, K, and Br plotted against the conservative component Cl. Cl is conservative since it is difficult to precipitate, it does not bind readily to mineral surfaces, and it is very low in abundance in most rocks. Cl therefore tends to remain at constant concentration (is conserved) in waters migrating through and reacting with bedrock. The three graphs in Figure 4 illustrate the three principal patterns that different chemical components have among the Saratoga mineral springs.

The Br-type pattern (Figure 4A) is representative of conservative chemical components. Neither Cl nor Br are removed from or added to the waters from the enclosing carbonate rock aquifer in significant amounts because of their low abundance in the rocks and low adsorption affinity. Cl and Br therefore define a straight mixing line.

The Ca-type pattern (Figure 4B) is shared with the components Ca, Mg, and HCO₃⁻. The pattern can be approximated with two end members, three distinct linear regression lines, and two line intersections. Rain and snow in precipitation start out as essentially pure water represented by end member **A**. Reaction with surrounding aquifer rock enriches the water in dissolved components. We think the hypothetical fresh groundwater in the deep carbonate aquifer is approximated line intersection point **B**, which is essentially "hard", fresh water. This is consistent with modeled water in contact with carbonate rocks though we have little firm constraint on the hard fresh water P_{CO2}. End member **D** represents the most saline deep water we have available from the Hathorn 3 Spring. The saline and intermediate springs can be approximated by two linear regression line

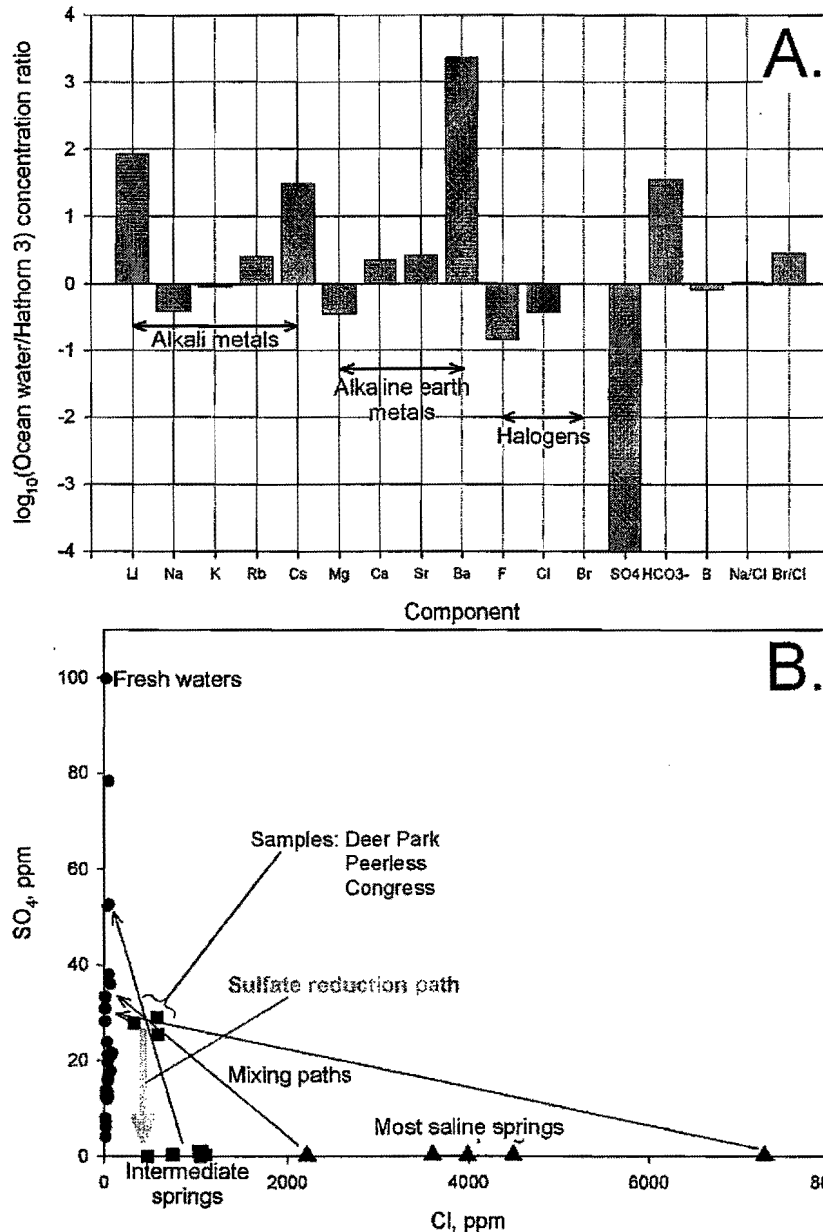


Figure 3.

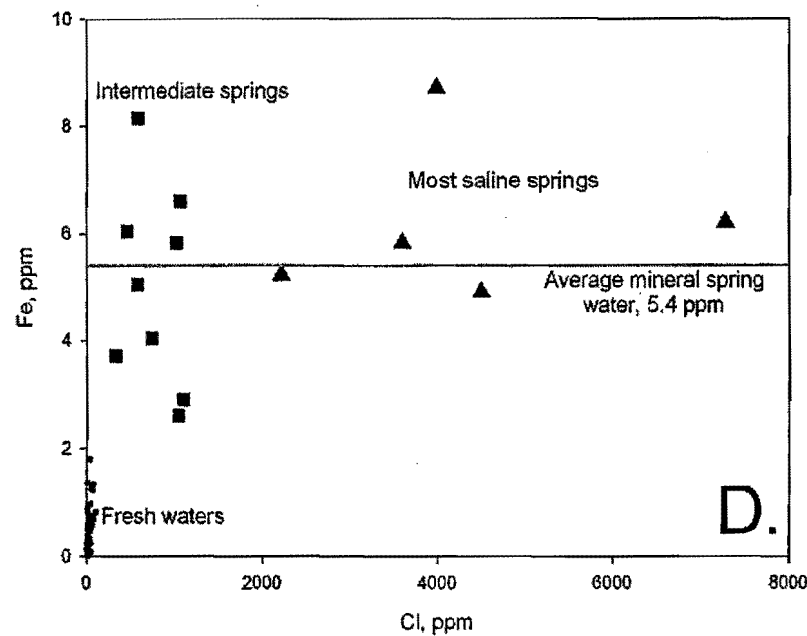
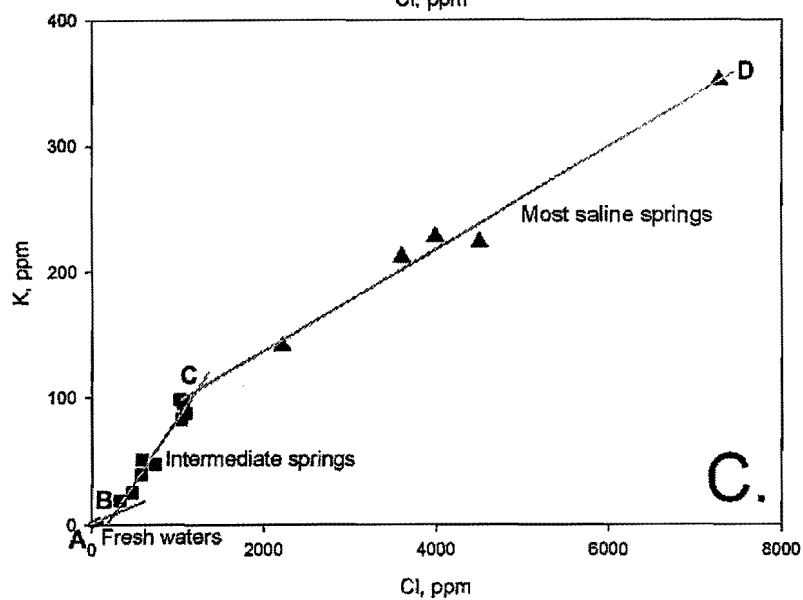
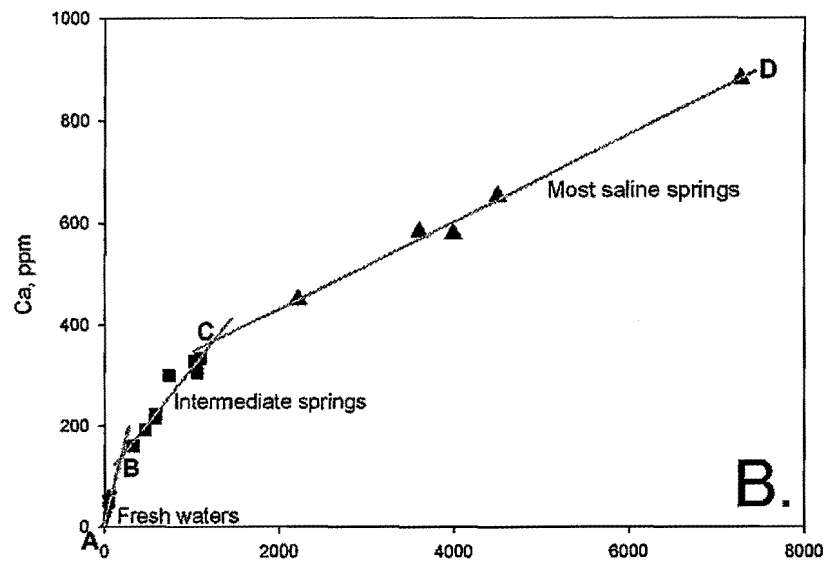
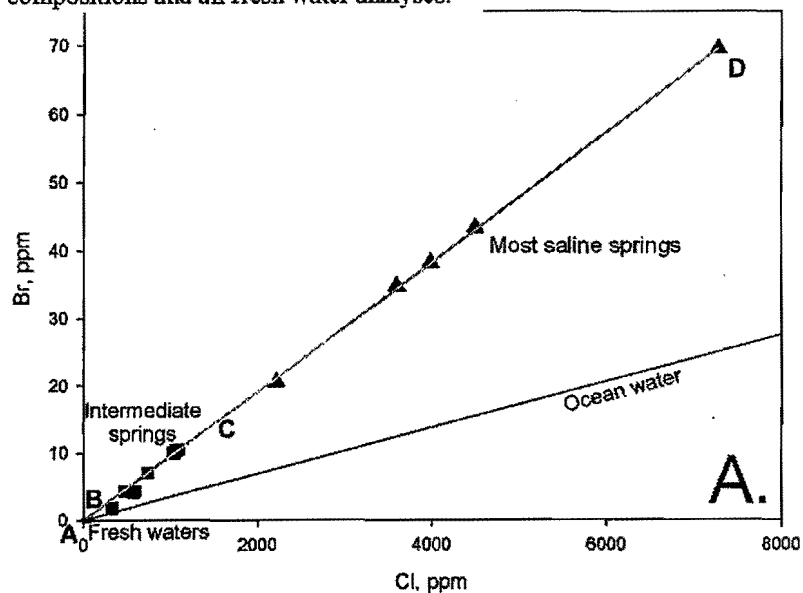
A. Concentration ratios relative to sea water of several chemical components in the most saline spring, Hathorn 3. High Ba ratio is permitted by very low sulfate ratio, inhibiting barite saturation. In general, larger ions are enriched over smaller ions for the alkali, alkaline earth, and halogen elements. The Li enrichment, however, is exceptional and does not follow this pattern.

B. Surface waters have variable but generally high concentrations of sulfate, derived partially from atmospheric deposition but primarily from the weathering of sulfides in rocks. The mineral spring waters are generally low in sulfate (~0.2 ppm) because of long-term equilibration under reducing conditions (calculated redox potential about -200 mV) that reduce most sulfate to sulfide. Mixing of saline and fresh, sulfate-rich waters soon before the water flows to the surface may permit sulfate-rich mixed waters to reach the surface. Longer term storage of mixed waters in the deep aquifer may allow sulfate reduction to proceed essentially to completion.

Figure 5 shows calculated CO₂ partial pressures for waters having different dissolved solid concentrations, but all with the same dissolved component proportions as the Hathorn 3 Spring. The model calculations were constrained by assuming that the waters were in equilibrium with calcite, dolomite, chalcedony, kaolinite, and pyrite. Calculated P_{CO₂} required to maintain this equilibrium varies strongly with concentration. The particular point of interest here is that the P_{CO₂} curve for water in equilibrium with these minerals is concave up. All mixtures of more saline and less saline waters therefore become CO₂-enriched over that required to maintain saturation with calcite and dolomite. This means mixed waters are undersaturated with respect to these carbonate minerals and can dissolve their host carbonate aquifer rock and so reattain equilibrium by becoming enriched in Ca, Mg, and HCO₃⁻ relative to a straight mixing line between end member D and ground water B. It is likely that the intermediate and most saline mineral waters, and mixture C, lie along an asymmetric curved line (not shown) rather than along the two regression line segments shown.

The K-type pattern (Figure 4C) is shared with the components Rb, Cs, B, and NH₄⁺. Li and Na may also be of this pattern, but for these elements deviation from a straight mixing line is small. The K-type pattern is similar to the Ca-type pattern except that ground water composition B is at a lower concentration than a straight A-C mixing line might suggest. Hard fresh ground waters in the carbonate aquifer probably do not become strongly enriched in Li, Na, K, Rb, Cs, B, and NH₄⁺ because they are not abundant in carbonate rocks, and because, though some are

Figure 4. Graphs of average mineral spring compositions and all fresh water analyses.



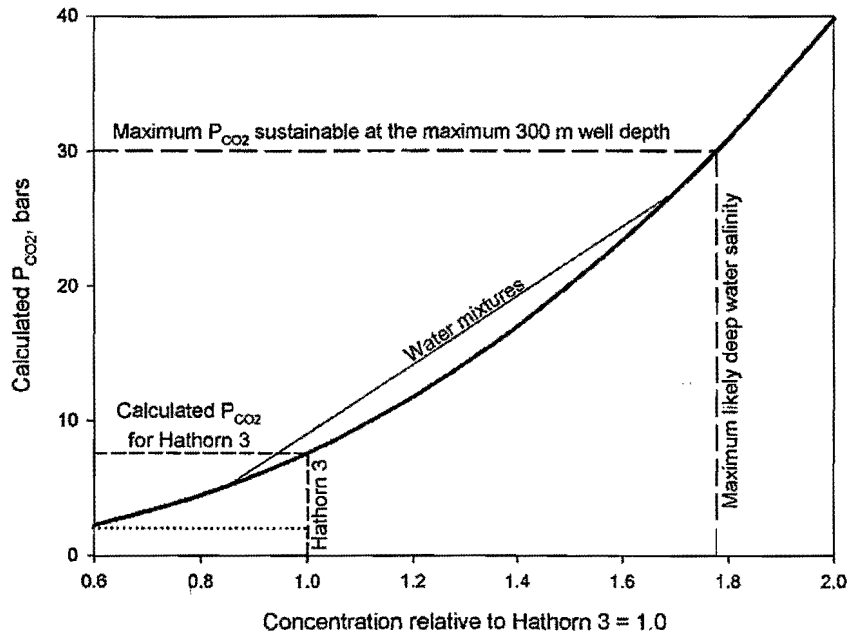


Figure 5. Model P_{CO_2} in water spanning a concentration range of 0.6 to 2.0 times that of the Hathorn 3 spring (Table 1). Hathorn 3 water requires a P_{CO_2} of ~ 7.8 bars to maintain calcite and dolomite saturation. Model water at >1.8 times the Hathorn 3 concentration requires >30 bars P_{CO_2} , exceeding the hydrostatic head of the overlying 300 m water column of the deepest drilled mineral water well. Mixtures of fresher and more saline water that are at CO_2 saturation become undersaturated with respect to calcite and dolomite and so will dissolve them. Shallowing of CO_2 -rich carbonate-saturated waters will allow them to evolve CO_2 gas bubbles.

components of silicates, these are rather insoluble. Intersection point **C** has elevated K concentrations compared to a straight **B-D** mixing line. This may be caused by dissolution of or ion exchange with newly exposed clay and other minerals that are exposed as subsurface mixing promotes dissolution of the enclosing impure carbonate aquifer rock.

Fe (Figure 4D) and Mn (not shown) have essentially flat, though rather scattered concentration patterns having more or less constant 5.4 and 0.1 ppm Fe and Mn, respectively. Fresh waters have much lower and more variable concentrations of Fe and Mn. Calculations indicate that Fe and Mn are almost entirely in the 2+ state, and are undersaturated with respect to various carbonate, hydroxide, and oxide minerals under the low redox potentials in the deep aquifer. However, the Fe and Mn available from carbonate rock dissolution may be relatively constant, resulting in only modest scatter of the data about the average line.

The other chemical components (e.g., Co, As, Mo, Pb, U) either have compositional distributions resembling random scatter, or they follow straight Br-type mixing lines but with a lot of scatter about the line. Though all elements have not been subject to modeling, none of those that have are close to saturation with any model phase. It seems likely that these trace components have variable sources in the rocks undergoing dissolution, and are not buffered.

CONCEPTUAL MODEL AQUIFER SYSTEM

Figure 6 shows our schematic conceptual model for the mineral springs aquifer system. Surface precipitation has a very low content of dissolved solids and represents water component **A**. It picks up CO_2 from the atmosphere and soil and percolates into fractures and solution voids in the Beekmantown Group carbonates in the Adirondack foothills to the north and west of Saratoga Springs (Figures 1 and 2). The residence time of the aquifer water is not known, but water tends to reach equilibrium with carbonate minerals within a matter of days or weeks. The result is a hard fresh water component **B** containing an enhanced dissolved load of carbonate rock components, most notably Ca^{2+} , Mg^{2+} , and HCO_3^- . This water probably has a pH near neutral and a $P_{CO_2} \ll 1$ bar. We assume that at least some of this water remains modestly oxidizing and sulfate-rich.

The composition of the most saline and carbonated deep water is not known. The most saline and carbonated water at the surface is from the Hathorn 3 Spring, and modeling indicates that the deep water at the 300 m depth of the Hathorn 3 well is unlikely to be more than twice as concentrated as the surface Hathorn 3 water. In any case, we use Hathorn 3 as the model saline water end member **D**. As this water flows along the fault zone, from unknown sources to the south, it partially mixes with hard fresh water **B** in the vicinity of Saratoga Springs to create a density stratified aquifer system. Depressurized waters may evolve CO_2 bubbles which may redissolve into CO_2 -undersaturated fresher waters above. Mixed saline-fresh waters also form. Mixing and incorporation of CO_2 by fresher water both undersaturate the waters with respect to carbonate minerals, and so will tend to dissolve carbonate rock in the aquifer zone, enlarging the zone to form a cave system. As indicated in Figure 4B, mixed waters are

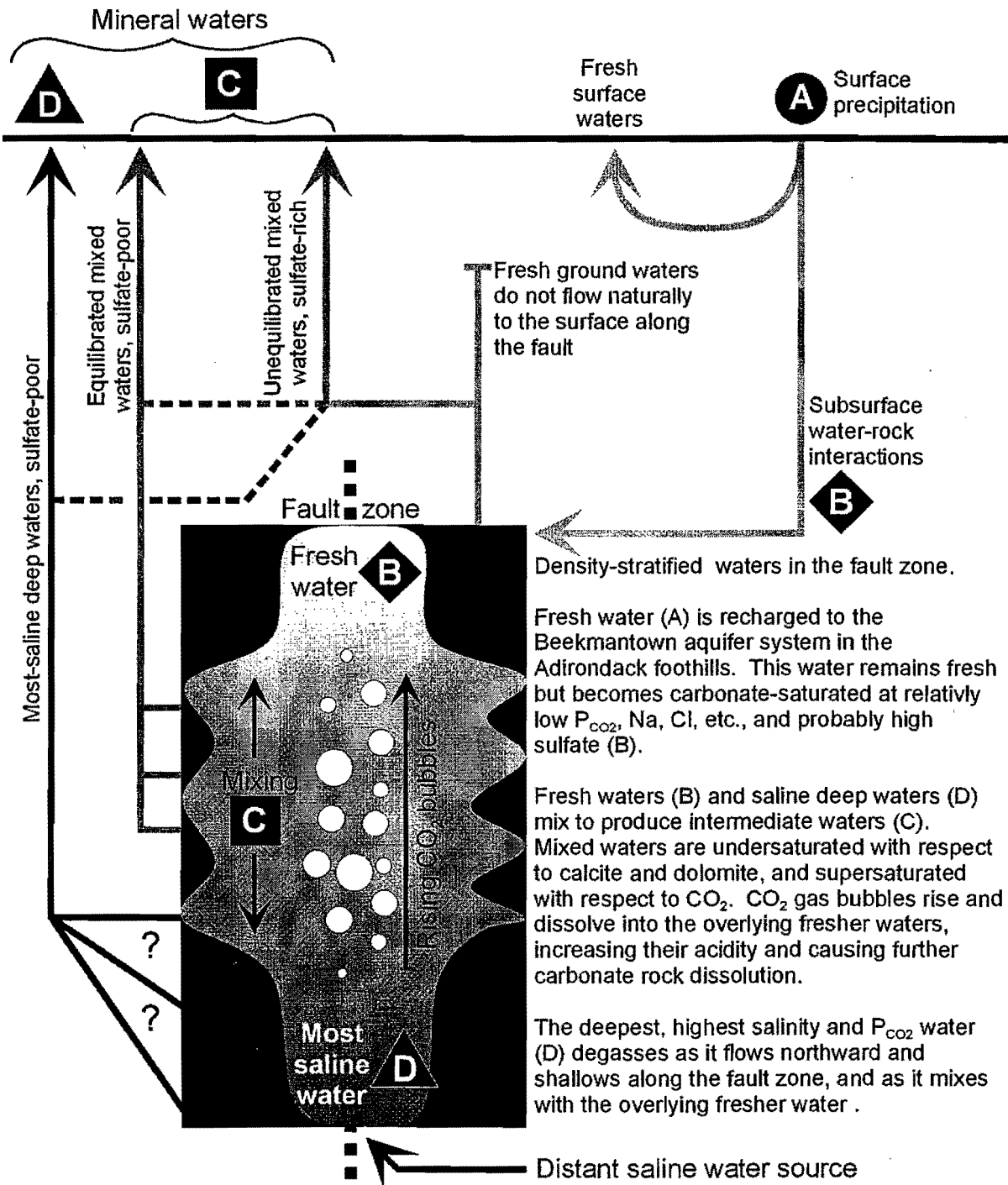


Figure 6. Conceptual model for water mixing, rock dissolution, and tapping of the mineral waters in the aquifer. indeed enriched in Ca, Mg, and HCO_3^- . The result is mixed waters that have elevated concentrations of various chemical components above those expected from a straight mixing line between water components B and D.

SOURCE OF THE SALINE WATERS AND CO_2

There is a long history of speculation as to the origin of the Saratoga spring waters, generally divided into the problems of the recharge water source, the CO_2 source, and the source of dissolved minerals. Possible sources for these, culled from the literature, are given in Table 2. The Saratoga mineral waters were compared with a wide

Table 2. Several concepts for the origin of the Saratoga Springs mineral waters, specifically regarding origin of the water proper, the mineral content of the water, and the CO₂ content of the water. Details of citations are too complex to cite specifically here, but are derived from Sylvester (1893), Kemp (1912), Cushing and Ruedemann (1914), Ruedemann (1937), Strock (1941); Putman and Young (1985), Siegel (1996); Quintin (2000); Lesniak and Siegel (2000).

Source	Attempts to explain			Concept	Problems
	Water	CO ₂	Minerals		
Magmatic	✓	✓	✓	Crystallization of igneous bodies, and interactions of magmas with surrounding rocks, can release large quantities of mineralized water and CO ₂ .	The springs are cold and there is no recent magmatic activity or local thermal anomaly. The cited Starks Knob "plug" to the northeast of Saratoga Springs is a Taconian thrust slice of oceanic pillow lavas.
Meteoric	✓			Meteoric water is an abundant and obvious source of spring water.	Does not account for the mineral or CO ₂ content of the mineral waters.
Trapped sea water	✓	✓	✓	Sea water was trapped in sediment pores at the time of deposition, providing a source of salty water. CO ₂ could be derived from slow decomposition of buried organic material.	Spring waters do not have compositions derivable from sea water by dilution. The organic matter in the shales and other rocks in the area is mostly high-carbon, high molecular weight material not subject to ready bacterial decomposition.
Metamorphism at depth	✓	✓		Metamorphism releases water and CO ₂ from various sedimentary rocks.	No reason to suspect active metamorphism at depth; continental margin has been more or less stable for ~200 Ma.
Mantle degassing		✓		CO ₂ released from the mantle via deep fractures.	Deep fractures unlikely to remain open due to ductile flow of rock and precipitation of minerals during fluid cooling and depressurization.
Deep sedimentary basin	✓	✓	✓	Meteoric water percolates downward and mixes with saline deep formation brines and equilibrates with thermally-derived formation gasses (CO ₂ , CH ₄ ?). Water flows northward along the fault into the Saratoga Springs area. High elevation in the water source are drives hydrostatic flow.	Distant water source, not nearer than beneath the Catskills or Pennsylvania. Requires an enormously long flow conduit. Mechanism of interaction between meteoric water and saline formation waters and gasses unclear.

range of waters from other sources (White et al., 1963; Carpenter, 1969; Campbell et al., 1970; Young and Putman, 1978; Drever, 1982). These indicate that the Saratoga Springs mineral waters are most similar to "oil field brines" and "deep sedimentary basin brines". Though the range of scatter of each water type is tremendous, it seems that it is unlikely that the Saratoga Spring waters are from any type of shallow or hydrothermal source, or that they are from a source closely associated with common gypsum or halite evaporites.

Many seemingly unlikely hypotheses have been proposed for the origin of the unusual Saratoga Spring water components, from clearly outrageous (local magmatic source; Kemp, 1912) to at least superficially implausible (from the north along the Saratoga Springs-McGregor fault, derived from crystalline rocks in the Adirondack highlands; Lesniak and Siegel, 2000). Our concept, which we hope is not worse than superficially implausible, is that the waters and their excess CO₂ is derived from the deep sedimentary basin beneath the Catskills or farther south in Pennsylvania. The higher elevation in these regions causes fresh groundwater to percolate downward, into some region where the meteoric waters can mix with deep basin brines and trapped or dissolved gasses. The hydrostatic head forces the mixed water to flow northward along solution and fracture porosity in the Saratoga Springs-McGregor fault zone, finally mixing in the Saratoga Springs region with local hard, fresh ground waters and finally coming to the surface.

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ROAD LOG

The starting point is the Wilton Square Mall adjacent to Rt. 50 in Saratoga Springs, just east of the Northway (I-87). To reach the starting point from either direction on I-87 take exit 15 for Rt. 50, Saratoga Springs. At the top of the exit ramp, turn east onto Rt. 50 towards Gansevoort. Cross through the traffic lights at Weibel Ave., stay in the right lane, and turn right at the next set of lights into the Wilton Square Mall (large sign advertising many stores). Take an immediate left into the Price Chopper parking lot adjacent to Rt. 50 and wait there (approximately 43.084°N, 73.741°W). Unfortunately the most recent topographic sheet does not have the new mall, so a more precise location is difficult. Figures 7 and 8 show the trip route and spring locations.

Total miles	From last	
0	0	Start in the Price Chopper parking lot, as described above. Turn right out of the parking lot exit and get in the left lane to turn left onto Rt. 50 toward Saratoga Springs. <i>Reset trip odometers to zero at the light.</i> Turn left onto Rt. 50.
0.2	0.2	Cross Weibel Ave.
0.6	0.6	Cross over I-87.
1.2	1.2	Turn left at the traffic lights onto Veterans Way (note: the road on the right side of the intersection is Gick Rd., not Veterans Way).
1.4	1.4	Turn right at the stop sign (T intersection) onto Excelsior Ave.
1.6	1.6	Brewery on the right.

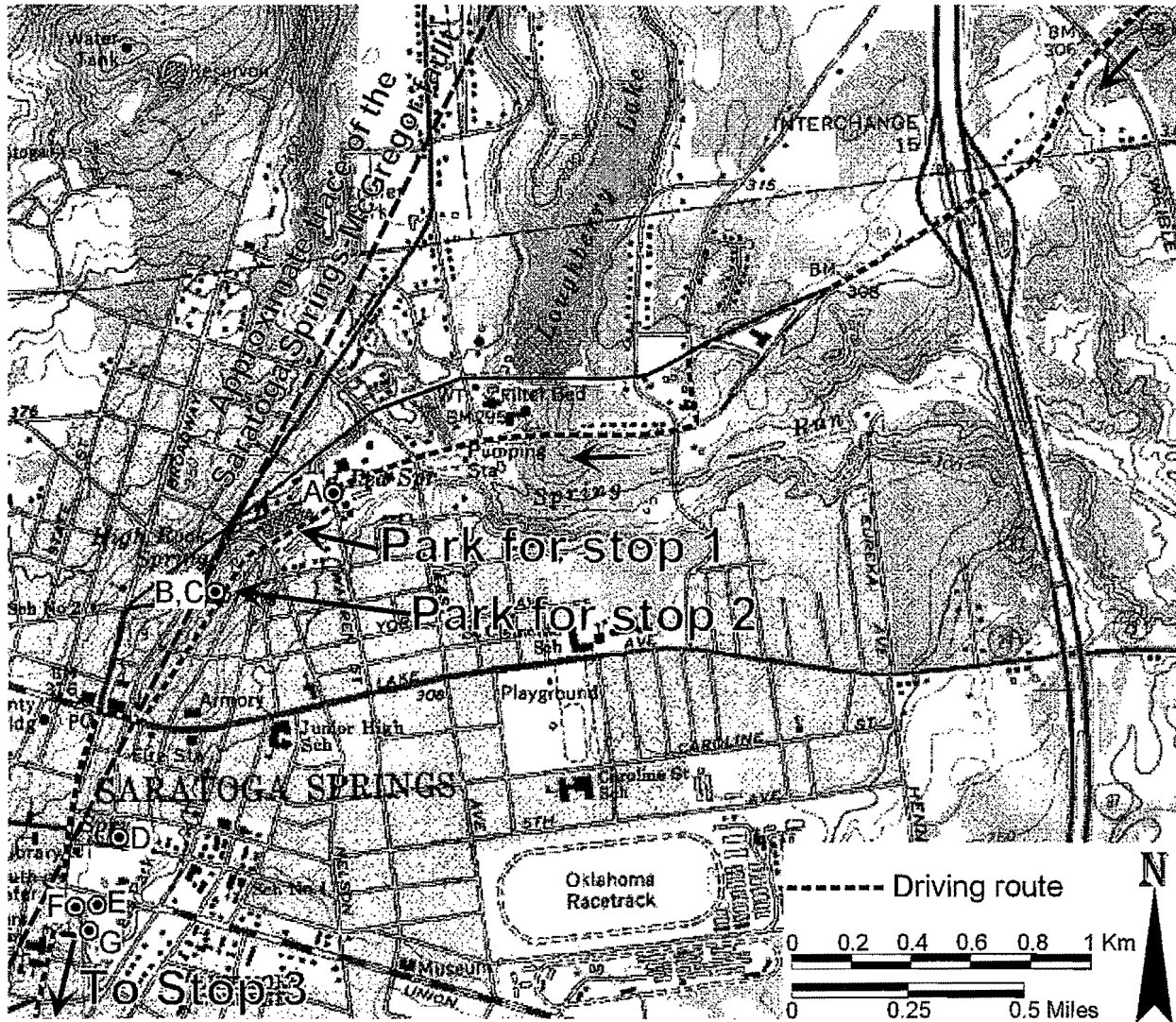


Figure 7. Route from near the start of the trip to Stops 1 and 2, and continuing toward Stop 3 through the Saratoga Springs downtown. Dashed line is the driving route. Springs are labeled A-F: A, Old Red; B, Peerless (the least saline mineral spring has nearly stopped flowing); C, Governor, D, Hathorn I; E, Congress; F, Columbian (Saratoga Springs municipal drinking water supply); G, Deer Park.

- 2.1 2.1 Turn left onto Warren St. and then an immediate right onto High Rock Ave. A small pavilion for the Old Red Spring is at this intersection.
- 2.2 2.2 Park on the right side of the street outside the light yellow building with many columns in front.

STOP 1. OLD RED SPRING. (10 minutes) The Old Red Spring (0.24% TDS, intermediate type, A in Figure 7) is the north-easternmost and one of the least saline of the existing Saratoga-type mineral springs. Some older literature describes this spring as being highly iron-rich, though chemical analysis shows this water to be unremarkable. It has the second lowest salinity of all of the flowing springs and so is more popular than some of the other saltier and smellier waters.

- 2.2 0 Continue straight on High Rock Ave.
- 2.3 0.1 Road curves to the left.
- 2.4 0.2 Park along the road next to the spring pavilion.

HOLLOCHER, QUINTIN, AND RUCITTO

STOP 2. CONGRESS PARK AND ENVIRONS. (1 hour 15 minutes) This is a walking stop at which we will see all of the flowing springs in the Saratoga Springs downtown.

High Rock Spring, originally known as the Big Medicine spring, was the first mineral spring in the area to be introduced to European settlers in 1767 (Siegel, 1996). Though the spring conduit has been cleaned with hand tools repeatedly, the original spring has long since sealed its own conduit by calcite precipitation. Any flowing water in the High Rock Pavilion actually flows by gravity through a pipe from the nearby Governor spring. The cliff to the west of the pavilions is of the Beekmantown Group (Amsterdam Limestone), faulted above the Utica Shale on which the pavilions are built. The fault displacement, calculated at the now vanished Star spring that was located ~100 m northeast of the High Rock Spring, is ~49 m, much less than the total carbonate section here of ~140 m (Cushing and Reudemann, 1914).

Peerless Spring (0.15% TDS, intermediate type, B in Figure 7) is the least saline of the flowing springs. Its salinity has been decreasing over the past decade. Based on the salinity curve over time, we predicted that it would stop flowing in 2001, which in fact it did. However, we found in spring 2002 that it was flowing again if only a trickle. It is called Peerless probably because it is the least saline and so least bad-tasting of the Saratoga Springs.

Governor Spring (0.35% TDS, intermediate type, C in Figure 7) is in the same pavilion as Peerless, though both are piped from the well head across the street.

Hathorn 1 Spring (0.71% TDS, saline type, D in Figure 7) is the first and northernmost of the saline-type springs as defined in Figures 3B and 4. The drilled well is just over 300 m deep and penetrates ~80 m into Cambrian clastic rocks. This spring outlet and pavilion were moved in 1999 from across the street to make room for the parking garage currently at the original spring location.

Congress Spring (0.28% TDS, intermediate type, E in Figure 7) is perhaps the most frequently visited of the springs, its handsome pavilion being a prominent landmark in Congress Park.

Columbian Spring (0.026% TDS, fresh water, F in Figure 7) is actually from the municipal water supply for the City of Saratoga Springs, derived from the Loughberry Lake reservoir. This was once a natural spring or drilled well, converted to municipal water in order to give justification for the pavilion.

Deer Park Spring (0.30% TDS, intermediate type, G in Figure 7) has a miniature pavilion that is unique among the Saratoga Springs. Curious ducks sometimes congregate to watch people collecting samples and making field measurements. Ducks are not, however, big fans of the mineral waters.

- 2.4 0 Continue straight on High Rock Ave.
- 2.7 0.3 Turn right (west) onto Lake Ave. (Rt. 29), the first real cross street. Get into the left lane as you climb the hill.
- 2.8 0.4 Turn left (south) onto Broadway (Rt. 50 and 9), which is the main street in town.
- 3.3 0.9 Rt. 50 turns off to the right, continue straight on Rt. 9 south.
- 4.0 1.6 Museum of Dance on the right.
- 4.1 1.7 Lincoln Baths on the right, the only operating public bath house in Saratoga Springs. This is the location of the Lincoln Spring, for which there is a small monument. The spring has been turned off for many years, presumably to supply mineral water to the baths.
- 4.2 1.8 Turn right onto the Avenue of Pines, enter Saratoga Spa State Park. This road travels through a remarkable tunnel made of pine trees.
- 5.0 2.6 Complicated intersection; bear right, following a sign toward Rt. 50.
- 5.2 2.8 Turn left following the sign to the Hall of Springs Museum. The "Bottling Plant" is on the right (historic; now a car museum).
- 5.3 2.9 Turn right into the large parking lot after the "Bottling Plant" and park.

STOP 3. SPA PARK SPRINGS AND OTHER WATERS. (2 hours) This is also a walking stop at which we will see all of the flowing springs in the Saratoga Spa Park and much of the park itself including the Saratoga Performing Arts Center (SPAC), the new antique car museum ("Bottling Plant"), and Geyser Brook, the valley for which hosts several of the springs.

State Seal Spring (0.030% TDS, fresh water, A in Figure 8) is by far the most popular spring in the area. There are usually droves of people filling up jugs, canteens, and carboys to bring home for drinking. Little do they realize that this fresh water is completely unrelated to the mineral springs, but in fact is pumped from a nearby shallow well in unconsolidated glacial outwash. The proximity of the well to the surrounding golf course causes this water to have the highest NO₃⁻ concentration (24 ppm) of any water sampled in this project by a factor of ~50. Doubtless there are organic residues as well, though these were not analyzed by us. The water is tested periodically

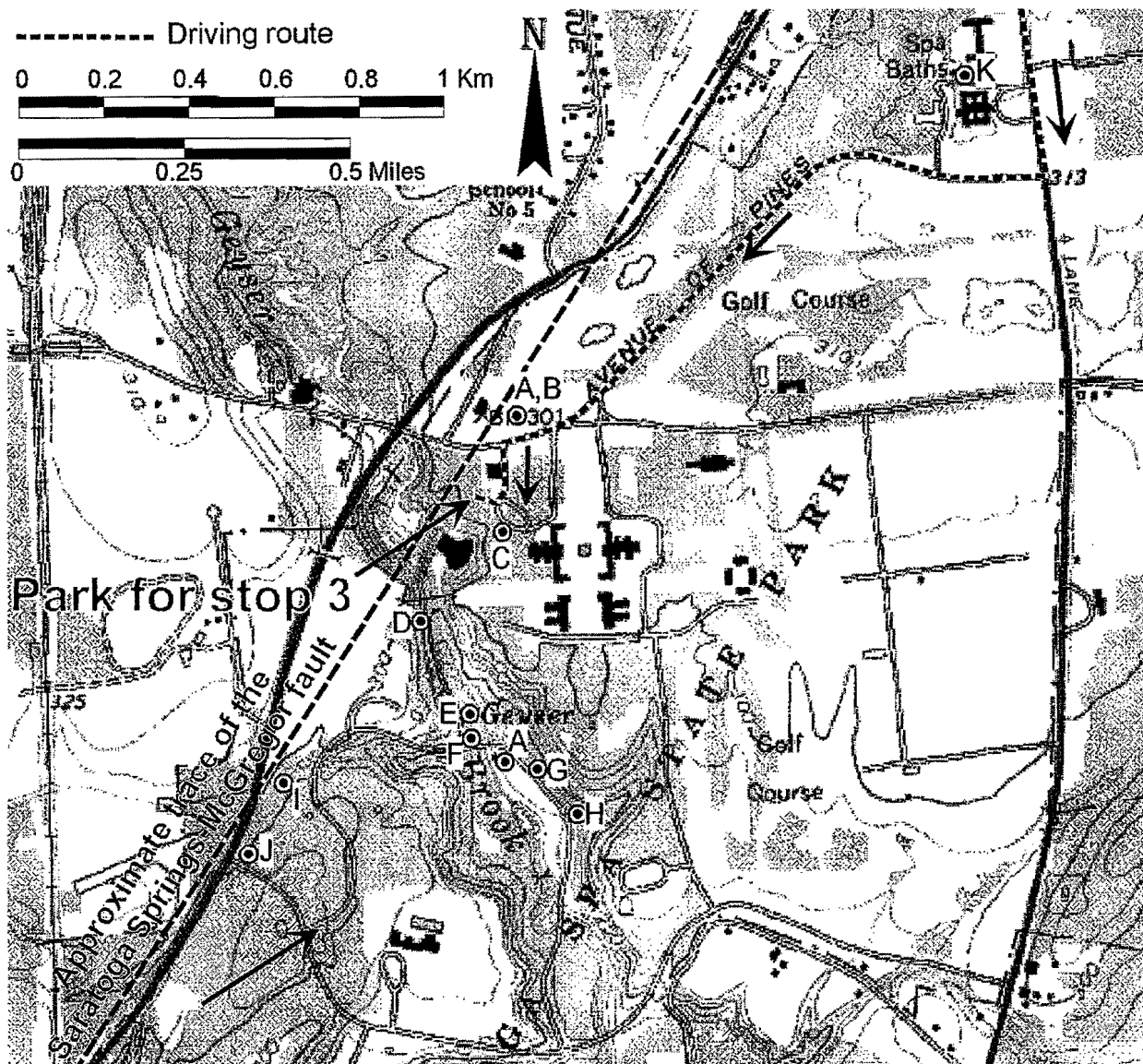


Figure 8. Route from Rt. 9 south from the Saratoga Springs downtown to Stop 3. Dashed line is the driving route. Springs are labeled A-K: A, State Seal (pumped from shallow glacial outwash); B, Geyser; C, Charlie; D, Orenda; E, Island Spouter; F, Hayes; G, Polaris; H, Fendell; I, Coesa (under a pond); J, Hathorn 3 (the most saline spring); K, Lincoln (dry; diverted to the adjacent Spa Baths).

and is safe for drinking. This water is also piped to a State Seal Spring outlet to the south, that we will see later today.

Geyser Spring (0.51% TDS, intermediate type, B in Figure 8). The original location of this spring was just west of the "Bottling Plant" across the street. As of this writing it is unclear if this water will be piped to the new pavilion at the new location of State Seal Spring. If so, you will see that people are *not* lining up to fill jugs with this real mineral water.

Charlie Spring (0.54% TDS, intermediate type, C in Figure 8) is the only spring water accessible from within the gates of SPAC. When it is flowing, it comes out on both sides of an ornamental wall. Note trace fossils on the stone slabs surrounding this spring.

Orenda Spring. (1.18% TDS, saline type, D in Figure 8) Orenda is the most boisterous of the mineral springs, enthusiastically belching forth CO_2 and traces of H_2S . This is also the most energetic precipitator of travertine, the amount of travertine deposition being estimated at ~ 2000 kg/year. The travertine mound is mostly along the slope down to Geyser Brook, on the banks of which it forms a fine travertine platform along which a path goes.

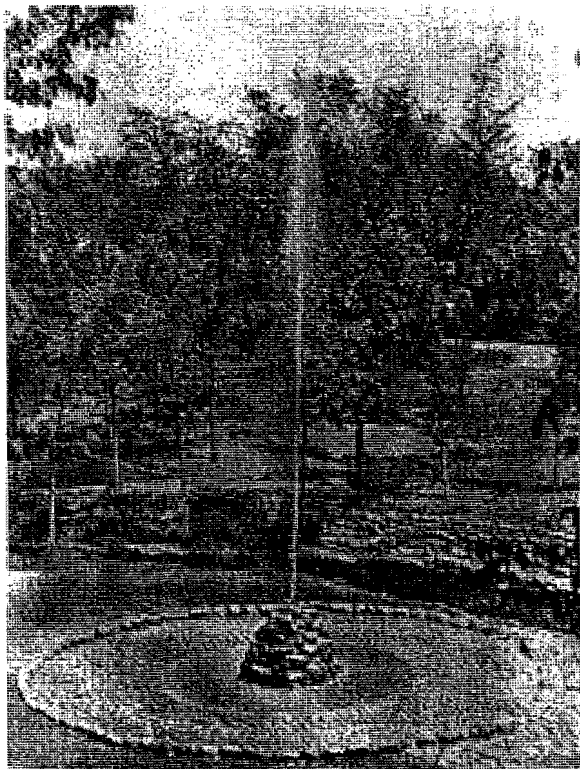


Figure 9. Photograph circa 1930 of the Island Spouter Spring, shown soon after it was ornamented with stonework. Photo source uncertain.

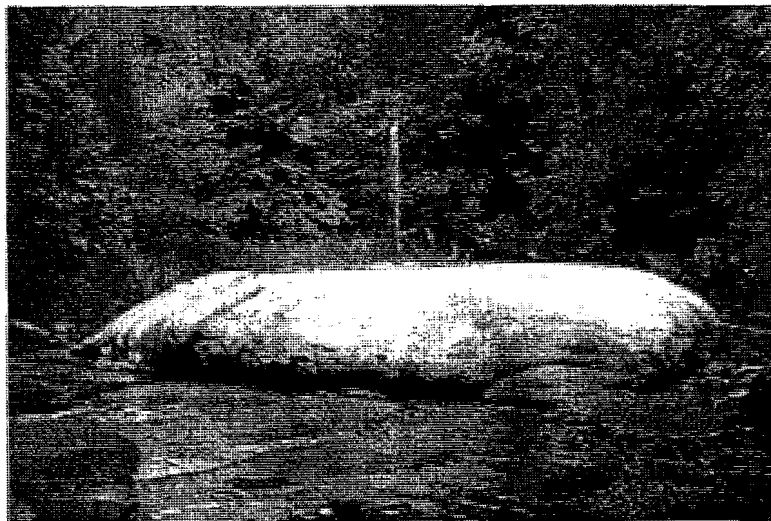


Figure 10. Photograph in 1999 of the Island Spouter Spring, long after the ornamental stonework was eroded away and covered with nearly 2 m of tufa.

Island Spouter Spring (1.05% TDS, saline type, E in Figure 8) is the most enthusiastic geyser among the flowing springs, spouting these days up to ~7 m high. Originally drilled in the early 1900's for CO₂ production, it was turned into an ornamental island in Geyser Brook in 1930. The ornamentation has either been eroded away or has been buried beneath the nearly 2 m of travertine deposited by the spring in the past 70 years. This spring usually runs through a cycle of varying geyser height that lasts perhaps 30 seconds, terminating in a short period of gas venting without water. Sampling this spring is a wet experience. Figures 9 and 10 show how the appearance of Island Spouter has changed as erosion has taken its course and as nearly 2 m of travertine has been deposited.

Hayes Spring (1.14% TDS, saline type, F in Figure 8) is the third most saline spring after Hathorn 3 and Orenda.

Polaris Spring (0.42% TDS, intermediate type, G in Figure 8) is a gentle continuous geyser typically spouting ~1 m high.

Ferndell Spring (0.44% TDS, intermediate type, H in Figure 8, BEWARE OF POISON IVY) flows to the surface without a notable geyser. It has deposited a broad, low travertine mound that is the third most notable after those of Orenda and Island Spouter.

Coesa Spring (not sampled, presumably saline type, I in Figure 8) bubbles to the surface beneath a small pond. Though it is occasionally seen to be connected to a hose, the pond and fence have so far discouraged sampling.

Hathorn 3 Spring (1.81% TDS, saline type, J in Figure 8) is the most saline spring currently available. It is an enthusiastic belcher that has deposited a modest travertine sheet on the floor of its pavilion and downstream. Crystalline calcite crusts can commonly be found floating on the surface of quiet pools of the spring water, precipitated as CO₂ degassing raises the pH and supersaturates the water with respect to calcite. This spring, which has a total dissolved solids content ~½ that of sea water, is the worst tasting and smelliest of the currently flowing springs. This spring is used in most of our modeling as being the most saline water end member (**D**), though modeling suggests that more saline waters can exist at depth. In our data set of old spring analyses, the Hathorn 2 spring was probably equivalent to Hathorn 3 in salinity, and the Glacier Spring was

slightly more saline. Neither of these two springs are currently flowing and there are no complete analyses of them.