

THE PUZZLE OF SARATOGA --

An Old Solution with a New Twist

by
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and
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The famous naturally carbonated springs of Saratoga Springs, New York were in vogue in the mid-nineteenth century when curious "mineral" springs the world over were touted for their beneficent medicinal properties. Resort spas sprung up and flourished around many of them, as thousands of people came yearly to drink, bathe, and soak in the waters often prescribed by the physicians of that time. Hotels sprung up to house the pilgrims and pleasure seekers and it was common for one to boast of its own mineral spring with its own peculiarly beneficent properties. For those who could not afford the luxury of a personal visit to the spas, bottling plants were constructed to bottle and ship the water to grocery stores and apothecaries. Today, only a single active bottling plant and a single hotel with a mineral spring remain in this resort town of the many once raised around its springs.

Since interest in the springs first arose, speculation concerning their origin has continued, rising and falling largely with the fortunes of popularity. The various theories have largely fueled the mystique of the waters because the question of their origin has never been satisfactorily answered. Plausible explanations for the presence of different components of the water have been advanced from time to time, but no single theory has been able to account for the collective major characteristics of the water which are: natural carbonation (from 2 - 10+ volumes gas/litre water); high total dissolved solids up to 22,000 PPM; the presence of NaCl as the most abundant dissolved salt; negligible or absent sulfate; and the presence of significant amounts of minor and trace constituents including barium, bromine, strontium, potassium, boron, silica, and zirconium. These characteristics are illustrated in table 1 where several sets of analyses made over the last 70 years show essentially the same values and patterns.

Before beginning a detailed discussion of the chemistry of the waters, however, a brief resume of the physical parameters is in order. First among these is the fact that while the term "springs" is used the vast majority are, in fact, driven wells that penetrate a thin shale cap into fracture zones in the water-bearing Gailor Dolostone (Little Falls dolomite of old reports). Only in a few instances has the water had suffi-

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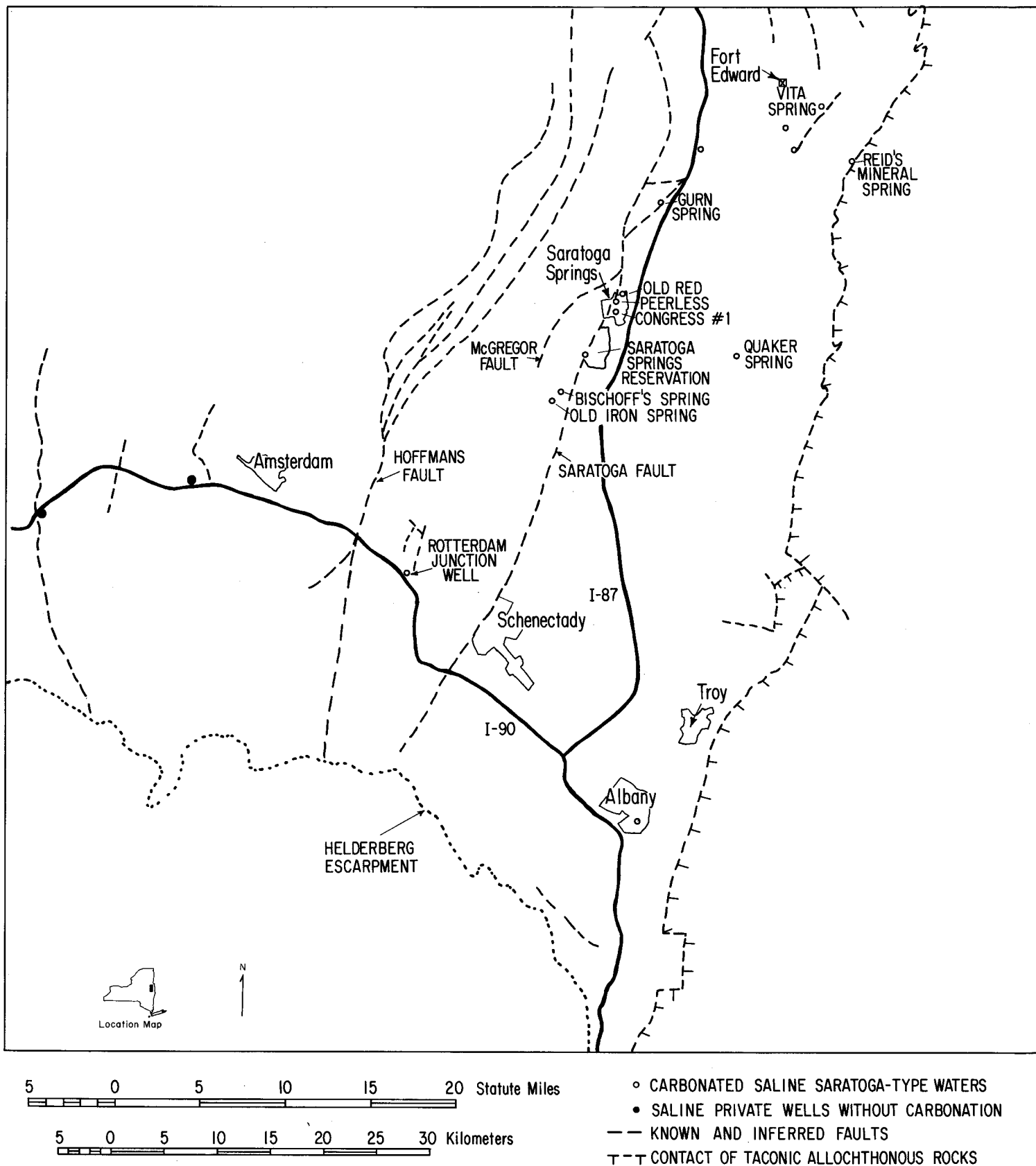


FIGURE 1. LOCATIONS OF WELLS WITH SARATOGA TYPE WATERS OR SALINE WATERS IN THE SARATOGA BASIN

Geology from Geologic Map of New York, 1970, New York State Museum and Science Service Map and Chart No. 15

cient "force" to drive its way to the surface: at Gurn Spring, Reid's Spring, the Old Iron Spring in Ballston Spa, and the original (now inactive) High Rock Spring in Saratoga Springs. Most of the waters are tapped by drilling anywhere east of the Saratoga Fault, a structure which has helped form a vast reservoir of the carbonated waters from Ballston Spa to Saratoga (Figure 1).

A second point on which all previous investigators have agreed (and, perhaps, the only one) is that the Saratoga Fault, an extension of the large McGregor Fault to the north of the city, is the controlling mechanism of the carbonated reservoir and natural springs. In the few places where shearing and crushing along the fault have produced sufficiently permeable zones, natural springs like the High Rock Spring (north edge of Saratoga Springs, not shown in Figure 1) have flowed for a time. More important, however, is the fact that a pumping test, involving three wells, conducted in the early 1900's, showed that the movement of the waters was essentially south to north along the strike of the fault. Apparently, the fault acts as a conduit for the northerly migrating waters at least in this area.

A third point which we adjudge to be very important is that these waters are spatially distributed over the entire Cambrian-Ordovician basin from Albany north to Whitehall and west along the Mohawk Valley at least as far as Amsterdam. Many of these occurrences possess as much carbonation as the wells of Saratoga (notably the Vita Spring, private wells near the Town of Fort Edward, and the private well at Rotterdam Junction) and all contain varying amounts of NaCl and other salts characteristic of the Saratoga waters. The private well drilled into the Little Falls Dolostone at Rotterdam Junction contains the highest total dissolved solids of all the known wells in current use (21,700 PPM); most contain from 1,500 to 8,000 TDS. The areal extent of the waters is therefore quite large, but bounded by the Helderberg Escarpment to the south, the Precambrian basement of the Adirondack Mountains to the north and the Hoffman's Fault to the west (with the exception of the Mohawk Valley). For convenience, this area is referred to here as the Saratoga basin. Nowhere east of Albany in the Taconic allochthon or in the similar Paleozoic carbonates surrounding the Adirondacks are these waters known to occur. Furthermore, as can be seen in the accompanying map, all of the known occurrences are either along recognized faults and linears or in topographic lows which may represent faults beneath glacial debris, thus lending credence to the conclusion of fault controlled water movement and sources throughout the Saratoga basin.

A final observation concerns the temperature of the waters which have recently been remeasured by Isachsen (personal communication) with much the same results as earlier published by Kemp (1912). The wells of Saratoga Springs and Ballston Spa span a range from 48°F to 56°F with most falling between 50°F and 54°F (Kemp, 1912). Seasonal variations are noted due to an admixture of surface waters, yet the range of temperature fluctuation is more subdued than in gravel aquifer wells of the same area. Because the mean annual air temperature of Saratoga Springs is 48°F, the wells average about 4°F above normal for this area. This slight anomaly could be explained in terms of the normal geothermal gradient (approximately

Table 1
 REPRESENTATIVE ANALYSES OF SARATOGA WATER
 RESULTS IN PARTS PER MILLION OR MGS. PER LITRE

Spring & Year of Analysis	Hathorn 1905	Hathorn No. 2 1959	Hathorn No. 2 1971	Lincoln 1905	Lincoln 1959
Cl	4675	6130	4000	4068	1538
Br	47	74		76	34
SO ₄	3.4	Nil		3.5	Nil
HCO ₃	4147	4550		4221	2606
SiO ₂	16	12	12	33	51
Na	2952	3727	1695	2688	1150
K	198	357	250	244	219
Li	7.4	12	9	2	6
Ca	765	872	656	676	348
Ba	7.5	25		12	8
Mg	328	374	151	326	171
Fe, Al	6.7	6.6		14	11
NH ₄	13	16	5	7.3	6
Total Dissolved Solids	13,370	16,188	11,000	12,372	6,166

No Entry = Not Determined

Tr = Trace

Source: N.Y. State Museum Bulletin 159
 New York State Reservation at Saratoga Springs
 N.Y.S. Department of Health

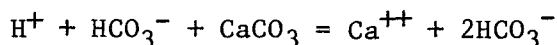
Table 1 Continued

Spring/Well & Year of Analysis	Lincoln 1971	Geyser 1905	Geyser 1959	Geyser 1971	Hyde- Franklin (Ballston)	Gurn 1921	Bischoff 1926
Cl	1180	1025	820	1030	7170	855	4264
Br		12	16		60	5	40
SO ₄		1.4	Nil		3.0	Tr	Tr
HCO ₃		4353	2562		6566	2557	3259
SiO ₂	29	21	12	15	28	54	16
Na	686	2011	850	830	4833	801	2658
K	88		83	80	346	128	188
Li	<0.1	3.6	2.1	4.3	16	1.7	7.2
Ca	336	116	375	240	991	356	583
Ba		2.6	13		13	4.4	14
Mg	146	61	75	163	469	112	269
Fe,Al		8.4	8.1		21	15	38
NH ₄	3.2	11	12	6.7	15	4.4	9.8
Total Dissolved Solids	3779	7656	4836	4185	20543	4896	11363

19.2222100
 10°F/100 ft. depth), although there is no direct correlation between well depth and temperature. In fact, the only pattern that appears from the available data is a rough inverse relationship between temperature and the amount of HCO_3^- . Wells with 3,000 to 5,000 PPM HCO_3^- have uniformly lower temperatures (48° to 51°F) than wells with less HCO_3^- , independent of depth. This suggests that the evolution of gaseous CO_2 as water rises up the last few hundred feet of well pipe from the carbonated reservoir slightly lowers and stabilizes the water temperatures measured at the wellhead.

The chemistry of the waters may be naively summed up with one word - complex. Aside from the constituents reported in Table 1, virtually every trace element that has been sought has been found in detectable quantities, much as is true of sea water. Most of these, however, are not individually germane to the question of the derivation of the waters, at least on the basis of present knowledge. Those elements and characteristics which we believe to be important in this respect are discussed below.

First and foremost among the features or oddities presented by the waters is the widespread presence of large amounts of CO_2 in nearly all of the waters. From two to ten litres or more of gas per litre of water exist in the wells, thereby posing a sufficient vapor pressure to drive some of the waters to the surface without the aid of a pump. Field pH measurements of the waters at the wellhead range from 6.0 to 6.8, yet values below 6.0 in the reservoir in many cases are probable since the pH rises rapidly with gas evolution even while measurements are being made. The actual gas pressures involved are on the order of several atmospheres pCO_2 . These values reinforce the presence of large amounts of CO_2 dissolved in the waters and are difficult to explain by a shallow mechanism of derivation particularly for pH values less than 6.0. Such solutions of CO_2 in water produce carbonic acid and substantial bicarbonate ion concentrations; the acidity results in active corrosion or dissolution of carbonate wall rocks contacting the waters thus increasing both the bicarbonate and calcium and magnesium ion contents; i.e., the alkalinity of the waters. An equation to represent this reaction might be:



from	wall	dissolved
carbonic	rocks	species
acid		

Neutralization of the acidity by this process is not attained in most of the waters, suggesting either dynamic carbonation (continued gas addition with time), or insufficient contact of the waters and carbonate wall rocks to reach equilibrium.

This aspect is shown in Figure 2, a plot of bicarbonate ion vs. chloride ion contents for Saratoga waters. The latter ion is used to represent the saline component alone. A possible dilution line is drawn for this plot to indicate the effect of mixing surface water (low in dissolved solids) with water(s) of relatively high salinity. As can be

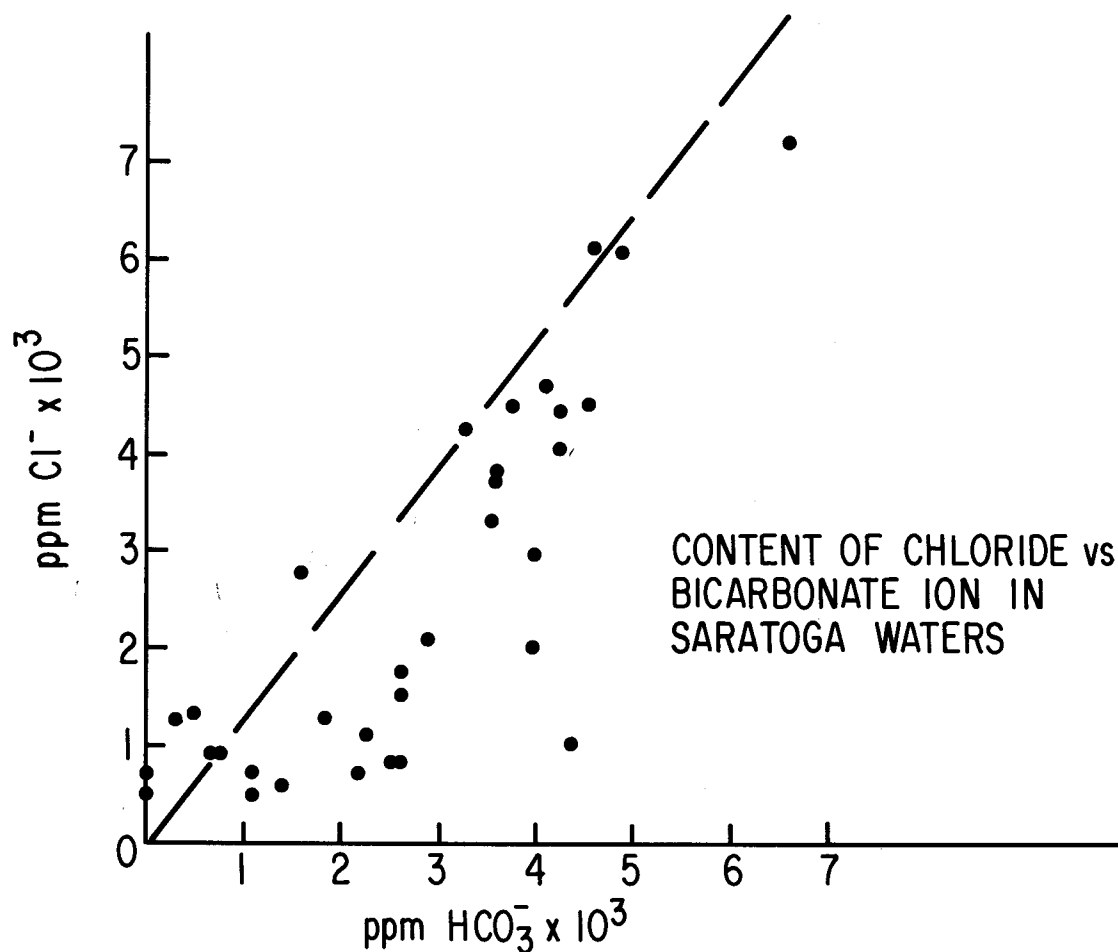


FIGURE 2. CHLORIDE AND BICARBONATE ION
CONTENTS OF SARATOGA

A possible dilution line for more saline initial waters is shown (changes in ion activities with concentration are neglected). Points to the right reflect increased alkalinity and presumed greater wallrock reaction; points to the left reflect neutralization or carbon dioxide gas loss on dilution.

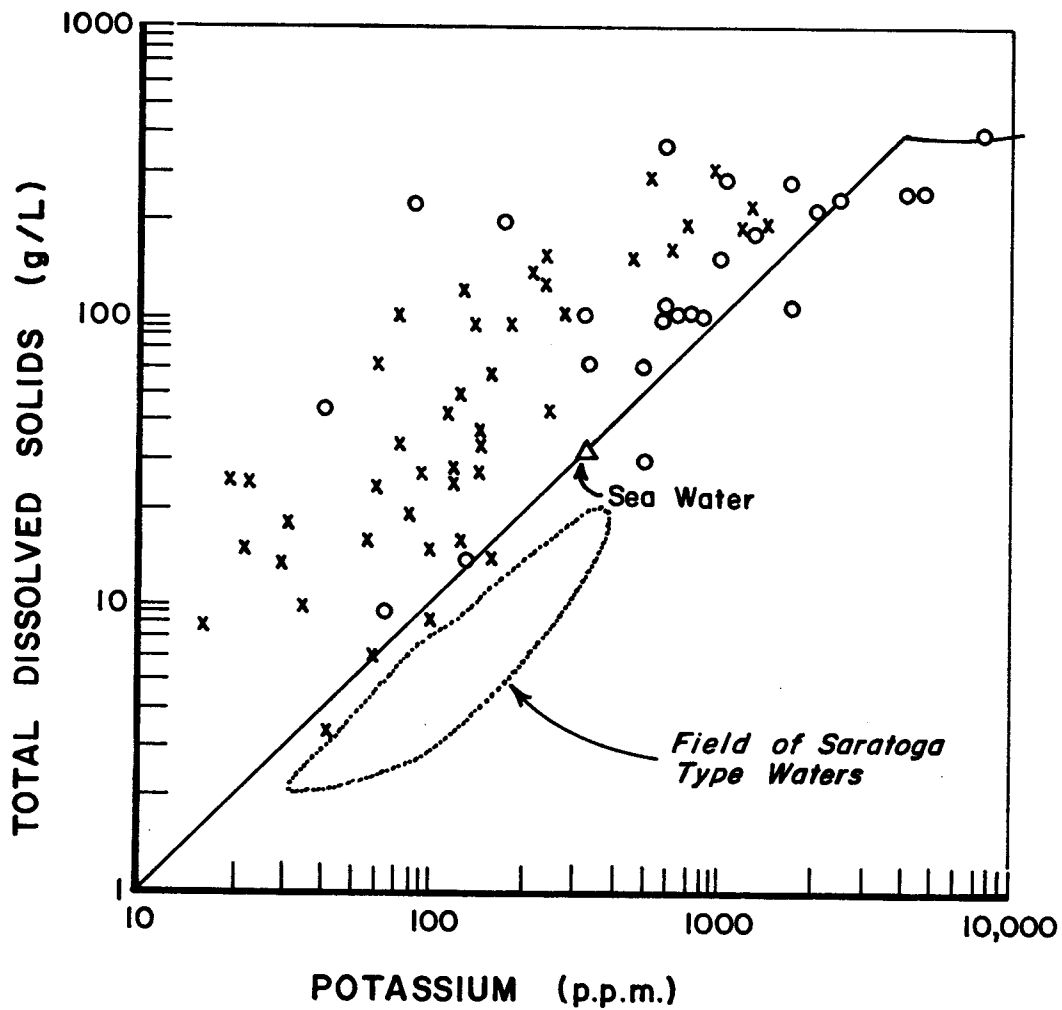


FIGURE 3. POTASSIUM CONTENTS vs. TOTAL DISSOLVED SOLIDS IN OIL FIELD BRINES AND SARATOGA WATERS

OIL FIELD WATERS FROM SANDSTONE (o) & CARBONATE (x) RESERVOIRS

from Rittenhouse, G. et al. 1968

seen, many of the analysed wells show evidence of a variable increase in bicarbonate content (and higher Ca and Mg contents) relative to a process of simple dilution of a reservoir fluid of a given composition.

Another aspect of the CO_2 problem is the relative absence of significant sulfate or nitrates in the water. Moreover, the low contents of these anions can be seen to vary inversely with the amount of total dissolved solids (TDS). The high TDS wells (10,000 PPM to 22,000 PPM) have little or no sulfate or nitrate, while the less saline wells with 2,000 - 10,000 PPM total dissolved ingredients have progressively more of these two latter constituents. Sulfate is produced by the surface and near surface oxidation of sulfide minerals, such as pyrite, and also from the decomposition of organic detritus. An increased presence of sulfate in the dilute waters can thus be explained by the admixture of surface groundwater, especially from the shales in which it is ubiquitous. Small amounts of CO_2 in ground water are produced throughout the outcropping carbonate rocks of the northeast U.S. by the interaction of weak H_2SO_4 and H_2CO_3 (produced by weathering) with the CaCO_3 of limestones and, to a lesser extent, dolostones. Carbon dioxide may also be produced by the direct oxidation of carbonaceous beds, such as coal or peat or by organic decomposition with accompanying production of methane. The amount of CO_2 at Saratoga, however, is at least an order of magnitude greater than occurs in waters normally associated with these latter processes, while the quantity of sulfate, nitrate, and methane is substantially less. Kemp (1912) first interpreted these points to rule out a shallow, oxidizing derivation for the gas. We concur completely with this interpretation now supported by even more complete analytical data, and can only conclude that the source of the gas is beneath the reservoirs and deep seated - a problem to which we will return.

The second major point concerning the waters is their obvious saline nature. Older analyses of some Saratoga waters, as well as the previously mentioned Rotterdam Junction well, exceeded 21,000 PPM total dissolved solids, the majority of which is NaCl - common salt. In general order of abundance follow calcium, magnesium, and potassium in amounts usually above 100 PPM in the wells of higher TDS. These constituents, in diversity and relative abundance for the most part are characteristic of world wide occurrences of basinal brines. We can, however, note in Saratoga waters several anomalies in their chemical make-up that are distinctly different from most basinal brines.

As can be seen in Figure 3, the relative amount of potassium contained in the Saratoga waters is distinctly higher than that of other North American basinal brines or ordinary sea water. While most brines of younger basins contain far higher total dissolved solids (from 200,000 to 300,000 PPM or more) some, such as the Illinois Basin, contain less (from 5,000 to 8,000 PPM). In all cases, the relative abundance of potassium is less than that of seawater, except for Saratoga type waters. In fact, the discrepancy for Saratoga waters is even larger than illustrated, since the dissolved solids in Saratoga waters includes appreciable amounts of bicarbonates not found in other basinal brines. While leaching from near-surface potash beds can produce anomalous potassium in groundwaters, and, presumably, become an increment into basinal brines, no evaporites including

salt beds, potash, or gypsum beds are known anywhere in the brine-bearing Beekmantown carbonates - nor is there any reason to suspect their presence. Another plausible method by which "excess" potassium may be produced involves the leaching of, or alkali exchange equilibria with, potassium-bearing minerals by waters at elevated temperatures - in other words a metamorphic reaction. In this same context it is to be noted that appreciable "excess" sodium is present in some wells, i.e. sodium which is in excess of chloride ion and which must be ionically balanced by bicarbonate. This also suggests a leaching or reaction of the carbonated waters with appropriate wall rocks, in this case the basal Potsdam Sandstone and the Proterozoic Basement.

Finally, there is the presence of a diverse suite of trace constituents and anions in the waters varying from 1 to 100 PPM, and including silica, strontium, barium, fluorine, lithium, iron, ammonia, bromine, boron, and zirconium - to name a few (unpublished analyses, New York State Department of Health). These elements are common to all basinal brines though not in quite the same relative abundances. Several wells show excess amounts of lithium (Hyde South, Ballston Spa), ammonia (Geyser), and silica (Lincoln, the latter two are in the Saratoga State Reservation on Figure 1) when compared with waters of similar salinity from other wells.

Strontium and barium also appear to be slightly enriched and a possible source might be in the low contents of these elements in the Beekmantown Carbonates. The anomalous silica content of the Lincoln Well, as well as several others, in respect to Saratoga waters is at present of unknown significance since basinal brines exhibit values from 10 to 100 PPM in an apparently random fashion. Zirconium, however, is uniformly present in amounts distinctly anomalous for basinal brines, for example two emission spectroscopic analyses by Strock (1941) show levels of about 350 PPB.

Although any attempt at a final resolution of these various observations with a theory of genesis must await the results of ongoing research, some basic conclusions can be reached at this time from the available data. Further, some speculation can also be offered, since the range of possible processes or mechanisms is already rather constrained by the data.

First, the Saratoga waters represent a complexly mixed system with at least four major components. They are (A) normal surface groundwaters of meteoric origin; (B) basinal brines of low salinity, probably through progressive dilution, which may be as old as the Paleozoic; (C) a gaseous phase consisting primarily of CO_2 ; and (D) constituents added by reactions between wall rocks and the saline carbonated waters.

Second, the source of the CO_2 is deep-seated in the basin east of Saratoga and the gas probably emerges along faults and fracture zones in the Grenville basement to encounter saline basinal waters at various points.

Third, the carbonated waters travel westward up the aquifer created by the fracture porosity of the dolostones and limestones of the Beekmantown

Group. The charged and possibly heated water pursues this path of least resistance because the overlying shales create a very effective caprock.

Fourth, during their long, slow rise to the surface the waters react with and variously equilibrate with their surroundings. Their temperature then reflects the local geothermal gradient in the surficial rocks of the basin.

Fifth, the distribution of charged waters at the surface is primarily controlled by faults which create channels up which the waters can rise through the impermeable shales.

Past workers have concluded that the source of the CO_2 was a metamorphic reaction between the dolostones of the Beekmantown or the marbles of the Proterozoic with an igneous intrusion. Kemp first proposed this theory in 1912 in his exhaustive study of the mineral waters and offered Stark's Knob, a volcanic "plug" situated north of Schuylerville, as evidence of volcanic action in the area. Cushing and Ruedemann (1914) concurred with Kemp's hypothesis but offered excellent evidence for the allochthonous position of the plug, a position agreed with by later workers on Taconic geology. Subsequent workers have either skirted the problem or vaguely agreed with Professor Kemp and ascribed the CO_2 to be a product of the last dying fires of the Grenville Orogeny!²

More recent observations on various carbonated waters from many localities suggest several source mechanisms, but also commonly with an implied thermal requirement (Farmer, 1965). Some carbonated waters have an obvious association with volcanic areas either through intrusion induced decarbonization reactions in appropriate rocks, or by means of metamorphic reactions in the aquifer rocks of attendant geothermal fluid systems. Other carbonated waters occur in orogenic zones of above normal geothermal gradient and represent the surface discharge of thermal waters associated with metamorphism at depth (Barnes and O'Neil, 1976).

Still other carbonated waters with $\text{Na} + \text{HCO}_3^-$ and variable Cl^- have been recognized as probable metamorphic waters associated with major fault or active tectonic zones such as the San Andreas Fault of California (Irwin and Barnes, 1975). Carbon isotope determinations in the latter case even suggest that the CO_2 may be mantle origin, and thus P_{CO_2} approximates the lithostatic pressure from the base of the crust to the surface (Barnes, personal communication, 1978). Surface temperatures of these waters are variable, however, and in some cases a near normal geothermal gradient may prevail.

Some carbon dioxide-rich (soda) springs have also been noted in areas which lack volcanism, but where carbon isotopes suggest a source from decarboxylating organic matter in the rocks without pronounced thermal degradation (Barnes, personal communication, 1978). Such a mechanism at Saratoga, however, is precluded by the absence of analogous organic material in the lower Paleozoic or Protozoic basement rocks.

As noted by previous investigators, the saline component of Saratoga waters is comparable to that of many connate waters in marine sedimentary

basins (White, 1965) and may have a similar origin. At least two other factors, however, appear to deserve consideration at this time. First the younger Paleozoic cover presumably present over the Saratoga basin included the easternmost margins of the Salina Group which has been stripped away in Tertiary erosion. The former position of this Group in the area now occupied by the Adirondacks is unknown, but a contribution of saline waters to the Saratoga basin by leaching of this Group upon removal may have occurred. Saline components by either of these sources, however, are residual, and a progressive dilution with time by surficial meteoric water would be expected, as perhaps is seen in the data of Table 1.

A second and non-residual source of saline materials is possible if a heated metamorphic type water component is associated with the CO_2 generation and added to the system. One cannot expect any significant water addition via dehydration reactions upon metamorphism of any already dehydrated Proterozoic basement, but flow along fault zones is possible. Sources of Cl^- by this process are admittedly limited to such things as chloride bearing scapolites in Proterozoic marbles and calc-silicate granulites, but no more likely source rocks for Cl^- are apparent in a number of other occurrences of thermal CO_2 -bicarbonate-chloride waters. A series of new analyses of Saratoga type waters, including carbon, hydrogen and oxygen isotopes is in progress, and hopefully will permit a distinction among these processes as to carbon source(s), water types and mixing, and thermal effects.

A principal concern of the study of Saratoga waters is, of course, the potential for thermal anomalies responsible for the CO_2 gas evolution. In almost any other setting, waters of this type could reasonably be ascribed to evident volcanism, metamorphism at depth, or igneous intrusion. Before speculating on this aspect, it must be noted that radiogenic heating is well known in the eastern U. S. as a means of producing local heat flow anomalies, especially in granitic rocks enriched in potassium and uranium. Heat flow measurements on the 175 m. y. Conway Granite of New Hampshire, for example, uniformly exceed 2 H.F.U., considerably above the average of 1.0 H.F.U. in Mesozoic or older continental rocks. Minor uranium provinces exist to the north and south of the basin in Proterozoic rocks near Lake George and in the Hudson Highlands at Bear Mountain. Thus, a possibility exists for some localized anomalous radiogenic heating in the basement beneath the insulating cover of the basin, which under optimum conditions might raise temperatures to about 100°C. While thermal waters thereby result, this mechanism appears inadequate to produce the temperatures of metamorphic decarbonization reactions within the upper 5 km. of the earth's crust. Higher geothermal gradients extending to greater depths can be postulated, but seem inconsistent with the scale of known Proterozoic radiogenic anomalies. Further, no known thermal waters in the eastern U.S. derived by radiogenic heating are carbonated.

For these reasons, radiogenic heating is not favored at this point as the primary causative mechanism, although it may be a fortuitous contributing factor. Obvious igneous activity in eastern New York and western Vermont ended with the dike swarms of the Cretaceous but tectonic activity continues. This is manifested by current uplift of the Adirondacks (Isachsen, 1975); suspected Quaternary age of some faulting or renewed activity on older faults

(Wold and Isachsen, 1977) and known historic seismic activity in the region (King and Zietz, 1978).

The New York-Alabama lineament in Proterozoic basement rocks terminates (or loses expression) beneath the Saratoga basin, and a notable Bouguer gravity low between Albany and Bennington, Vermont coincides with the eastern part of the basin and is likewise attributed to a source largely in the basement rocks (King and Zietz, 1978).

Are Saratoga type waters then the tangible expression of the embryonic stages of the development of a N-S rift zone in the crust in eastern New York? By analogy with current plate tectonic concepts, igneous activity is a likely feature during this development. We cannot deny, at this point, that an intrusion into the upper few kilometers of the Proterozoic basement beneath the Saratoga basin, or several dikes intruded into faults in the same would provide for the characteristics of these waters in virtually all particulars.

While the prior popularity of its waters may have waned, at least for geologists Saratoga may have enhanced its potential for excitement; for the moment, too, it can also claim to be exceptional.

ACKNOWLEDGEMENTS

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