THE BUBBLES REVISITED: THE GEOLOGY AND GEOCHEMISTRY OF "SARATOGA" MINERAL WATERS[1]

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ABSTRACT

Carbonated-saline-bicarbonate mineral waters of a pH < 6.5 occur within an area of more than 1000 square miles in east-central New York, extending from Fort Edward to the Mohawk Valley. The most notable occurrences are from wells 150-1000 feet in depth in Lower Paleozoic carbonate rocks near an eastward downstepping fault complex in the cities of Saratoga Springs and Ballston Spa. Other occurrences to the east in the overlying shales tend to be carbonated $NaHCO_3$ types of lower salinity with occasionally significant sulfate-ion contents as well.

The presence of residual uncarbonated saline formational waters in the same Paleozoic aquifer rocks around the region of carbonation, as well as temporal and areal variation patterns of the carbonated waters, indicate that at least four major components are present, (1) saline formational waters of approximate NaCl stoichiometry, with low alkalinity and salinities to 12,000 ppm or more; (2) an aqueous, dissolved carbon dioxide phase apparently generated by carbon dioxide outgassing along faults in basement rocks beneath the deeper and denser saline waters; (4) dissolved salts added as a result of reactions between the carbonated waters, i.e., saline carbonic acid solutions and the wallrocks with Ca, Mg, Na, and K bicarbonates as the major constituents.

Consideration of the dynamics of the system with P_{CO_2} up to 5 atmospheres, exsolution of a free gas phase, and of the isotopic chemistry of C, H, and O, suggest that the carbon dioxide is of a thermal, inorganic origin. The relatively low geothermal gradients of the area (15° to 20°c/km) suggest a carbon dioxide source via deep crustal or mantle degassing with access to the surface by "leakage" along deep faults.

INTRODUCTION

The City of Saratoga derives its name from the famous naturally carbonated mineral waters that emerge from numerous driven wells in the eastern portion of the city. The first spa in this country, the city is situated in eastern upstate New York halfway between the Adirondack resort of Lake George and the capital city of Albany. It is one of America's most picturesque towns, hosting a racetrack and stables, mineral baths, state park and performing arts center, golf courses, a college, and numerous historic homes. Though it lies in the Hudson Valley lowlands, the lower Adirondacks frame the city, jutting out as they do from the main massif to the immediate northwest. In short, the area is one of many attractions which have evolved about the sources of the carbonated waters. While Saratoga Springs thus serves as the historic focal point, in actuality the waters occur over an area of more than 2500 square kilometers (Figs. 1, 3) which is the topic of this report.

This study of the waters follows many previous ones conducted with varying degrees of comprehensiveness. We cannot consider this effort to be the last work since the final resolution of the source of these most peculiar waters (i.e. with an apparent inorganic, thermal carbon dioxide source) awaits the development of more sophisticated data that are presently available. However, we have at least narrowed the possiblities by defining a geological, geochemical framework encompassing the answers from which the reader may judge.

THE PROBLEM AND ITS WORKERS - PAST AND PRESENT

The puzzle that the springs of Saratoga represent and partial resolution represented by this work are very much functions of time. We are doubtful that our hypothesis could have been properly phrased at an earlier time; at the same time we do not feel that the problem would have long remained unresolved for it only needs to be reexamined in the light of modern chemical techniques and the now accepted basic tenets of plate tectonics. In short, the data and their interpretation presented herein are very much the cliched idea whose time has come.

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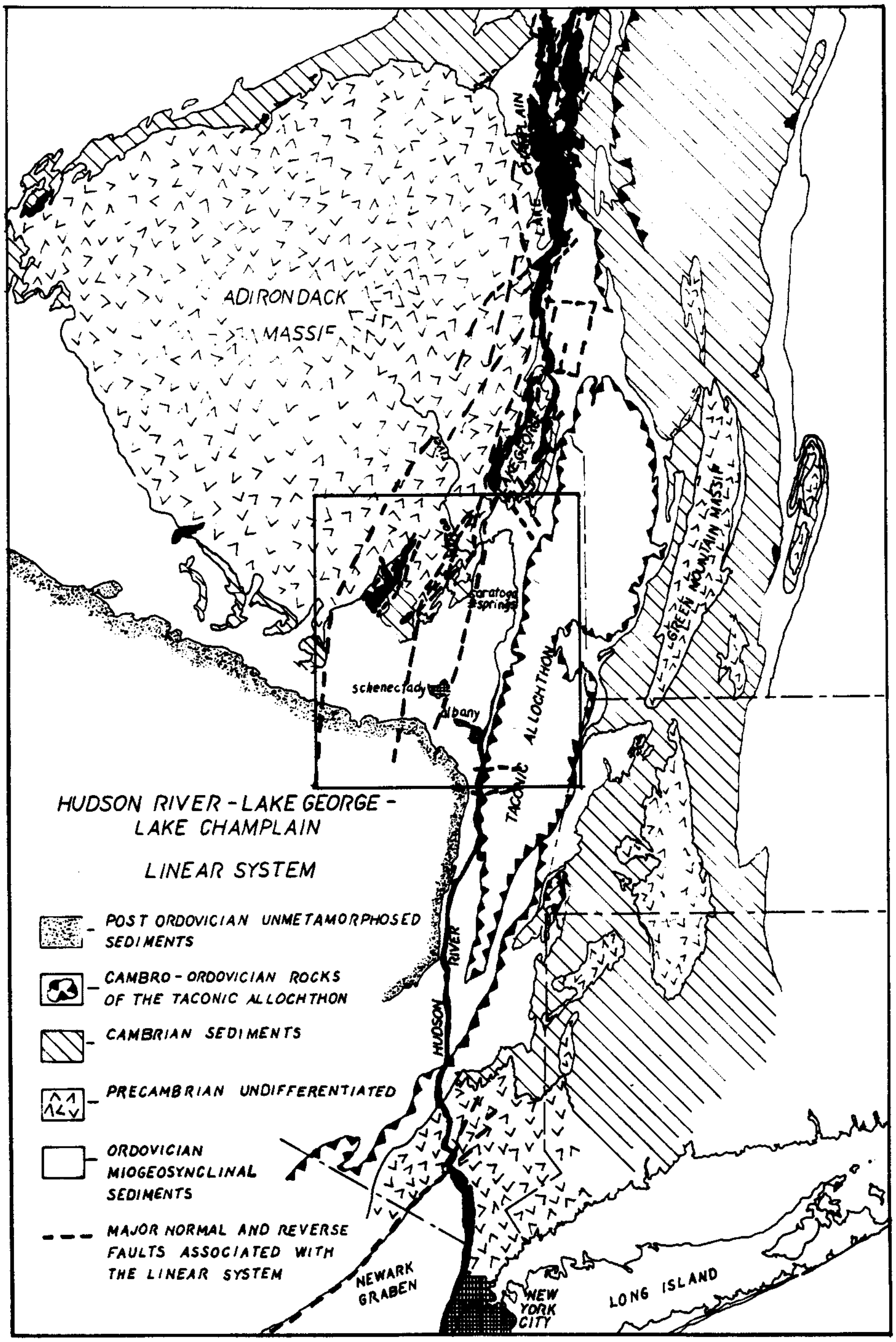


Figure 1. Generalized geologic map, eastern New York and western New England, and location of the study area.

To properly frame the apparent enigma of Saratoga it is necessary to look at the previous work as well as contemporary theories of subsurface CO_2 generation while elucidating other unique aspects of the system, for truly the CO_2 is not the problem, but rather the context in which it occurs.

Currently identified processes of subsurface carbon dioxide generation (Land, 1959; Farmer, 1965; Hunt, 1979; Irwin and Barnes, 1980) relevant to this study are briefly discussed in the section on water chemistry. They may be subdivided into organic and inorganic mechanisms as follows.

(a) Organic Processes:

1) Decay of organic matter and burial decarboxylation,

2) Catagenetic degradation of hydrocarbons during thermal maturation (75-125°C).

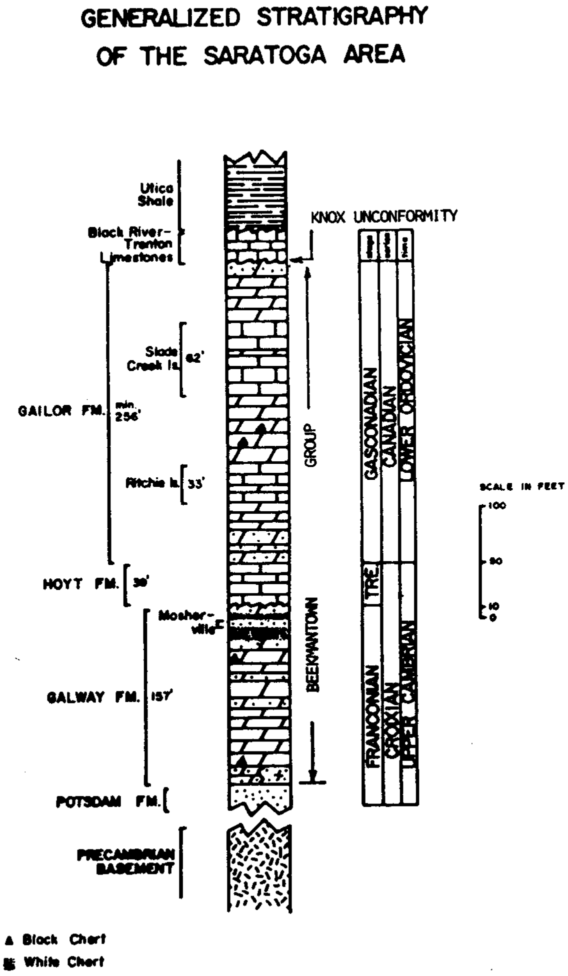
b) Inorganic Processes:

1) Degassing of igneous melts, mantle degassing, or formation of carbon dioxide rich melts,

2) Metamorphism of carbonates (decarbonation) or reactions between host rocks and connate brines during prograde metamorphism of sedimentary basins, CO_2 generation via thermal dissolution of carbonates has been reported at temperatures as low as 100-150°C.

All but the first organic process are considered to be thermally derived. However, all the organic sources also result in the concurrent production of much more methane than carbon dioxide. Present techniques of carbon and oxygen isotope analysis as used in this study may permit an identification of the sources(s) of carbon, as, for example, "igneous" or organic origins.

As America's oldest spa, Saratoga Springs affords a rare opportunity in geochemical studies, that of being able to examine trends in water chemistry over a period of time exceeding 100 years. In fact, the early interest in the late eighteenth and early nineteenth centuries fostered many studies that were largely "pseudoscientific" in nature and mostly designed to tout the curative properties of the waters. However, a reputable set of analyses may date as far back as 1840, as performed by Dr. John Steele, and a later more thorough set was made by Professor Charles F. Chandler in 1875. Their analytical work can be considered relatively accurate for many of the major dissolved constituents in the waters. The first interpretation of the mineral water system was attempted by Professor James F. Kemp (1912), who combined the prior analytical work and other data with new sets of analyses by the U.S. Department of Agriculture to produce an exhaustive study of the waters.



(Modified after Mazzullo et al. 1978)

Figure 2. Generalized stratigraphic column, Saratoga area.

Kemp's work still remains as an outstanding example of scientific analysis even though it was performed over 70 years ago. Not only does he compile a complete historical/analytical sketch of the Saratoga area springs and wells, he cites other occurrences from Albany north to Whitehall and links them into a unified interpretation. Among some of Kemp's more noteworthy conclusions are these: (1) that "faults furnish an upward passage for the gas and dissolved mineral matter...but the tight cap of slates above the limestones act as a roof to prevent their escape, except in the springs and bore holes"; (2) the gas (CO_2) is one of the most important features of the water and is generally present in amounts between one to five volumes gas/volume solution (approximately one gas volume per atm. P_{CO_2}); and (3) that the carbon dioxide is thermally generated and the source of the gas and mineral waters was probably due to the action of silicic acid on limestone (i.e. metamorphism) or else a result of expiring volcanic activity (citing the volcanic "plug" of Northumberland, Stark's Knob, as evidence) somewhere deep-seated in the "basin" to the east.

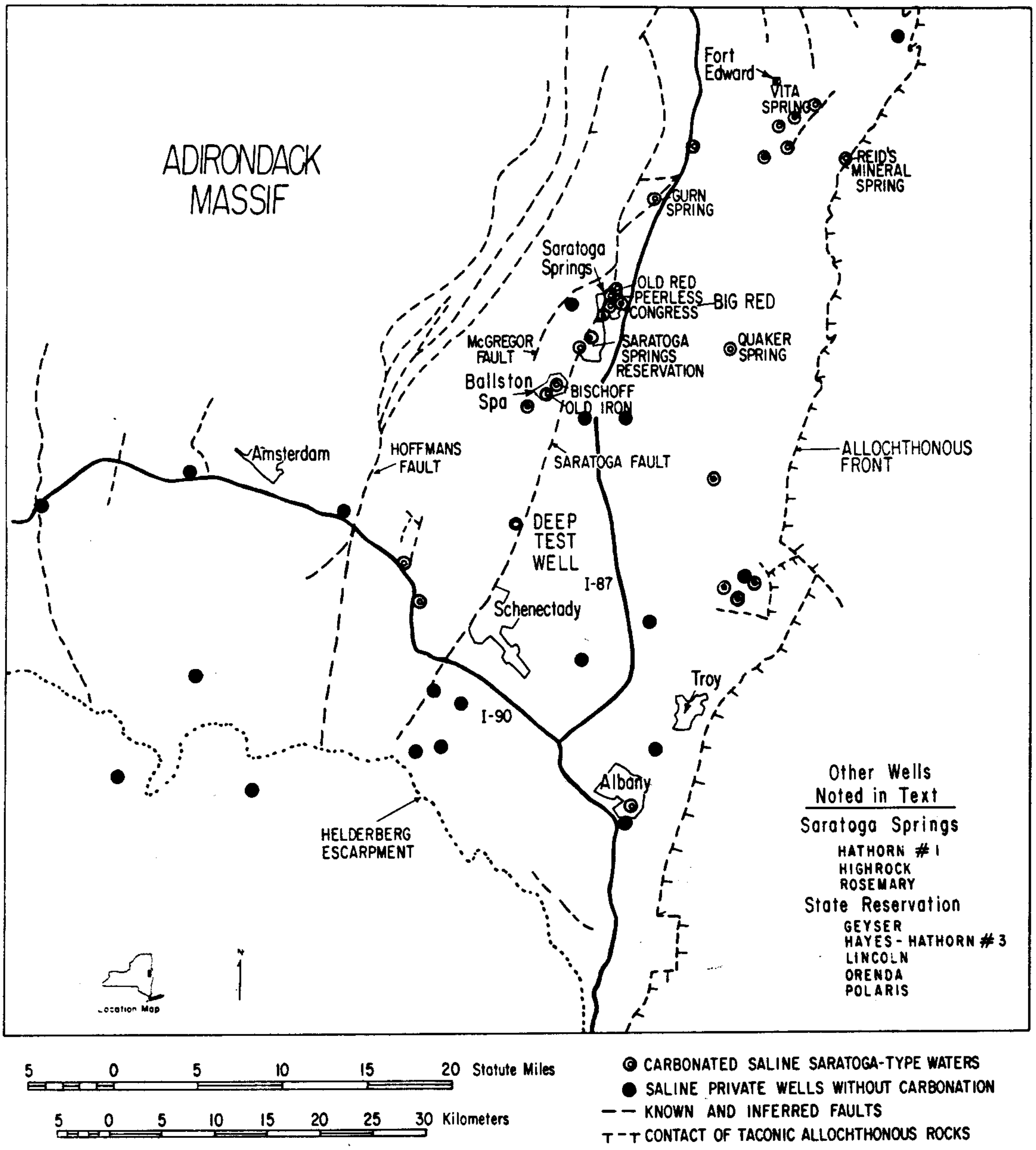


Figure 3. Location map of wells and water types of the study area.

Cushing and Ruedemann (1914) next touched upon the springs in their study of the geology of the Saratoga area. While they did not attempt an in-depth look, stating that such an effort would be redundant after Professor Kemp's work, their mapping supported the conclusion that the points of issuance of the water were fault controlled. They also suggested two other observations of note based on Kemp's work. First, that it was quite possible that the waters were a mixed assemblage of at least three components: meteoric water, connate water, and a separate juvenile source for the CO_2, rather than the waters being entirely of juvenile origin. Second, they pointed out the essential difficulty with Kemp's ideas when they stated that: (1) the waters are not thermal, and (2) "there is no direct evidence of igneous activity of recency in the vicinity, or anywhere else in the eastern United States." While still not choosing to refute a thermal process, they succinctly describe the core of the Saratoga problem in its present status with these final observations.

The last significant study of the waters was conducted by R.J. Colony for the specifically appointed Saratoga Springs Commission under the aegis of the Sate of New York in 1930. While the commission's primary concern was the well-being of the large health resort, considerable data were collected about the waters themselves. Among these were new sets of chemical analyses arranged in a table corresponding to a north-south well progression. These showed a somewhat inconsistent but general increase in total salinity and various separate salts from north to south, which relates to a greater admixture of meteoric water in the shallower, more open northern portion of the carbonate aquifer.

From a historical perspective, the inference of thermally-generated carbon dioxide (or carbonated waters) was based on its presence in volcanic gases, the known partial pressures of the gas (>1 atm), the high bicarbonate alkalinity of the carbonated waters (indicating reactions with carbon dioxide), the presence of certain dissolved constituents (e.g. potassium) in amounts atypical of formation or connate waters of comparable salinity, and the issuance of the carbonated waters along faults of presumed deep penetration. The first four characteristics were known to occur in some hot springs of volcanic association (e.g. see Clarke, 1924), while the last has, at least recently, been described by Irwin and Barnes, (1975), and Barnes et al., (1975).

This report is the outgrowth of several different lines of work by both authors. A specific project was commenced in 1978 under the aegis of NYSERDA-DOE was designed to explore possible thermal effects associated with the carbonated mineral waters. Much of the data has been discussed by Young (1980) and all project results, including those of newly drilled wells, have been detailed in a series of reports by NYSERDA which are available upon request. This report includes a more comprehensive discussion of water chemistry than appears elsewhere and a few revisions of prior reports by Young (1980) and Young and Putnam (1979). Where possible a regional and comparative approach to the problem is taken. The authors did not participate in the final NYSERDA report; (Sneeringer, et al., 1983) views expressed therein will not necessarily agree with the conclusions presented here.

GEOLOGY

Essential to an understanding of the Saratoga-type mineral waters is a knowledge of the general geology of the area and, particularly, the bedrock structural pattern of the area whose fault-generated pathways govern the distribution of the carbonated waters. The local pattern of the immediate study area integrates well with the larger emerging structural framework of the eastern Adirondack massif and the Lake Champlain-Lake George-Hudson River Valley linear system, a topic whose significance is addressed in a forthcoming separate paper. A brief overview of the geology is first offered here as it pertains to the mineral waters.

STRATIGRAPHY

A large body of geologic literature exists concerning the Paleozoic stratigraphy of eastern New York State, especially the siltstones, wackes, and pelites of the Taconic sequence and the Cambro-Ordovician carbonates of the eastern Mohawk Valley. These sediments formed during the earliest Paleozoic as a shallow, marine, continental shelf sequence on the margin of the North American craton that later subsided and was covered by the westward transgressive flysch of the Taconic stage. Subduction and subsequent collision during the Taconic orogeny has resulted in a complex pattern of deformation, thrust transport, and synchronous erosion/deposition within the flysch sequence which varies from autochthonous in the eastern Mohawk Valley to completely allochthonous in the eastern part of the study area. Local variations in the lithology, structure, faunal ages, and deformation features have spawned a large number of stratigraphic names (e.g., Utica, Canajoharie, Schenectady, Snake Hill, Normanskill, and Austin Glen as applied to various portions of the flysch). For convenience in this discussion, we refer to those names of common or original usage in the study area. However, a review of the Paleozoic structural/tectonic history of these rocks is beyond the scope of this report, and we do not imply any resolution of the nomenclature. A generalized stratigraphic column for the area is depicted in Fig. 2. Except for deformed portions of the flysch sequence, all Paleozoic rocks in the study area are approximately flat-lying.

Precambrian Basement

Precambrian basement rocks outcrop in the north-central and northwest portions of the Saratoga quadrangle and underlie the Paleozoic rocks of the entire upper Hudson Valley study area. Most of the basement rocks are believed to have a primary age of 1-2 b.y., but all have been metamorphosed to the upper amphibolite to granulite facies during the Grenville orogenic episode at 1.0 to 1.2 b.y. Geothermometry and geobarometric estimates place the peak of the Grenville metamorphism in the Adirondacks at 700-750°C and 7-9 kilobars (20-36 km), an unusually deep episode of metamorphism in now exposed crustal rocks and for which a former double thickness of continental crust has been suggested (McLelland, 1979). Stratigraphic and structural relationships in these rocks are commonly inferred to be complex with some authors suggesting as many as 5 distinct episodes of folding (Turner, 1980) while others suggest multiple zones of ductile shear and/or flattening, and transposed fabrics (Anderson, 1983). Consequently there is little agreement about a recognizable stratigraphy.

The rocks consist of mixed metasediments and metaigneous rocks with iron and titanium-rich anorthosites and metagabbros forming the Adirondack core some 75 miles north of Saratoga Springs. Metasedimentary rocks outcrop immediately north of the city and consist of quartzites, locally highly graphitic schists, garnet-sillimanite, microcline gneisses (Khondalite), thinly interbedded graphite-pyrite-sillimanite schists, and coarse calcitic to dolomitic marbles often containing graphite in large disseminated flakes. Granitic to charnokitic gneisses and other quartzo-feldspathic gneisses of uncertain origin are common with local migmatite and pegmatite. Some granitoid gneisses are enriched in radioactive materials with or without magnetite.

The Cambro-Ordovician Aquifer

Resting unconformably on the Precambrian basement, the Potsdam Formation is a massive, heavily bedded orthoquartzite, well-cemented by quartz itself. It is comprised of well-rounded quartz grains and is relatively insoluble in groundwater, and, presumably, only slightly more soluble in the carbonated mineral waters. While not porous, the beds are brittle and probably have some limited reservoir characteristics due to secondary fracture permeability.

Long interpreted as a prograding beach sand, the bulk mineralogy is rather monotonous except in the basal portions where much of the sandstone is arkosic with numerous stream channels in the lowermost 20 feet as exposed near Whitehall, NY. Alkali feldspars and perthite derived from the underlying Precambrian basement comprise up to 20 percent of the lower beds and decrease to less than 5 percent 20-200 feet from the base of the formation. The stream channels and the basal 1-10 feet of the Potsdam in this area are arkosic conglomerates, which contain magnetite, ilmenite, zircon, uranothorite, etc. and locally exhibit pervasive chloritization. At the only outcrops in which the basal contact is visible (on Route 22 outside Comstock and Putnam Station, N.Y.) the unconformity appears to be almost "welded" and certainly would not serve as a conduit for the present mineralized waters if it persists in this fashion further south in the Saratoga area.

The Potsdam sandstones are transitionally replaced upwards by the quartzites, quartzose dolostones, and dolostones of the Galway Formation without a distinct stratigraphic boundary. Colony (1930) used the term Theresa "passage beds" to describe the Galway, but this alternating transitional sequence has since been renamed because the type Theresa near Watertown, NY is Ordovician in age whereas the section in the eastern Mohawk Valley is Cambrian, hence, the preferred name Galway (Fisher and Hanson, 1951; Rickard, 1973).

In the Saratoga area this formation averages about 160 feet thick but thickens rapidly to the west to a possible maximum of about 300 feet in the Galway area. The lowermost 60 feet has only been penetrated by a single drillhole in the Pallette Quarry 2 miles west of the City of Saratoga Springs. Here the lower portion is known to be an alternating series of orthoquartzite (similar to the upper Potsdam sands just below) and quartzose dolostones, both averaging 5-10 feet in thickness. The quartz content of the dolostones and the thickness of the quartzites decreases upward in the formation. Authigenic alkali feldspar (microcline) is ubiquitous throughout the formation further to the west (Braun and Friedman, 1969) and presumably in the Saratoga area as well. Present locally 2 miles west of Saratoga Springs is a strongly reactive limestone unit known as the Hoyt Limestone. The Hoyt is very fossiliferous and possesses abundant cryptozoa that are well-exposed at Lester Park on the Pompa Quarry road. Abundant oolites and local sands also characterize the Hoyt as a reef facies. As far as is known this lithology is very local and is not picked up in the boreholes of the mineral wells several miles to the east in the City of Saratoga Springs.

The Gailor Formation transitionally tops the Galway and consists of 256 feet or more of medium- to thick-bedded, light- to medium-crystalline, slightly cherty dolostone with two prominent intercalated limestones in the Saratoga area. Characteristically dark-gray, both these limestones are also fine- to coarsely-crystalline calcilutites which are difficult to distinguish from one another in the field (Mazzullo, _et al_., 1978). The lower limestone is thought to be the Ritchie member after the type section near the Pompa Quarry described by Fisher and Hanson (1951) and redescribed by Fisher and Mazzullo (1976). The upper limestone is 62 feet thick in the Pellette core and is termed the Slade Creek member.

The remainder of the formation consists of light-gray, medium- to coarsely-crystalline dolomites similar to those of the underlying Galway Formation. Field distinction of the two can often be very difficult in areas of poor outcrop. Complicating this are rapid facies changes to dark-gray, silty and sandy (quartzo-feldspathic) medium-crystalline dolostone over distances of only a few kilometers (Mazzullo, _et al_., 1978). These two facts pose serious functional problems for the stratigrapher in this area.

The Gailor Formation hosts most of the mineral water wells in the City of Saratoga Springs. In this respect the intercalated limestones and the 40 feet thick Hoyt Limestone immediately beneath, assume some potential significance for the chemistry of the carbonated mineral waters due to relative solubilities and dissolution rates in carbonic acid. The fault and fracture zones constituting permeability pathways in the otherwise impermeable formation (also the similar underlying Galway) are probably undergoing slow enlargement due to dissolution by the carbonic acid of the mineral waters. However, this effect is interpreted to be limited overall due to the lack of recent karsting in the exposed, exhumed limestones immediately west of the city.

While not a large factor in the general vicinity of Saratoga Springs, the very reactive Trenton Black River limestones are now known to thicken southward to a minimum depth of 70 feet where they were encountered in the 2300 foot exploratory hole at Ballston Lake for the NYSERDA-DOE (Sneering, _et al_., 1983). This post-Knox group is only about 40 feet in thickness at Saratoga Springs and has only been penetrated there by the boreholes drilled to tap the mineral waters. The Knox unconformity is also known to rise stratigraphically south of Saratoga Springs, e.g. in the Ballston Lake drillhole about 500 feet of Tribes Hill carbonate rock units above the

Gailor was reported (Sneeringer, et al., 1983). The Trenton limestones could also host considerable karsting from action of the carbonated waters although direct evidence is lacking at this time.

The Ordovician Shale "Caprock"

Transitionally overlying the Cambro-Ordovician aquifer rocks are a series of impermeable autochthonous and parautochthonous to completely allochthonous shales in the Hudson Valley lowlands. In much of the Saratoga area the Canajoharie Shale (Ruedemann, 1912; Cushing and Ruedemann, 1914) is the surface bedrock. It extends north and south from Ballston Spa and east to the folded and perhaps thrust-faulted exposures of the Snake Hill Shales in the vicinity of Saratoga Lake. The formation consists of 1000-1100 feet of soft black, carbonaceous, argillaceous, and variable calcareous shales distinct from those to the east termed the Snake Hill. Much of the shale contains abundant pyrite that oxidizes to fill the cleavage and bedding planes with rusty brown limonite that is probably responsible for the minor H_2S gas and SO_4 ion noted in some of the mineral water wells. The formation also contains anomalous but low-level contents of uranium scavenged by the carbonaceous matter in what was probably an anoxic or reducing environment during deposition.

The Schenectady Formation, as described by Ruedemann (1912), overlies the Canajoharie Shale in much of the study area west of the Snake Hill Shale and other allochthonous Taconic rocks. In the lower Mohawk Valley the formation consists of about 2000 feet of light bluish-gray to dark-gray shales forming monotonous, uniformly alternating series. Resembling a turbidite sequence, these rocks were probably deposited in a relatively distal shelf or proximal slope environment. The principal point of note for this study is that there is no substantial lithic difference between either of these shale units nor the allochthonous ones to the east.

STRUCTURAL GEOLOGY

Saratoga Springs is coincidentally situated at the confluence of several geologic provinces (Figs. 1 and 3) whose juxtaposition is a result of the fault development and continued movement in the region accompanying the domical rise of the Adirondacks (Isachsen, 1975, 1981). The very large McGregor Fault system, which is 85+ km long and continues northward into Canada as part of a zone of high-angle faults that define the eastern border of the Adirondack uplift (Geraghty and Isachsen, 1981), breaks up into several faults of lesser displacement at Saratoga Springs. The dominant N10E and N20E strike is manifest in at least two traceable faults, the Saratoga Fault (Cushing and Ruedemann, 1914) and the southern extension of the Ballston Lake Fault which was identified by Ruedemann in 1930. Another unnamed, less prominent system strikes generally westward and aids in defining the southern limit of the Adirondack periphery, which otherwise forms a series of cuestas on the gently south-dipping Paleozoic carbonates. The most notable of these is the Helderberg escarpment. The carbonates of the western part of the area provide the best evidence of overall fault patterns because of their brittle nature. It is this area that we have examined in some detail with the intention of relating exposed patterns here to the shale-covered areas further east.

The dominant fault pattern in the nearly flat-lying Paleozoic rocks around the southern periphery is the same as that through the Adirondacks, viz north-northeast. Several of the larger breaks extend southward out of the massif into the Paleozoic cover. Like their more numerous northern counterparts, these faults are generally normal and upthrown to the west at high angles, usually between 70° and 90°. Approximately 12 of these faults with measurable vertical displacements over 30 meters extend southeasterly from the Adirondacks into the Mohawk Valley (Fisher, 1954). All decrease in throw to the south and many tend to "hook" to the west at their southernmost limits (D. Fisher, 1954 and pers. comm.). There is a tendency for these major faults to strike from approximately N20E in the western Little Falls area to almost N-S just east of Saratoga.

In addition to the major north to northeast high-angle step faults there are several sets of shorter individual faults in the Paleozoic cover around the southern Adirondack periphery with less apparent vertical displacement. The major component of these sets strikes from N60E to E-W while a lesser conjugate set strikes from N30W to N-S. These faults can be most easily seen in the brittle carbonates west of Saratoga that are quite literally "diced" by small, high-angle breaks. Faults with only 10 meters or less of vertical displacement may manifest sharp topographic scarps with a relief of several meters. As a whole, this subordinate set of faults forms block-faulted topography with many small horsts and grabens traceable from Saratoga westward to Little Falls.

The largest exposed fault in the area is the McGregor system, along whose southern extension, the Saratoga Fault, issue most of the classic Saratoga "springs". Recent studies of this fault system indicate at least two (and probably more) periods of reactivation with a tectonic history extending as far back as the late Precambrian (Williams, et al., 1983). We view this fault as being deep-seated and probably being the surface expression of a more fundmental, long term zone of weakness in the lithosphere. From the following discussion on the chemistry of the mineral waters it seems likely that the Saratoga Fault acts as a conduit for the discharge of CO_2 rather than as a barrier. So, too, do several inferred more easterly faults.

In relating the faulting patterns discussed above to the lowlands to the east where shale bedrock is covered by glacial drift, it is most reasonable to assume that there is no significant change in these patterns. In fact, when we consider that the visible fault pattern in the carbonates enjoys a lateral exposure of almost 80 km, it actually becomes unreasonable to assume a marked change in the 10-20 km wide swath of shale up to the western limit of Taconic deformation*. With regard to the major NNE trending step faults, there is some indirect evidence to suggest that at last two such features may be hidden under the shale cap between the City of Saratoga Springs east to the Hudson River. Drillhole data from the Big Red well identifies the depth to the nearly flat-lying carbonates as approximately 1400 feet, whereas one mile west near the Saratoga Fault scarp the depth is less than 50 feet. Therefore one or more subparallel faults may lie within one mile of the McGregor Fault.

Less directly visible, but perhaps even more important as far as controlling the distribution of the waters is concerned, may be a large fault or fault zone inferred to lie under Saratoga Lake. It is interesting to note that the strike of this linear is approximately N5E, which fits the observed tendency of the major high-angle step faults to strike more nearly north-south as one proceeds eastward.

Subordinate cross faulting may also be inferred to persist beneath the masking shale caprock. This faulting would yield a pattern of many separate, sharply-bounded blocks of carbonates of varying heights capped by shale, which in turn probably contributes to the heterogeneity of water types found in the Saratoga wells.

In the largest sense then, the pattern of grabens and major step faults as evidenced by Lakes George and Champlain most probably continues southward under the masking shale cover of the upper Hudson Valley lowlands. These faults appear to fan outward to the south and perhaps become widest in distribution somewhere near the latitude of Albany. From the pattern in the western carbonates it is possible that the cumulative vertical displacement and frequency of the faulting also reach a maximum beneath the shale. These inferred major structural breaks, then, most likely would serve as conduits for issuance of the postulate deep seated CO_2 beneath the eastern lowlands.

MINERAL WATERS OF THE GREATER SARATOGA REGION

General

As commonly used, the term "mineral water" refers to naturally occurring waters that contain sufficient amounts of dissolved solids and gases to be distinguished from overlying meteoric derived ground waters. For most people familiar with the Saratoga "Springs", the term mineral water brings to mind waters from the better known wells, but probably even more people are familiar with a low salinity bottled version with enhanced carbonation under such labels as 'vichy', 'sparkling', or 'Geyser' water.

These well known examples are but part of a larger group of carbonated mineral waters with free CO_2 gas as typified by the Saratoga wells, observed over an area of more than 1000 sq. mi. that extends from Albany north to Whitehall, east to the Taconic margin, and along the Mohawk Valley westward at least as far as Rotterdam Junction (Fig. 1). Locally, carbonated waters occur in wells in Canajoharie or Snake Hill shale which intersect fracture zones or faults but do not actually penetrate to the underlying carbonates. South, and perhaps east, of the area of carbonated waters proper is a "fringe" zone of neutral bicarbonate-saline waters within a larger region of typical uncarbonated saline mineral waters. These latter waters occur in the same lower Paleozoic rocks over a wide area, notably south of the Mohawk Valley and westward along the Valley beyond the limits of the region of study in Fig. 3.

The mineral waters occur, for the most part, in fractures, faults, bedding-plane partings and in such other permeability as exists in the shale or carbonate host rocks and commonly underlie groundwater of meteoric origin. Under static hydrologic conditions with only seasonal variations in groundwater level, only a very slow dilution or mixing with the lower saline waters occurs because of their higher density.

The distributions of water types shown in Fig. 1 reflect gross variations both in the relative proportions of dissolved constituents and in carbonation; specific water types are recognized on the basis of compositional regularities. Non-systematic variations in salinity and dissolved gas species (mainly carbon dioxide methane) are superimposed and reflect local factors and dilution at a given well site. The chemistry of these water types, or components in the case of evolved or mixed waters, are discussed in more detail below.

Temperature and Other Physical Aspects of the Waters

Past temperature measurements of Saratoga carbonated waters (Kemp, 1912) as well as those obtained in this study over a larger area, fall in a narrow range of 9-13°C (48-56°F) for the well or spring discharge. A recent compilation, including down well measurements, has been prepared by Sneeringer, <u>et al.</u> (1983). Some seasonal variation is noted, but the range of temperature variation is more subdued than in groundwater wells in surficial sand and gravel aquifers of the same area. With a mean annual air temperature of 9°C in Saratoga Springs, the carbonated waters average about 2°C higher, which is consistent with the temperature range of meteoric groundwater wells of similar depth

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*Low angle Taconic thrust of listric detachment faults at depth have been inferred for deformation of the shale unit (e.g. Snake Hill) west of the actual Taconic allochthon (Bosworth, 1980).

in this region. From temperature profiles in five unused wells, 270 to 710 meters in depth, as reported by Sneeringer, et al. (1983), we have obtained thermal gradients of 15-20^{o}C/km which is normal for areas of stable continental crust (Roy, Blackwell, and Decker, 1972). Wells of the more highly carbonated waters (i.e. with CO_2 partial pressure of 2-5+ atm tend to have the lower discharge temperatures in the above range due to the cooling effect of exsolution of the gas phase as the water rises in the well. The evolved gas produces considerate sputtering in the discharge of some wells; in others with less gas, bubbles are evident. In some wells the internal pressure of the exsolving gas phase in a rising water column creates a hydraulic "head" sufficient to force water to the surface in a manner akin to artesian behavior. If the flow in these wells is stopped and gas allowed to separate to the top of the well column, then the well must first be artifically pumped before spontaneous discharge will resume (see discussion of "gas seal" by Kemp, 1912). In other wells a build-up of gas pressure may occur at depth which upon release produces transient "geysers" up to heights of some 25 meters (e.g. Ballston Spa deep well and Rotterdam Junction well; reported by Sneeringer, <u>et al.</u>, 1983).

In many mineral water wells that have been studied, minor seasonal fluctuations in static water levels and pH have been noted, but without much change in salinity (i.e. concentration of dissolved solids). In a few cases the water type discharged from a new well has changed markedly upon pumping for a time (e.g. see Smith Well; Colony, 1930), the discharge of natural springs may show seasonal fluctuation or flow only at time of high water table (e.g. Bischoff "Spring", Ballston Spa), and in still other cases the discharge of a well has shifted rather abruptly from a mineral water type to typical ground water (e.g. Bennett well, vic. Fort Edward, NY, 1979-1980; Young 1980). These effects suggest a density stratification of waters in the aquifer and interaction with an overlying meteoric ground water zone which tends to dilute or displace the mineral waters beneath.

When the waters of adjacent wells are compared, variations in salinity are common, and in some cases, changes in the relative proportions of dissolved solid or gaseous constituents, or even in the basic water type, may occur. At least part of this variation can be explained by differences in well depth, stratigraphic units penetrated, and the nature and position of fault or fracture "feed zones" intersected in the well.

Types of Waters and Their Chemistry

For this study five main water types were recognized, and representative analytical data compiled from a series of analyses (1978-1980) by the Division of Laboratories and Research of the New York Department of Health are shown in Table 1. Compositional patterns and distinctions among these types are summarized in Table II below, and subsequent illustrations, and a discussion of their chemistry follows.

Saline mineral waters of lower salinity than sea water (and thus not brines) occur marginal to carbonated waters in the Cambro-Ordovician formations of the Mohawk Valley and to an undetermined extent to the south and west of the limits of the area studied (Fig. 1). In sampling to date, these uncarbonated mineral waters have shown salinites < 12,000 mg./liter (total dissolved solids = TDS), with either a near 1:1 molar ratio of Na and Cl ion or a slight excess of Cl, low Ca and Mg content, and maximum alkalinity of a few hundred mg./l. (Table I, No. 9). Minor Br, I, Sr, K, Li, and Ba are invariably present in amounts approximately proportional to salinity, and B, F, Fe, Al, and N (in ammonia) are common trace constituents.

These proportions of major and minor constituents (see Table II) are very similar to connate basinal brines of the NaCl type (White, 1965) except for the much lower salinity. Such brines were originally derived from sea water which furnishes the dissolved components, but the bulk composition may subsequently be modified by ion exchange, diagenetic reactions, and osmotic filtering within the host rocks (White, 1965) as well as by later dilution by meteoric waters. A comparison of the saline waters and sea water in Table 2 points out the relative loss of K and Mg + Ca, with enhancement in Br and I (^{I}/Cl x 1000 = 1-4 vs. .003 in sea water) in the former in this particular case.

These contrasts, especially in halogen ratios, make it very unlikely that the saline waters originated by post depositional ground water dissolution of first stage evaporite salts (gypsum-halite) with markedly lower halogen ratios, rather than from diluted Paleozoic connate waters.

All examples of typical saline formation waters obtained in this study are from wells south of the Mohawk River in the Schenectady-Canajoharie shale-Snake Hill (Normanskill) formations. North of the river and in the Saratoga lowlands the same saline components (Na, Sr, Cl, Br, I) with similar halogen ratios occur in the carbonated mineral waters in both shale and carbonate aquifers, with equivalent salinities up to about 13,000 mg./l. observed in the latter. One example of a saline water (∿ 8000 mg./l. TDS) with weak alkalinity (∿ 800 mg./l.) and low Ca + Mg was once reported from Round Lake (Round Lake Journal, July 1879; C.F. Chandler, analyst; aquifer not stated); others have been alluded to, but not documented by analysis. Normally deep wells in the Saratoga area were abandoned if carbonated mineral waters were not recovered.

TABLE I

WATER ANALYSES	(1) CARBONATED ALKALINE SALINE	(2)	(3)	(4) $NaHCO_3$ TYPES ———	(5)	(6) + SULFATE	(7) NEUTRAL ALKALINE - SALINE - $NaHCO_3$ TYPES	(8)	(9) SALINE WATER	(10) GROUND WATERS IN DOLOMITE	(11) IN SHALE
	HATHORN #3	ORENDA	BIG RED	PEERLESS	MARTIN WELL	VITA SPRING	CARR WELL	HARRINGTON WELL	FRANKLIN WELL	POMPA WELL	SARATOGA VET. HOSP.
pH (field)	6.0	5.9	6.0	5.9	6.3	6.5	6.9	7.6	7.4	7.5	8.5
Cl (mg/liter)	6900	3800	2300	1000	190	230	120	800	5800	6	3
Br	110	61	40	20	21	10	N.A.	25	130	N.A.	< 0.10
I	3.6	2.0	0.7	0.4	0.17	0.04	.044	3.0	18	0.01	0.09
Alkalinity	4100	3020	2500	1925	2270	1220	1430	2410	250	300	216
SO_4	4	20	7	11	21	1300	5	180	16	80	3
F	0.45	0.78	0.20	0.7	0.2	0.2	0.5	2.6	2.4	0.26	1.7
Na	4400	2420	1500	800	630	510	530	1630	3610	5	76
K	320	240	100	93	18	46	50	13	39	3	2.4
Ca	950	700	340	420	100	390	99	12	140	130	6.3
Mg	410	270	260	100	58	130	32	5	43	29	3.5
Li	10	7.8	4.8	2.4	1.1	0.84	1.7	5	14	<.05	0.20
Ba	21	15	6.3	3.1	5.6	<0.5	3.4	<0.5	17	<0.5	0.5
Sr	17	13	12	4.2	7.7	10	2.8	3.3	91	1.4	1.0
Br	3.0	3.4	1.5	1.1	2.0	1.3	0.50	1.3	0.4	0.20	0.5
Fe	2.2	2.7	11	1.9	1.7	1.5	0.40	<.05	5.9	0.33	0.11
SiO_2	12	10	55	10	13	14	9	9	7	7.2	10
Zr	.03-.32	0.23	0.04	0.08	0.12	0.04	N.A.	N.A.	<.003	<.01	<.01
TDS	15190	10370	6460	3820	2590	3720	1640	4070	10600	438	250
Br/Cl x 1000	6.1	7.1	7.7	8.9	49	19.3	--	13.9	9.9	--	--
K/Na	.043	.06	.04	.069	.017	.053	.055	.0047	.0064	--	--
P CO_2 (atm)	4.3	3.25	2.65	2.0	2.3	1.2	0.17	0.052	.008	.010	<.001

NOTES: NA = not analyzed.
- = not calculated.
Alkalinity expressed as CaCO equivalent.
Water sample (1) from 806' free flowing well in carbonates; (2) 344' free flowing well in carbonates; (3) 1800' pump assisted flowing well in carbonates; (4) 151' pump assisted flowing well in carbonates; Samples 1-4 from Saratoga Springs; (5) 293' pumped well in shale, Town of Moreau, Fort Edward vicinity. Sampled from tap; (6) 248' free flowing well reported to reach carbonates, located in Durkeetown, Saratoga County; (7) 400' pumped well in shale, Ballston Spa; (8) Approx. 400' well in shale, Altamont. Sampled from tap at well head before entry to holding tank; 99) 290' idle well, downhole sampler used. Aquifer unknown. Delanson, Schoharie County; (10) 90' pumped well in Galway dolomites, Pompa Quarry, west of Saratoga Springs; (11) 300' pumped well in shale, Wilton, Saratoga County.

Table II: Composition Patterns of Water Types,
East Central New York

Constituent(s) or Ratios	Saline Fm. Waters	Carbonated		Neutral Alkaline Saline	Meteoric Groundwater	Average Sea Water
		Alk.-Saline Waters	NaHCO Bearing			
Max. Obs. TDS	11-12,000	∿ 17,000	< 6,000	<5,000	< 400	34,500
Molar Na/Cl	∿ 1:0	1.0-1.1w/ TDS > 10,000	>1.1	>>1.0	>> 1.0	0.86
Alkalinity*	< 300	2000- 4000^+(a)	HCO^-Na Cl	>1000	< 500	147
Total SiO	7-12	10-70	10-15	9-12	8-12	6-7
Ca+Mg/Na	(<0.08) low	(>0.4) high	variable	$low^{(b)}$	$low^{(b)}$	0.13
Significant minor ions	Br,Sr,I	Br,K,Zr	K,Zr	--	variable Ca,Mg,SO	K,Br,Sr,I
molar Br/Cl x 1000	5-10	$5-20^+$	10-30	--	--	1.5
K/Na	.005- .008	.015- .08	.01- .12	.002- .01	variable, up to .10 or more	$.02_1$
pH	7.2-7.7	5.5-6.5	5.7-7.0	7.0-8.9	8-9.5	8.15

Analyses in mg/liter
(a) molar Na,Cl > HCO_3^-
(b) relatively high ratios may occur
in wells reaching carbonates

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*Alkalinity = Total anion equivalents minus [Cl + $2SO_4$ + Br + F] and thus in samples with low borate and silica contents, as here, is essentially equivalent to HCO_3^- and/or $CO_3^=$ ion depending upon pH. In reported analyses, alkalinity is variously expressed as HCO_3^-, $CO_3^=$, or the $CaCO_3$ equivalent (mg/liter), even though bicarbonate ion is the predominant form in the waters of concern here. For convenience, valence symbols have usually been omitted from dissolved ions shown by chemical symbol in the text.

Carbonated Mineral Waters

The discharge of wells in this group constitute the famed carbonated "springs" of Saratoga, but numerous other examples occur at various points over an area of more than 1000 sq. mi. (Fig. 3). An introduction of carbon dioxide into the saline formation waters produces saline carbonic-acid solutions, which in turn react with the aquifer wall rocks to form bicarbonates; hence the term carbonated-alkaline-saline waters. A generalized form of this reaction for carbonated water in contact with a dolomite acquifer is

$$2\,H_2CO_3 + CaMg(CO_3)_2 = Ca^{++} + Mg^{++} + 4HCO_3 \qquad (1)$$

Hydrolysis and leaching reactions with authigenic alkali feldspars present in the Beekmantown carbonates and detrital feldspars in the basal Potsdam Formation also contribute alkalis (e.g. see Garrels and McKenzie, 1971). These and possible ion exchange reactions are also probable in shale-siltstone aquifer lithologies, with the result that the carbonted waters are marked by increased Ca, Mg, K and Na ion contents balanced by bicarbonate anion (alkalinity) relative to the saline waters, or the saline component; e.g. compare nos. 1-6 and 9, Table I; see Table II. Carbonated waters from a shale-siltstone aquifer, in particular, have enhanced proportions of alkali ions with molar Na/Cl > 1.1 and maximum K:Na ratios, but lower total salinity and in some cases lower Ca + Mg contents (Table I, Nos. 4, 5; Table II, carbonated-$NaHCO_3$ bearing).**

**Based on available data (Clays and Shales of New York State, Dept. of Commerce, 1951, and unpublished carbonate analyses on file by New York State Geological Survey), much of the Beekmantown carbonate section (upper Galway, Gailor, and Tribes Hill Fms.) averages about .05 wt.% Na_2O, but more than 1.5 wt.% K_2O derived from authigenic alkali feldspar and argillaceous matter. A few analyses of Trenton-Black River limestones average 0.2% Na_2O, and about 0.5% K_2O, but no data are available for units in the

Uncarbonated low salinity (< 5000 mg./l.) waters of pH $\geq$ 7, but with > 10 meq./l. alkalinity, occur in a number of wells in shale within and adjacent to the localities of actively carbonated waters. Because of their distribution and similarity to the latter waters, except for higher pH and lack of CO_2 gas exsolution, they are considered in most cases to represent the neutralized and probably diluted equivalents of formerly carbonated waters (Table I, Nos. 7, 8) and are referred to here as neutral-alkaline saline waters, or more simply as 'fringe' $NaHCO_3$ waters (Table II). As a group these waters have low TDS (only one known example exceeds 3000 mg./l.) consisting mainly of equivalent $NaHCO_3$ and NaCl, and low K/Na ratios which overlap those of the strictly saline formation waters but are less than ratios from actively carbonated waters in shale (Figs. 5, 8).

In two cases encountered in this study, neutral or near neutral (pH = 6.9) waters with a typical $NaHCO_3$ component also possessed relatively high Ca, Mg, and K contents (e.g. no. 7, Table I). Although the wells are collared in shale, at depth they may be in close proximity to the top of the carbonate section and may actually be fringe versions derived from that aquifer.

A high alkalinity in these mineral waters then serves as a measure of the extent of wall rock reaction, but not of the degree of carbonation; i.e. the partial pressure of dissolved or aqueous carbon dioxide, and the consequent acidity (pH). Compositional variations and evolution among the mineral waters are shown in the accompanying plots illustrating the progress of wall rock reaction and the influence of the aquifer lithology. Figure 4 is a modified Piper diagram (Romani, 1981) showing the proportions (mole %) of the major dissolved ions; saline carbonated waters of highest salinity are all from a carbonate aquifer and form a trend line away from the saline waters, per se, as shown. This trend line corresponds to a molar Na+K/Cl value of 1.1; all other carbonated or fringe mineral waters have a higher ratio with an equivalent $NaHCO_3$ component of salinity. A similar trend line for proportions of the major cations corresponds to Mg x 100 Ca + Mg values of 34-43% in the saline carbonated waters, but with much more overlap of the two groups.

On this type of plot waters on a linear trend can be inferred to be related by 'mixing', i.e. saline formation waters plus a Ca+Mg+(K) bicarbonate component produce alkaline-saline waters, and the added Ca+Mg ions are consistent with the dissolution of dolostones. In general, $NaHCO_3$ bearing waters are not related by any simple mixing trend derived from the saline formation waters.

An enhanced potassium content of the carbonated waters relative to the saline types (see K/Na ratios) was described and speculated upon by Kemp (1912) and Strock (1941), and the latter also noted the presence of anomalous zirconium in solution (e.g. up to 0.4 ppm). This potassium enhancement appears to hold as a general feature as shown in Fig. 5, where K vs. TDS in the mineral waters of this study are compared with other saline formation waters and connate brines. The potassium anomaly is actually more pronounced than as depicted in this plot because the dissolved solids content (TDS) of carbonated waters is increased by added bicarbonate relative to the other mineral waters.

Quantitative concentration relationships (rather than ratios) among the major dissolved species of the mineral waters are illustrated in Figures 6, 7, 8; saline and alkaline components are compared in Fig. 6. Carbonated waters of the highest saline content also have highest alkalinity with Cl > HCO_3, and have only been obtained from a carbonate aquifer. In waters of lower total salinity from either major aquifer lithology this relation is reversed. On this plot saline formation waters lie near the base line, and examples with intermediate alkalinity (15-40 meq./l.) are only known in diluted form (< 30 meq./l. Cl ion in solution). For comparison, one example of uncarbonated ground water from a well in Galway dolostones (Table 1, no. 10) is included. The trend of decreasing chloride ion contents among the mineral waters is testimony to dilution by meteoric waters; a dilution of the most saline-carbonated water, without addition of CO_2 or additional wallrock reaction, generates the dilution line shown on Fig. 6. Such dilution would produce no trend on the Piper type plot of Fig. 4 since the molar ratios of ions would remain unchanged. Wall rock dissolution (e.g. eqn. 1), however, produces bicarbonate ion with at least a one-half molar equivalent consumption of dissolved carbon dioxide, and it is evident in Fig. 6 that mineral waters plotting above the dilution line have evolved separately with added CO_2 and alkalinity during dilution.

Fig. 7 uses the same data as Fig. 6, but contrasts Ca + Mg bicarbonates with other components of alkalinity. Samples near the base line correspond to molar Na $\simeq$ Cl, and any alkalinity is essentially equivalent to Ca + Mg gained by wall rock dissolution. A slight negative alkalinity here indicates an equivalent calcium/magnesium chloride solute, as

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Saratoga-Glens Falls region. For comparison, shales of the Snake Hill and Schenectady Fms. average about 1.0% Na_2O with 1.8-4+%K_2O; the latter range being equalled or exceeded by many intervals of the Beekmantown section. Base cation exchange (or absorption) on argillaceous matter tends to retain potassium relative to sodium during wall rock leaching or dissolution by mineral waters, hence a shift from dolomite to shale lithogies will also influence alkalis in solution. This effect, however, is complicated by the presence of the saline (NaCl) water component.

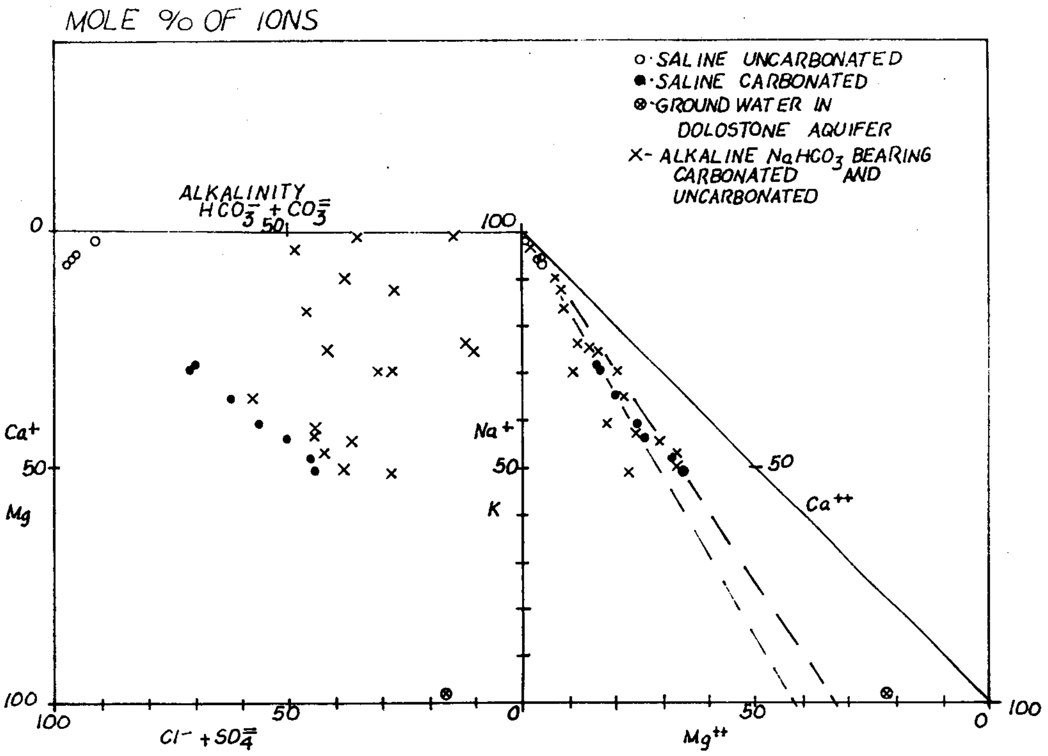


Figure 4. Proportions of major ions in Saratoga mineral waters.

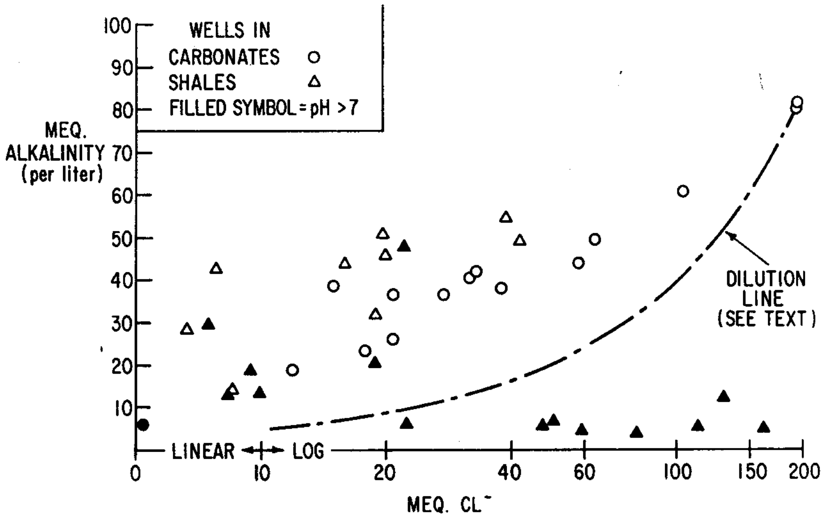
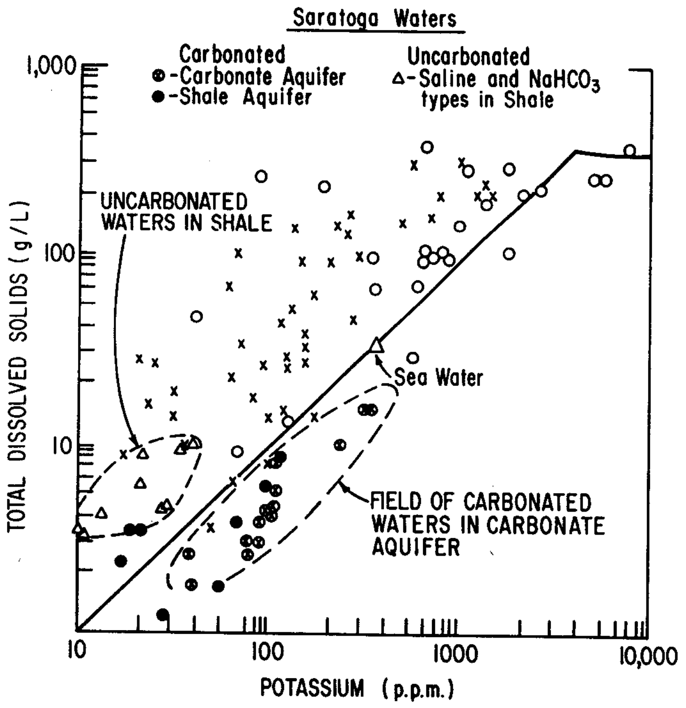


Figure 6. Alkalinity vs. salinity of Saratoga area mineral waters.



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

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

(Rittenhouse et al, 1968)

TDS/K ~100 DIVIDING LINE REPRESENTS SEA WATER RATIO EXTRAPOLATION.

Figure 5. Plot of potassium content vs. total dissolved solids in mineral waters.

appears in some saline formation waters with molar Na slightly less than Cl.* Waters having a dissolved $NaHCO_3$ component plot above the base line in proportion to the content. A "formation water" influence is seen on this plot where carbonated waters in a shale-siltstone aquifer tend to have the highest $NaHCO_3$, and lower Ca + Mg, contents than waters in a carbonate aquifer. Less clear is a reason why apparently no carbonated waters with $>$ 60 meq. chloride ion from a carbonate aquifer have any significant $NaHCO_3$ content relative to more dilute versions.

K/Na ratios of the same waters, plus a few added examples from shales with relatively low TDS, are plotted versus pH in Fig. 8. High ratios occur in strongly carbonated waters with consequent pH $<$ 7 (compare Fig. 5) regardless of salinity and aquifer lithology, but this dependence means that little correlation exists between K/Na ratios and alkalinity or $NaHCO_3$ content of the waters.

Other mineral waters and groundwaters

Many waters from wells in shale have low concentrations ($\lesssim$ 0.33 millimol/liter) of sulfate ion, but locally this ion becomes dominant in both carbonated and neutral sulfate waters with contents up to 3000 mg./l. or more. An example of a carbonated type from the Vita Spring, east of Saratoga Springs, is cited in Table I, no. 6. All of the known sulfate waters have Ca + Mg as major cations with variable Na and Cl ion. K/Na ratios in all cases regardless of pH are similar to those of the carbonated waters in Fig. 8. A localized source of sulfur, as via the weathering oxidation of disseminated sulfides (bedding and fracture surfaces) present in the shales in particular, seems apparent and adequate.

Aside from wells in soils and glacial deposits, most shallow, and even many deeper, wells (to 100 meters or more) in bedrock encounter low salinity ground waters of $<$ 400 mg./l. TDS, and $<$ 5 meq./l. alkalinity for which the term mineral water is inappropriate. These values are typical of waters in equilibrium with the carbon dioxide contents of air or soil gas, and commonly $NaHCO_3$ is the dominant solute. Locally calcium and magnesium bicarbonates (minor sulfate) are important, especially for groundwaters underlain by carbonate terrains (see Table I, nos. 10, 11; Table II). The chloride content of all these groundwaters is low and rarely exceeds a few mg./liter, pH is commonly 8-9.5, and they are quite typical in character by comparison with many other ground, stream, and river waters of the northeastern United States.

Dissolved Gases and pH of the Waters

Analytical results for the gas phase exsolved or separated from various mineral waters are listed in Table III. Carbon dioxide is the major gas component in carbonated waters, with lesser, but variable methane, nitrogen, argon, oxygen and helium in approximate order of abundance. In uncarbonated water types methane is dominant and carbon dioxide becomes a very subordinate component.

The data in Table III were obtained on gas samples recovered as bubbles beneath water at the point of discharge. The gas displaces water from the collection vessel, and every effort was made to exclude air from the system during the process. In private pumped wells, however, a holding tank with a pressurized gas "chamber" is common, and an air bleed to maintain gas volume may be incorporated as well. Samples cited in Table III are considered to be least influenced by direct contamination with air, but some bias in gas proportions of samples from pumped discharges may still be present.

At ambient well temperatures of the gases listed, carbon dioxide is the most soluble and twenty times more so by volume than methane, fifty times more than nitrogen, and argon and helium are still less soluble. At saturation furthermore, carbon dioxide is kinetically slower to exsolve than the less soluble gases; the result is that the latter tend to be preferentially fractionated into the gas phase at natural discharges, but possibly a reverse effect occurs in pressurized holding tanks. At any rate, the data of Table III are representative of the gross gas compositions involved, but the relative volume proportions may be somewhat biased.

As seen in Table III, normally the mineral waters have very low oxygen contents, and the presence of this gas can be used to check for immediate air contamination. Methane, in particular, is indigenous to the carbonaceous matter-bearing shale-siltstone lithology, and is present in virtually all wells which penetrate it. Singificantly, carbonated waters from wells which penetrate only carbonates (e.g. Orenda, Hathorn #3) have the lowest contents not only of methane, but nitrogen, argon and helium as well. This suggests these gases (especially methane), like many other hydro-carbon dominated natural gases, are formation derived. Dilution of the mineral waters by meteoric waters containing dissolved air (from which oxygen is subsequently removed by oxidation reactions with the wall rocks or with organic matter in the soil zone) could also be a factor in sources of nitrogen and argon. Contributions of argon and helium isotopes by radioactive decay processes within the Paleozoic sediments and Proterozoic basement rocks, as well as uranium/thorium bearing fault zones, are still another possibility. A resolution of these sources requires isotopic analyses of the gases; moreover, the implications of

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*Normal analysis error for each constituent can be compounded by this type of plot, and points within a few milliequivalents of the base line cannot be consistently reproduced.

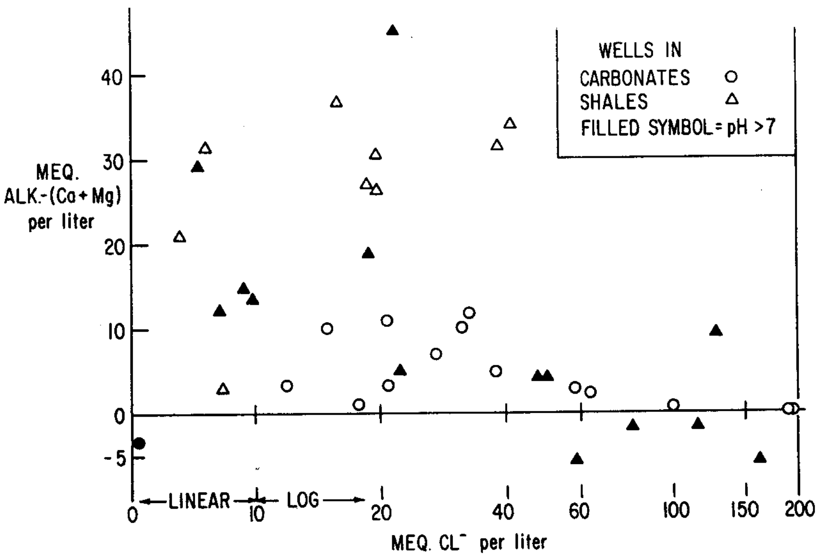

Figure 7. Effective alkalinity vs. salinity of mineral waters.

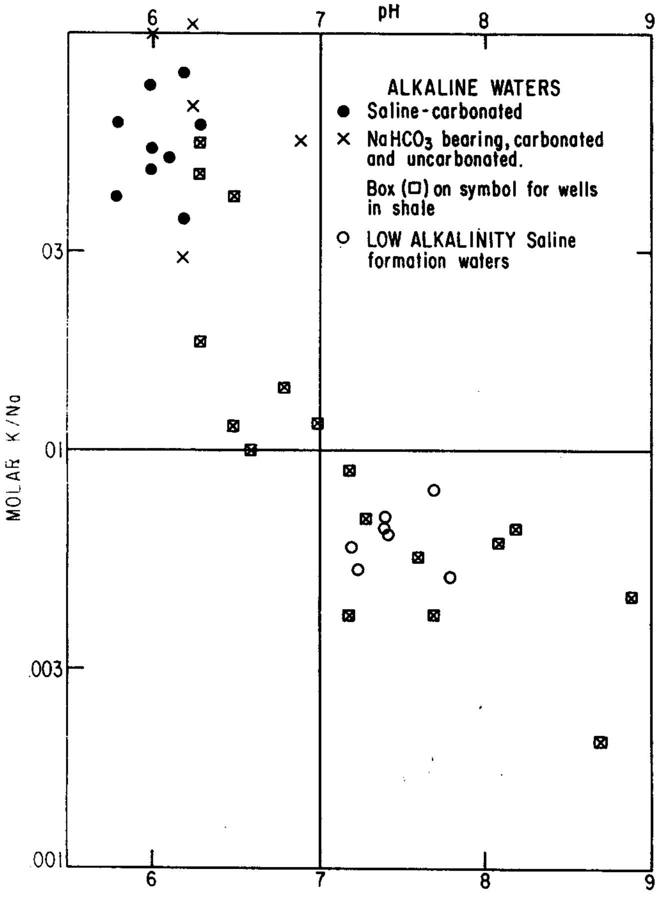

Figure 8. Alkali ion ratio vs. pH of mineral waters.

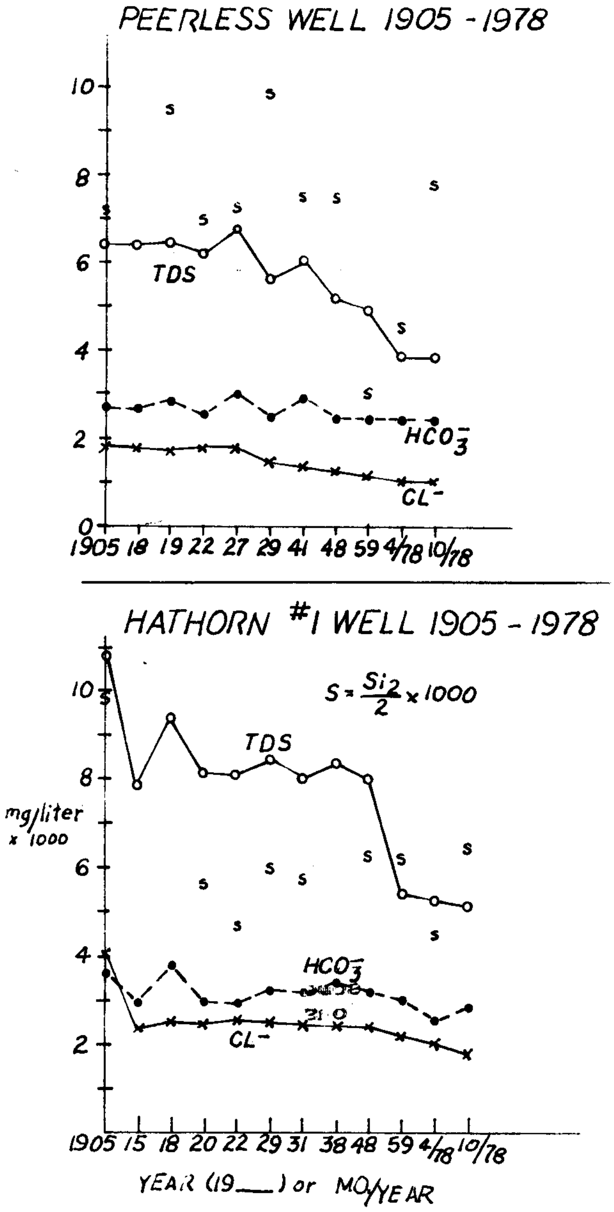

Figure 9. Time trends of analyses.

Table III: Composition of the gas phase from mineral waters.

GAS ANALYSES

	(1) HATHORN #3	(2) ORENDA	(3) BEG RED	(4) BENNET	(5) MARTIN #1	(6) MARTIN #2	(7) GUILDERLAND WELL
-ppm He	--	--	17	500	2700	1894	35
wt.% Ar	<.02	<.02	.04	.09	0.57	0.93	0.21
O_2	0.02	0.37	0.18	0.02	0.06		
N_2	0.14	1.37	1.80	4.06	45.25	46.2	8.17
CH_4	0.50	0.42	2.26	6.30	13.39	11.9	84.3
C_2H_6	<.01	<.01	<.01	0.01	0.01	0.027	--
CO_2	99.08	97.52	95.77	89.64	40.73	40.8	0.38

NOTES:

- = not analyzed or not detected.

Samples collected from exsolved gases at discharge.

Well sites as in Table I.

Guilderland Well is 310' in shales (Route #20, Albany County) and is pumped. Water is predominantly a saline type similar to no. 9, Table I, with 8810 ppm TDS and 640 ppm alkalinity.

Bennet well is ~200' in shales in Town of Moreau, vic. of Fort Edward, New York, and is pumped. The carbonated water was a $NaHCO_3$ type with ~3800 ppm TDS and similar to no. 4, Table I, except for somewhat lower Ca and Mg. This well has subsequently reverted to discharge normal groundwater.

Samples 1-5 (collected 1978) analyzed by J. O'Neil and I. Barnes, U.S.G.S., Menlo Park, California. Samples 6, 7, and He in samples 3 analyzed by Chemical Projects, Ltd., Toronto, Ontario, Canada (1980).

such data, especially that of helium, may have a bearing on the proposed origin of carbon dioxide, and it is hoped that such analyses become available soon.

In all the water types described previously with pH 8, bicarbonate ion concentration, carbon dioxide partial pressure, and pH are related by the ionization equilibrium of carbonic acid:

$$\frac{a_{H^+} \cdot \gamma_{HCO_3^-} \cdot [HCO_3^-]}{P_{CO_2}} = K_{eq.} \simeq 1.86 \times 10^{-8}$$

@ 10°C (Clark, 1966)

where a_{H^+} = activity of hydrogen ion (pH)
$[HCO_3^-]$ = molar concentration of bicarbonate ion
$\gamma\ HCO_3^-$ = activity coefficient for bicarbonate ion
P_{CO_2} = partial pressure of carbon dioxide in the gas phase or internal vapor pressure of aqueous CO_2.

Most of the dissolved carbon dioxide exists in molecular form (aqueous CO_2) with a very minor fraction associated with water as true carbonic acid. In a solution with no dissolved solids and P_{CO_2} = 1 atm, dissolved CO_2 is about .045 molar and the bicarbonate ion concentration (and $[H^+]$) is about 1.3×10^{-4} mol/liter or equivalent to an alkalinity of 0.13 meq./l (8 mg./l and pH of about 3.9.

Mineral waters with significant alkalinity as a result of wall rock reaction become buffered with respect to the above equilibrium, and have a higher pH for a given P_{CO_2}; e.g. most of the carbonated waters sampled here are in a pH range 5.8-6.3 with calculated P_{CO_2} of 1-5 atm. A rise in pH and alkalinity slows the rate of wall rock reaction, so that at some point little additional dissolution occurs relative to the rate of transport or withdrawal of mineral waters. Note that this condition does not imply any necessary decrease in P_{CO_2}, or that saturation in respect to a solid phase has necesarily been attained. However, this aspect of the carbonate solution chemistry is very difficult to treat further, simply because dilution by shallower ground water, prior to and during discharge, is probable in most wells.

For the above equilibrium, it is evident that a decrease in P_{CO_2} means less carbon dioxide in solution and therefore a rise in pH. In the more highly carbonated waters, wherein considerable exsolution of gas takes place upon ascent to the surface, the measurement of pH is difficult in two respects, viz: 1) pH is unstable due to degassing of the waters during discharge; 2) bubbles of gas nucleate on the electrode probe of the pH meter which creates instability in the electrolyte concentration at the probe surface.

Relatively stable pH determinations are obtained in waters removed from the discharge where the rate of gas exsolution is slowed, but such values are upper limits displaced above the actual pH of waters in the aquifer by an uncertain amount. For example, using the data of the Big Red well (Table I, No. 3) to represent a carbonated water, a P_{CO_2} of 3 atm in the aquifer produces a pH of about 5.9. A loss of 1 atm. in P_{CO_2} via exsolution during ascent and discharge raises the pH to about 6.1. This latter value may or may not be closely estimated at the point of discharge depending upon the rate of loss of the remaining 2 atm. P_{CO_2}.

The pH, and P_{CO_2} values calculated therefrom, cited in Table I are based on electrode measurements at the point of discharge; commonly these pH values are lower by 0.1-0.3 than those made subsequently in the laboratory on bottled samples. At the ambient temperatures of the mineral waters, carbon dioxide is soluble at a proportion of about one volume per volume of water per atm. P_{CO_2}. Since in the discharges of some wells, e.g. Orenda and Hayes, the volume fractions of gas and water are subequal, the example cited above of the effect of one atm. CO_2 exsolution on pH can reasonably be expected to apply. Thus, it appears certain that the carbonated waters are of significantly lower pH (more acid) at depth and the effect is approximately proportional to the P_{CO_2} present in the aquifer.

Carbonate Equilibrium and Saturation of the Waters

Of the major constituents in solution in these waters, only solubility/precipitation relations for calcium are considered here. This approach is based on the known presence of calcite in veins and fractures within the Paleozoic wallrocks, and in tufa or travertine deposits about the well discharges. The situation is complicated by the probable initial precipitation of metastable carbonate phases, especially in the Tufas, which is not considered. At any rate, no other carbonate mineral phases, such as dolomite, have been noted among the above precipitates. The general pattern of carbonate equilibria, including cases applicable here, has been treated in detail by several workers, e.g., Garrels and Christ (1965); interested readers should consult such sources for a full discussion.

Solution equilibria among carbon dioxide, carbonic acid and bicarbonate ion and the general nature of wall rock dissolution have been briefly discussed above. Bicarbonate ion in solution also coexists with carbonate ion by the ionization equilibrium $HCO_3 = H^+ + CO_3$; in turn, the concentrations of carbonate ion and dissolved calcium at saturation are related by the solubility product of calcite:

$$(K_{CaCO_3} = [Ca^{++}] \cdot \gamma\, Ca^{++} \cdot [CO_3^{=}] \cdot \gamma\, CO_3^{=}) = 10^{-8\cdot15} \quad (10°C;\ \text{Clark, 1966})$$

In any water where the product of calcium and carbonate ion activities reaches or exceeds K_{CaCO_3}, then normally calcite deposition ensues or dissolution stops and the water is saturated in this phase. With a fixed amount of carbon in solution, decreasing pH (increased acidity) favors carbonic acid and bicarbonate over carbonate ion, and a larger concentration of calcium ion in solution can be tolerated before saturation; increasing pH favors carbonate ion and the opposite behavior. Using the water analysis data, measured pH values, reference equilibrium constants at 10°C for bicarbonate ionization and calcite solubility, and estimated activity coefficients* for bicarbonate, carbonate and calcium ions, the calcium content to produce calcite saturation of each water at the point of discharge can be calculated. This value can then be compared with the analyzed calcium in solution, and the results for some representative waters are given below in Table IV.

Reference to Table IV discloses that while the mineral waters are generally appreciably undersaturated at discharge, at least one example of a carbonated-saline water (Orenda Well) and of a neutralized-$NaHCO_3$ water (Harrington well) are near or at saturation. Both of these waters deposit calcite tufa (M. Liston, unpub. research, 1981) at the well discharge in qualitative support of these relations; the deposit about the Orenda well is particularly copious, reflecting the calcium content. However, all carbonated waters will ultimately become saturated subsequent to discharge via loss of carbon dioxide and tufa deposits of this derivation occur about several wells where the discharge is not immediately drained away.

This calculation of saturation is very sensitive to pH, and in view of the probable slight pH decrease with depth in the carbonated waters, all the waters are apparently unsaturated in some degree in respect to a carbonate aquifer. However, the general pattern of appreciable calcite undersaturation in most carbonated waters of intermediate salinity in Table IV reflects dilution rather than a lack of wallrock dissolution.

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*Activity coefficients derived from mean ion data tabulated by Garrells and Christ (1965). In waters of ionic strength 0.15 activity coefficients were corrected for ion pair formation by calculations based on data cited by the same.

Table IV

Calculated calcium contents at calcite saturation
in mineral waters of east central New York

well or spring	total dissolved solids (mg/l)	pH	alkalinity meq/l	analyzed calcium mg/l	calculated calcium at saturation mg/l
Big Red	6500	5.9	49	380	621
Rosemary[1]	2500	6.0	38.8	260	521
Peerless	3820	5.9	36.5	420	853
Orenda	10370	6.0	61	700	752
J. Martin	2200	6.3	42.6	100	271
A. Bohl[2]	3190	7.5	6.8	27	163
Harrington[3]	4070	7.6	48.0	12	13

Notes:
1 - 425 ft. well into Dolostones, Route 9, south edge of Saratoga Springs
2 - 150 ft. well into shales, Town of Bethlehem, Albany Co.
3 - See Table I, #8.

Using Orenda as an example, a 1:1 dilution with groundwater would immediately reduce $^{P}CO_2$, HCO_3^-, Ca^{++}, and salinity by one-half, but increase pH by less than 0.1 unit. If information on rates of dissolution versus pH were available then perhaps estimates of residence times in the aquifer could be attempted, but at present this is not possible.

The data of Table IV also serve to illustrate the contrasting effects of pH and alkalinity upon water type. High calcium (and magnesium) contents in mineral water of substantial alkalinity are only possible at relatively low pH; with neutralization the contents must decrease, and the water thus becomes a $NaHCO_3$ type (see Figs. 7, 8).

Discussion of Water Characteristics

Temporal Trends

Analytical records of mineral waters in Saratoga Springs exist for more than 100 years, and the data suggest that an irregular but continuing dilution of saline components of the waters occurs with time. This effect is difficult to assess quantitatively because few wells have been active for this entire time period, and most wells have been modified at one time or another in terms of retubing, packing and sealing, or cleaning which commonly produces some variation in salinity of the discharge. A plot of the analytical results for two wells (Peerless, 151 ft. in depth, and Hathorn #1, ∿1000 ft.; compiled from Kemp, 1912; Colony, 1930; records of the Saratoga Springs Reservation, and data of this study) in which these disruptions have been minimal is shown in Fig. 9. The data cover a span of some 75 years and show a clear temporal trend of decreasing salinity (but not alkalinity) such that recent values are some 50-60% of the initial analyses. Long term changes in other wells are not all as large, and in particular, wells in the north portion of the city (like those cited) seem most affected by temporal dilution. This may reflect the relative thinness or lack of a shale caprock beneath the surficial glacial deposits (50-60 ft. or more) on the east side of the Saratoga fault in this vicinity.

The separate long-term trends in alkalinity versus salinity as seen in some wells (e.g. Fig. 9) suggests separate sources for these constituents; i.e. an open system or steady state CO_2 source, as reflected in alkalinity, as contrasted to a fixed reservoir for saline components. Other data implications for continuing carbonation have been noted previously, and added confirmation is seen in the record of commercial gas production at Saratoga Springs.

Wallrock dissolution by carbonated waters is certain to enlarge fractures and increase permeability, and it seems reasonable to expect this effect to be more intense at points where carbon dioxide is added. Past observations of apparent local water flow directions during pumping have been made in Saratoga Springs (Kemp, 1912; Colony, 1930), but such data are not interpretable as to CO_2 source or flux.

While it is clear that the incidence of mineral waters reflects fault and fracture zone control, it is not clear how pervasive the carbonated waters are within the carbonate aquifer throughout the area of Fig. 1. Most of the area is underlain by the shale-siltstone "caprock", in which local incidences of carbonated waters occur, but virtually no deep wells east of the Saratoga-Ballston Lake fault penetrate to the carbonates beneath (Sneeringer et al., 1983).

Variations in Water Types

The influence of the aquifer on the chemistry of carbonated waters is reflected in the shift from Ca-Mg to Na bicarbonate dominated types, irrespective of the saline component. This relation is to be expected as a result of dolostone/shale-water interaction, and implies appropriate formation residence times as well as stratification or density segregation of waters. Carbonated waters with the highest salinities and highest alkalinities in the Saratoga Springs vicinity also have the highest calculated P_{CO_2}, which is consistent with an entry of CO_2 via faults into waters of highest density at the bottom of the aquifer. Aside from these general interpretations, however, it is clear that the lack of information on hydrologic properties and water compositions at depth for most of the area limits further comment on possible parameters of, or models for, the carbonated water system. A case in point is a suitable interpretation for the $NaHCO_3$ component of some carbonated waters within the carbonate aquifer (see Figs. 4, 7).

As far as is known from past and current annalyses, all waters in which a $NaHCO_3$ component is significant have less than 7000 mg/l. TDS, and commonly have less than 5000 mg/l TDS. Present wells of this water type include Rosemary, Geyser, Peerless and Lincoln in Saratoga Springs, and the Gurn Spring at Wilton as a natural example; all with less than 4500 mg/l TDS. These waters are all derived from the upper portion of the carbonate aquifer (Trenton-Black River Section; three, and possibly four, of the above wells do not penetrate the Beekmantown section, Fig. 2); they tend to have anomalous silica contents (12-15 ppm background), very high K/Na, and low, but greater sulfate concentrations than deeper waters of higher salinity.

Waters with a $NaHCO_3$ component from a carbonate aquifer were discussed by Kemp (1915, 1916; unpublished reports to the Saratoga Springs Commission) who suggested increments of a carbonated-$NaHCO_3$ bearing "fluid" were injected into the Paleozoic aquifer along the Saratoga fault. This view was considered by Young (1980), and Young and Putman (1979) and discussed in relation to other carbonated waters. On Figs. 6, 7, for example, such a primary carbonated water would appear as a vector more or less parallel to the ordinate at low chloride contents, and other water types could be described as various mixtures with typical (uncarbonated) saline waters. One problem with this idea is the apparent lack of a major or even significant $NaHCO_3$ component in the deepest and most saline waters, which should be hydrostatically closest to the entry points of carbonation. Another is that the $NaHCO_3$ types apparently do not have the highest P_{CO_2}.

At least two other interpretations appear to be as consistent with the chemical data as the above view, viz: 1) the waters in question, like those in shales, have a lithic interaction or 'formation' character derived from the upper part of the carbonate aquifer (essentially above the Knox unconformity) or 2) the waters are mixtures of the deeper, high salinity alkaline-saline type and the $NaHCO_3$-bearing type developed in shales.

The latter interpretation would require that some $NaHCO_3$ type waters in shales be displaced stratigraphically downward, or laterally westward across faults, into the upper part of the carbonate aquifer and raises hydrologic questions. The first alternative is consistent with the presence of ± 16 meters of shale interbeds in the Trenton limestone lithologies above the Knox unconformity, but the abrupt transition from dolostone to limestone does not appear to be reflected in other aspects of the water chemistry (e.g. Mg/Ca ratio) among wells sited in these respective lithologies.

Unfortunately, a resolution of these interpretations appears to await additional information.

Silica Distribution

Silica contents of waters with active carbonation and $pH < 7$ tend to be > 10 mg/l and greater than in all other water types. A formation influence is seen in that wells in shale seldom exceed 15 mg/l silica, while some wells penetrating carbonates consistently have > 15 mg/l and range up to a maximum of 70 mg/l as recorded for the Big Red well. Wells in shale thus show an inverse effect of that for $NaHCO_3$, discussed above (Figs. 7, 10) However, temporaral variations in silica content for a given well are usually not reflected in corresponding changes for other dissolved constituents or in total salinity (e.g. Fig. 9). This seems to suggest some independence in either the source(s), or the kinetics of solution of silica.

Dissolved silica values < 10 ppm could reflect equilibrium with quartz, whereas higher solubilities occur with less ordered forms (e.g. up to ~ 100 ppm with silica gel at $10^{o}C$, Fournier et al., 1974). The degradation or attack of silicate minerals by soil waters also results in higher , dissolved silica, e.g. up to ~ 60 ppm in waters in equilibrium with kaolinite through the alteration of feldspar (Garrels and MacKenzie, 1971). In Figure 10, a measure of the effect of wallrock reaction or dissolution among waters is attempted by plotting SiO_2 vs. effective alkalinity (i.e. [meq. total alkalinity-molar Ca + Mg] to estimate the amount of HCO_3^- ion obtained from carbonic acid reaction and not from wall rock carbonates). This latter quantity assumes all Ca + Mg is derived by carbonate dissolution and may not equally well estimate reaction progress with wall rock silicates, but no better index seems available. Symbols in Fig. 10 with bars represent long term averages and ranges of silica contents.

Silica solubility also increases with temperature (Fournier et al., 1974), and the metastable persistence of anomalous contents in waters of ambient temperature has been used as a tracer for hidden thermal systems. A resolution among these factors, based merely on the range of silica contents in Saratoga waters (10-70 ppm) is thus ambiguous.

In Fig. 10 a series of wells near the Saratoga-Ballston Lake fault with generally $<$ 5000 mg/l total salinity and penetration mainly in the upper (Post Knox or Trenton) part of the carbonate section (Old Iron, Polaris, Geyser #2, Lincoln series, Rosemary, Peerless, Red, High Rock and Gurn Spring) consistently show $>$ 15 ppm dissolved silica. Higher salinity and deeper wells along the same trend (Hathorn #1 and #3, Bischoff) consistently have $<$ 15 ppm silica, as does the Orenda well which is reported to reach only the Trenton-Black River section, but is otherwise similar. This pattern could suggest a relationship between wall rock dissolution of the post Knox carbonates and enhanced silica contents, but on the other hand the Big Red well east of the fault reaches well into the Beekmantown carbonate section, has moderately high salinity ($\sim$ 7000 mg/l) and has the highest analyzed silica contents (46-70 mg/l). Obviously, the presence of the shale "caprock" east of the Saratoga-Ballston Lake fault makes it difficult to test the silica distribution in deeper mineral waters, and the problem is compounded by possible dilution or mixing effects with shallower waters in deep wells. The controlling factors for the $NaHCO_3$ and silica aspects of the water chemistry thus remain somewhat unresolved and pose a fitting topic for future work.

CARBON DIOXIDE SOURCE

The dimensions of this carbonated water system, and the potential free gas content (in terms of aqueous CO_2), place it among the more energetic examples known globally.

All past workers who have considered the question of source (e.g. see discussion by Kemp, 1912; Cushing and Ruedemann, 1914) have faced the same dilemma: the intensity of carbonation suggested thermally generated carbon dioxide while there was little, if anything, in the known geologic relations of the region to support this inference. Today, some additional, and more subtle, variations in source mechanisms for carbon dioxide are known (Lang, 1969; Farmer, 1965), but with the same basic conclusion. Current data and inferences of a carbon dioxide source also tend to emphasize the geologic contrast of the Saratoga system with others of similar carbonated waters (Barnes et al., 1978; Irwin and Barnes, 1980).

Non-thermal waters with moderate to even substantial alkalinity can be a result of equilibria with soil gases (Deines et al., 1974), decarboxylating organic matter, warm water hydrolysis of carbonates, and ionic filtration/exchange processes during the diagenesis of sediments (White, 1965; Kramer, 1969) or, in some cases, of ground water flow between contrasting surficial deposits (Krothe and Parizek, 1979). None of the examples cited for these processes, however, are waters with true carbonation, let alone several atm. CO_2 and a pH less than 6.

Thermal processes of carbon dioxide generation include: a) de-gassing of igneous melts, directly evident during volcanic activity as a component of eruption clouds and fumarolic emissions; some CO_2 may also be present in associated geothermal fluid systems, e.g., Steamboat Springs, Colorado; b) deep crust or upper mantle degassing with "leakage" along deep faults such as transforms (Irwin and Barnes, 1975; Kolotov et al., 1979) and in rift zones (Mazor, 1972; Bailey, 1977) commonly without accompanying volcanicity or shallow geothermal fluid systems; c) inorganic decarbonization reactions during metamorphism; other fluids, such as H_2O, are not essential; d) decarbonization equilibria with thermal fluids during metamorphism at depth (White, et al., 1973), e.g. Salton Sea geothermal system (Muffler and White, 1969), Pannonian Basin (Barnes and O'Neil, 1976), Alpine Fault, New Zealand (Barnes, et al., 1978). A related aspect is the thermal maturation of organic matter in sedimentary basins with the production of CO_2 as well as hydrocarbons (Hunt, 1979).

Many of the well known geothermal provinces with commercial steam production contain a minor fraction of CO_2 in the discharges as a result of process (d) above, in combination with a primary heat source related to recent volcanism or a shallow intrusion, e.g. Larderello, Italy (Ellis, 1967), Wairakei, New Zealand (Ellis and Mahon, 1966).

Obviously, clear distinctions among these thermal processes may not always exist in actual cases, and is not of concern here. Whatever the inferred origin of carbon dioxide at Saratoga (using this term to apply to the region of carbonated waters), it must be consistent with the observations previously cited, viz a) quantity appropriate to P_{CO_2} and commercial gas extraction; b) probable multiple fault controlled localities of carbonation; c) source independent of aquifer lithology and formation waters; d) no obviously associated thermal waters; and e) no evidence of CO_2 gas or a CO_2-bearing gas field noted in exploration wells within the thicker Taconic flysch sediments to the east.

Stable isotope analyses of the carbonated waters can provide clues to the source of carbon dioxide as well as the water itself, and the available data are discussed in the next section.

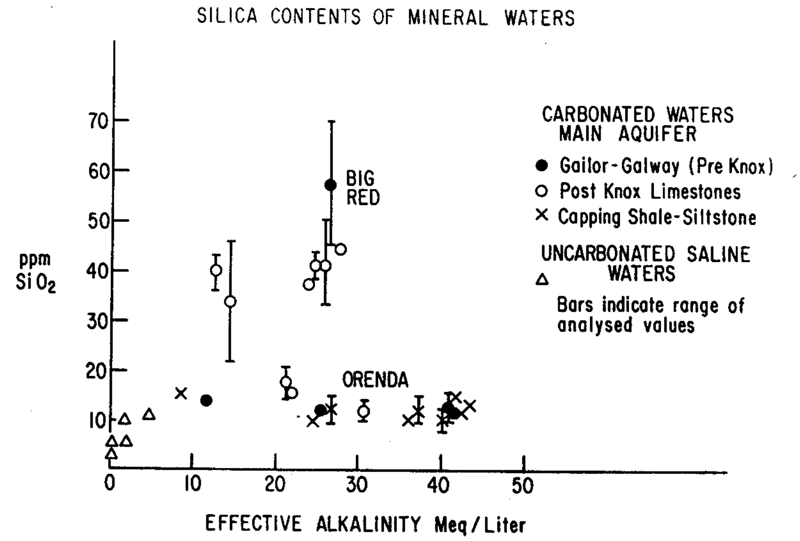
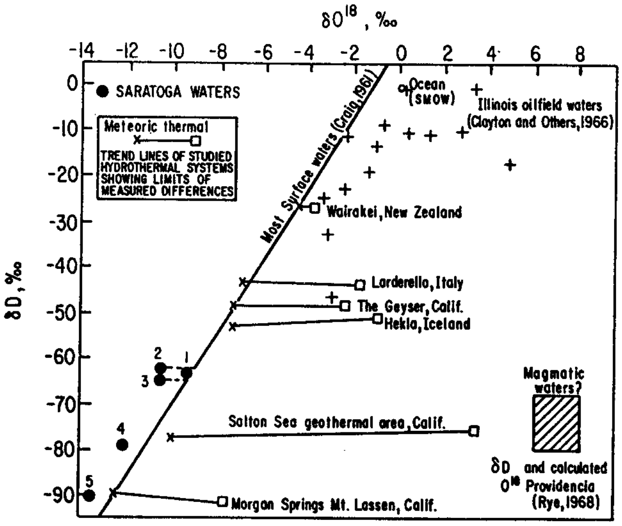


Figure 10. Silica contents of mineral waters.



Isotropic trends of Saratoga and other thermal and mineral waters (modified after White, Barnes and O'Neil, 1973)

Figure 11. Isotopic trends of Saratoga and other thermal and mineral waters.

TABLE V

STANDARD ISOTOPE RATIO ANALYSES IN SELECTED MINERAL WATERS OF EAST CENTRAL NEW YORK

			δ^{13}C in -				
SAMPLE	δ D	δ O	Carbonate ppt.	CO_2 gas	Total Allkalinity (Meq/l.)	Derived Alkalinity	P_{CO_2}(est.)
1) Hathorn #3	-64.2	- 9.22	+ .57	-5.03	80	40	4.3 atm.
2) Orenda	-63.6	-10.39	+ .60	-5.15	60.4	30	3.2
3) Big Red	-65.9	-10.36	- 3.92	-6.84	50	24	2.6
4) Bennett Well	-79.0	-12.10	-4.35	-7.55	45.2	9.2	2.4
5) Martin Well	-90.4	-13.26	-4.91	ND	43	6	2.3
Saratoga*	--	--	--	-5.7	--	--	--

NOTES;

δ = Isotope fractionation ratio in sample, expressed in parts per thousand (per mil) difference relative to SMOW for D,H,O and PDB for carbon.

D = deuterium isotope of hydrogen

^{18}O = oxygen isotope mass 18

^{13}C = carbon isotope mass 13

Total Alkalinity as defined previously in text; Derived Alkalinity estimted as the contribution by dissolution of wall rock carbonates

ND = not determined

All analyses made in the isotope geochemistry laboratory of the U.S. Geological Survey, Menlo Park, California by J.R. O'Neil and I. Barnes, 1979.

Samples collected by G. Putman and J. Young, 1978; identified by sample no. on Figure 11.

*Result calculated from data of Lang (1959) reported as C^{13}/C^{12}; the specific sample site is not identified.

ISOTOPE CHEMISTRY

Results of standard isotope ratio analyses of hydrogen, oxygen, and carbon in several carbonated Saratoga waters, and of carbon in carbon dioxide of the exsolved gas phase, are given in Table V. These data, when compared with oxygen and hydrogen isotope ratios of other mineral waters, sea water, and meteoric waters (Craig, 1963) in Figure 11, suggest that the water component is essentially meteoric in origin and is consistent with values for current precipitation ($\delta D \sim -60$-65) at Saratoga Springs. Waters from the northeast area of the basin, however, have much lower δ D values that are consistent with subartic precipitation and appear to represent ice age water retained in this portion of the Paleozoic aquifer.

Because of isotopic exchange with host rocks, basinal brines and connate waters have higher $\delta^{18}O$ ratios, and commonly higher δ D, than meteoric waters (Hitchon and Friedman, 1969) and plot to the right of the meteoric water line in Figure 11. Substantial dilution of a high salinity brine with meteoric water (new or old) could produce the δ D values observed in Saratoga waters, but larger (less negative) $\delta^{18}O$ ratios would be expected. Precisely this effect has been noted in other thermal and mineral waters, e.g. in the Coast Ranges of western North America (White, et al., 1973). Low salinity wells comparable to Saratoga in shallow parts of the Illinois basin (Graf, et al., 1966) clearly exhibit flushing and plot closer to the meteoric water line than deep wells in the same basin (Clayton, et al., 1966).

In contrast, the most saline Saratoga water (Hathorn #3, Table I) lies approximately on the meteoric water line and the other samples show a pronounced negative shift of ~ 1 per mil $\delta^{18}O$ relative to meteoric waters. Meteoric waters show a normal scatter of about ± 1/2 per mil ^{18}O about the line (Craig, 1961), but no locality has a consistent deviation. A negative oxygen isotope shift of this magnitude exceeds the (condensed) steam-water fractionation effect found in some thermal water systems (Clayton and Steiner, 1975), and has been predicted for carbon dioxide - water systems where thermal CO_2 subsequently exchanges with cooler water (I. Barnes, personal communication, 1979) but has not heretofore been observed in natural waters.

The significance of this negative shift lies in the implication that the carbon dioxide was originally in isotopic equilibrium with rocks at elevated temperature; i.e. $> 300^{o}C$ and $\delta^{18}O < +10$ per mil. If the CO_2 subsequently encounters and isotopically exchanges with water at normal surficial temperatures, a strong ^{18}O fractionation takes place with the CO_2 (as an aqueous CO_2 phase) becoming enriched and therby depleting the water in this isotope. Any itosopic exchange between the mineral waters and carbonate wall rocks ($\delta^{18}O > +20$) would lead to a reduced or opposite effect and thus is not a cause of the shift relative to meteoric waters.

If a CO_2-water exchange as above is assumed, then simple mass balance using fractionation factors from Friedman and O'Neil (1977) requires about twice as much CO_2 to produce a -1 per mil ^{18}O shift, as is actually dissolved in the waters of highest P_{CO_2}. If valid, this approach implies a net CO_2 flux through the aquifer, or continual degassing, as suggested previously.

The interpretation of the carbon isotope data of Table V is less straight forward because of mixed carbon sources, e.g. aqueous carbon dioxide species and methane, and bicarbonate and carbonate ion added by wall rock dissolution. Isotope ratios of the carbonate precipitate* are bulk estimates for total inorganic carbon in the water samples; those for CO_2 gas refer to this component of the gas phase collected at the well discharge.

If equilibrium isotope exchange occurs, the isotope ratios of CO_2 gas, methane, aqueous CO_2, and ionic carbon species (HCO_3^- , $CO_3^=$) are related by temperature dependent isotope fractionation factors (Deuser and Degens, 1967, Friedman and O'Neil, 1977); however, incomplete isotope exchange among carbon species at the ambient temperatures of these waters (10-14°C) is a common experimental problem, and is probably reflected in the variable $\delta^{13}C$ differences (3-6 per mil) between CO_2 gas and precipitated carbonate in the samples of Table V.

Some variation in ratios is also to be expected since the precipitate represents mixed carbon whose sources have different proportions in each sample, i.e. bicarbonate ion derived from wall rocks with $\delta^{13}C < +2$ and > -1.5 per mil (J.R. Young, 1980), bicarbonate ion derived from a carbonic acid - aqueous CO_2 source consistent with the reported $\delta^{13}C$ of the gas phase (< -5 per mil), and carbon from aqueous CO_2 fixed during precipitation, but whose concentration depends on P_{CO_2}.

These relations may partly explain the trend in Table V, where samples with the lowest $\delta^{13}C$ values also have the least amount of wall rock-contributed bicarbonate ion. Other factors which could influence the observed carbon isotope data are the extent of any isotope exchange with dissolved methane, possible exchange between the mineral waters and carbonates of the wall rocks (isotope buffering), and the extent of degassing of the waters prior to discharge (Pearson, et al., 1978).

The observed range of carbon isotope values in the exsolved carbon dioxide of Saratoga waters is similar to that observed in discharges from many areas marked by thermal activity (Panicki and Tongiorgi, 1976) and partly overlap values cited for carbon dioxide of igenous or mantle origin ($\delta^{13}C \sim -4$ to -8; Taylor, et al., 1967). $\delta^{13}C$ values (total carbon) similar to some observed at Saratoga have also been noted for meteoric groundwaters

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*Precipitated by addition of ammoniacal strontium chloride solution. Procedure described by Barnes, et al., 1978.

in carbonate aquifers by Plummer and Back (1980), where the CO_2 source is essentially soil gas. Meteoric waters with dissolved atmospheric CO_2 ($\delta^{13}C \sim -7$) in contact with carbonates may also have similar δ ^{13}C ratios, but all such groundwaters are not an analogy for Saratoga waters/CO_2 source because of much lower CO_2 contents and alkalinities, and higher pH. Because of mixed carbons the data of Table V do not provide unequivocal indication of the carbon dioxide source in Saratoga waters; however, at least two limiting inferences seem apparent: First, a mass balance for isotope ratios < -3 per mil in both the precipitate and free gas of several samples eliminates simple decarbonation of the Paleozoic carbonates or marbles in Proterozoic basement rocks as a source; Second, carbon of biogenic origin is characterized by very light δ ^{13}C values (usually < -15 per mil) and is also eliminated as a source (e.g. as by oxidation of methane or carbonaceous matter in the wall rocks, or thermal decarboxylation of the latter).

The present carbon isotope data thus are at least permissive of carbon dioxide from an "igenous" source, including mantle degassing. On a global scale many nonvolcanogenic carbon dioxide discharges are associated with intracontinental rift zone tectonics (Barnes et al., 1978), and the implications of this pattern for the geologic setting of northeastern New York are examined in a subsequent paper.

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