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# Origin of halite brine in the Onondaga Trough near Syracuse, New York State, USA: modeling geochemistry and variable-density flow

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**Abstract** Halite brine (saturation ranging from 45 to 80%) lies within glacial sediments that fill the Onondaga Trough, a bedrock valley deepened by Pleistocene glaciation near Syracuse, New York State, USA. The most concentrated brine occupies the northern end of the trough, about 10km downgradient of the northern limit of halite beds in the Silurian Salina Group, the assumed source of salt. The chemical composition of the brine and its radiocarbon age suggest that the brine originally formed about 16,700 years ago through dissolution of halite by glacial melt water and later mixed with saline bedrock water. Two hypotheses regarding the formation of the brine pool were tested through variable-density flow simulations using SEAWAT. Simulation results supported the first hypothesis that the brine pool was derived from a source in the glacial sediments and then migrated to its current position, where it has persisted for over 16,000 years. A second hypothesis that the brine pool formed through steady accumulation of brine from upward flow of a source in the underlying bedrock was not supported by simulation results, because the simulated age distribution was much younger than the age estimated from geochemical modeling.

**Résumé** Des saumures riches en halite (saturation comprise entre 45 et 80%) se situent dans les sédiments glaciaires qui remplissent le Bassin d'Onondaga Trough, vallée rocheuse approfondie par la glaciation pléistocène à proximité de Syracuse (Etat de New York, Etats-Unis). Les saumures les plus concentrées occupent l'extrémité nord du bassin, à environ 10km à l'aval hydraulique de

la limite nord des lits de halite du Silurian Salina Group, la source supposée du sel. La composition chimique de la saumure et son âge radiocarbone suggère qu'elle s'est initialement constituée il y a environ 16700 ans, par dissolution de la halite par l'eau de fonte glaciaire, et s'est ensuite mélangée avec l'eau de la roche-mère saline. Deux hypothèses sur la formation d'une ressource sursalée ont été testées par simulation d'écoulements à densités variables, sous SEAWAT. Les résultats de la simulation confirment la première hypothèse : la ressource sursalée prend son origine dans les sédiments glaciaires et a migré vers la position actuelle, où elle se maintient depuis plus de 16000 ans. La seconde hypothèse était que la ressource sursalée s'était formé par accumulation de saumure sous un flux ascendant issu de la roche-mère sous-jacente; elle n'a pas été validée par les résultats de la simulation, parce que les âges simulés apparaissaient bien inférieurs aux âges estimés à partir des modélisations géochimiques.

**Resumen** Una salmuera de halita (con una saturación que oscila entre el 45 y el 80%) se encuentra en sedimentos glaciares que rellenan el Onondaga Trough, un valle rocoso excavado por la glaciación Pleistocena cerca de Siracusa, en el estado de Nueva York, USA. La salmuera más concentrada ocupa el extremo norte del valle, a 10km aproximadamente aguas abajo del límite norte de los estratos de halita en el Grupo Silúrico Salina, la supuesta fuente de sal. La composición química de la salmuera y su edad medida por radiocarbono sugiere que se formó originalmente hace aproximadamente 16,700 años a partir de la disolución de halita por el deshielo de agua glacial y su posterior mezcla con agua de los cuerpos salinos. Se han considerado dos hipótesis observando la formación de la salina mediante simulaciones de flujo de densidad variable usando SEAWAT. Los resultados de la simulación confirmaron la primera hipótesis, consistente en que la salina derivó de una fuente en los sedimentos glaciares y entonces migró hasta su posición actual, donde ha permanecido durante más de 16,000 años. Una segunda hipótesis consistente en la salina se formó mediante la acumulación estacionaria de salmuera desde un flujo aguas arriba de una fuente en el estrato inferior no se vio confirmada por los resultados de la simulación, porque la distribución de edad simulada fue mucho más joven que la edad estimada de la modelación geoquímica.

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## Introduction

Saline formation waters occur at considerable depth in most sedimentary basins worldwide (Hanor 1987), but are found less frequently at shallow depths where, for example, (1) upward leakage may occur along fracture zones (Bense and Person 2006), (2) dissolution of salt beds by active fresh-water circulation may occur (Johnson 1981; Dutton 1989), or (3) pumping from deep boreholes produces saline formation waters that are subsequently released at the land surface or discharged to shallow aquifers (Novak and Eckstein 1988). Recently, Grasby and Chen (2005) suggested that brine springs discharging from the eastern margin of the Western Canada Sedimentary Basin originated as Pleistocene melt water that dissolved Devonian evaporites within the basin. Glacial loading and unloading had previously been suggested as the cause of salt dissolution in the Western Canada Basin by Anderson and Hinds (1997). Pleistocene recharge of subglacial melt water was also invoked by McIntosh and Walter (2006) to explain the geochemical evolution of saline waters in Silurian-Devonian carbonate aquifers along the margins of both the Illinois and Michigan basins in the USA. The potential recharge of subglacial melt water beneath the European Ice Sheet has also been demonstrated by Boulton et al. (1995) using numerical models.

For more than 50 years, geochemical investigations of saline formation waters have focused on chemical and physical processes responsible for the variations observed in brine compositions (Chebotarev 1955; Bredehoeft et al. 1963; Graf et al. 1966; Carpenter 1978; Hanor 1983; Kharaka and Hanor 2004; Frape et al. 2004, and references therein). Several environmental problems continue to be investigated in relation to the occurrence of saline waters in groundwater environments, including (1) disposal of radioactive wastes in bedded salt deposits (Lambert 1978) and their potential for release and transport in groundwater (Jones and Anderholm 1996), (2) contamination of fresh-water supplies by introduction of saline waters from improper disposal practices, leakage from improperly sealed deep wells, or intrusion of saline water in coastal aquifers, and (3) issues pertaining to the disposal of chemical wastes and sequestration of carbon dioxide and other wastes in deep-formation waters (Brasier and Kobelski 1996; Herzog and Drake 1998). To investigate the environmental impacts of occurrence of highly saline fluids in groundwater environments, models are needed that are capable of simulating variable-density flow and solute transport.

Density-dependent simulations of groundwater flow increasingly have been applied in the analysis of salt-water intrusion within coastal aquifers and a number of

codes have been used for this purpose, including SEAWAT (Dausman and Langevin 2005), SUTRA (Gingerich and Voss 2005) and FEFLOW (Pohlmann et al. 2002). These and other codes are described in Zheng and Bennett (2002). The application of simulation models to a number of benchmark problems has been described, but there are few published studies of field simulations of brine and groundwater interactions. Langevin and Guo (2006) applied SEAWAT to the salt-pool problem (Oswald and Kinzelbach 2004), a laboratory experiment in which a three-dimensional mixing zone was formed between saline water with a 10% mass fraction and an overlying layer of slow-moving fresh water; concentrations were measured by nuclear magnetic resonance imagery. Johannsen et al. (2002) applied a research code to the same problem; a model with nearly 17 million nodes was required to obtain an acceptable match to the measured concentrations.

Field-scale simulations typically have employed sensitivity analyses to examine the influence of flow and transport parameters on variable-density flow. Ranganathan and Hanor (1988) applied SUTRA in a two-dimensional model to determine the magnitudes of density and thermal effects on groundwater flow in the vicinity of salt domes in Louisiana. Lahm et al. (1998) also applied a model based on SUTRA in a two-dimensional simulation of the flushing of brine from a carbonate aquifer by infiltrating meteoric water in the western portion of the Appalachian Basin in Ohio, USA. A similar model was then used to simulate the effects of long-term groundwater withdrawals on the salinity of water in the carbonate aquifer (Lahm and Bair 2000). Ophori (1998) applied MOTIF in a three-dimensional model to investigate the combined effects of density, viscosity and temperature on groundwater flow beneath the Atikokan Research Area in Ontario, Canada. Mason and Kipp (1997) used HST3D to simulate brine movement beneath the Bonneville Salt Flats in Utah, USA and to quantify sources and discharges of salt from a shallow-brine aquifer.

Here SEAWAT-2000 (Langevin et al. 2003) has been used to investigate the origin of a brine pool found at relatively shallow depths within glacial drift at the northern end of the Onondaga Trough near Syracuse, New York State. Because of its shallow accessibility, the brine and groundwater flow system within the glacial drift provide an opportunity to simulate field-scale interactions that arise between fluids of sharply contrasting densities. Unlike the previous study by Grasby and Chen (2005) that addressed the origin of brine within a regional flow system at the margin of a deep sedimentary basin, this study is concerned with the origin and stability of a brine pool in a shallow local flow system that resides in glacial drift. This study combines data on major ion chemistry and isotopic composition of brines and saline waters with simulation results from a two-dimensional, variable-density flow model constructed using SEAWAT-2000 to test two hypotheses for the origin of the brine pool: (1) that the brine pool could have migrated through glacial sediments to its current position and persisted until the present, and (2) that the brine pool formed through steady accumula-

tion of brine from upward flow of a source in the bedrock underlying the Onondaga Trough. The two-dimensional model described herein was based on a transient, three-dimensional, variable-density flow model described by Yager et al. (2007) that was calibrated to both observations of water levels and chloride concentrations, and water and chloride mass discharges measured in the glacial aquifer system within the Onondaga Trough.

### Hydrogeologic setting

The brine in the Onondaga Trough is confined within a narrow bedrock valley that was deepened and widened by the southern expansion of the Laurentide glacier from eastern Canada during the late Pleistocene Epoch. The trough extends from the north end of Onondaga Lake, 40 km south through the Tully Valley and connects to another bedrock valley that continues 24 km south to the town of Cortland (Fig. 1). Glacial downcutting in the Onondaga Trough eroded the northern limit of halite beds within the upper Silurian Salina Group near its confluence with the West Branch Valley (Fig. 2). The halite removed by erosion could have been incorporated in glacial till at the base of the ice during the glacial advance and later

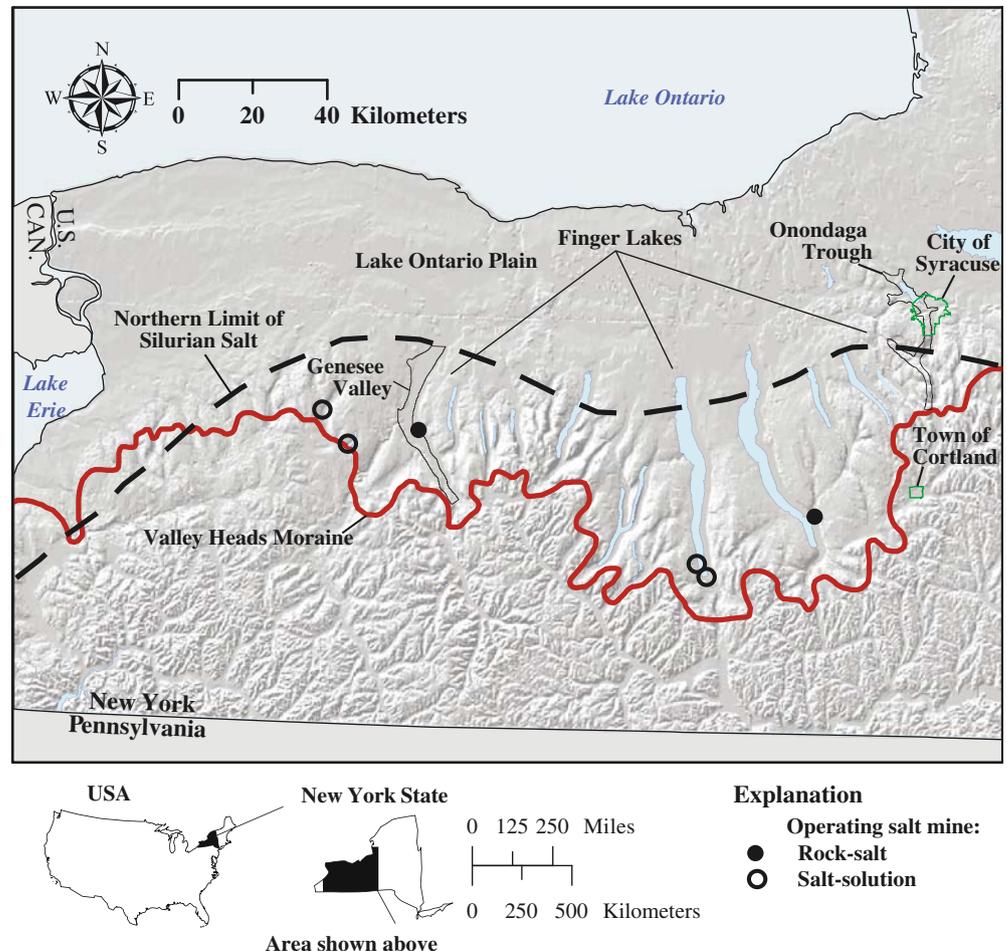
exposed to dissolution by glacial melt water during the glacial recession.

### Bedrock geology

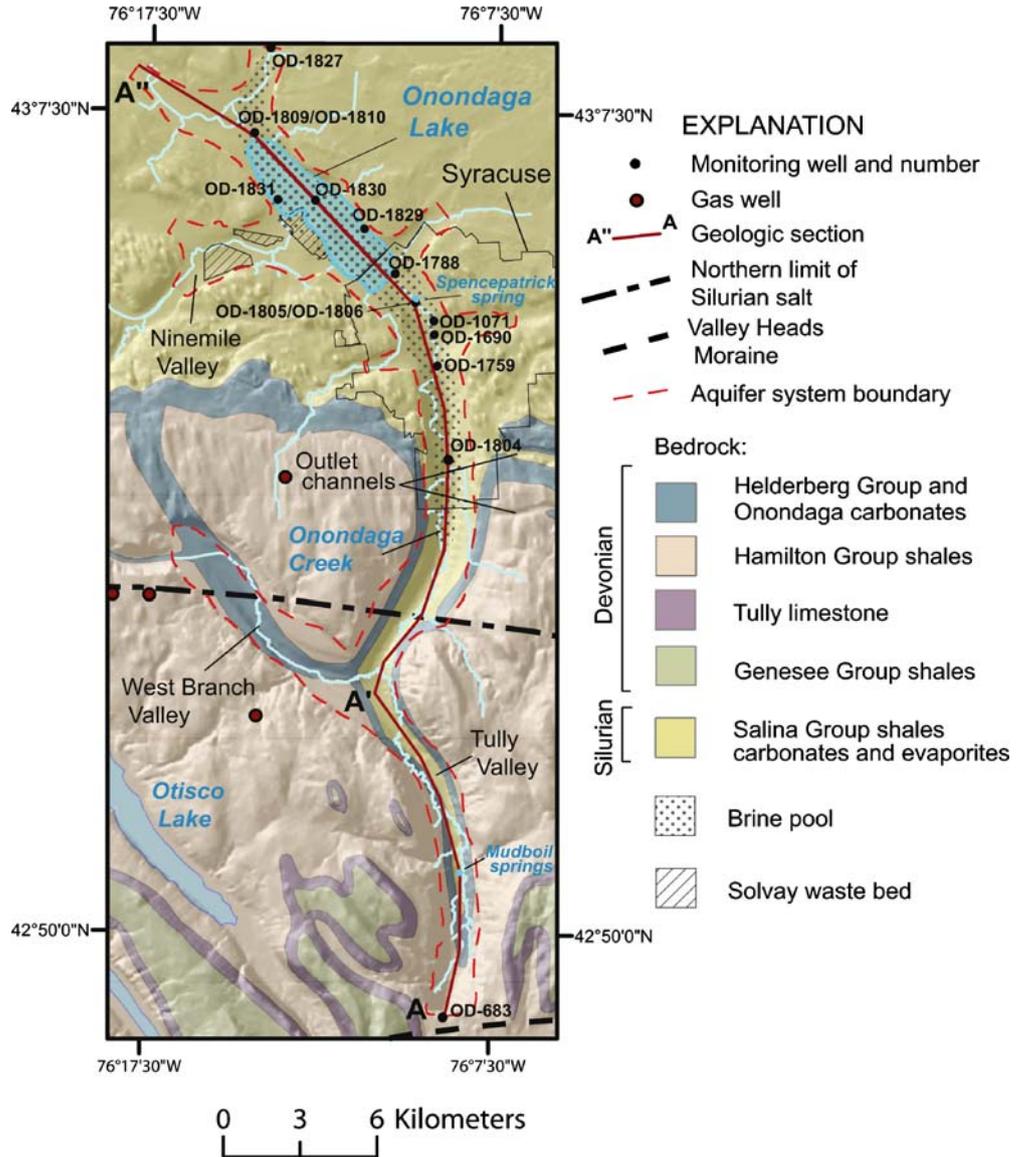
The Onondaga Trough is underlain by Silurian and Devonian sedimentary rocks that dip southward at about 9.5 m/km. The bedrock units strike E–W and extend across western New York and into southern Ontario. Most of the bedrock valley floor is underlain by shale of the Silurian Salina Group, which is overlain by Devonian carbonate that outcrops south of Syracuse (see Fig. 2). The carbonate is overlain in turn by Devonian shale and limestone that forms the surrounding uplands.

Shale is interbedded with halite and gypsum in the Syracuse Formation of the Salina Group. The evaporite beds subcrop beneath the Onondaga Trough, thicken southward into the Appalachian Basin and are contemporary with evaporite beds in the Michigan Basin to the west (Rickard 1969). Halite is found in four extensive beds with an aggregate thickness of about 45 m in the southern end of the Tully Valley, and over 150 m along the New York–Pennsylvania border. Halite is currently mined at several locations in western New York (see Fig. 1). Interpretation of geophysical logs from gas well boreholes

**Fig. 1** Geographic features in western New York State, showing northern limit of Silurian salt, Valley Heads Moraine, Finger Lakes, and location of Syracuse



**Fig. 2** Bedrock geology in the vicinity of the Onondaga Trough, showing surface drainage and springs, extent of brine pool, location of monitoring wells and Solvay waste beds. *Shaded relief* is bedrock surface within the trough and land surface outside the trough



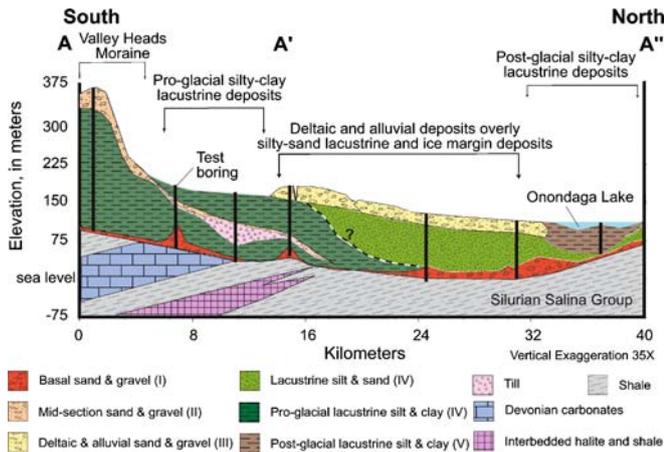
(see Fig. 2) suggests that the halite beds pinch out about 19 km south of Syracuse, although isolated salt lenses probably occur within the Syracuse Formation north of this limit.

**Glacial sediments**

The Onondaga Trough is filled with glacial drift deposited during the last deglaciation. The trough was occupied by ice about 17,300 years B.P. when the Valley Heads Moraine was formed during the last major southward surge of the ice front (Mullins et al. 1996). The Valley Heads Moraine extends across central New York (see Fig. 1) and marks the present drainage divide between streams that flow north to the St. Lawrence River and streams that flow south to the Susquehanna River. Most of the drift in the Onondaga Trough was deposited during the northward retreat of the ice from the moraine, which has been dated at 16,500 years B.P. (Mullins et al. 1996).

Glacial deposition in the trough ceased by about 14,300 years B.P. with the formation of glacial Lake Iroquois, which occupied the depression now filled by the present-day Onondaga Lake. The formation of Lake Iroquois marked the final recession of the ice margin from the Onondaga Valley. The drift thickness increases from north to south, ranging from 75-m thick beneath Onondaga Lake, to about 120-m thick in the Tully Valley and over 240-m thick beneath the Valley Heads Moraine (Fig. 3).

The glacial drift in the Onondaga Trough is primarily composed of lacustrine sediments that were deposited in a series of pro-glacial lakes dammed by glacial ice to the north and the uplands to the south. Coarse-grained sediment (sand and gravel) 3–30 m thick was deposited at the base of the ice where melt water entered the lakes and formed subaqueous fans. Silty-clay lacustrine sediments, as much as 30 m thick, overlie these coarse-grained, ice-marginal sediments and were deposited in a



**Fig. 3** Generalized section A-A'' along Onondaga Trough showing glacial and bedrock stratigraphy. Roman numerals are numbers of units referenced in text. Section location shown on Fig. 2

deep-water lake that occupied the Tully Valley. A till layer overlain by sand and gravel within the mid-section of glacial drift in the Tully Valley and at land surface on the Valley Heads Moraine suggests a readvance of the ice in the southern part of the Onondaga Trough (Kappel and Miller 2003). Another depositional sequence of coarse-grained sediments overlain by fine-grained lacustrine sediments is repeated in the Tully Valley. The lacustrine sediments in the Onondaga Trough are overlain by deltaic coarse-grained sediments as much as 30 m thick that were deposited by a series of deltas built out eastward from the West Branch Valley and northward into the Onondaga Trough. The top elevations of the deltas decrease northward and correspond to a series of outlet channels that were cut east of the trough by proglacial lake drainage (see Fig. 2; Hand 1978). As the ice margin receded northward onto the Ontario Plain, the relatively shallow and long-lived Lake Iroquois formed in the lowland. A sequence of silty-clay lacustrine sediments, up to 40 m thick, was deposited beneath Onondaga Lake.

The generalized depositional history described above formed the basis of a three-dimensional geologic model developed for the glacial drift (Yager et al. 2007). The sediment sequence in the Onondaga Trough is similar to that described by Mullins et al. (1996) for several Finger Lake valleys in central New York on the basis of marine seismic surveys. A similar geologic model described by Yager et al. (2001) formed the framework for a groundwater flow model in the Genesee Valley, located 160 km west of the Onondaga Trough (see Fig. 1). The geologic model for the Onondaga Trough was developed by interpolating stratigraphic contacts shown on sections from Kappel and Miller (2005) to form continuous units consistent with assumed depositional history.

## Hydrology

The distribution of coarse-grained sediments has created an aquifer system that consists of (1) a lower aquifer that

is assumed to be hydraulically continuous throughout the Onondaga Trough, (2) a middle aquifer in the Tully Valley, and (3) an upper aquifer in the Onondaga Valley. These aquifers are separated by thick confining layers of lacustrine sediment. Most of the groundwater in the aquifer system flows through the upper aquifer which is unconfined and receives recharge through precipitation on the valley floor and infiltration of runoff from surrounding upland areas. Groundwater in the upper aquifer discharges to Onondaga Creek, the principal stream that drains the valley (see Fig. 2). Recharge reaches the middle aquifer in areas where it is exposed on the Valley Heads Moraine and perhaps locally through alluvial fans emanating from large tributary valleys. Artesian pressure in the middle aquifer in the Tully Valley causes groundwater to discharge through breaches in the overlying confining layer to springs within a 4-ha area where numerous mudboils discharge water and sediment, causing land subsidence (Fig. 2; Kappel et al. 1996). Recharge to the lower aquifer is limited to infiltration of runoff along the walls of the bedrock valley and from leakage from the upper and middle aquifers. Groundwater discharges from the lower aquifer through upward flow to Onondaga Creek.

Little information is available concerning groundwater flow through the bedrock surrounding the Onondaga Trough. The rocks are relatively undisturbed, so groundwater probably flows through a network of bedding plane fractures and joints similar to fracture networks found in other bedrock terrain in western New York (Yager 1996). Carbonates that underlie the uplands adjacent to the Lake Ontario Plain probably intercept most of the meteoric water that recharges these areas. Some of the remaining recharge could infiltrate downward to the deeper shale units that underlie the carbonate, but this water would flow across the bedding, which would limit the rate of flow. Meteoric water could enter the lower aquifer through bedding plane fractures that intersect the Onondaga Trough, but the rate of flow is probably small throughout most of the trough. For this reason, the representation of a possible hydraulic connection between the aquifer system and the bedrock was not considered in the flow modeling presented later on.

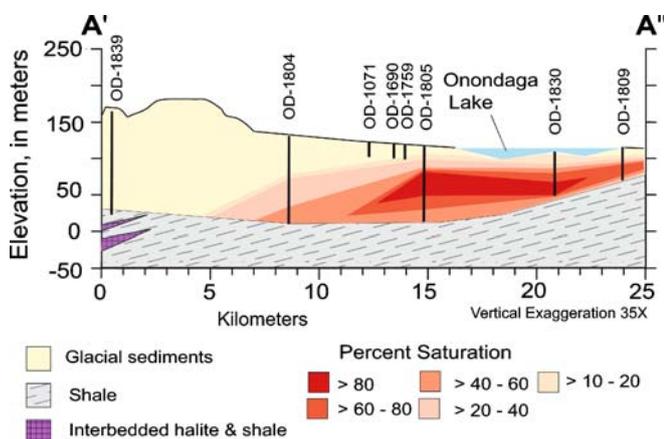
## Occurrence of brine and history of brine production

A brine pool of Na–Cl dominated water (referred to as ‘halite brine’ herein) covers an area of about 26 km<sup>2</sup> within glacial sediments at the northern end of the Onondaga Trough, and extends southward about 18 km (see Fig. 2). The brine pool occupies the lowest part of the trough and is confined beneath Onondaga Lake by silty-clay lacustrine sediments. Measured brine densities in the brine pool currently range from 1.09 to 1.16 g/cm<sup>3</sup>, corresponding to halite saturations of 45–80% (Yager et al. 2007). Saturations are highest beneath Onondaga Lake and generally increase with depth (Fig. 4). The brine is slightly less saturated at the bottom of the glacial sediments beneath the southern shore of

Onondaga Lake, possibly reflecting removal of brine through pumping in the nineteenth century. The mass of halite in the current brine pool is estimated as  $4.5 \times 10^{10}$  kg and the mass produced by pumping from the Onondaga Trough in the nineteenth century was about  $1.0 \times 10^{10}$  kg (Phalen 1919). The total mass of halite present prior to pumping in 1800 would, therefore, have been  $5.5 \times 10^{10}$  kg, equivalent to a 4-km slab of salt 5-m thick extending across the trough (1,300 m).

Halite brine that discharged from springs around the southern shore of Onondaga Lake was collected and boiled down to produce salt by European settlers in the eighteenth century. Solar evaporation of the brine was introduced in the 1800s after wells were constructed to pump more concentrated brine from the confined aquifer beneath Onondaga Lake. Upon completion of the Erie Canal in 1825, the salt works became the most important source of salt in the United States (Kurlansky 2002). Salt was produced from the aquifer system between 1797 and 1917, primarily from brine wells (Phalen 1919). During this period, halite saturations of brine pumped from the deepest wells declined from more than 75% to less than 60% (or from 200 to 170 g/L dissolved solids; Kappel 2000).

A chemical plant was constructed along the western shore of Onondaga Lake in 1888 to manufacture sodium carbonate or soda ash ( $\text{Na}_2\text{CO}_3$ ) from the halite and limestone resources found within local rocks using the Solvay process (Effler 1996). Saline waste materials from the Solvay Process plant were deposited in extensive waste beds covering more than 8.1 km<sup>2</sup> around the western shore of Onondaga Lake (see Fig. 2). The runoff of saline water from these waste beds caused hypersaline conditions in Onondaga Lake by the middle of the twentieth century, resulting in chemical stratification of lake water and failure of spring turnover during a number of years (Effler and Perkins 1987). While the salinity of lake water decreased significantly following closure of the plant in 1980, continuing remedial activities seek to collect and treat leachate from the waste beds, and thereby limit the discharge of saline



**Fig. 4** Generalized section A'-A'' showing percent saturation of brine at the northern end of the Onondaga Trough. Section location shown on Fig. 2

water, which currently accounts for about 30% of the total chloride loading to the lake (Onondaga County Department of Water Environment Protection 2002).

The natural salt springs known in the eighteenth century are now buried by fill materials and have ceased to flow at the land surface. Brine currently discharges at about 28 L/s from Spencepatrick Spring, located in Onondaga Creek about 1.5 km south of Onondaga Lake (see Fig. 2), contributing about  $9.0 \times 10^7$  kg of NaCl annually to Onondaga Lake. This discharge rate would have depleted the brine pool in about 600 years, so it is likely that flow from Spencepatrick Spring is relatively recent. Spencepatrick Spring is located in an area where brine wells were drilled in the nineteenth century, and may be the site of an abandoned well. Brine also discharges directly to Onondaga Lake, but the rate of flow is limited by lacustrine sediments that underlie the lake. The mass of halite discharged annually by groundwater to Onondaga Lake was estimated to be  $5.3 \times 10^6$  kg by Effler et al. (1990).

### Geochemistry and origin of brine

A series of chemical and isotopic measurements were made on the brine and other local waters to investigate the origin and age of the waters in the Onondaga Trough. Samples of groundwater in the Onondaga Trough were analyzed using standard methods by US Geological Survey laboratories for: (1) major and minor ions by a National Research Program (NRP) laboratory (Reston, VA, USA), (2) <sup>2</sup>H and <sup>18</sup>O by the Stable Isotopes Laboratory (Reston, VA, USA), (3) dissolved gases by the Chlorofluorocarbon Laboratory (Reston, VA, USA), and (4) <sup>11</sup>B by a NRP laboratory (Menlo Park, CA, USA). Samples of dissolved inorganic carbon were analyzed for (1) <sup>13</sup>C by the University of Waterloo Environmental Isotope Laboratory, Canada and (2) <sup>14</sup>C by Rafter Radiocarbon Laboratory, New Zealand and the Laboratory of Isotope Geochemistry at the University of Arizona, USA. A list of analytical results for the wells discussed in the text is presented in Table 1. The full table of analytical results is presented in Yager et al. (2007).

### Major and minor ions

Sodium and chloride are the principal constituents of the halite brine (e.g. well OD-1805, Fig. 5), but significant concentrations of potassium, magnesium, calcium and sulfate also are present. The brine also contains bromide (40–120 mg/L), iron (1–14 mg/L) and boron (1–5 mg/L). Salt solutions prepared by dissolving samples of halite from the Salina Shale with distilled water contain smaller amounts of these constituents (Fig. 5), suggesting that the halite brine in the Onondaga Trough is not solely derived from halite. The halite brine differs from that of saline bedrock water sampled in and around the Onondaga Trough (e.g. well OD-1827, Fig. 5) in both ionic composition and the relative proportions of chloride and

bromide. The chemical composition of saline bedrock water contains higher concentrations of cations (except sodium) and bromide, and lower concentrations of chloride and sulfate than the halite brine water, and is similar to Appalachian Basin brine typically found in western New York (NYSDEC 1988). Bedrock waters in the Onondaga Trough generally have weight ratios of chloride to bromide concentration (120:1) that are similar to Appalachian Basin brine (Fig. 6), although three bedrock wells located along the shore of Onondaga Lake have much larger Cl:Br ratios (1,300:1) that are typical of the halite brine.

**Isotopic composition**

*Hydrogen and oxygen*

Most samples of halite brine have isotopic compositions of hydrogen ( $\delta D$ ) and oxygen ( $\delta^{18}O$ ) that plot along the local meteoric water line (MWL; Burnett et al. 2004). The  $\delta D$  values have been corrected for electrolyte-water interaction resulting from the high concentrations of NaCl using the experimental calibrations of Horita et al. (1993); no corrections were made for  $\delta^{18}O$  measurements because such corrections are negligible for NaCl (Taube 1954). The mean isotopic values are  $-76.6\text{‰}$   $\delta D$  and  $-11.3\text{‰}$   $\delta^{18}O$  (Fig. 7a). These values are slightly more depleted than those typically found in recent recharge in western New York, suggesting that either the water infiltrated to the aquifer when the average temperature was cooler than at present, or that the samples are mixtures containing various fractions of melt water. Saline bedrock water contains even more depleted isotopic values, indicating recharge under still colder conditions. Two saline-water samples from the lower aquifer plot below the local MWL and have enriched isotopic values. These samples are probably mixtures of waste slurry discharged from the Solvay Process plant, because the production of sodium carbonate required heat ( $\sim 300^{\circ}C$ ) that evaporated some of the water, and produced a waste stream enriched in  $\delta D$  and  $\delta^{18}O$ .

*Boron*

Halite brine samples generally have  $\delta^{11}B$  values that are less than 22‰, while the  $\delta^{11}B$  values of saline bedrock water are larger and closer to values typical of marine waters (39‰; Spivack et al. 1987; Fig. 7b). Salt solutions created by dissolving samples of halite from the Salina Group have very little boron and  $\delta^{11}B$  values that are near zero, which indicates that the boron in the brine was not derived from halite. Solutions created by leaching powdered samples of Salina Group shale with distilled water yield  $\delta^{11}B$  values (10–28‰) that overlap the range of values in halite brines (Fig. 7b). This evidence suggests that the boron in the brine originated from desorption from glacial sediments, which are largely derived from the local shale. The process of sorption and desorption of boron from sediments results in fractionation (Oi et al. 1989),

**Table 1** Chemical and isotope composition of brine and groundwater, Onondaga Trough

Well number	pH	Specific conductance mS/cm	Density g/cm <sup>3</sup>	Saturation percent	Ca g/L	Mg g/L	Na g/L	K g/L	Cl g/L	SO <sub>4</sub> g/L	HCO <sub>3</sub> g/L	Fe mg/L	Br mg/L	$\delta^2H^a$ ‰ VSMOW	$\delta^{18}O$ ‰ SMOW	<sup>3</sup> H pCi/L	B mg/L	$\delta^{11}B$ ‰	<sup>14</sup> C <sup>b</sup> pmc	$\delta^{13}C$ ‰ PDB
OD-683	7.9	0.5	0.998	0	.035	.014	.043	.001	.028	.067	.160	.5	0.5	-74.34	-10.71	0	1.9	4.25	50 <sup>c</sup>	-12 <sup>c</sup>
OD-1788	6.9	196	1.119	62	2.200	.370	63	.420	98	3.900	.110	4.1	36	-75.29	-11.34	0.1	1.3	21.73	3.8	-13.2
OD-1804	6.7	167	1.098	51	1.280	.200	49.4	.200	74	4.240	.160	13.3	47	-76.74	-11.41	2.6	5.1	19.98	15.5	-7.5
OD-1805	6.9	210	1.131	65	1.810	.350	66.3	.340	102	3.260	.092	13.5	86	-76.75	-11.30	-0.3	1.6	20.98	5.1	-13.5
OD-1806	6.8	159	1.087	43	1.740	.230	41.4	.180	69	4.520	.140	6.8	45	-76.70	-11.46	2.6	5	15.98	13.4	-8.6
OD-1827	7.3	94.8	1.046	25	9.900	2.100	12	1.600	41.1	1.300	.029	30.1	510	-90.12	-12.40	1.6	2.9	44.21	4.0	-11.5
OD-1831	6.6	111	1.055	30	9.900	.170	19	.320	46.4	1.100	.043	5.5	360	-67.01	-9.89	1.6	2.5	37.71	93.8	-18.1

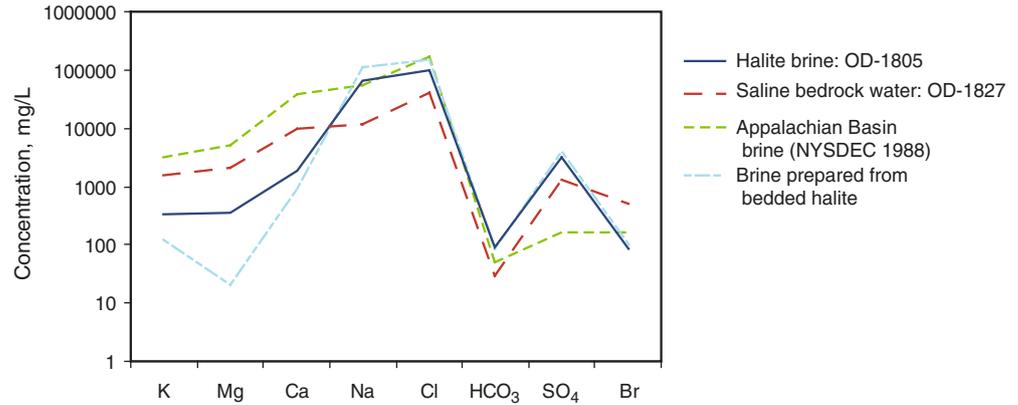
<sup>a</sup> Adjusted for salinity

<sup>b</sup> Dissolved inorganic carbon

<sup>c</sup> Not analyzed, estimated assuming closed system evolution

VSMOW: Vienna Standard Mean Ocean Water; pCi/L: picoCuries per liter; pmc: percent modern carbon; PDB: Pee Dee Belemnite

**Fig. 5** Concentrations of major ions in halite brine from a representative well in the Onondaga Trough (well OD-1805), in saline bedrock water (well OD-1827), bedded halite, and in Appalachian basin brine (NYSDEC 1988, Table 15.4)



and could explain the difference between  $\delta^{11}\text{B}$  values found in bedrock waters (over 40‰) and the values found in the halite brine (less than 22‰).

**Carbon**

The halite brine samples contain relatively low concentrations of dissolved inorganic carbon (DIC), ranging from 0.5 to about 2.5 mmol/L with log CO<sub>2</sub> partial pressures of 10<sup>-3.4</sup>–10<sup>-2.2</sup> atm (atmospheres). The halite brines are near calcite saturation (the average calcite saturation index is -0.05±0.32). The <sup>14</sup>C activities of DIC in the concentrated halite brines generally range from 4 to 15 percent modern carbon (pmc). Four samples from the wells near the Onondaga Lake shore (OD-1809, OD-1810, OD-1829 and OD-1831) have values ranging from 40 to 90 pmc (Table 1 and Yager et al. (2007)), and because some of these samples contain small amounts of tritium, could reflect mixing with recent (post-nuclear detonation) meteoric waters. The <sup>14</sup>C values of bedrock waters range from 4 to 90 pmc.

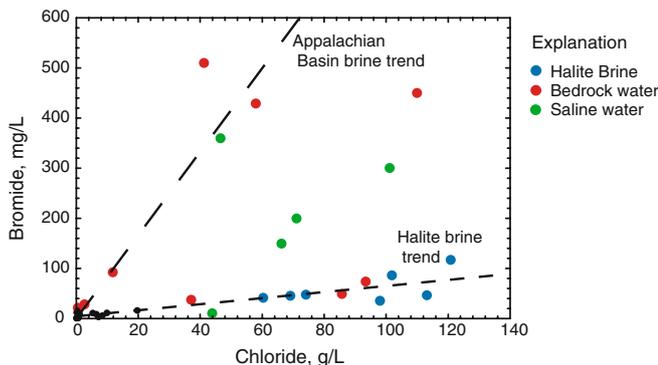
Halite brine samples with <sup>14</sup>C values less than 15 pmc could be as old as 15,000–25,000 years. The DIC in these samples have  $\delta^{13}\text{C}$  values of -8 to -15‰, which could result from dissolution of marine carbonate rocks ( $\delta^{13}\text{C} \sim 0\text{‰}$ ) with soil CO<sub>2</sub> derived from organic carbon ( $\delta^{13}\text{C} \sim -25\text{‰}$ ) in a closed system (Clark and Fritz 1997). The addition of “dead” carbon from dissolution of carbonate rocks containing negligible amounts of <sup>14</sup>C

dilutes the <sup>14</sup>C content, resulting in unadjusted radiocarbon ages that are biased old. The age of the DIC in the halite brine was estimated through geochemical calculations by using NETPATH (Plummer et al. 1994), as described below.

**Geochemical modeling**

The geochemical composition of the halite brine differs markedly from that of saline bedrock water in that: (1) the Cl:Br ratio of brine samples is much larger (Fig. 6), (2) the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values are more enriched (Fig. 7a), and (3) the  $\delta^{11}\text{B}$  values are lower (Fig. 7b). This evidence suggests that the halite brine was not derived directly from saline water in the local bedrock. The presence of potassium and magnesium and other minor ions in the halite brine, however, suggests that the brine probably mixed with bedrock water, as these elements are not present in the halite beds in the Syracuse Formation.

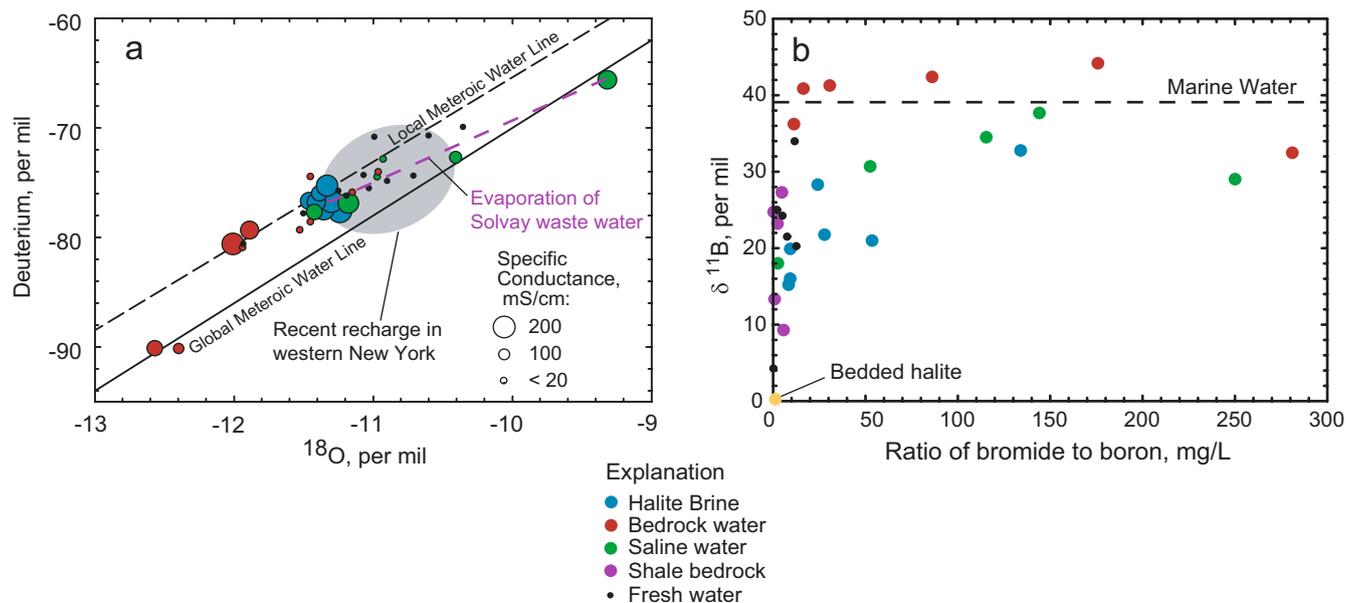
Geochemical modeling using the computer program NETPATH was conducted to determine whether mixtures of representative waters and accompanying water–rock reactions could account for the observed geochemical composition of the halite brine. The two end-member waters included in the mixing scenarios were fresh water and saline bedrock water. The fresh water was represented by the sample from well OD-683, which is screened in the lower aquifer beneath the Valley Heads Moraine and contains the most dilute water sampled in the study area (wells are located on Fig. 2). Saline bedrock water was represented by the sample that appears to contain the oldest groundwater, based on the measured <sup>14</sup>C value of 4 pmc from well OD-1827 located north of Onondaga Lake (see Fig. 2; Table 1).



**Fig. 6** Relation between chloride and bromide in groundwater in the Onondaga Trough

**Modeling approach**

The aqueous speciation calculation indicated that charge imbalances were typically less than 2% in the most saline waters. Though small, charge imbalances of even several percent can lead to large uncertainties in calculated mass transfer in geochemical mass-balance calculations involving highly saline fluids. Most affected are the calculated mass transfers of “neutral” phases such as organic matter



**Fig. 7** Isotopic concentrations of brine and saline waters in the Onondaga Valley: **a** Deuterium and oxygen-18, scaled on the graph with reference to the concentration indicators in the legend. **b** Boron-11 and Br:B ratio

or  $\text{CO}_2$  that are not formed by combination of positive and negative charges. Therefore, the charge-balance algorithm of NETPATH was invoked to adjust the compositions of all initial and final waters prior to making the mass-transfer calculations.

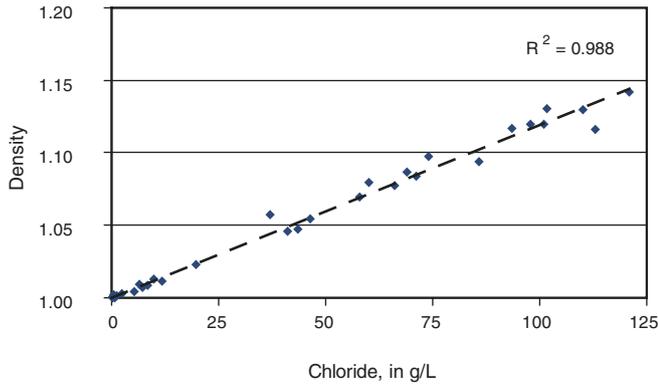
Mixtures of waters were assumed to react with the principal carbonate minerals (calcite and dolomite) and evaporite minerals (halite and gypsum) found in the study area. Additional reactions considered the possibility of (1) iron reduction (from goethite), (2) sulfate reduction accompanying the oxidation of organic carbon, (3) precipitation of iron sulfide, (4) cation exchange (involving  $\text{Ca}^{2+}$  and  $\text{K}^+$  for  $\text{Na}^+$ ) on surfaces of clay minerals and (5) exsolution of a  $\text{CO}_2$ - $\text{CH}_4$  gas mixture containing 5%  $\text{CH}_4$  (as indicated by analyses of gas bubbles sampled from Spencepatrick Spring, OD-1819). The models were constrained by measured concentrations (adjusted for charge imbalance) of the elements Ca, Mg, Na, K, Cl, S, C, Fe, and Br; and an electron balance constraint (conservation of electrons in redox reactions) was included. Carbon containing  $^{14}\text{C}$  was assumed to originate from soil  $\text{CO}_2$  and organic matter present in the valley. Because  $^{13}\text{C}$  and  $^{14}\text{C}$  analyses were not available for these materials, a range of potential values (-22 to -25 per mil and 50–100 pmc, respectively) was considered for both these carbon sources. Inorganic carbon sources (calcite and dolomite) were assumed to have  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  activities of 0 per mil and 0 pmc, respectively.

#### Reaction models

One reaction model was found that satisfied all the constraints and predicted the observed  $^{13}\text{C}$  of DIC of concentrated halite brine in well OD-1805 (65% saturation). This well is screened in the lower aquifer and located

near the center of the brine pool at the southern end of Onondaga Lake. The reaction model indicated a mixture of fresh water (83%) and saline bedrock water (17%), dissolution of 2.8 moles/ $\text{kg}_{\text{water}}$  of halite, 0.033 mole/ $\text{kg}_{\text{water}}$  of gypsum, and 0.029 moles/ $\text{kg}_{\text{water}}$  of cation exchange ( $\text{Ca}^{2+}$  for  $\text{Na}^+$ ). The rest of the mineral mass transfers were comparatively small (<0.001 moles/ $\text{kg}_{\text{water}}$ ). The computed age of DIC in water from OD-1805 (5.1 pmc), following adjustment for the modeled geochemical reactions, was 16,700 years.

The computed age is sensitive to the initial  $^{14}\text{C}$  content specified for OD-683; increasing the  $^{14}\text{C}$  value from 50 to 100 pmc increased the computed age at OD-1805 from 16,700 to over 22,000 years. The initial  $^{14}\text{C}$  content specified for OD-683 is unknown, but assumed to be near 50 pmc, a value consistent with geochemical evolution in a system closed to  $\text{CO}_2$  gas exchange. Closed system evolution is commonly observed in humid areas where a relatively high recharge rate causes rapid infiltration to the water table, followed by subsequent, closed-system evolution in saturated zones that contain carbonate rocks (Deines et al. 1974). At calcite saturation, the bicarbonate content of the resulting groundwater in the recharge area contains about half its carbon from soil gas  $\text{CO}_2$  (100 pmc) and half its carbon from old carbonate rocks (0 pmc). In arid regions where the recharge rates can be quite low, open-system evolution is more common resulting in initial  $^{14}\text{C}$  activities near 100 pmc. Although open-system conditions are unlikely to apply to recharge in the glacial drift system of Onondaga Trough, partially open systems could prevail in some areas, so the adjusted radiocarbon age of DIC in water from well OD-1805 could be older than 16,700 years. Another brine sample from well OD-1788, located within 1 km of OD-1805, contained  $^{13}\text{C}$  and  $^{14}\text{C}$  values of DIC similar to those from



**Fig. 8** Relation between chloride and density in halite brine samples

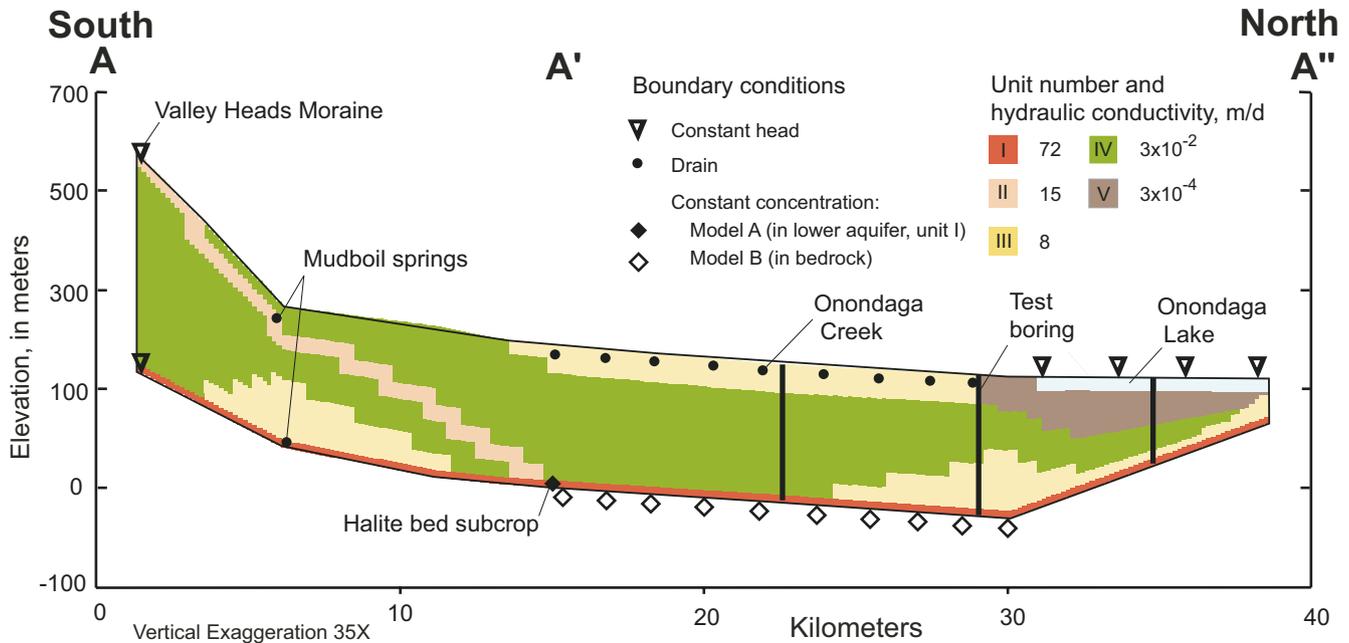
well OD-1805 (see Table 1), suggesting a comparable age for this sample. Although the mineral saturation indices and compositions of these two brine samples are similar, a valid reaction model for OD-1788 was not found, owing to compositional variations that resulted from uncertainty in the charge imbalance calculation.

The same reaction model as that presented above for the brine sample from well OD-1805, with only minor modifications, also reproduced the observed chemical concentrations and  $\delta^{13}\text{C}$  of DIC in more dilute brines at wells OD-1804 and OD-1806 (51 and 43% saturation, respectively). Both of these wells are located near the periphery of the brine pool where fresh water from upgradient areas to the south flows upward and over the brine pool and discharges to Onondaga Creek. Well OD-1804 is screened in the lower aquifer at the southern end of the brine pool and well OD-1806 is screened in coarse sediments about 60 m above well OD-1805. The specified  $^{14}\text{C}$  content of fresh water was increased to 100 pmc in

these reaction models to reflect a recent source of meteoric water in the mixing model, and the ion exchange reaction ( $\text{Ca}^{2+}$  for  $\text{Na}^+$ ) was modified to include  $\text{Mg}^{2+}$  to account for the enriched  $\delta^{13}\text{C}$  ( $-7.5$ ) observed at OD-1804. Both reaction models indicated a mixture of 91% fresh water and 9% saline bedrock water, and the occurrence of the dedolomitization reaction (dissolution of dolomite and gypsum accompanied by precipitation of calcite) as the predominant water–rock reaction. The adjusted radiocarbon ages of the DIC in water from wells OD-1804 and OD-1806 calculated from the geochemical models was 2,000 and 2,400 years, respectively. Although the modeled and measured  $\delta^{13}\text{C}$  were in close agreement at well OD-1804, the calculated  $\delta^{13}\text{C}$  was enriched by 4 per mil in DIC at well OD-1806 compared to the measured value ( $-8.6\text{‰}$ ). This difference could have resulted from uncertainties related to the adjustment of charge imbalances in water compositions, or other uncertainties in the model. The amount of calcite precipitation predicted by both of these models is consistent with observations of calcite rinds that encrust sand and gravel obtained from core samples at shallow depths ( $\sim 20$  m) near the southern end of the brine pool. The younger computed ages probably reflect mixing of the brine with recent meteoric recharge.

**Age and origin of brine**

The halite in the brine in the Onondaga Trough probably originated from the halite beds in the Salina Group that were eroded by glacial downcutting in the Pleistocene during the southern expansion of the Laurentide glacier from eastern Canada, and were later exposed to dissolution. Potential sources of water for the dissolution of halite include recent meteoric recharge and glacial melt water. If



**Fig. 9** Design of two-dimensional variable-density flow model

recent meteoric recharge were the source of the halite brine, then the spatial distribution of salt saturation in the Onondaga Trough would reflect a 20-km plume of high salinity water flowing northward from the halite-bed subcrop area to Onondaga Lake. Saturation data, however, suggest the opposite, because the highest salinities occur at the northern end of the trough beneath Onondaga Lake and decrease southward to the subcrop area (see Fig. 4). The computed age range of concentrated halite brine at well OD-1805 estimated from geochemical modeling (16,700–22,000 years) also indicates that the brine is not derived from recent meteoric recharge.

The estimated age of halite brine compares favorably with the timing of deglaciation in the Onondaga Trough (14,300–16,500 years B.P.), and supports the hypothesis that the halite brine is largely derived from glacial melt water. There are two possible explanations for how the brine pool at the northern end of the trough could have formed through the transport of halite by glacial melt water. Under the first hypothesis (scenario A), halite beds that intersected the trough and were eroded by glacial ice remained within the trough, perhaps embedded in the glacial till, which is largely derived from local bedrock (B. Stone, US Geological Survey, personal communication, May 2005). The halite brine formed following the glacial recession from the Valley Heads Moraine about 16,500 years B.P., when melt water dissolved the exposed salt. The brine composition was later modified through mixing with saline bedrock water and cation exchange with glacial sediments as it migrated northward through the lower glacial aquifer under the hydraulic gradient established between the Valley Heads Moraine and the Ontario Plain. The brine pool was trapped at the northern end of the trough by lacustrine sediments beneath Onondaga Lake, which limited discharge of the brine to surface water.

An alternative hypothesis for the origin of the brine pool (scenario B) assumes a source of halite brine in the shale bedrock that underlies the Onondaga Trough. Under this second hypothesis, subglacial recharge during the advance or retreat of the ice sheet dissolved halite in situ and later mixed with saline bedrock water, forming a brine pool within the bedrock. The bedrock brine entered the lower aquifer in the glacial sediments through upward flow or dispersion under the regional hydraulic gradient established following deglaciation. Upward transport of brine from the bedrock could explain the observed increase in salinity of water in the lower aquifer along a northward flow path from the Tully Valley toward the northern end of the Onondaga Trough. Upward flow of groundwater discharging to Onondaga Lake and Onondaga Creek subsequently formed a brine pool in the glacial sediments. There is no information on the quality of bedrock water directly beneath the trough between the delineated brine pool and the halite subcrop area to the south to either support or refute this hypothesis. Both of these hypotheses for explaining the origin of the brine pool were considered in variable-density models described below.

## Variable-density flow model

A two-dimensional variable-density, transient groundwater flow model of the glacial aquifer system was developed to assess these two hypotheses for the formation of the brine pool in the Onondaga Trough. The flow model was constructed using SEAWAT-2000 (Langevin et al. 2003), a computer program that combines a modified version of MODFLOW-2000 (Harbaugh et al. 2000) with MT3DMS (Zheng and Wang 1998). While there are a variety of codes available that are suitable for this purpose, SEAWAT-2000 affords the flexibility of supporting several different boundary conditions and provides a choice of numerical methods for solving the transport equation. SEAWAT-2000 has accurately reproduced the solutions to several benchmark problems commonly applied in the literature (Guo and Langevin 2002).

The SEAWAT program solves the variable-density flow equation by formulating the matrix equations in terms of fluid mass and assuming that the fluid density is solely a linear function of solute concentration (Guo and Langevin 2002). The flow and transport equations were explicitly coupled using a one timestep lag and solved alternately until the maximum difference in fluid density was less than  $10^{-6}$  kg/m<sup>3</sup>, which provided a mass-balance error less than 0.01%. The effect of variable fluid viscosity on flow was not considered in these simulations because the temperature range in this shallow aquifer system is small. Langevin and Guo (2006) showed that accounting for variable viscosity in their SEAWAT simulation of fluids with sharply contrasting densities in the salt-pool problem had a negligible effect on model results. An implicit finite-difference (FD) method was selected to solve the advection equation and central-in-space weighting was specified to minimize numerical dispersion.

## Modeling approach

The two-dimensional simulations were used to represent the two hypothetical scenarios proposed to explain the formation of the brine pool over an approximate 17,000-year period since the deglaciation of the Onondaga Trough. The transient simulation was divided into two periods in the first scenario: (1) a 2000-year period that represented dissolution of halite within the lower aquifer and accumulation of brine in the glacial sediments, and (2) a 15,000-year period following cessation of dissolution that represented flushing and dilution of the brine by fresh groundwater. In the second scenario, a constant source of salt (or saturated brine) located in the bedrock beneath the lower aquifer created a brine pool in the glacial sediments during a single 17,000-year period. Chloride was selected as the migrating solute in the transport simulation because the relation between chloride and density in brine samples is relatively linear (Fig. 8). The transport of a second solute was also simulated in both scenarios to compute the groundwater age distribution. This calculation used a zero-order reaction to trace the increase in age during the simulation; the initial age was specified as zero in both scenarios.

The two-dimensional model was based on the three-dimensional model described in Yager et al. (2007). The three-dimensional model was calibrated to changing aquifer conditions over a 215-year period from 1790 to 2005 to reproduce observations of water levels, chloride concentrations, and discharges of water and chloride. Eight parameter values, including hydraulic conductivity and recharge, were estimated in the three-dimensional model through nonlinear regression using UCODE (Poeter and Hill 1998), a computer program that uses weighted least-squares to minimize model residuals. The parameter values estimated through calibration of the three-dimensional model were specified in the two-dimensional model.

The two-dimensional model afforded a higher degree of resolution than the three-dimensional model, while still permitting simulation of the 17,000-year period within an acceptable computation time. The model simulated flow in the vertical section A-A" (see Fig. 2) along the longitudinal axis of the Onondaga Trough. Although the two-dimensional model cannot represent converging groundwater flow where the West Branch Valley intersects the Onondaga Trough, groundwater north of this intersection flows mainly parallel to the line of section. The two-dimensional model did not represent hydraulic connections along the bedrock valley walls that could allow groundwater from the lower aquifer to flow upward to the upper aquifer. The magnitude of flow along the valley walls is probably much less than the upward flow through the lacustrine sediments that overly the lower aquifer, however. The two-dimensional model, therefore, provides a reasonable simulation of flow conditions in the area of interest, from the halite subcrop area to the north end of the trough beneath Onondaga Lake.

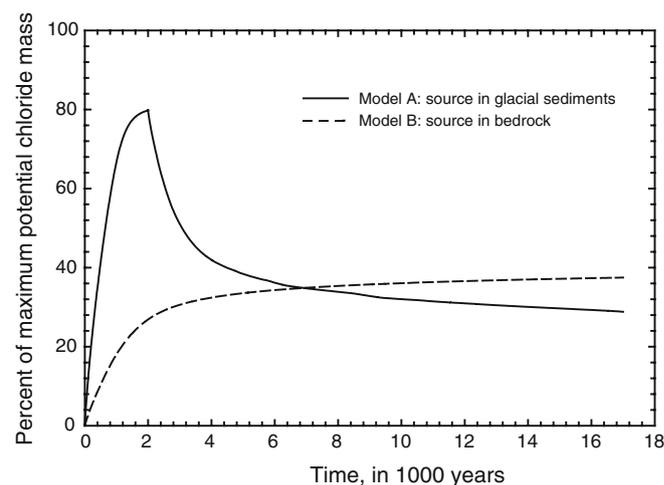
The depictions of the aquifer system, including both the initial conditions and the distribution of hydraulic properties, are highly generalized, so the models were not calibrated to observed chloride concentrations. Moreover, the selection of a two-dimensional representation precludes the comparison of chloride mass computed by simulation with the mass estimated from observed concentrations and discharges. Simulation results were compared with observed chloride concentrations to determine whether the models could reproduce the general dimensions of the observed brine pool. The observed chloride concentrations were measured in pore-water samples extracted from continuous sediment cores that were obtained from three boreholes completed within the brine pool (OD-1804, OD-1805 and OD-1830, see Fig. 2). A sensitivity analysis was later conducted to identify the significant factors that controlled the simulated concentration distributions.

### Model design

The design of the two-dimensional variable-density flow model was based on the geologic model presented earlier. Five geologic units were represented in the models: (I) basal sand and gravel (lower aquifer), (II) mid-section sand and gravel (middle aquifer), (III) deltaic sand gravel

(upper aquifer), (IV) lacustrine silt and sand and (V) lacustrine silt and clay (Fig. 9). The model domain extended northward 37 km from the Valley Heads Moraine to Onondaga Lake and was initially divided into a grid with 245 columns and 11 layers to correspond to the grid used in the three-dimensional model. This coarse grid (column and layer spacing of 152 and 15 m, respectively) was divided to form a finer grid (column and layer spacing of 38 and 3.8 m, respectively) with 46,060 cells that were used in the simulations described below. The effects of spatial discretization on the simulated concentration distribution were assessed and described below under the discussion of model sensitivity. Specified hydraulic and transport properties were based on values estimated for the three-dimensional model of Yager et al. (2007), with the exception of the dispersivity values. The dispersivity values (20 m and 1.5 mm for the longitudinal and transverse directions, respectively) were chosen large enough to minimize artificial oscillations in the numerical solution, yet small enough to prevent excessive dispersion of mass from the simulated brine pools. The effective porosity was specified as 30%, likely a maximum value for coarse sediments that would yield a conservative estimate of travel time.

Constant head and drain boundaries were specified in both model scenarios (1) at land surface to represent recharge on the moraine and discharge to Onondaga Lake and its inlet, Onondaga Creek, and (2) in the lower aquifer in the Tully Valley to represent underflow through the moraine and discharge from confined aquifers through springs in the area of mudboil formation (Fig. 9). In the first scenario (relict brine source in glacial sediments), a constant concentration boundary was specified in the lower aquifer during the initial time period in the area where halite beds subcrop on the bedrock valley floor (Fig. 9); this boundary condition was removed during the second time period. In the second scenario (continuing



**Fig. 10** Chloride mass simulated in aquifer system by *model A* (brine source in glacial sediments) and *model B* (brine source in bedrock), expressed as percentage of the total possible mass in storage

brine source in the bedrock), an additional layer representing the bedrock below the lower aquifer was added and a constant concentration boundary was specified within this layer northward from the subcrop area to the deepest part of the trough beneath Onondaga Lake (Fig. 9). The hydraulic conductivity of the bedrock layer was specified as zero to prevent advective transport, and dispersivity values of 15 m were specified to allow dispersion of saturated brine into the lower aquifer.

**Simulation results**

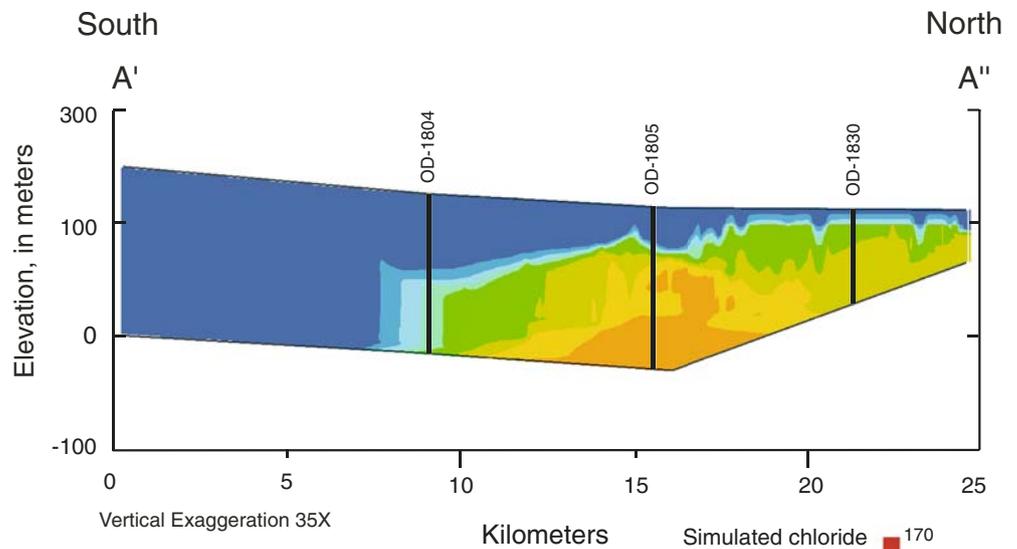
The simulated mass of chloride in the aquifer system computed by the first scenario (model A-brine source in glacial sediments) approaches a maximum after

2,000 years when sediments downgradient of the halite subcrop become nearly saturated (Fig. 10). The simulated chloride mass declines rapidly following the cessation of halite dissolution, but then is depleted very slowly after about 7,000 years. The simulated chloride mass computed by the second scenario (model B-brine source in bedrock) follows a different trajectory, increasing rapidly over the first 3,000 years and then slowly over the remainder of the simulation. Both simulations result in brine pools of comparable mass, but the pool predicted by model B covers a larger area (Fig. 11). Chloride concentrations simulated by the models are similar in magnitude to the observed concentrations, but do not match the concentration profiles exactly at each borehole (Fig. 12).

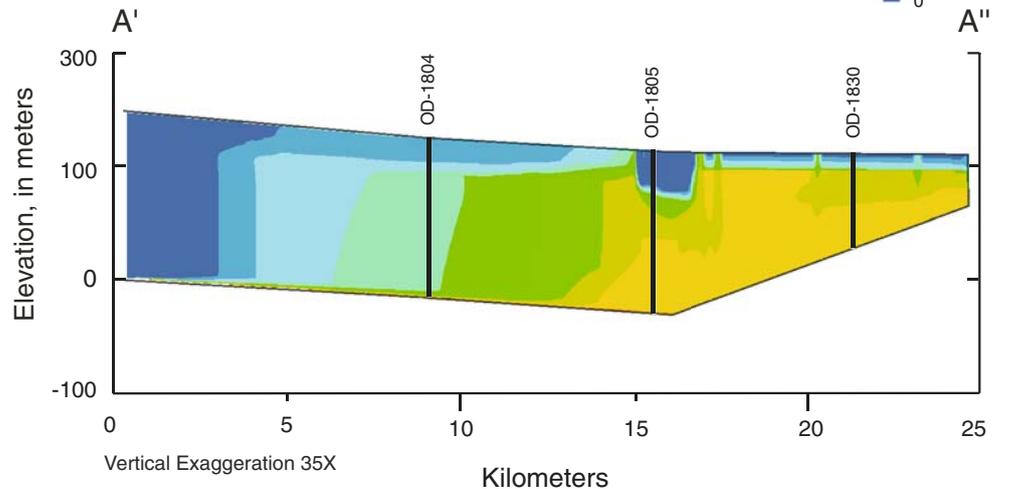
The brine pool predicted by model A results from the interaction of concentrated brine with fresh water flowing

**Fig. 11** Chloride concentrations simulated at the end of 17,000-year period with **a** model A (brine source in glacial sediments) and **b** model B (brine source in bedrock)

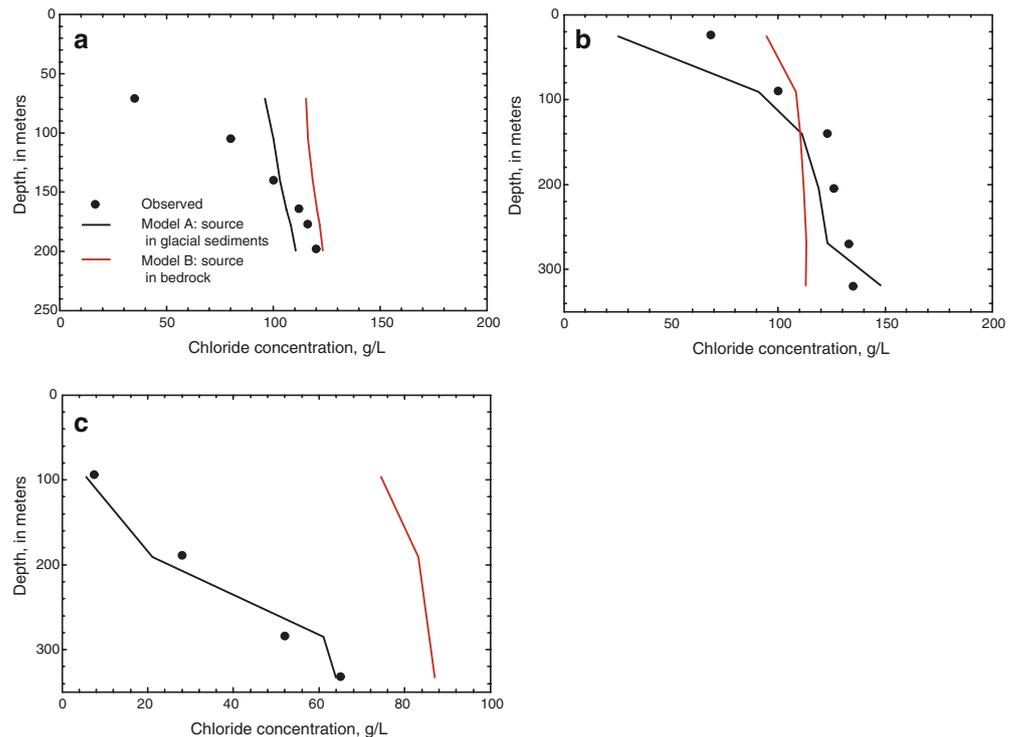
**a: Brine source in glacial sediments**



**b: Brine source in bedrock**



**Fig. 12** Chloride-concentration depth profiles simulated with model A (brine source in glacial sediments) and model B (brine source in bedrock): **a** well *OD-1830* beneath Onondaga Lake; **b** well *OD-1805* 1km south of lake; **c** well *OD-1804* 5km south of lake



from upgradient areas south of the pool. In the simulation, fresh water in the lower aquifer intrudes beneath the concentrated brine and creates an unstable density distribution. The effects of the instability are magnified along sharp vertical boundaries that occur between areas of large and small hydraulic conductivity. In these areas, lower density water moves upward and higher density water moves downward, forming convection cells. Upward flow through these convection cells and subsequent discharge of saline water to Onondaga Creek and Onondaga Lake result in a loss of brine from the pool. The displacement of brine from these simulated convection cells creates a complicated chloride-concentration distribution, particularly beneath Onondaga Lake where the bottom of the aquifer system slopes southward against the regional hydraulic gradient. The density distribution ultimately attains a stable configuration, as reflected by the time series plot of chloride mass in Fig. 10.

In contrast, the brine pool predicted by model B results from the steady accumulation of brine in the aquifer system. The brine pool forms from south to north and the regional hydraulic gradient forces the concentrated brine to the northern end of the trough. Under this scenario, higher density water always underlies the lower density water, so areas of instability do not form. The mass of chloride in the brine pool simulated with model B is 30% greater than that simulated with model A, and is still increasing at the end of 17,000-year simulation.

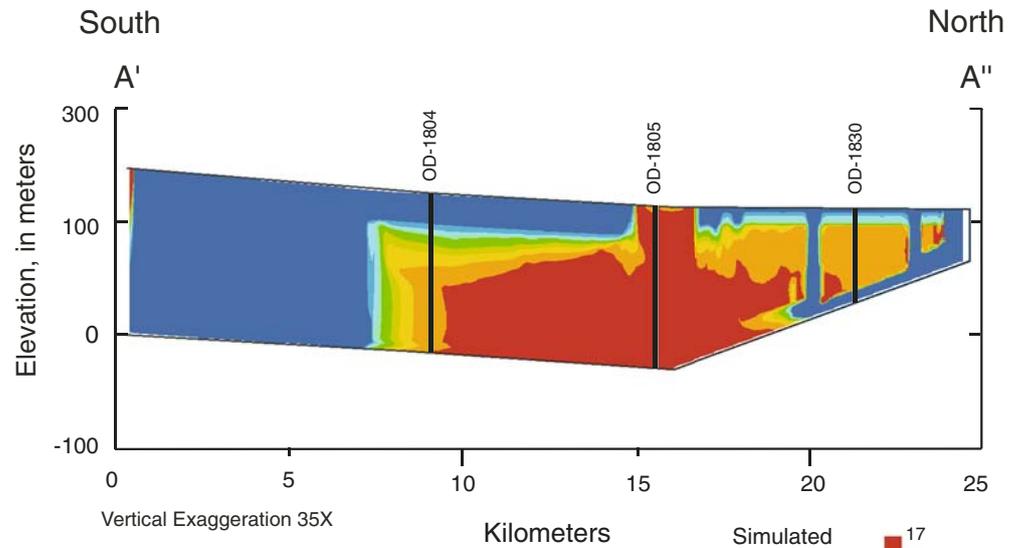
Although the concentration distributions simulated by models A and B are similar, a comparison of the distributions of groundwater age reveals a significant difference between these two scenarios (Fig. 13). The age of the brine is nearly 17,000 years throughout the pool

simulated by model A, while only small areas of brine older than 13,000 years are simulated by model B. The difference in the age distributions can be explained by comparing vector plots that indicate the simulated direction of groundwater flow (Fig. 14). In model A, most of the groundwater from upgradient areas south of the brine pool is deflected upward by denser water toward discharge areas along Onondaga Creek. Some of the lower density water flows horizontally over the brine pool, but the velocity is one order of magnitude lower than upward-flow velocities south of the pool. A circulation pattern opposite to the direction of the regional hydraulic gradient is simulated within the thick, relatively permeable sands that overlie the lower aquifer beneath the southern end of Onondaga Lake. This flow delivers saturated brine to a mixing zone at the south end of the brine pool and is similar to the pattern of flow observed in coastal areas where fresh water overlies a salt-water wedge. The lowest groundwater velocities (less than  $10^{-5}$  m/d) are simulated beneath Onondaga Lake where the remnants of convection cells create a complicated pattern of flow.

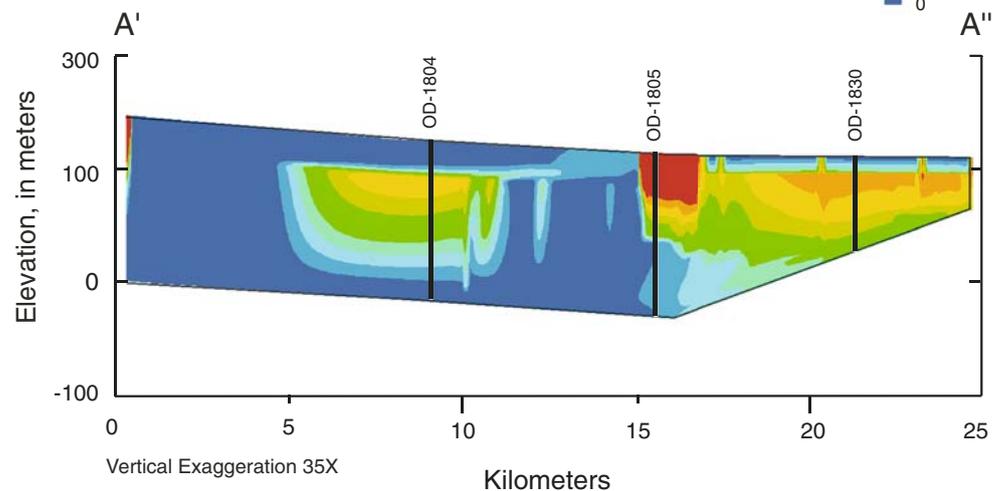
In model B, groundwater from upgradient areas also flows upward and discharges to Onondaga Creek, but water in the lower aquifer flows northward with the hydraulic gradient to the end of the trough. The simulated discharge to Onondaga Lake is one order of magnitude greater in model B than in model A. No convection cells are formed under this scenario. As a result, groundwater velocities within the thick permeable sands beneath the southern end of Onondaga Lake are five times larger than in model A, and result in a larger discharge of saline water to the north end of Onondaga Creek.

**Fig. 13** Groundwater age distributions simulated with **a** model A (brine source in glacial sediments) and **b** model B (brine source in bedrock)

**a: Brine source in glacial sediments**



**b: Brine source in bedrock**



**Model sensitivity**

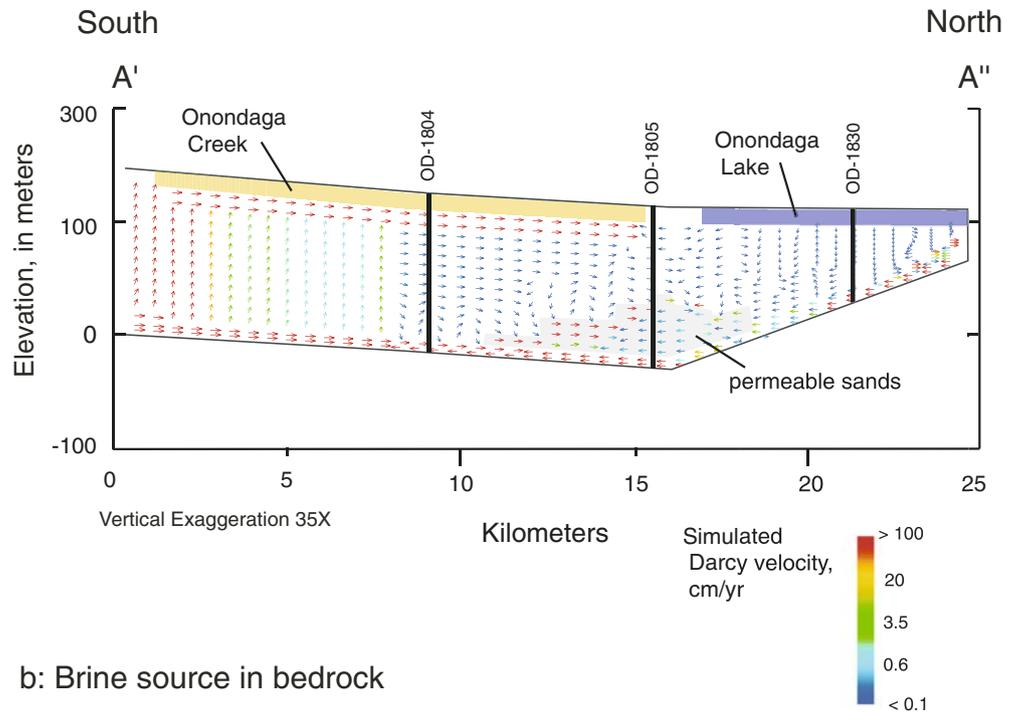
Specified values of several model parameters affect the dimensions and mass of the simulated brine pools obtained at the end of the 17,000-year simulations. The instabilities that arise in the density distribution simulated by the flushing and dilution of brine in model A are particularly sensitive to these parameters. The mass of the simulated brine pool in model A was diminished when the rate of flow through glacial sediments was increased either by increasing the permeability of the lacustrine silt and sand ( $K_{lac}$  in unit IV) or decreasing the effective porosity of all glacial sediments. Increasing  $K_{lac}$  by one order of magnitude or decreasing the effective porosity by one-half reduced the simulated mass by either 40 or 25%, respectively. Increasing the longitudinal or transverse

dispersivity intensified mixing of fresh and saline water in the simulations and also reduced the simulated mass. Increasing the specified values of either longitudinal or transverse dispersivity by a factor of two decreased the simulated mass by 50 or 10%, respectively.

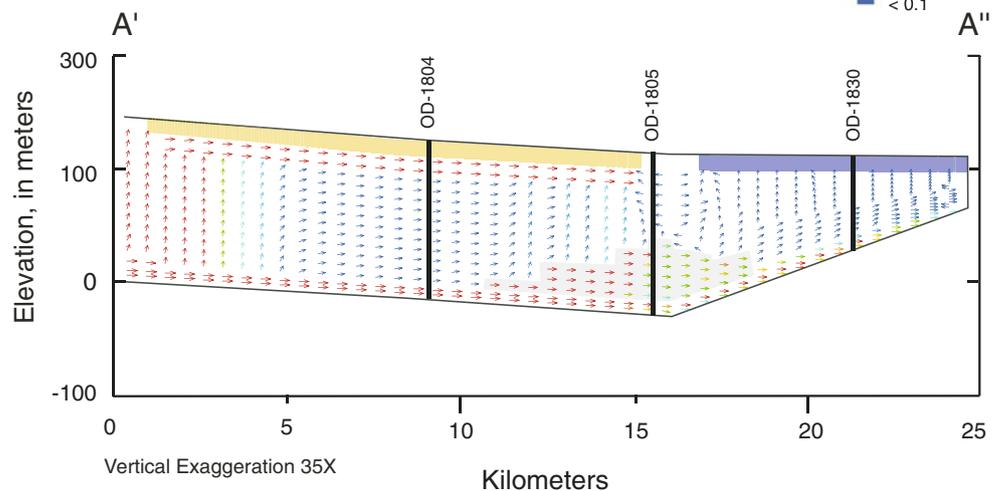
The degree of spatial discretization used in the simulations also affected the mass of the simulated brine pools. Increasing the grid spacing by a factor of two increased numerical dispersion and decreased the simulated mass in model A by 25%. The simulated brine pools were also affected by assumed characteristics of the chloride sources used to create the pools. The duration of dissolution in the first time period in model A and the location of the chloride source in model B can both be altered to adjust the mass of the simulated pools. An

**Fig. 14** Groundwater velocity distributions simulated with **a** model A (brine source in glacial sediments) and **b** model B (brine source in bedrock). *Arrows* indicate direction of flow and *colors* indicate magnitude of flow

**a: Brine source in glacial sediments**



**b: Brine source in bedrock**



alternative simulation was conducted with model B in which the constant concentration boundary was replaced by a constant-flux boundary that more than doubled the flux of saturated brine into the lower aquifer. The resulting mass of chloride in the simulated brine pool was only 65% greater than that obtained with the constant-concentration boundary with model B, because the simulated capacity for brine storage in the aquifer system is limited.

Model sensitivity to these factors indicates that the simulated concentration distributions presented above are not unique and that a detailed representation of the brine pool is not possible with the present models. Moreover, the distribution of glacial sediments specified in the models is highly generalized and the actual permeability

distribution is certainly more heterogeneous than represented. This heterogeneity would likely cause instabilities in the density distribution, which would create a more complex pattern of flow than obtained by model simulation. However, the processes responsible for formation of the brine pools under the two scenarios considered (flushing and dilution of brine in model A and steady accumulation of brine in model B) are unaffected by changes in parameter values or the grid spacing. Therefore, while a brine pool with bulk characteristics similar to those observed could be produced by either model A or model B, only the age distributions simulated with model A are consistent with brine age estimated by geochemical modeling. This conclusion was supported by all of the sensitivity results for either model A or B.

## Conclusions

The Na–Cl dominated brine in glacial sediments at the northern end of the Onondaga Trough was probably derived from halite beds in the Silurian Salina Group. The halite brine differs markedly from that of saline bedrock waters adjacent to the trough in that: (1) the Cl:Br ratio of brine is much larger, (2) the  $\delta D$  and  $\delta^{18}O$  values are more enriched, and (3) the  $\delta^{11}B$  values are lower than those of the saline bedrock waters, respectively. Geochemical modeling with NETPATH indicates that the brine could have formed from a mixture of fresh water (83%) and saline bedrock water (17%), which reacted with halite and gypsum and resulted in cation exchange of  $Ca^{2+}$  for  $Na^+$ . The estimated radiocarbon age of this mixture (16,700 years) suggests that the fresh water was derived from glacial melt water rather than recent meteoric recharge. The estimated brine age is consistent with the timing of deglaciation in the Onondaga Trough and deposition of glacial sediments (16,500–14,300 years B.P.).

The formation of the brine pool within glacial sediments 10 km north of the halite subcrop area can be explained by two hypotheses. Under the first hypothesis, the brine pool was derived from a relict source of salt that was dissolved by glacial melt water and then migrated through glacial sediments to its current position, where it is slowly being depleted. Under the second hypothesis, the brine pool has been sustained indefinitely by upward flow or dispersion from a separate brine pool in bedrock that was originally derived from subglacial recharge. There is no information on the quality of bedrock water directly beneath the Onondaga Trough to either support or refute the second hypothesis. Both hypotheses were tested using two-dimensional, cross-sectional variable-density flow models to determine whether the simulated chloride concentration and age distributions were consistent with the observed data.

Variable-density flow simulations support the first hypothesis that the halite brine was derived from dissolution of halite by melt water in the glacial sediments. The simulations indicate that there has been sufficient time for the brine pool to migrate from the halite subcrop area to the northern end of the Onondaga Trough, and that the brine pool could have persisted for over 16,000 years. The simulated age throughout the brine pool was about 17,000 years, which is consistent with the estimated age from NETPATH modeling (16,700 years). The simulated concentration and velocity distributions indicate that brine is slowly depleted through a mixing zone formed by upward flow of fresh water over the southern end of the brine pool.

Variable-density flow simulations suggest that a brine pool similar to that observed could also have formed by steady accumulation of brine through upward flow from a source in the bedrock that underlies the Onondaga Trough. The simulated age distribution in the brine pool resulting from this simulation is much younger than the estimated radiocarbon age, however, suggesting that this second hypothesis is not correct. The different age distributions

computed by the two models result from differences in the simulated velocity distributions. Under the first hypothesis, younger water is deflected upward and over the brine pool and discharges primarily to Onondaga Creek, while under the second hypothesis, the younger water penetrates further northward into the brine pool and a larger portion of the flow discharges to Onondaga Lake.

The simulations, consistent with the first hypothesis, suggest that the brine pool is a finite resource that could be largely depleted within 1,000 years at the current rate of saline discharge to Onondaga Creek, which has probably been accelerated within the past 150 years by leakage through abandoned well casings. This conclusion is also supported by the observation of declining salt saturations following removal of brine through pumping in the nineteenth century (Kappel 2000). Salt saturations in the lower aquifer have never recovered to their original levels in the nearly 100 years since the production of brine was halted as would be expected, according to the second hypothesis, if the brine pool was sustained by a continuing source in the bedrock beneath the Onondaga Trough.

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