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SEASONAL GEOCHEMISTRY OF TWO TUFA-DEPOSITING SPRINGS IN SOUTHWESTERN WISCONSIN

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ABSTRACT

Two small springs in southwestern Wisconsin, which emerge from Middle Ordovician dolomite, form water falls flowing over massive tufa mounds. Both springs were sampled in summer and winter at the spring outlet and at the base of the falls. Both springs contain hard water of a calcium-magnesium-bicarbonate type which is supersaturated with carbon dioxide in comparison to the atmosphere. Seasonal comparison of the water quality at the spring outlets shows a summer decrease in pH, saturation with respect to calcite and dolomite, and bicarbonate concentration; and a summer increase in temperature and pCO_2. These effects are due to carbonic-acid recharge available during the growing season. As the spring water emerges and travels over the algae- and ice-covered tufa mound or both and downward, carbon dioxide is rapidly lost to the atmosphere. This causes a dramatic increase in carbonate mineral saturation and pH. Calcite or aragonite is precipitated and results in a subsequent loss of dissolved calcium, bicarbonate, total hardness, and conductivity. Contrary to other studies, for these springs the greatest loss of calcium carbonate occurs in the winter. The top-to-bottom increase in carbonate mineral saturation in the summer indicates that deposition is inhibited during that season, perhaps because of the effects of magnesium ions retarding calcite precipitation at higher temperatures. Evaporation does not play a significant role in tufa deposition at this locality.

INTRODUCTION

Many previous studies have indicated that tufa deposition of non-thermal springs, as well as speleothem deposition in caves, occurs mainly during periods of comparatively warm weather such as summer or interglacial periods. Enhanced tufa deposition during warm weather is thought to be due to greater evaporation, plant growth, and higher concentrations of carbonate minerals during low flow conditions (Pitty, 1971; Moore, 1962).

Springs which deposit tufa are not abundant in Wisconsin. Two such springs, however, are locally well known. Both of these emerge from Middle Ordovician dolomite where thin shales locally concentrate ground-water flow. This study examines the seasonal variation in the carbonate geochemistry of these two springs and how it pertains to tufa deposition. Unlike previous studies, both of these springs were found to have enhanced tufa deposition in winter.

SPRING DESCRIPTION

The spring locally known as Platteville tufa falls is located 7 kilometers southwest of the town of Platteville, Wisconsin (NE1/4NW1/4 sec. 5.

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T. 2 N., R. 1 W., Dickeyville quadrangle). The water issues from a sand-choked opening in the base of the Middle Ordovician Guttenberg Dolomite on the steep south bank of Blockhouse Creek, and flows over a massive mound of tufa which overhangs the creek. The total vertical drop of the water is approximately 15 m. Potosi tufa falls is located 14 km northwest of the town of Potosi, Wisconsin, 300 m. south of the bridge over the Grant River formed by Camel Ridge Road (NW1/4NE1/4 sec. 17 T. 3 N. R. 4 W., Balltown quadrangle). In this location the water emerges from the base of the Pecatonica Dolomite, at a vertical cliff formed by the erosion of the Grant River through the St. Peter Sandstone. A large mound of tufa overhangs the river here as well, with the total vertical drop from the spring to the river approximately 20 meters. In this location the river bottom is littered with large irregular blocks of tufa which have fallen off the mound in the past.

Both springs have a relatively uniform year-round flow of approximately 40 and 60 liters per minute, respectively. The water of both springs are clear and sediment-free. Both Tufa mounds support the abundant growth of filamentous algae, mosses, and grasses. Ice buildup on the tufa mounds is considerable in the winter.

Tufa accumulation is most rapid at the top of the tufa mound where a thin water layer passes over the tufa barrier before falling to the river below. The fall of the mineral-laden spring water causes aeration and turbulence which results in the loss of carbon dioxide, evaporation, and plant growth. All of these promote carbonate mineral precipitation on the tufa mound.

METHODS

Water samples were taken at both springs as close to their respective outlets as possible, and also at the base of the falls. The springs were sampled in June 1981 (air temperature approximately 20 °C) and again in February 1982 (air temperature approximately 5 °C). Conductivity, temperature, and pH were measured in the field. Bicarbonate concentration was measured (standard HCl titration) on the chilled unfiltered samples within several hours of collection. The samples were then acidified with nitric acid, and the remainder analyses were performed in the laboratory several days later. Computer analysis of the data (from a program designed by Jacobson, 1973, and modified by E. Werner) was used to calculate the theoretical electrical conductivity at 25 °C, the saturation indices for calcite and dolomite, the theoretical aqueous partial pressure of carbon dioxide, the calcium to magnesium equivalence ratio, and the ion charge-balance error. The results are shown in table 1.

DISCUSSION OF CHEMICAL DATA

The geochemistry of both the Platteville and Potosi springs shows very hard water of a calcium-magnesium-bicarbonate type, as would be expected from a dolomite aquifer. The calcium-to-magnesium equivalence ratio is also typical of dolomite dissolution. The water is very close to saturation with carbonate minerals as it emerges, and exceeds the carbon dioxide partial pressure in equilibrium with the atmosphere (log $pCO_2 = -3.5$).

Table 1. Results of chemical analyses for seasonal comparison of top (spring outlet) and bottom (base of falls) of Potosi and Platteville tufa falls springs. Symbols and units used: SPC- conductivity in mhos/cm at 25 °C (calculated); TH- total hardness in mg/l $CaCO_3$; pCO_2- base 10 logarithm of the theoretical aqueous carbon dioxide partial pressure; SIc- log saturation index for calcite; SId- log saturation index for dolomite; Ca/Mg- calcium to magnesium equivalence ratio; all other parameters in mg/l except for pH and T° C. ERR- analysis charge-balance error (percent).

	Summer Potosi 6-16-81		Winter Potosi 2-27-82		Summer Platteville 6-7-81		Winter Platteville 2-27-82		
	top	bottom	top	bottom	top	bottom	top	bottom	Analytical error
pH	7.20	7.95	7.30	8.00	7.20	7.90	7.30	7.90	0.05
T°C	10.0	12.5	9.0	7.0	9.0	9.8	8.0	5.0	.2
SPC	771	708	747	679	749	750	770	755	--
HCO^-_3	437	418	439	396	435	431	450	439	5
TH	364	348	364	327	364	366	373	369	20
Ca^{+2}	88.3	80.8	80.8	67.3	80.6	82.1	87.9	79.1	4
Mg^{+2}	34.8	35.4	39.4	38.6	39.4	39.2	37.2	41.5	2
Cl^-	5.6	4.9	5.9	5.9	3.9	4.2	4.5	5.2	.5
SO_4^{-2}	14	14	10	10	35	31	31	30	2
Fe_{TOT}	0.005	0.005	0.009	0.009	0.006	0.012	0.009	0.060	0.02
Na^+	5	5	5	5	5	5	5	5	
Ca/Mg	1.54	1.38	1.24	1.06	1.24	1.27	1.43	1.16	--
SIc	0.09	0.83	0.14	0.70	0.04	0.75	0.17	0.67	0.05
SId	-0.05	0.72	0.04	0.61	-0.07	0.65	0.03	0.56	0.05
PCO_2	-1.65	-2.41	-1.75	-2.50	-1.66	-2.36	-1.75	-2.37	0.05
ERR	5.4	2.8	3.5	4.2	3.6	2.9	3.8	3.3	--

Seasonal comparison of the chemical quality of the water at the outlet of both springs shows a summer decrease in pH, decrease in saturation with respect to calcite and dolomite, decrease in bicarbonate concentration, and an increase in temperature and theoretical aqueous carbon dioxide partial pressure. During the summer growing season, the carbon dioxide partial pressure in the soil zone should be greater because of the higher temperature, rate of organic matter decay, and plant root respiration. Percolation of water through this zone would tend to increase the carbon dioxide partial pressure of the shallow ground water during the summer. This results in a pH decrease because of the formation of carbonic acid, which then partially dissociates to bicarbonate. The summer recharge of carbonic-acid rich ground waters causes a decrease in the degree of carbonate saturation because greater bicarbonate and hardness values are needed in the ground water to achieve saturation at the lowered pH levels. The summer decrease in bicarbonate concentration in the springs is harder to explain, as a summer increase should be expected due to the dissociation of carbonic-acid recharge. The slight summer decrease may be a result of the lower bicarbonate solubility in warmer water.

Comparison of water quality between the spring outlet at the top and the bottom of the falls shows that as the water travels out of the opening, over the tufa mound and downward, its conductivity, total hardness, calcium and bicarbonate concentrations, and theoretical aqueous carbon dioxide partial pressure all decrease, especially for the Potosi spring in the winter. The pH and saturation indices for calcite and dolomite both increase dramatically. The increase in carbonate mineral saturation between the top and the bottom of the falls is especially noticeable in the summer for both springs. As would be expected the temperature of the spring water increases in summer and decreases in the winter as the water reacts with ambient atmospheric temperatures, or flows over the winter ice accumulation.

As water travels over the tufa mound it approaches equilibrium with the atmospheric partial pressure of carbon dioxide, which is much lower than the carbon dioxide content of the spring water. This rapid degassing causes a sudden rise in pH and subsequent precipitation of calcium carbonate, which removes calcium and bicarbonate ions from solution, thereby decreasing the total hardness and electrical conductivity. If calcite precipitation were rapid enough to keep pace with degassing, the spring water would reach the bottom of the falls at equilibrium with carbonate minerals. However, the water actually arrives at the base of the falls in a supersaturated state, indicating that the rate of carbon dioxide degassing is much faster than the rate of tufa deposition. Similar results have been found by Dunkerley (1981) and Barnes (1965) for tufa-depositing springs in Queensland, Australia, and Brich Creek, California, respectively.

The chemical results shown in Table 1 also indicate that tufa deposition is occurring by a precipitation of calcite or aragonite only. The small gains or losses in dissolved magnesium shown are within experimental error and are not significant. The loss of calcium and preservation of dissolved magnesium from the top to the bottom of the falls causes the calcium-to-magnesium equivalence ratio to approach unity at the bottom.

The most interesting problem with both the Potosi and Platteville tufa falls springs is that most of the calcite deposition occurs in the winter rather than in the summer, as would be expected. Table 2 indicates direct

Table 2. Top-to-bottom gain (+) or loss (-) in selected aqueous geochemical species. Symbols and units are the same as for table 1.

	Summer Potosi 6-16-81	Winter Potosi 2-27-82	Summer Platteville 6-7-81	Winter Platteville 2-27-82
pH	+0.75	+0.70	+0.70	+0.60
T° C	+2.5	-2.0	+0.8	-3.0
SPC	-63	-68	+1	-15
HCO^-_3	-14	-43	-4	-11
TH	-16	-37	+2	-4
Ca^{+2}	-7.5	-13.5	+1.5	-8.8
Mg^{+2}	+0.6	-0.8	-0.2	+4.3
Ca/Mg	-0.16	-0.18	+0.03	-0.27
SIc	+0.74	+0.56	+0.71	+0.50
SId	+0.77	+0.57	+0.72	+0.53
PCO_2	-0.76	-0.75	-0.70	-0.62

gains and losses of relevant dissolved species between the top and bottom of the falls. The greatest loss in dissolved calcium and bicarbonate occurs in the winter. The slight gain in calcium for Platteville tufa falls in the summer is insignificant. The greatest gain in carbonate mineral saturation from top to bottom occurs in the summer because less calcite is deposited during that season.

Previous research has indicated that tufa deposition from non-thermal springs occurs mainly in the summer due to greater evaporation and plant growth during the warm season (Pitty, 1971). In addition, Moore (1962) indicates that stalactite growth in caves is greater in the warm season and in warm climates because ground water contains more carbon dioxide from organic matter decay and plant root respiration in the soil zone. This lowers its pH and allows it to dissolve more carbonate minerals from the bedrock. When this slowly percolating ground water eventually reaches saturation and subsequently migrates to an air-filled cave passage, carbon dioxide is rapidly lost and stalactite growth results. However, stalactite growth will not occur if percolation is so rapid that the water cannot reach saturation. In the winter, on the other hand, the ground water has less ability to dissolve (and hence precipitate) minerals because less carbon dioxide is available. Platteville tufa falls shows higher concentrations of carbonate minerals in the summer, as predicted by this model, as do other springs in the area (Heller, manuscript in preparation). However, deposition of calcite occurs as a function of calcite saturation rather than total concentration. As noted previously, both tufa falls springs are more saturated with carbonate minerals, and hence more likely to deposit tufa, in the winter.

Moore's model has been challenged by Atkinson (1981), who has studied stalactite growth in Castleguard Cave, British Columbia, which is located beneath the Columbia Icefield. Atkinson maintains that the abundant speleothems in this alpine cavern are a result of supersaturation of ground water caused by complex mineral dissolution of dolomite and sulfates rather than loss of carbon dioxide. If this is true then the speleothem deposition in Castleguard Cave is not strictly climatically controlled.

Herlinger (1977) notes that tufa deposition along Fall Creek, Idaho, occurs as spherical granules attached to algal filaments in the summer, and denser, non-granular zones deposited in the winter when darkness and cold preclude or inhibit algal activity. Examination of eroded, inactive tufa mounds reveals cycles of porous, granular layers alternating with denser, non-granular zones.

In contrast to the studies above, Hennig, and others (1982) plotted age data for 660 speleothems and 140 spring-deposited travertines. The plots clearly show periods of increased speleothem/travertine growth between approximately 130,000 and 90,000 years ago and since about 15,000 years ago, periods which correspond to warm, humid interglacial climatic phases.

CONCLUSION

The results of this study and the research cited above show that climatic controls of tufa (or stalactite) deposition are far from simple. For whatever reason, calcite tufa deposition at Platteville and Potosi tufa falls occurs mainly in the winter. The top-to-bottom increase in carbonate mineral saturation in the summer indicates that deposition is inhibited during that season, perhaps because of the effects of magnesium ions retarding calcite precipitation at higher temperatures. Evaporation of the water is not thought to play a significant role in the tufa deposition for two reasons: 1) tufa deposition occurs mainly in the winter while evaporation is strongest in the summer, and 2) in order to cause calcite supersaturation to occur by evaporation, an increase or at least maintenance of solute concentrations should be expected from top to bottom of the falls. This does not occur.

The conclusions of this study are based on a total of eight water samples, so the results should be considered preliminary. Unfortunately, because of the exposed locations of the springs, obtaining water samples from them at all is physically challenging, particularly in winter.

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