

## Geochemical Controls on a Calcite Precipitating Spring

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*Abstract.* A small spring fed stream was found to precipitate calcite by mainly inorganic processes and in a nonuniform manner. The spring water originated by rainwater falling in a 0.8 km<sup>2</sup> basin, infiltrating, and dissolving calcite and dolomite followed by dissolution of gypsum or anhydrite. The Ca<sup>2+</sup>/Mg<sup>2+</sup> indicates that calcite is probably precipitated in the subsurface from a supersaturated solution. This water emerges from the spring still about 5 times supersaturated with respect to calcite and continues calcite precipitation. When 10 times supersaturation is reached, due to CO<sub>2</sub> degassing the precipitation is more rapid. The calcite accumulation from the stream with a flow of 5 l/s is calculated to be 12600 kg/yr with the highest rates in areas where CO<sub>2</sub> degassing is the greatest. The non-equilibrium, as shown by the high calcite supersaturation, is also reflected in a variable partitioning pattern for Sr<sup>2+</sup> between the water and calcite.

### Introduction

The study was initiated to examine in detail the formation of calcite in a small stream. Relatively large amounts of calcite appeared to be precipitating; and the precipitation also appeared to be taking place in the absence of organisms, which would allow the problem to be examined by studying inorganic geochemical processes. Careful, detailed chemical measurements were made on the stream in order to determine the saturation of the water with respect to calcite as it emerged from the spring, and how the water chemistry changed as it flowed as a stream. These measurements made it possible to determine where and why the precipitation took place.

### Description of the Study Area

The study area is located approximately 1 km southwest of the village of Westertshof, which is 30 km north of Göttingen in east-central West Germany. A calcite precipitating spring is located in the Triassic Upper Muschelkalk formation which is predominantly limestone. This is underlain by Middle Muschelkalk which is dolomite with gypsum lenses. The spring lies approximately 250 m from a fault striking E–W, and 100 m from one striking N–S (Geol. Map 'Northeim' 1:25000).

The water exiting at the spring appears to circulate through both Upper and Middle Muschelkalk. The discharge measured below Station 9 (Fig. 1) averaged between 5 and 6 liters/second (l/s) varying only slightly throughout the year, depending on the rainfall. At the end of August, 1973, which had less than 10 mm of rain for the month, the flow was 5.0 l/s. However, at the end of February and August, 1974, which had respectively 38 and 43 mm of rain per month, the discharge was 5.9 and 6.0 l/s. During the year of the study, approximately

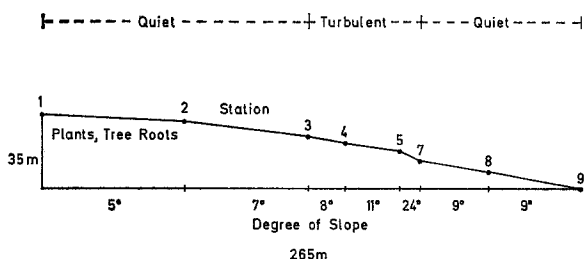


Fig. 1. Profile of the calcite precipitating stream near Westerhof

500 mm of precipitation as rain and snow fell. Assuming approximately 40% infiltration as an average for carbonate terrain (Parizek, White, and Langmuir, 1971, and Jacobson and Langmuir, 1974)  $1.63 \times 10^8$  l/yr of water could be discharged from the observed surface drainage area of 0.81 km<sup>2</sup>. This compares well to  $1.58 \times 10^8$  l/yr of water actually leaving the area based on an average flow of 5 l/s. Both numbers are subject to uncertainties, but the fact remains that the small basin immediately above the spring could supply the observed discharge.

The stream formed from the spring water initially has slower flowing water and flows through branches and partial grass and weed-choked stream bed to Station 2 (Fig. 1). From this point to the end, the only material to contact the water other than precipitated calcite is a few small patches of moss (*Cratoneurum cummutatum* and *Brachythecium rivulare*) and liverworts (*Conocephalum conium* and *Pellia fabbroniana*). These plants had little or no effect on the water chemistry changes (Freitag, personal communication). Inorganic processes are therefore controlling the calcite precipitation.

### Analytical Procedures

Because of the nature of the water being studied, most measurements were conducted in the field to minimize changes. Temperature was measured with a mercury thermometer divided in 0.2°C intervals with uncertainty  $\pm 0.1^\circ\text{C}$ . Specific electrical conductivity (SpC) was measured in the field to give a rapid but accurate check of the dissolved species. This measurement exactly reflects the precipitation pattern. It was carried out with a "Wissenschaftlich-Technische Werkstätten" (LF 56) meter and electrode, and the values were corrected to 25°C using a correction curve based on a 1:1  $\text{Ca}(\text{HCO}_3)_2$ : $\text{CaSO}_4$  solution. The uncertainty for SpC is approximately 1%. The pH was measured using a Portamess Knick 902 meter and electrode. The electrode was calibrated using the 4.01 and 6.86 pH buffers, and the calibration was checked before and after each measurement. The pH uncertainty is  $\pm 0.03$ . The concentration of  $\text{HCO}_3^-$  was titrated in the field using 0.01 N HCl and a pH electrode. The end point was determined as the maximum pH change per unit of added HCl with an uncertainty of 2%. Both  $\text{Ca}^{2+}$  and the sum of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  were titrated in the field with 0.01 N EDTA, with an uncertainty of 2%. Murexide and Eriochrome Black T were respectively the two indicators used. The concentrations of both  $\text{Na}^+$  and  $\text{K}^+$  were determined by standard atomic absorption techniques with an uncertainty of 2%. A turbidometric technique was used to determine  $\text{SO}_4^{2-}$  (Taras *et al.*, 1971). This technique had an uncertainty of approximately 5%.

### Results

The spring was studied in detail at 2 times during the year, when normally the maximum variation in the chemical species occurs (Jacobson and Langmuir, 1974,

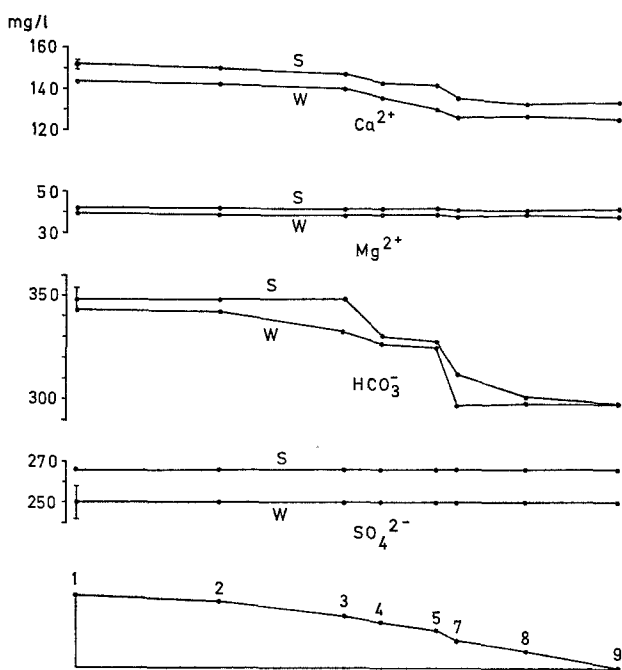


Fig. 2. Variations of chemical species along the profiles of the Westerhof stream. S: August 1974, W: February 1974. All concentrations are in mg/l. Vertical lines indicate analytical uncertainties

and Shuster and White, 1971). One sampling was undertaken in August when maximum temperature and plant growth occur, but when spring discharge is normally a minimum. February was chosen when just the opposite conditions exist. Fig. 1 presents a general profile of the stream as it flows down the hillside from the spring. The actual source of the spring is 75 m up the slope from Station 1. At this point the spring emerges, but sinks almost immediately into coarse gravel to reappear at Station 1; therefore the profile originates at Station 1. The quiet and turbulent zones of water flow are only a visual estimate, but are also related to the degree of slope, so therefore are representative.

In Fig. 2 only  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  show any variation with distance, which is reasonable because only calcite is observed to precipitate. The other species,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cl}^-$  were constant, indicating there was no significant evaporation or additional inputs of different water. The difference in water chemistry between summer and winter is small, but as expected the winter flow shows lower concentrations due to dilution caused by larger amounts of water in the system.

The temperature (Fig. 3) dropped in winter and rose in summer as expected. It was supposed that the precipitation would be more dramatic in summer, but this was not supported by the data as indicated by the approximately parallel summer and winter curves for  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  (Fig. 2) and for SpC (Fig. 3). The pH continued to increase to Station 3 from which point it was more or less constant. This constant pH indicated that precipitation and  $\text{CO}_2$  degassing were approximately equal, with the first producing  $\text{CO}_2$  and the second releasing it from the water.

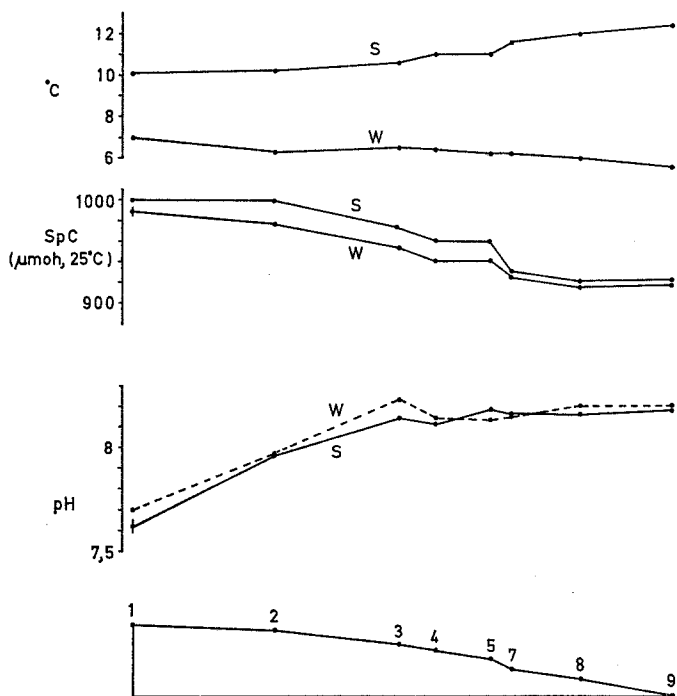


Fig. 3. Variations of temperature, SpC, and pH along the profile of Westerhof stream. S: August 1974, W: February 1974. SpC is corrected to 25°C. Vertical bars indicate analytical uncertainties

The spring chemistry during a 24-hour period was found to be constant. The stream chemistry, however, measured at Station 9 showed some variation over the same period (Fig. 4). Less precipitation occurred at night perhaps due to several factors including lower temperature at night and absence of sunlight which effects plant photosynthesis. The intergrowth of grass, weeds and tree roots (Fig. 1), which was not examined thoroughly, is the most probable cause of the day-night cycle. This did not cause significant  $\text{CaCO}_3$  precipitation between Stations 1 and 3 (Fig. 2), but did change the  $\text{CO}_2$  production and consumption. This is similar to the situation in which the spring water  $\text{CO}_2$  changes. Since the stream behaved in a similar manner during winter and summer, the temperature effect is minimal, and plant photosynthesis and respiration from Station 1-3 is the major influence in causing greater calcite precipitation in the lower part of the stream during the day. During the day the plants take up  $\text{CO}_2$ , increasing supersaturation and precipitation of calcite; and at night  $\text{CO}_2$  is given off causing decreased supersaturation (Fig. 4). Because the plants in and near the stream are kept from freezing by the running water, photosynthesis and respiration take place in both winter and summer.

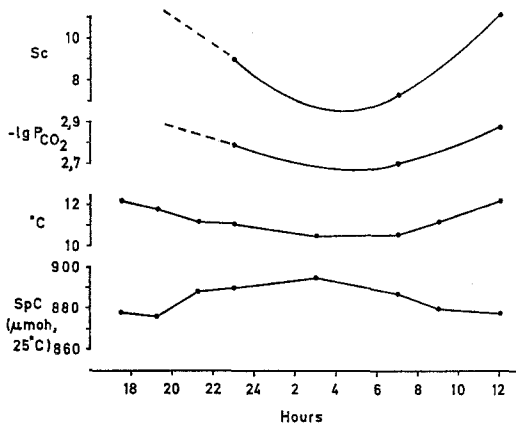


Fig. 4. Water chemistry variations at Station 9 for 19 hrs, August 1974. The locations of  $S_c$  and  $P_{CO_2}$  minimums are estimates from temperature and SpC.  $S_c$ : see expression (6)

**Discussion**

Starting with pH,  $mHCO_3^-$ , total ionic strength and temperature, it is possible to calculate a theoretical  $CO_2$  pressure ( $P_{CO_2}$ ), which would be in equilibrium with the spring water, by using expression 1:

$$P_{CO_2} = \frac{aH^+ \cdot aHCO_3^-}{k_0 \cdot k_1} \tag{1}$$

$a$  is activity of species indicated,  $k_0, k_1$ : see expressions 3 and 4.

This calculation is useful in observing the rate of  $CO_2$  degassing and the distance (proportional to time) required to reach an atmospheric value of  $10^{-3.5}$  atm (Fig. 5).

A computer program (Jacobson and Langmuir, 1972) was written to aid in the calculations of  $P_{CO_2}$ , activities of species, saturation with respect to minerals, and the amount of each species ion paired. The water from the Westerhof spring exhibited a marked  $CO_2$  decrease to Station 3, and then remained more or less constant to Station 9. The data for  $P_{CO_2}$  from the spring to Station 3 lie, with some scatter, on a straight line on a  $\log P_{CO_2}$ -distance ( $s$ ) plot. This means that degassing can be described as

$$-\frac{dP_{CO_2}}{ds} = kP_{CO_2}; \quad k = 8.5 \cdot 10^{-3} \text{ m}^{-1} \quad (\text{m: meters}).$$

This is identical with a first order reaction and shows that the dissolved  $CO_2$  has a constant probability of degassing between the spring and Station 3. Therefore degassing is the only factor in depletion of  $CO_2$  in the water, and is in agreement with the increase in supersaturation ( $S_c$ , Fig. 5). First order laws have been reported to describe formally the hydration of  $CO_2$  and dehydration of  $H_2CO_3$  (Kern, 1960). The constants cannot be compared because the flow rate is not uniform along the stream and cannot be measured accurately. The amount of calcite precipitated before Station 3 is relatively small, and it may be assumed that no precipitation occurs. Expressions 2-5 and Table 1 are utilized to explain the events.

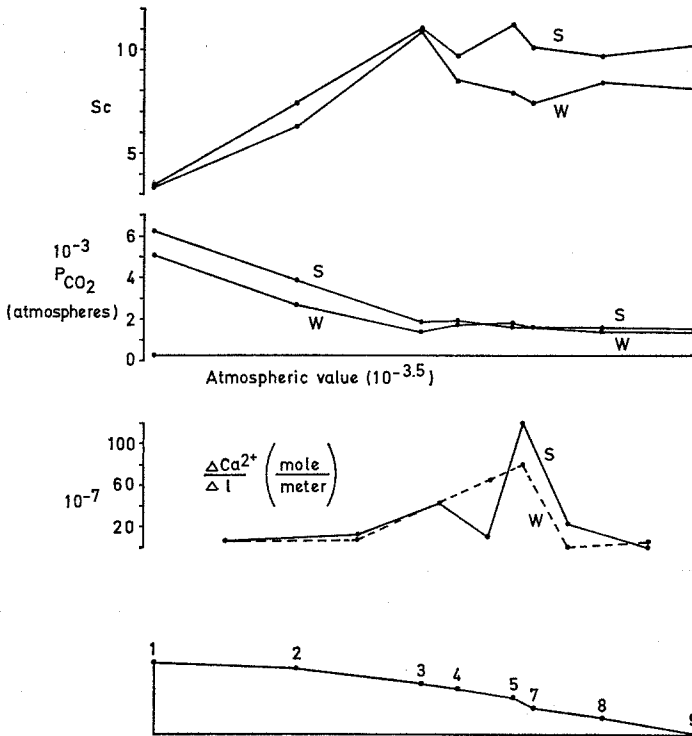


Fig. 5. Variation of calculated variables along the profile of Westerhof stream, S: August 1974, W: February 1974



$$k_0 = \frac{a_{\text{H}_2\text{CO}_3}}{P_{\text{CO}_2} \cdot a_{\text{H}_2\text{O}}}; \quad a_{\text{H}_2\text{O}} = 1, \quad (3)$$

$$k_1 = \frac{a_{\text{H}^+} \cdot a_{\text{HCO}_3^-}}{a_{\text{H}_2\text{CO}_3}}, \quad (4)$$

$$k_2 = \frac{a_{\text{H}^+} \cdot a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}}. \quad (5)$$

The spring water has a higher  $\text{CO}_2$  pressure than the atmosphere and therefore  $\text{CO}_2$  is lost from the water, decreasing  $\text{CO}_2$  at the left of expression (2). Expression (3) indicates that  $\text{H}_2\text{CO}_3$  is also reduced. The  $a_{\text{H}^+}$  is observed to be lowered, causing equal consumption of  $\text{H}^+$  and  $\text{HCO}_3^-$ . The pH change can be measured easily, but  $m_{\text{HCO}_3^-}$  is several orders of magnitude less sensitive, and appears constant. If  $a_{\text{H}^+}$  decreases while  $a_{\text{HCO}_3^-}$  remains virtually constant, then through expression (5)  $a_{\text{CO}_3^{2-}}$  must increase (Table 1). The increase in  $\text{CO}_3^{2-}$  while  $a_{\text{Ca}^{2+}}$  is more or less constant means that the ion activity product (IAP) for calcite increases and thereby the water becomes more supersaturated with respect to calcite (Fig. 5 and expression 6).

$$S_c = \frac{\text{IAP}}{k_c} = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}}{a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}} \quad \frac{(\text{in water sample})}{(\text{at equilibrium})} \quad (6)$$

Table 1. Change in chemical species between Stations 0 to 3 and 3 to 9 in August 1974

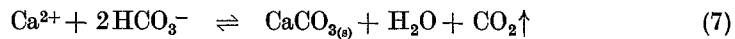
-lg (m/l)	Station			
	0	3	$\Delta$	$\Delta\%$
Ca <sup>2+</sup>	2.421	2.436	3.890	- 3.4
H <sup>+</sup>	7.38	8.14	7.463	-82.6
HCO <sub>3</sub> <sup>-</sup>	2.244	2.244	—	—
CO <sub>3</sub> <sup>2-</sup>	5.188	4.420	4.501	+486.4
H <sub>2</sub> CO <sub>3</sub>	3.216	3.982	3.298	-82.8
P <sub>CO<sub>2</sub></sub>	1.949	2.704	2.033	-82.4

-lg (m/l)	Station			
	3	9	$\Delta$	$\Delta\%$
Ca <sup>2+</sup>	2.436	2.476	3.492	- 8.8
H <sup>+</sup>	8.14	8.18	9.196	- 8.8
HCO <sub>3</sub> <sup>-</sup>	2.244	2.313	3.077	-14.7
CO <sub>3</sub> <sup>2-</sup>	4.420	4.490	5.247	-14.9
H <sub>2</sub> CO <sub>3</sub>	3.982	4.106	4.587	-24.8
P <sub>CO<sub>2</sub></sub>	2.704	2.802	3.399	-20.2

(m/l) = moles/liter.

The supersaturation with respect to calcite steadily increases to Station 3 (Fig. 5), and then with small fluctuations either declines or remains constant. The data shows that precipitation in the presence of calcite begins at a supersaturation of less than 5 times, but is more rapid at values greater than 10 times supersaturated. The increase in saturation because of CO<sub>2</sub> degassing causes significant precipitation to begin below Station 3. The Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> combine to form CaCO<sub>3</sub> shifting the reaction at *k*<sub>2</sub> in expression (2) to the right. Utilizing Eqs. (3), (4), and (5) with a nearly constant pH, there is a decrease in *a*HCO<sub>3</sub><sup>-</sup> and H<sub>2</sub>CO<sub>3</sub> and a release of CO<sub>2</sub> to the atmosphere. Thus, the reaction at *k*<sub>2</sub> is exactly balanced by the reaction at *k*<sub>1</sub> (Table 1). The total reaction is best summarized by expression (7):



This reaction causes calcite to precipitate and produces an equivalent amount of CO<sub>2</sub>. The CO<sub>2</sub> escapes from the water at a rate similar to its production, and therefore the CO<sub>2</sub> remains constant (P<sub>CO<sub>2</sub></sub>, Fig. 5).

Expression (7) shows that ideally 1 mole of Ca<sup>2+</sup> should be consumed with 2 moles of HCO<sub>3</sub><sup>-</sup>, however in the summer of 1974 and winter of 1974 samples, 2.6 moles of HCO<sub>3</sub><sup>-</sup> and 1.6 moles of HCO<sub>3</sub><sup>-</sup> were reacted respectively for every mole of Ca<sup>2+</sup> from Station 3-9. This scatter about the ideal value of 2 is attributed to analytical error of small changes in large numbers. The overall change for the summer of 1974 was 1.9 moles of HCO<sub>3</sub><sup>-</sup> for every mole of Ca<sup>2+</sup> which is close to the expected value.

The change in  $\text{Ca}^{2+}$  concentration with distance ( $\Delta\text{Ca}^{2+}/\Delta l$ , Fig. 5), or amount of calcite precipitated, was found to be the greatest where the water was the most turbulent. Because  $\text{CO}_2$  is escaping most rapidly in the turbulent zone, this aids the formation of calcite [Expression (7)]. The amount precipitated per distance between Stations 5 and 7 was several times larger than the average. This precipitation pattern was also supported by placing natural sponges as used for household purposes in the stream between Stations 2–3 and 5–7 to observe rate of calcite accumulation. Nearly identical spherical natural sponges were utilized, with a diameter of 24 cm and a large surface area. Only 2 g of calcite were precipitated on a sponge between Stations 2 and 3 in 3 weeks, however, 300 g were precipitated on a sponge between Stations 5 and 7. The sponge between Stations 2 and 3 was in a small pool and the other sponge was placed in a small waterfall.

The difference in precipitation rates is also demonstrated by the variation of the distribution factor  $b$  for the trace element  $\text{Sr}^{2+}$ .

$$b = \frac{\text{ppm Sr}^{2+} \text{ in calcite}}{\text{ppm Sr}^{2+} \text{ in water}}$$

In addition to temperature, pressure and activity coefficient of the trace element, the factor  $b$  depends on the crystallization rate (Burton, Prim and Slichter, 1953). The Westerhof precipitation has an average  $b$  of 240, but ranges from 190 to 285 at a constant 2 ppm  $\text{Sr}^{2+}$  in the water. The temperature, pressure and activity of  $\text{Sr}^{2+}$  are constant or changing only slightly, and thus the amount of  $\text{Sr}^{2+}$  which enters the calcite structure is primarily controlled by precipitation rate. Laboratory data on partitioning of  $\text{Sr}^{2+}$  obtained under equilibrium conditions have to be applied with some caution to geochemical systems in which non-equilibrium situations prevail.

The rate of calcite precipitation that is neither in equilibrium with calcite or the  $\text{CO}_2$  in the atmosphere is approximately 12 600 kg/yr or 47 kg/yr/m of stream length. The rate of accumulation between Stations 5 and 7 based on the submerged sponge is 230 kg/yr/m of stream length. Using the figure of 12 600 kg of calcite/yr, assuming a density of 2 because it is tuffaceous, estimating the area of the deposit to be 50 000  $\text{m}^2$ , and taking an average thickness it is possible to calculate the probable age for the deposit. The average thickness is at present unknown but is believed to be from 1–10 m. A one meter thickness would give an age of 8 000 years, assuming a constant discharge and precipitation. Any age of much greater than 10 000 years is believed to be unrealistic because of glaciation in the area. The thickness tends toward uniformity because as the precipitate builds up in the stream bed it is elevated above the surrounding terrain, at which time the stream breaks out of its channel and begins a new one at a lower elevation.

The spring water begins precipitation of calcite immediately upon emerging from the ground and is supersaturated with respect to calcite at this point. Based on this observation and a chemical analysis of the spring water (Table 2), it is possible to reconstruct the history of the spring water. It is proposed that the infiltrating water first dissolved  $\text{CO}_2$  from the soil zone, followed by dissolution of calcite and dolomite. After significant amounts of calcite and dolomite were dissolved gypsum or anhydrite dissolution began, which increased the  $\text{Ca}^{2+}$



Table 2. Spring water chemistry in relation to possible dissolved minerals. Small concentrations of Na<sup>+</sup>, K<sup>+</sup>, and Cl<sup>-</sup> are not shown

	Ca <sup>2+</sup>	Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Total epm	7.59	3.46	5.70	5.54
From CaMg(CO <sub>3</sub> ) <sub>2</sub>	2.24	3.46	5.70	
From CaSO <sub>4</sub>	5.35			5.35
				$\Delta = 0.19$

$$\text{epm} = \frac{\text{ppm} \cdot \text{charge}}{\text{molecular weight}}$$

activity causing calcite to precipitate and an enrichment of Mg<sup>2+</sup> relative to Ca<sup>2+</sup>. The equivalents per million (epm) balance shown in Table 2 demonstrates clearly that excess Mg<sup>2+</sup> is present, as represented by 3.46 epm Mg<sup>2+</sup> versus 2.24 epm Ca<sup>2+</sup>. Dissolution of MgSO<sub>4</sub>·nH<sub>2</sub>O from salt deposits may be considered. This source has to be ruled out because in agreement with the petrology of marine evaporites any MgSO<sub>4</sub> precipitation is accompanied by chloride minerals, predominantly NaCl. Less than 10 ppm, of Cl<sup>-</sup>, Na<sup>+</sup>, or K<sup>+</sup> were ever measured in the spring water, and therefore the dissolving of any marine salt deposit is unlikely. CaSO<sub>4</sub> dissolution rather than that of MgSO<sub>4</sub> is also suggested by Savelli and Wedepohl (1969) based on Ca/Sr ratios and sulfur isotopes.

### Summary

A small calcite precipitating stream was studied to obtain information on the source of the water and dissolved species, and on the factors causing CaCO<sub>3</sub> precipitation. The study area is a small drainage basin with an area of 0.8 km<sup>2</sup> underlain by carbonates of the Upper and Middle Muschelkalk formations. The spring in the basin had a discharge between 5 and 6 l/s. Most measurements of water quality were made in the field to minimize changes. Determination of H<sup>+</sup> (pH), Ca<sup>2+</sup>, and HCO<sub>3</sub><sup>-</sup> are particularly critical in a calcite precipitating stream. These were the only chemical species exhibiting a decrease with distance of flow, which is consistent with calcite precipitation.

The calculated CO<sub>2</sub>-pressure also steadily decreased along the stream until calcite precipitation increased, at which point CO<sub>2</sub> stayed constant. The loss of CO<sub>2</sub> also caused the water to increase its supersaturation with respect to calcite from 5 to 10 times. The high supersaturation resulted in calcite precipitation and because CO<sub>2</sub> production accompanies the precipitation, the calcite accumulation was the greatest in the turbulent zone where CO<sub>2</sub> could degass most rapidly. The rapid calcite precipitation caused a non-equilibrium condition for Sr<sup>2+</sup> partitioning between water and the calcite.

Based on water chemistry changes it was calculated that 12600 kg/yr of calcite was precipitated. This precipitate originated from dissolution of calcite and dolomite followed by dissolving of anhydrite or gypsum.

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