

Hydrochemistry of springs from dolomite reefs in the southern Alps of northern Italy

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ABSTRACT Ca/Mg-ratios of water in the Italian 'Dolomites' (=type area) indicate congruent dissolution of dolomite. Surface water sampled at high altitude before infiltration into the dolomite has low Ca- and Mg-concentrations, and lower than atmospheric CO₂-pressures. Concentrations in springs around the reefs, and $\delta^{13}\text{C}$ -values in a number of the springs, are consistent with open system dissolution during flow through fissures from high altitude to spring level; the fissures must therefore be large enough for air circulation. A rapid dissolution of dolomite is suggested, which was confirmed by dissolution experiments with polished dolomite slabs immersed in water charged with air for a period of two months. The results indicate that only a few days would be needed to reach concentrations near saturation in the field. Some springs have lower $\delta^{13}\text{C}$ and show small concentration increases; these are considered to reflect an additional flow component draining vegetated soil in the area surrounding the reefs.

Introduction

The northern Italian Dolomites show a characteristically rugged landscape with mountain blocks made up of dolomitized reefs of Triassic age. The reefs are embedded in softer rocks of the same age (volcanics, marls and limestones) which were partly eroded to a Late Pleistocene level of 2100 m, and now rise 1000 m above this elevation. Engelen (1974) has given a detailed hydrogeological description of one reef and surrounding rocks. The present study aims to interpret the evolution of spring water composition for pure dolomite rock, using information on dissolution kinetics from laboratory experiments and carbon isotopes to determine reaction mechanisms.

Kinetic information can be used to obtain a residence time (or contact time) of water in dolomite. It is essential, however that the reaction mechanism is correctly stated in terms of an open versus closed system with respect to CO₂, and atmospheric versus additional biological CO₂. This can be achieved by calculating isotope balances based on mass-transfer and mass-balances (Deines *et al.*, 1974; Mook, 1976; Wigley *et al.*, 1978; Plummer *et al.*, 1983).

Busenberg & Plummer (1982) concluded from dissolution experiments with dolomite that equilibrium would take an 'extremely long time'. Mercado & Billings (1975) have calculated rate data for dolomite dissolution in the Florida aquifer, and mentioned equilibration times of 15,000 years. Such a very slow dissolution rate is at variance with our observations, in that intermittent springs, or snow melt trickling over the dolomite-surface, had Ca- and Mg-concentrations which approached equilibrium. The following account gives (1) the results

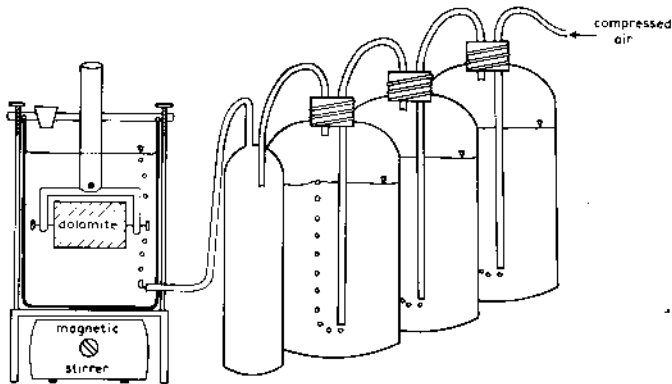


Fig. 1. Equipment used for kinetic experiments.

of new dissolution experiments, (2) a general scheme of carbon isotope evolution in a dolomite aquifer, and (3) an interpretation of spring water composition using kinetic and isotope data.

Kinetic experiments

In the present work, the dissolution rate of dolomite was measured in free drift experiments using the technique described by Roques & Ek (1973) (Fig. 1). Compressed air was led through three washing bottles and one empty bottle, and bubbled through a pyrex glass reaction-vessel containing 600 ml water and a 46 cm² slab of dolomite. The dolomite was cut with a diamond saw, polished, washed with 2N HCl and rinsed with water before insertion into the reaction vessel. The gas inlet was sideways to leave space for a magnetic stirring bar and the outlet was below water level to ensure a complete gas/water equilibrium. Temperature was kept at $22 \pm 2^\circ\text{C}$.

Electrical Conductivity (EC) was measured daily over a 1483 hour period, and eight 10-ml samples were taken at regular intervals for chemical analysis of cations. The reaction vessel was weighed before and at the end of the run. It was found that about 30 ml water was lost, either via the bubbling gas-stream, or through drops adhering to the conductivity cell when it was removed from the solution after measurement. The rate data given here, are corrected for changes in the surface/volume-ratio which result from these water losses, by recalculating increases in surface/volume towards the initial value. Eight samples from different locations in the reefs were processed, of which four were found to yield 'pure dolomite' Ca/Mg-ratios in solution, and the other half to yield higher Ca/Mg-ratios. Chemical analyses of the dolomite samples are given in Table 1.

EC-values are plotted against time in Fig. 2A for two samples. EC was also recalculated as solution composition using the linear relationship between EC and analysed Ca + Mg-concentrations:

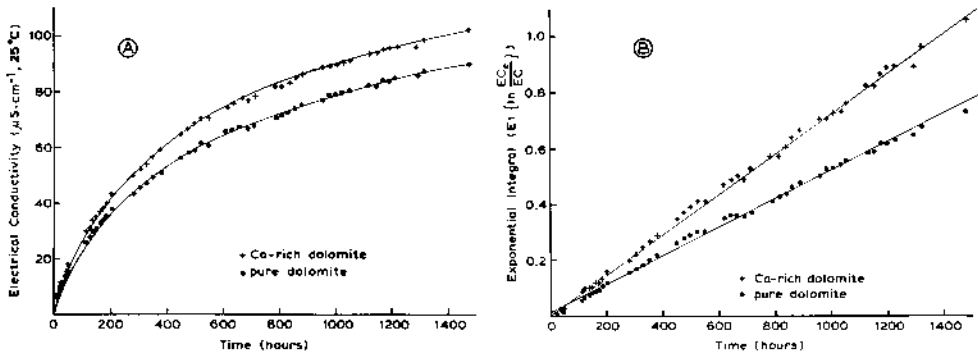


Fig. 2. Increase of Electrical Conductivity (EC) with time during dissolution of dolomite.

Table 1. Chemical composition of dolomite samples used in the dissolution experiments. Rate constant is defined in eq. 3 of text.

Sample	Dolomite-formula	Ca/Mg-ratio in solution	Rate- constant (k)
4B	Ca _{.503} Mg _{.497} Fe _{.000} CO ₃	1.03 ± .03	1.22E-10
A	Ca _{.515} Mg _{.483} Fe _{.001} CO ₃	1.07 ± .07	1.28E-10
8*	Ca _{.505} Mg _{.495} Fe _{.001} CO ₃	1.03 ± .02	1.18E-10
17	Ca _{.498} Mg _{.502} Fe _{.000} CO ₃	1.03 ± .03	1.07E-10
2B	Ca _{.537} Mg _{.460} Fe _{.002} CO ₃	1.30 ± .13	1.21E-10
2D	Ca _{.515} Mg _{.482} Fe _{.002} CO ₃	1.29 ± .08	1.44E-10
10A*	Ca _{.526} Mg _{.472} Fe _{.001} CO ₃	1.42 ± .15	1.63E-10
2C	Ca _{.549} Mg _{.449} Fe _{.002} CO ₃	1.28 ± .04	1.24E-10

* Dissolution shown in Fig. 2.

$$EC = 7.04 + 189.3 \cdot (Ca + Mg) \quad (R = 0.996; n = 60) \quad (1)$$

where Ca + Mg is given in mmoles/l, and EC in $\mu S/cm$. The solution composition was then calculated fully with PHREEQE (Parkhurst *et al.*, 1980), and compared with the rate equation given by Busenberg & Plummer (1982). It was found, however, that after only 300 hours of reaction time, the calculated rate became **negative**, although the solution was undersaturated, and in fact a positive reaction-rate could be measured in the reaction vessel.

An alternative rate-formulation was therefore derived, and a very good fit was obtained with the equation :

$$dc/dt = -k \cdot A/V \cdot \ln(IAP/K) \quad (2)$$

where dc/dt is the reaction rate in $mmole\ cm^{-3}s^{-1}$, k is the apparent rate constant in $mmole\ cm^{-2}s^{-1}$, A/V is the ratio of dolomite surface to solution

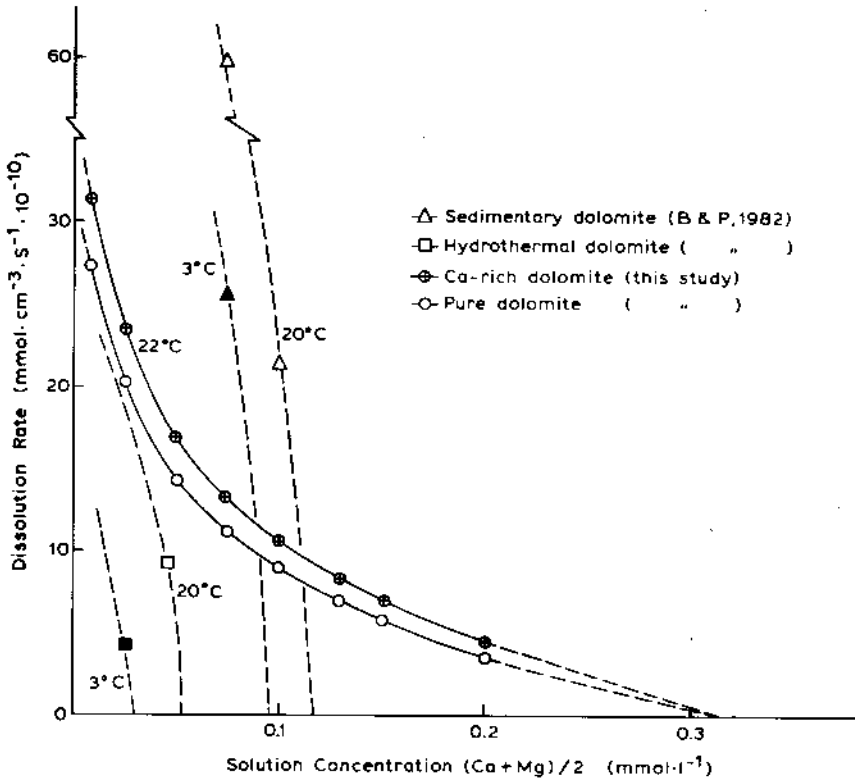


Fig. 3. Comparison of dissolution rates found in the present experiments with those given by Busenberg & Plummer (1982).

volume, and K and IAP are respectively the equilibrium constant and ion activity product for dolomite. This equation represents a thermodynamic formulation, since it relates rate of dissolution to free-energy differences of the solution with its value at equilibrium.

At a constant CO_2 -pressure, one may express IAP or K in terms of Ca -concentration if the difference between activity and molality is neglected (cf. Stumm & Morgan, 1970) :

$$IAP = 256 \cdot (Ca)^6 / P^2_{CO_2} \text{ and } K = 256 \cdot (Ca_e)^6 / P^2_{CO_2}$$

Substituting in eq. (2), and making the rate equal to the increase in Ca -concentration, gives:

$$d(Ca)/dt = -k \cdot A/V \cdot 6 \ln (Ca/Ca_e)$$

This equation can be integrated to give :

$$E_1 (\ln (Ca_e/Ca)) = \frac{k \cdot A/V \cdot 6}{Ca_e} \cdot t \tag{3}$$

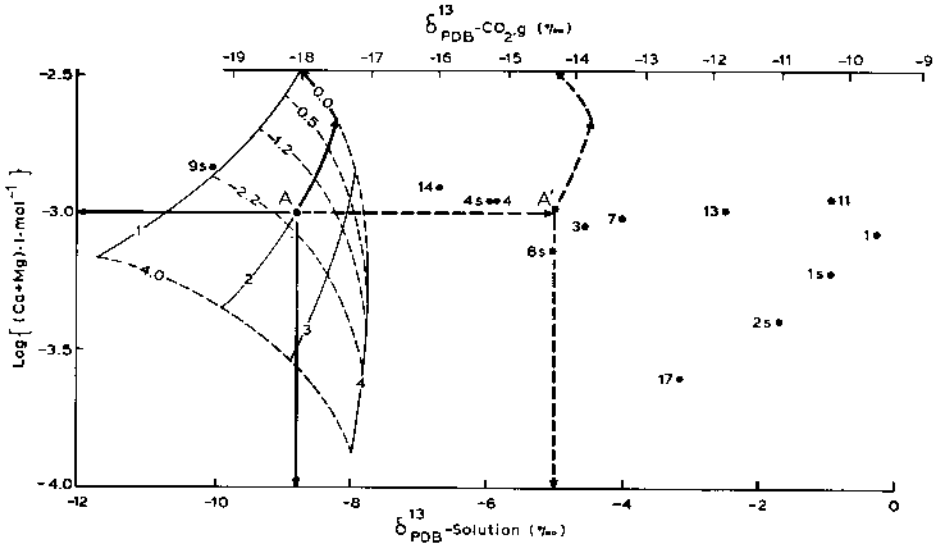


Fig. 4. The relationship between $\delta^{13}\text{Solution}$, $\delta^{13}\text{CO}_{2,g}$ and Ca + Mg in an *open system* dissolution of dolomite at 3°C. —0.0—saturation-index dolomite (= $\log(\text{IAP}/K_T)$); —1— reaction-path; i = initial, before dissolution of dolomite and f = final, solution is saturated with respect to dolomite. Reaction-paths: —1— $P_{\text{CO}_2} = 10^{-2.0}\text{atm.}$, $\text{pH}_i = 4$, $\text{pH}_f = 7.48$. —2— $P_{\text{CO}_2} = 10^{-2.5}\text{atm.}$, $\text{pH}_i = 4$, $\text{pH}_f = 7.81$. —3— $P_{\text{CO}_2} = 10^{-3.0}\text{atm.}$, $\text{pH}_i = 5$, $\text{pH}_f = 8.13$. —4— $P_{\text{CO}_2} = 10^{-4.0}\text{atm.}$, $\text{pH}_i = 6$, $\text{pH}_f = 8.79$. For example, dolomite spring-water with composition A ($-\log\{(\text{Ca} + \text{Mg})\} = 3$, $P_{\text{CO}_2} = 10^{-2.5}\text{atm}$ and $\delta^{13}\text{Solution} = -8.75\text{‰}$), has $\delta^{13}\text{CO}_{2,g} = -18\text{‰}$. When translating A to A' under the same chemical conditions, the $\delta^{13}\text{Solution}$ is -5‰ and $\delta^{13}\text{CO}_{2,g}$ will be -14.35‰ . ●1 = spring-water.

where E_i is the exponential integral, tabulated by Abramowitz & Stegun (1970). Alternatively, EC may be used instead of Ca-concentrations because of eq. 1. Fig. 2B indicates the results, with $\text{EC}_e - 7.0 = 121 \mu\text{S}/\text{cm}$ (from $\text{Ca}_e = 0.32 \text{ mmole}/\text{l}$); it shows excellent linearity ($R > 0.997$ for all 8 samples). Table 1 gives values of k as defined in eq. 3, with slightly smaller values for dolomite which dissolves stoichiometrically. At present it is not yet clear how dolomite, with bulk chemical formulas as given in table 1, can dissolve non-stoichiometrically. However, all samples showed micropores lined with finer crystals, and preliminary dissolution tests gave even higher Ca/Mg-ratios for non-stoichiometric dissolving dolomites (but equal Ca/Mg-ratios for the stoichiometric ones). It may be that part of the finer crystals have higher Ca/Mg-ratios than found for bulk dolomite.

Fig. 3 shows the overall rate vs. amount of dolomite dissolved, and also a comparison with values calculated from the Busenberg & Plummer (1982) formula at 3° and 20°C. Two lines have been drawn for 'sedimentary' and 'hydrothermal' dolomites of Busenberg & Plummer, and also two lines for pure and Ca-rich dolomite from present experiments. Although initial rates are

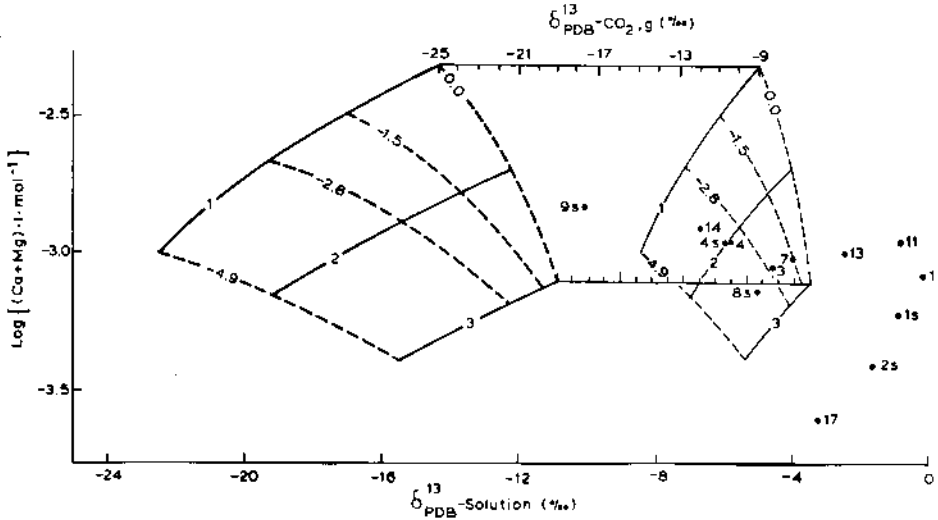


Fig. 5. The relationship between $\delta^{13}\text{C}_{\text{Solution}}$, $\delta^{13}\text{C}_{\text{CO}_2,\text{g}}$ and Ca + Mg in a closed system dissolution of dolomite at 3°C . --0.0-saturation-index dolomite; —1— reaction-path. Reaction-paths: —1— $P_{\text{CO}_2,\text{i}} = 10^{-1.0}\text{atm.}$, $\text{pH}_\text{i} = 4$; $P_{\text{CO}_2,\text{f}} = 10^{-1.54}\text{atm.}$, $\text{pH}_\text{f} = 7.19$. —2— $P_{\text{CO}_2,\text{i}} = 10^{-1.5}\text{atm.}$, $\text{pH}_\text{i} = 4$; $P_{\text{CO}_2,\text{f}} = 10^{-2.61}\text{atm.}$, $\text{pH}_\text{f} = 7.88$. —3— $P_{\text{CO}_2,\text{i}} = 10^{-2.0}\text{atm.}$, $\text{pH}_\text{i} = 4$; $P_{\text{CO}_2,\text{f}} = 10^{-3.82}\text{atm.}$, $\text{pH}_\text{f} = 8.66$. Because of a non-linear relationship between $\delta^{13}\text{C}_{\text{Solution}}$, $\delta^{13}\text{C}_{\text{CO}_2,\text{g}}$ and Ca + Mg in a closed system dissolution, two examples for the three reaction-paths have been drawn: one at $\delta^{13}\text{C}_{\text{CO}_2,\text{g}} = -25\text{‰}$ and the other at $\delta^{13}\text{C}_{\text{CO}_2,\text{g}} = -9\text{‰}$. Note different scales for initial $\delta^{13}\text{C}_{\text{CO}_2,\text{g}}$ at different P_{CO_2} .

comparable, the sharp drop in overall rate calculated from the Busenberg & Plummer relationship, clearly represents too great an extrapolation beyond experimental conditions.

The present rates extrapolate to 3981 and 3440 hours to attain 1/2 (Ca + Mg) – concentrations at 95% of equilibrium for respectively pure and Ca-rich dolomite dissolution under the given experimental conditions. Field-situations may have A/V-ratios, which are 100–1000 times greater, with consequently smaller equilibration times. Although no rigid extrapolation to the lower field temperatures in the Dolomites is possible (experiments are currently running at 4°C), one would expect from a comparison with Busenberg & Plummer's data (Fig. 3) that initial dissolution rate would be about five times slower than it is at 22°C . Equilibrium is therefore expected to require a few days under field conditions open to atmospheric CO_2 .

Carbon isotope evolution of dolomite-water

The computer model PHREEQE (Parkhurst *et al.* 1980) was modified to include isotope calculations and used for reaction path simulations as described

by Plummer *et al.* (1983). Congruent dissolution of pure dolomite was modelled since the sampled springs indicated that no secondary minerals were precipitating. The same conditions were assumed as reported by Deines *et al.* (1974), i.e. for closed systems an initial loading with CO₂ is followed by dolomite dissolution, and for open systems equilibrium with a large CO₂-reservoir is maintained while dolomite dissolves. No other CO₂-exchange is assumed (cf. Mook, 1976). Factors for isotope fractionation were taken from Friedman & O'Neill (1977).

Figures 4 and 5 show relationship between $\delta^{13}\text{C}$ and Ca + Mg-concentrations in water for open and closed systems in which dolomite dissolves congruently. Also plotted in these figures are the analyses of springs discussed below. Lines have been drawn along calculated reaction paths; these indicate $\delta^{13}\text{C}$ evolution of water as related to initial conditions in pH, $\delta^{13}\text{C}$ of gaseous CO₂ and CO₂-pressure. pH-values of the initial water were set by CO₂-pressure and addition of HCl. $\delta^{13}\text{C}$ of dolomite was fixed to + 2.2 ‰, the average of 11 determinations ranging from + 1.96 to + 2.69 ‰.

In an open system (Fig. 4), the evolution lines (drawn for an initial $\delta^{13}\text{C}$ of CO₂-gas of -18 ‰) can be shifted along the bar giving $\delta^{13}\text{C}$ -CO_{2,g}, to find $\delta^{13}\text{C}$ in solution with other initial values of $\delta^{13}\text{C}$ -CO_{2,g}. In the closed system (Fig. 5), such a linear shift is not possible, and evolution lines are shown for $\delta^{13}\text{C}$ -CO_{2,g} of -9 and -25 ‰.

Of particular value is that a comparison of carbon isotope and chemical data can indicate source-area conditions. For gaseous CO₂, the maximum range in $\delta^{13}\text{C}$ is from -9 to -25 ‰ for respectively atmospheric CO₂ and biological respiration; Figures 4 and 5 therefore show, that $\delta^{13}\text{C}$ in water-samples above -3.5 ‰ can only be explained by an open system dissolution with atmospheric CO₂. In a closed system other sources of acidity besides CO₂ must also be considered. The oxidation of ferrous iron or of pyrite may lead to dissolution of dolomite and raise $\delta^{13}\text{C}$ of the water. However, in our case the quantitative contribution is minor; ferrous iron is less than 0.2% of Ca in the analysed dolomite samples (Table 1), and therefore negligible; SO₄-concentrations show a small increase of 0.04 to 0.08 mmole/l with respect to snowmelt values, but this is generally accompanied by an increase in the Ca/Mg-ratio, and is therefore likely to be derived from gypsum dissolution.

Field samples from the Italian Dolomites

General description of the area

For the present study springs were sampled in the 'Sasso Lungo' and 'Putia' - groups of the Dolomite Mountains. Springs in both groups were found to have identical characteristics. Fig. 6 gives the geology of the Sasso Lungo, and includes a schematized cross section (from Engelen, 1974).

The geological formations are of Middle Triassic age. Two coexistent and laterally interfingering facies types occurred during that time: reef masses (bioherms) grew upwards in the Triassic sea, whereas at the same time clastic

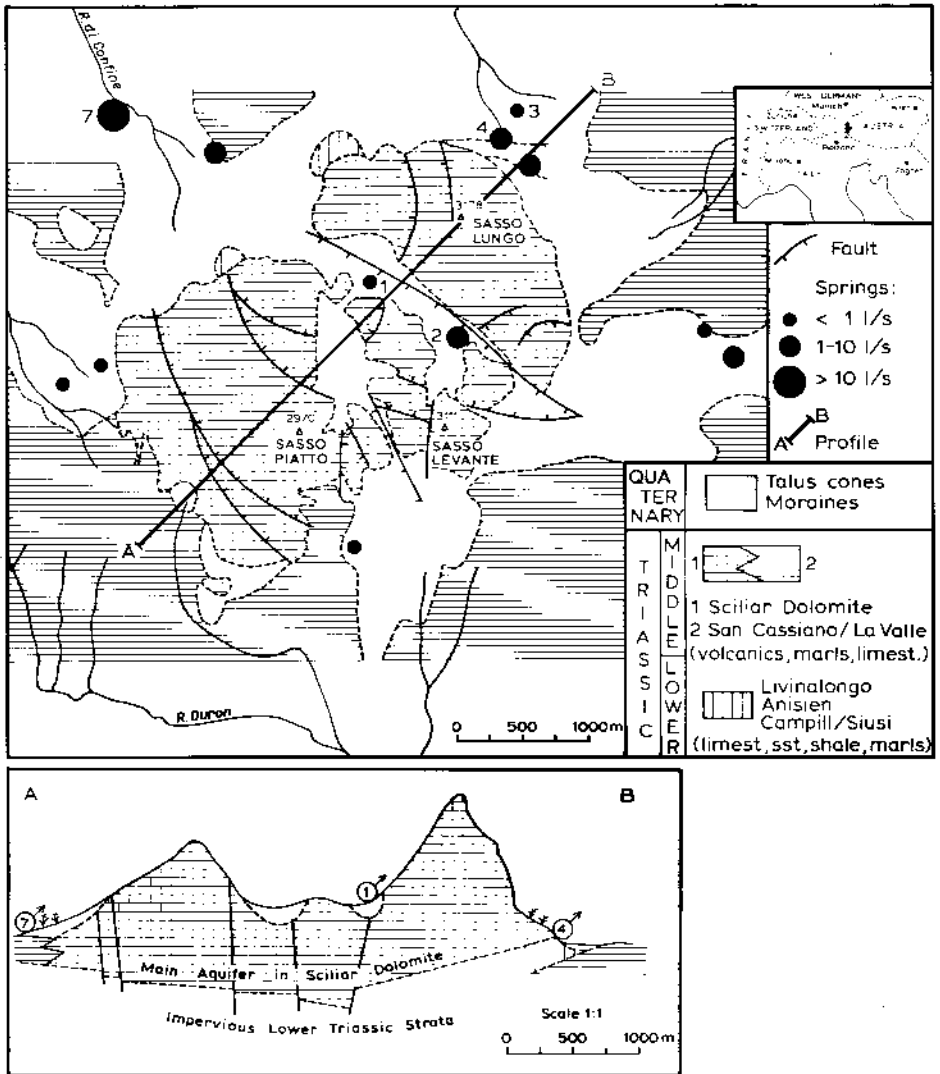


Fig. 6. Simplified geological map of the Sasso Lungo mountain group showing springs sampled in November 1982. Cross section indicates schematized spring locations.

volcanic rocks and lavaflows, interbedded with normal sedimentary marine strata, were deposited in the sea around the reef islands. The reef facies forms the present Sciliar dolomite formation with an estimated thickness of 800–1000 m. Present day morphology is determined by the great difference in resistance to erosion between the massive reefs and the surrounding formations. The latter were partly eroded to a Late Pliocene level of 2100–2200 m above sea level, with the result that these reefs now rise about 1000 m above the surrounding area.

Table 2. A selection of chemical and isotope analyses of spring water inside and outside Dolomite mountain groups.

Sample*	Inside Dolomite			Outside, atm. CO ₂			Outside, -biol. CO ₂			
	2S	1S	1S	11	13	7	4	4S	14	9S
Altitude (m)	2435	2255	2255	2100	2000	1780	2070	2070	1520	2170
Temp (°C)	0.2	2.0	2.2	2.0	2.0	3.1	2.5	3.0	5.0	4.0
pH	8.65	?	8.52	?	?	8.50	8.19	8.30	8.35	8.05
Q (l/s)	4	0.5	4	0.01	0.5	50	3	0.2	10	1
Mg (mmol/l)	0.20	0.42	0.29	0.60	0.52	0.47	0.55	0.55	0.62	0.76
Ca (")	0.22	0.49	0.34	0.64	0.55	0.59	0.62	0.60	0.66	0.80
Sr (µmol/l)	0.04	0.09	0.06	0.11	0.89	2.00	0.09	0.09	0.56	0.14
HCO ₃ (mmol/l)	0.87	1.63	1.25	2.43	2.06	1.87	2.33	2.26	2.44	2.97
SO ₄ (")	0.01	0.06	0.02	0.02	0.03	0.09	0.05	0.05	0.03	0.04
δ ¹³ C (‰/∞, PDB)	-1.7	-0.3	-1.0	-0.9	-2.5	-4.0	-5.9	-5.9	-6.7	-10.0
Tritium (TU)	22	40	31	49	71	64	44	44	147	42
log P _{CO₂}	-4.0	?	-3.8	?	?	-3.6	-3.2	-3.3	-3.3	-2.9
log(1AP/K _{dol})	-1.1	?	-0.7	?	?	+0.1	-0.3	-0.1	+0.2	-0.1

*S-coded samples taken in August 1983. Others in November 1982.

Mean annual precipitation is probably in the order of 900–1000 mm. The water is discharged through springs of different types as discerned by Engelen (1974):

(1) A few small springs in the central reef areas. (2) Springs of intermediate size at the border area of the reef, where it contacts the impermeable surrounding formations. (3) A few large springs away from the reef in Quaternary deposits.

Techniques for sampling and analysis

Field sampling for the present study was carried out in November, 1982 and August, 1983. Electrical conductivity (EC), temperature and pH were determined at the sampling point. pH was measured with a Metrohm field-meter, using an Ingold 'low temperature' glass electrode. The pH-measurements of 1982 samples are unfortunately less reliable than those taken later because of slow electrode response at the low (water-) temperatures. In August, 1983 samples were refreshed at least three times until successive samples gave the same pH within 0.02 unit. Electrode response was checked with buffers pH = 4 and 7 before and after every determination.

A sample of 100 ml was filtered through 0.45 µm Millipore filters, and acidified with 0.7 ml 65% HNO₃. This sample was used for the analysis of Na, Mg, Ca, Sr, Al, Si and Fe by ICP-emission, and of K using a flame-photometer. A 200 ml sample was taken for the analysis of HCO₃ by endpoint-titration, and of NO₃, SO₄, and Cl by Auto-Analyzer procedures. Samples of 250 ml were taken for analysis of ¹³C and ³H in the Groningen isotope laboratory. Conservation was with 5 drops of a 30 g KI + 15 g I₂ per litre solution in the 1982 samples, but hydrocarbons appeared nevertheless in a number of samples. The 1983 samples were therefore conserved with 10 drops of the same KI/I₂-solution, with better results.

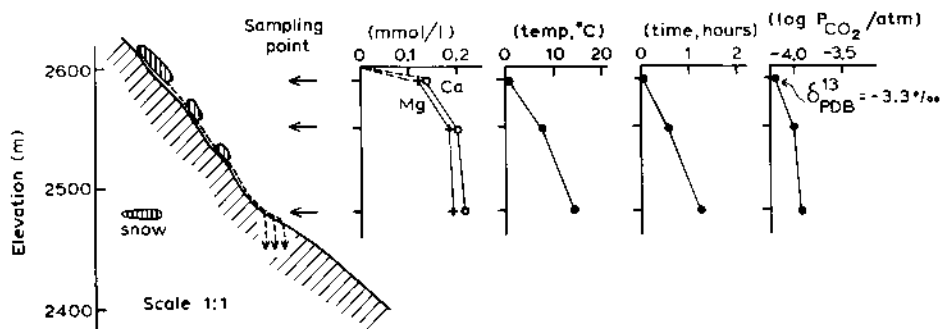


Fig. 7. Chemical evolution in snowmelt flowing over a dolomite surface.

Water at high altitude in the central reef

There is very little surface water within the dolomite at altitudes above 2200 m, either following rain or on warm days under snow melt conditions. This indicates a **high** porosity and infiltration capacity for the dolomite, even though it is barren rock. Water from the few intermittent springs can be traced back to snowfields somewhat higher up.

A few representative samples have been grouped together in Table 2, which shows that Ca- and Mg-concentrations vary from 0.2 to 0.5 mmole/l. The elemental contribution from rain and snow is not exactly known, but measurements in 1973 (Appelo, 1975) gave average concentrations of 18 $\mu\text{mole Ca/l}$ and 6 $\mu\text{mol Mg/l}$ during the summer months. These are almost negligible quantities when compared with concentrations given in Table 2. Most samples show a Ca/Mg-ratio of 0.98 to 1.05. Furthermore, $\delta^{13}\text{C}$ is higher than -3‰ , showing that no biological CO_2 has contributed to the alkalinity in these samples. Where the pH-measurements are sufficiently accurate to allow calculation of CO_2 -pressures, these are found to be lower than the atmospheric value of $10^{-3.5}$. This value is approached in springs with the highest Ca- and Mg-concentrations.

It is of considerable interest to show the concentration evolution in water from a snowfield trickling over fine-grained dolomite before infiltration and disappearance into the dolomite rock. Fig. 7 illustrates this situation with analysis results from three samples taken on a warm, sunny day in August, 1983. The highest sample was taken directly below the uppermost snowfield; the water has a very low CO_2 -pressure through lack of CO_2 in snow, and slow diffusion of air with respect to CO_2 -consumption by the dissolving dolomite. Forty metres lower, after a time lapse of about 30 min. CO_2 -pressure has increased somewhat and Ca- and Mg-concentrations have increased to 0.2 mmole/l. Cl-concentration remained constant at 6 $\mu\text{mole/l}$ in all three samples, showing that Ca- and Mg-increases were not caused by evaporation. About 50 minutes later and 70 m lower, the water had completely disappeared. Ca- and Mg-concentrations at this point exceeded 60% of the saturation values, but

were still the lowest found. The 1 to 2 hours that this snowmelt remained as surface water before infiltration is about the maximum lifetime of any surface-water observed.

Other springs in the central reefs can originate either where a talus cone ends near a rock step or from fissures (samples 2 and 1 respectively in Table 2). Water from these springs again rapidly infiltrates where dolomite debris and talus cones are sufficiently thick. The EC of the water was found not to change during the short transit period over the surface between emergence and infiltration, but Ca- and Mg-concentrations were already well in excess of 60% saturation. Differences exist between winter and summer, as shown by the analysis of fissure-spring 1 in Table 2. Discharge is about 8 times higher in summer, giving an admixture of rapid components which dilutes baseflow concentrations found in the winter sample.

It may be concluded from these data that in the central reef dissolution of dolomite is driven by atmospheric CO_2 , and is often faster than the rate at which CO_2 can diffuse into the water. This can lead to relatively low concentrations, especially in surface runoff which results from snowmelt.

Springs surrounding the reefs

Water composition of springs in the area around the reefs may be influenced by other formations, contributions from which can be expected to increase the Ca/Mg-ratio (because the formations are calcareous), and increase the SO_4 - and Si-concentrations (because gypsiferous layers occur and the formations have silicate minerals) as well as the Sr-concentration (an empirical criterion). Most 'pure dolomite' waters were found to have $\text{SO}_4 < 0.1 \text{ mmol/l}$, $\text{Si} < 8 \text{ } \mu\text{mol/l}$ and $\text{Sr} < 0.2 \text{ } \mu\text{mol/l}$.

First are discussed springs with $\delta^{13}\text{C} > -3.5 \text{ } \text{‰}$, since these have gained gaseous CO_2 from the atmosphere only. Such springs thus originate in the central reef where vegetation is absent. CO_2 -exchange near the spring outlets is unlikely, since discharge points are in grass-covered areas where any exchange with the soil atmosphere would lower the $\delta^{13}\text{C}$.

Springs with $\delta^{13}\text{C} > -3.5 \text{ } \text{‰}$. - In these springs Ca- and Mg-concentrations vary from 0.45 to 0.64 mmole/l, whereas the value at saturation is about 0.53 mmole/l (atmospheric CO_2 , 3°C). The higher concentrations probably result from gypsum dissolution, since samples with higher concentrations also have slightly higher SO_4 -concentrations up to 0.08 mmole/l and higher Ca/Mg-ratios. The concentrations are higher than for water sampled in the central dolomite, but $\delta^{13}\text{C}$ indicates that dolomite dissolution is still driven by atmospheric CO_2 . The concentration increase must take place *before* the water arrives at a continuous watertable where CO_2 -exchange stops, and *after* infiltration of snowmelt water (or rain) which has lower than atmospheric CO_2 -pressure and only half the concentration found in the springs. Ample reaction time is therefore available

to allow for equilibration with dolomite and atmospheric CO_2 : the dolomite rock is considered as essentially open to water and atmosphere alike, and fissures sufficiently large for atmospheric circulation are the main conduits for water flow. This may be termed 'shaft flow' of water flowing as films on the walls of vertical shafts (Gunn, 1981), with a residence of a few days allowing saturation with dolomite to be attained.

It is thus concluded that diffuse flow or vadose seepage through micropores is relatively unimportant; the necessary residence times can easily be obtained in shaft-flow, since the height difference to be bridged between the central reefs and the springs is about 900 m.

Springs with $\delta^{13}\text{C} < -3.5\text{‰}$. - A number of springs surrounding the reefs show $\delta^{13}\text{C} < -5.5\text{‰}$ and Ca- and Mg-concentrations which vary from 0.5 to 0.8 mmole/l (Table 2). Using the procedures outlined previously, $\delta^{13}\text{C}$ for the initial CO_2 -gas is calculated to vary from -15 to -20‰ for an open system, and from -14 to -22‰ for a closed system.

It is apparent from the analyses given in Table 2 that concentrations in springs with biological CO_2 are barely higher than those without; it can also be seen that CO_2 -pressures are only marginally higher than atmospheric. It seems, therefore, that vegetated areas surrounding the reefs contribute (at sampling times) only a small part of the springwater, the bulk being derived from the central dolomite.

The springs outside the central reef also show tritium-concentrations which are generally higher than for intermittent springs or snow melt in the central area (Table 2). The values suggest residence times of more than one year, at least for the bulk water component. This confirms the presence of a main aquifer within the dolomite as suggested by Engelen (1974).

Final remarks and conclusions

Spring water compositions derived solely from dolomite dissolution are relatively rare, since dolomites are often intercalated in other formations. The North Italian Dolomites however, occur as isolated reefs which are elevated from other formations, and are thus ideal to study the hydrogeochemistry of dolomite. Springs surrounding the reefs show chemical compositions which result from dissolution of 'pure dolomite' and have Ca/Mg-ratios of 0.98 to 1.05. The total concentrations in spring water indicate equilibrium with dolomite at CO_2 -pressures which are close to atmospheric.

The present study gives indications as to the origin of spring water concentrations by consideration of dolomite dissolution kinetics and spring water isotopic evolution. It was found that chemical concentrations mainly increase during flow through larger fissures between the dolomite surface at 3000 m and the spring levels at about 2100 m. These fissures must be large enough to allow a free circulation of air, since dissolution occurs under conditions open to atmo-

spheric CO₂. This was proven by $\delta^{13}\text{C}$ -measurements and from chemical analyses of water which infiltrates into the dolomite at high altitude. Associated laboratory dissolution experiments have shown that residence times in the fissures need only be a few days at most for equilibrium to occur. Since the dissolution process is open, diffuse flow or vadose seepage through micropores are considered to be relatively unimportant flow mechanisms in the upper parts of the Dolomites.

Spring water tritium values indicate that there may also be a large groundwater reservoir at lower levels in the dolomite reef, giving residence times of more than one year. It should be emphasized however, that a long residence time is not necessary to explain the measured concentration levels in springs; the Ca- and Mg-concentrations are in fact obtained in an open situation, before the water enters the closed environment of a groundwater reservoir.

Acknowledgements. – It is a pleasure to acknowledge the assistance of Mr. P. Overweg with the dissolution experiments and the chemical analyses. Isotope analyses were performed by Mr. H. J. Streurman of Groningen University. The authors wish to thank Prof. I. Simmers for his comments on this work, and also to thank Mr. H. Sion for drawing the figures and Mrs. R. de Vries for typing the manuscript.

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