

HYDROCHEMISTRY OF SPRINGS IN AN ALPINE CARBONATE/SERPENTINITE TERRAIN

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ABSTRACT

A reaction scheme is given to explain composition of springs originating from micaschists, calcareous schists, serpentinites and dolomite, with local gypsiferous layers. Dissolution experiments were performed on rock- and soil samples to obtain information on cation release. Solutions of soil samples show a great cation buffering capacity, with concentration levels found in spring-water rapidly reached, even with a relatively large dilution of 750 ml. water to 100 gr. soil. Results indicate a redistribution of elements within the soil. Solute uptake along a flow-line is therefore not continuous and difficult to define kinetically.

INTRODUCTION

A number of studies have appeared in which the chemical composition of natural water is compared with dissolution experiments in the laboratory. When concentrations change with changing runoff-volumes particular reactions may indicate "source-areas" or "flow-lines" (Kennedy, 1971; Pilgrim et al. 1979). Residence times have been estimated from the comparison of spring-water composition and kinetic experiments (Paces, 1973; Appelo, 1975). The chemistry of springs is thus used as a natural tracer for obtaining information of the subterranean part of the hydrological cycle.

The present investigation follows this line of thought and was carried out in an alpine terrain with a great variation of lithologies. It aims to 1) characterise spring-water compositions from flow-lines passing different lithologies and soil horizons and 2) give information on the kinetics of solute uptake along flow-lines.

Characteristics of the area

The studied area lies in the Italian alpine province of Bozen (Bolzano). It has a number of glaciated, hanging valleys about 5 km long and 1.5 km wide, draining to the river Ahr (Aurino) in the north. Mountain peaks at the divide exceed 3000 m and outlets in the Ahr are at 1020 to 1400 m. The valleys show morphological features of an alpine environment with steep relief, moraine deposits, slumps, avalanches and other high-alpine variations of mass transport and deposition. The area is wooded to 2000 m and sparsely cultivated with meadows used for hay in the more accessible, lower parts. Higher in the cirques grazing occurs during summer.

The high relief and steep incision of the U-shaped valleys give rise to a large number of closely spaced springs and seepage zones near the streams. Faults exist, feeding springs, but main drainage is along steep slopes perpendicular to the streams. Lithology shows a great variability, with the 'root zone' of three alpine nappes being exposed in the area. The nappes are wrapped around the Tauern orthogneiss, visible in a tectonic window north of the Ahr (fig. 1).

HYDROCHEMISTRY OF THE SPRINGS

A hydrological fieldwork in the summer of 1980 was completed with sampling for chemical analysis of 49 springs. Analytical procedures involved in-field measurement of pH and Electrical Conductivity (EC). K was determined by flame-emission, and Na, Mg, Ca, Al, Si, Mn, Fe, Cu by ICP-emission spectrometry in samples acidified to pH 1.5. For NH_4 , NO_3 , Cl and PO_4 Auto-Analyzer procedures were used, SO_4 was determined turbidimetrically, and HCO_3 by end-point titration.

The springs show a great variation in water composition which reflects lithological heterogeneity. Cl and Na remain more or less constant when compared with Mg, Ca, HCO_3 and SO_4 ; the following discussion is thus limited to these reactive ions. Minerals which actively contribute to spring-water composition will be gypsum, sul-

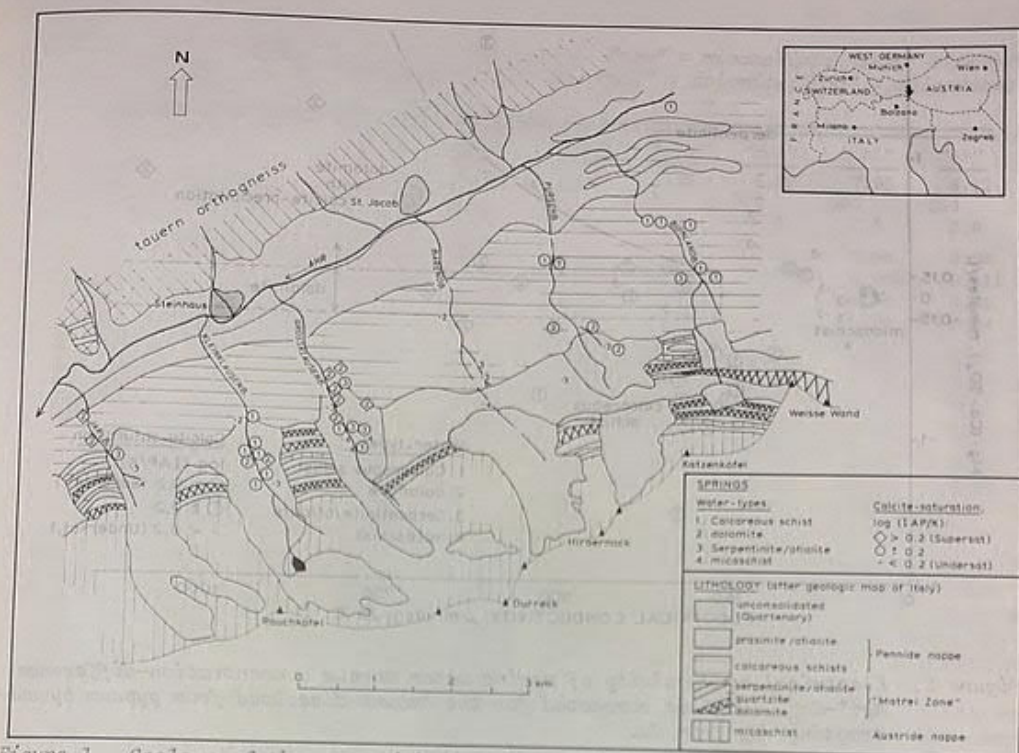


Figure 1. Geology of the area with location and classification of springs.

fides, calcite, dolomite and Mg-bearing minerals (notably talc, serpentine, chrysotile). Feldspar and mica are relatively unimportant, as seen from the low and uniform concentrations of Na and K.

Reaction scheme

Figure 2 shows spring-water EC versus the difference $(\text{Mg}-\text{Ca}_d)$, where Ca_d is Ca-concentration corrected for the part which is ascribed to gypsum dissolution ($\text{Ca}_d = \text{total Ca} - \text{SO}_4$). The figure allows discrimination into 4 groups of water composition:

1. Water from calcareous schists. This water has low SO_4 -content and shows slight supersaturation with respect to calcite: $\log(\text{IAP}/K_{\text{cc}}) = 0.11 \pm 0.13$ for 17 samples.
2. Water with equal proportions of Mg and Ca_d and an EC > 250 $\mu\text{mho}/\text{cm}$, described as dolomite-water. SO_4 -content is high in samples with high EC. Since gypsum is the likely source of SO_4 in these samples, Ca-concentrations increase to precipitate CaCO_3 ; Mg then becomes relatively high. 'Dolomite'-water having a high $(\text{Mg}-\text{Ca}_d)$ -number is strongly supersaturated with respect to calcite: $\log(\text{IAP}/K_{\text{cc}}) = 0.3-0.7$.
3. 'Serpentinite'-water shows $(\text{Mg}-\text{Ca}_d)$ -numbers about the same as for the 'dolomite' group, but with lower EC. Water is, with one exception, undersaturated with respect to calcite.
4. Spring water with EC < 100 $\mu\text{mho}/\text{cm}$ originates from micaschists. Water is strongly undersaturated with respect to calcite.

Figure 1 shows the geographical distribution of water types in the area, and table 1 gives a selection of representative analyses. Figure 2 can be seen as summary picture of the reactions which give different spring-water compositions. The portions of flow-lines where reactions take place leading to these compositions may now be considered.

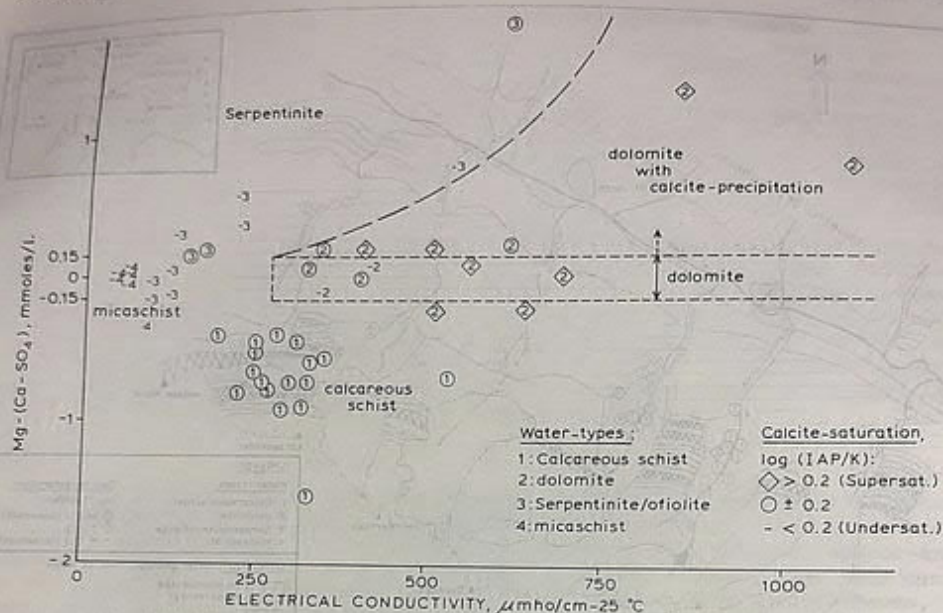


Figure 2. Electrical conductivity of spring water versus concentration-difference $Mg^{2+} - Ca^{2+}$. Ca^{2+} is corrected for the amount dissolved from gypsum by subtracting SO_4 from Ca .

DISSOLUTION EXPERIMENTS ON ROCK AND SOIL SAMPLES

Dissolution experiments were made to obtain information on rock- and soil influences leading to certain water qualities and to estimate time periods involved. Soil samples were dried at 105° C, stones and larger rock fragments were removed and 100 gr. was transferred to a 1 l. polyethylene bottle. 750 ml. of distilled water was added, and the bottles were regularly sampled for chemical analysis of pH, cations and SO_4 . (For SO_4 a colorimetric Auto-Analyzer technique was used, since sample coloring by humic acids interfered in the turbidimetric analysis). Sampling was carried out by pipette after vigorous stirring to hold the ratio mineral surface/distilled water roughly constant. Samples were filtered through a 0.45 μm Millipore filter. Rock samples were crushed in an agate mortar. 100 gr. of material was placed in bottles, and 750 ml. distilled water added. Neither size-fractionation nor removal of finer fragments (chemically or ultrasonically) were carried out on the crushed rock. 51 samples were processed and selected results are given in fig. 3.

Results

A description is given using the general reaction scheme, with discrimination of micaschist (fig. 3A, B, C) serpentinite/Mg-rock (fig. 3D, E, F) and carbonates (fig. 3G, H, I).

- In the micaschist soil solution an increase of Si with time is evident. Cation concentrations are more constant over the time period between 7 and 1300 hours (55 days). Ca- and Mg-concentration levels are within the range observed in spring-water. Si shows a steady increase with time to over 0.3 mmol/l, whereas Si concentration in spring-water was 0.051 ± 0.015 mmol/l (6 'micaschist'-spring samples). Al is below ICP-detection limits (1 μmol/l) in spring-water, but is present in elevated concentrations in the soil solutions. Also, soil solutions show much lower pH than spring-waters.
- In the dissolution of serpentinite the expected Mg increase is evident (fig. 3D).

Table 1. Typical composition of spring-waters. "mas" = micaschist; "serp" = serpentinite; "pras" = prasinite/ophiolite; "dol" = dolomite; "cc" = calcareous schist.

Geol. unit	"mas"	"mas"	"serp"	"pras"	"dol"	"dol"	"cc"
pH	7.63	7.70	8.47	7.41	8.00	7.93	8.12
EG (μmho/cm)	52	100	152	610	325	505	250
Temp (°C)	3.7	4.0	4.0	4.8	5.5	7.5	2.0
Na (mmoles/l)	0.04	0.03	0.02	0.06	0.04	0.04	0.04
K "	0.016	0.026	0.011	0.015	0.011	0.008	0.011
Mg "	0.11	0.12	0.44	2.30	0.67	0.93	0.31
Ca "	0.17	0.35	0.33	1.20	0.77	1.95	0.94
Cl "	0.05	0.05	0.06	0.05	0.04	0.06	0.05
HCO ₃ "	0.37	0.86	1.35	5.54	2.10	3.34	2.23
SO ₄ "	0.08	0.04	0.05	0.72	0.14	1.19	0.15
Si "	0.05	0.05	0.06	0.13	0.06	0.09	0.05
log PCO ₂	-3.37	-3.08	-3.67	-2.01	-3.00	-2.74	-3.11
log(IAP ^{ca} /K ^{ca})	-1.8	-1.1	-0.19	-0.18	-0.11	+0.37	+0.08
log(IAP ^{do} /K ^{do})	-4.1	-2.9	-0.48	-0.29	-0.47	+0.27	-0.82

However, only one sample of soil from Mg-rich rock shows larger concentrations of Mg than Ca (fig. 3F). Soil solutions show higher pH and lower Al concentrations than found for micaschist-soils. Si increases steadily in concentration, but at lower rates than in micaschist soils. Mg and Ca were normally found to increase with time, although concentrations after 1300 hours were still lower than given for 'serpentinite' spring-water in a number of samples (fig. 3E).

- In the carbonate containing soils differences are evident between pure calcite-rock soil (fig. 3G) and soils in which Mg is also present (fig. 3H, I). After 1300 hours the soil on calcareous schist (fig. 3G) shows higher concentrations of Ca than found in spring-waters associated with this unit. It may be that in this sample calcite fragments were mixed with calcite free soil, acid buffering of the latter being neutralized by dissolution of calcite. Figure 3H shows soil solution compositions which are comparable to 'dolomite'-water, with high SO₄, though the strong SO₄-increase is not coupled to an increase of Ca (as expected when gypsum would dissolve). High SO₄ concentrations were invariably found in samples containing plant roots, lichens and moss, indicating that decomposition of organic material in the experimental soil solution actively releases SO₄. A typical example showing "Alpenrose" (Rhodod. hirsutum)-roots with adhering soil is given in figure 3I. The experimental concentrations of Ca and Mg are in the range of spring-water values but Al- and Si concentrations are different, especially when pH is low.

Interpretation

Figure 3 shows a variety of results which can basically be explained from interaction of different processes :

- weathering of primary rock minerals
- dissolution of (secondary) clay minerals
- adsorption/desorption from the soil adsorption complex
- decomposition of organic material.

Si increases in all soil solutions. At lower pH (in micaschist soils) the rate of increase is greater, giving Si-concentrations which are about 6 times higher after 55 days than those observed in spring water. Cations in micaschist soil solutions show no increase in concentration. It may be that possible increases which result from weathering are buffered by uptake in the adsorption complex, just as initial cation concentrations are high through rapid desorption from the adsorption complex.

In more basic soil solutions with pH > 6 cation concentrations often increase, indicating that the primary rock fragments in these soils weather more rapidly. Initial concentrations of Ca and Mg (after 7 hours contact) are also higher. This sug-

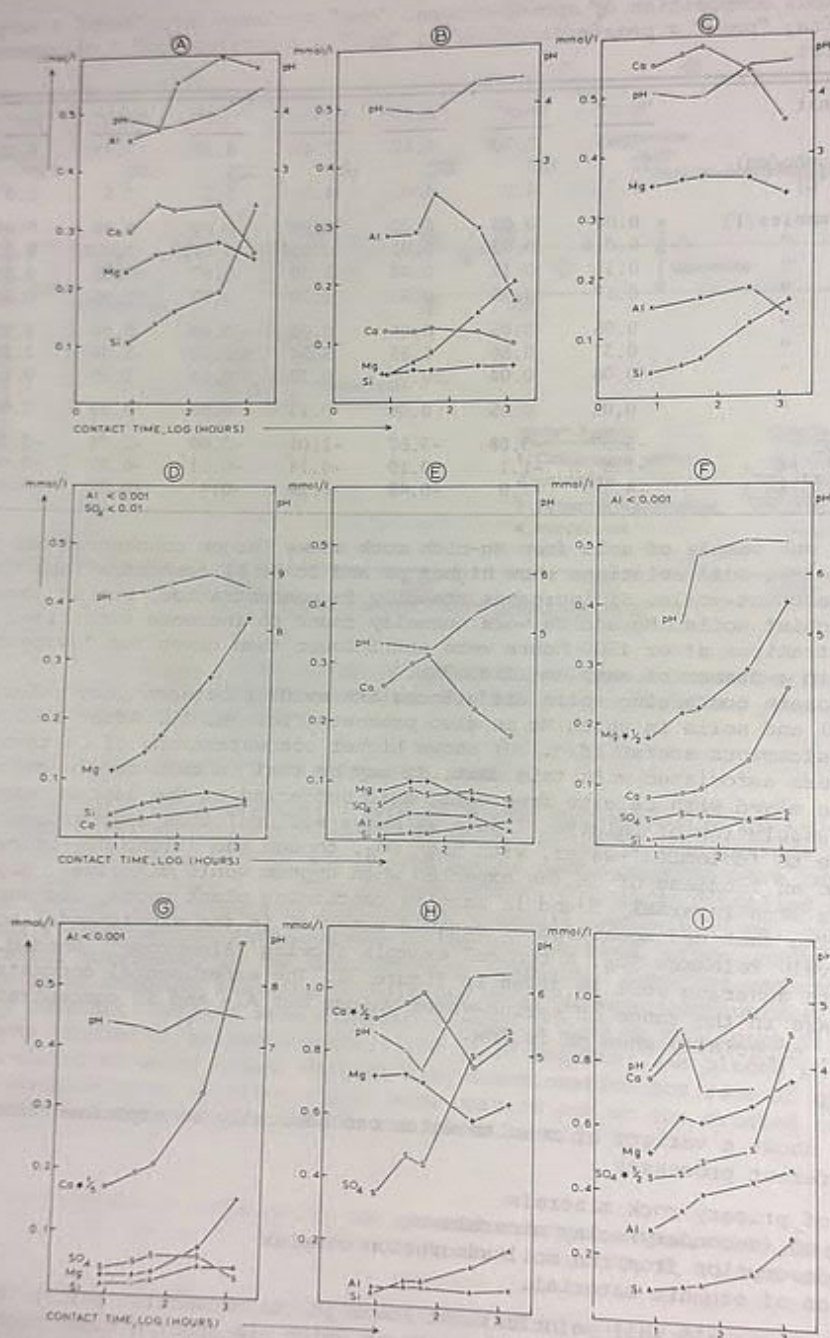


Figure 3. Dissolution of soil samples.
 A, B, C : A, B, C-horizon of brown forest soil on micaschist.
 D, E, F : Mg-bearing rock and soil; D : serpentinite-rock,
 E : brown soil on serpentinite, F : soil on serpentinite/dolomite.
 G, H, I : Carbonate containing soils; G : brown soil on marble;
 H : black topsoil on calcareous schist, I : roots of Rhod.
 hirsutum-roots with adhering soil from micaschist.

gests higher base saturations which cannot buffer further Ca- and Mg release from weathering as effectively as the more acid soils. Some acid buffering can still be found, however, and explains why Ca-concentrations increase to very high values as a result of calcite dissolution without a source of CO_2 being present (fig. 3G). At the same time, decomposing organic material acidifies with release of anions which can be buffered by desorption or increased mineral weathering. The increase of SO_4 seems to indicate decomposition (was highest in solutions of plant material with adhering soil).

FACTORS LEADING TO SPRING WATER COMPOSITIONS

Discrepancies may exist near spring outlets in the proposed reaction scheme relating water chemistry and local geology (fig. 1). Springs can be fed from faults which drain different lithological units, or moraine deposits may be present in the soil which plaster the rock with a mixture from several lithologies. Furthermore, springs often have mixing zone characteristics in which water from different flow-paths is combined. Different flow-lines are evident in springs having Golomite-water with high (Mg-Ca) numbers. It is unlikely that high SO_4 -concentrations result from organic material decomposition as suggested by the dissolution experiments, since decomposition products would be taken up by growing vegetation rather than being released and subsequently lost (Vitousek, 1977). The outlets of these springs show a wandering pattern as the outlets are repeatedly blocked by CaCO_3 deposition. This CaCO_3 -blocking cannot take place in the subsurface where it would immediately diminish permeability; separate flow-lines through gypsiferous layers in the (deeper) subsurface are therefore important contributors to springs with high SO_4 -concentrations.

All other concentrations observed in spring water can result from soil solution. Only a very short residence time is necessary, since the soil material is very effective in buffering cation concentrations.

Si and Al concentrations in soil solutions generally increase to far higher levels than observed in spring water, suggesting that these elements must precipitate in lower soil horizons before the water discharges to springs. There is therefore an active redistribution of elements within the soil, with higher concentrations in the A-horizon than in B- and C-horizon solutions. This also is invariably found when soil solutions are sampled in the field (Best & Monk, 1975; Appelo, 1975; Sollins, et al. 1980; Bruijnzeel, 1982).

The obtained soil solutions show that solute uptake along a flow-line is not a continuous process of water-rock interaction. In fact, rainwater may reach spring water composition for some elements on first contact with soil material, but solute redistribution and soil buffering reactions make it unlikely that exactly the same elemental molecules leave the area later as spring water. The active role of soil and vegetation is such that it may either increase or decrease solute concentrations, thus making kinetic definition of spring water composition along a flow-line very difficult.

ACKNOWLEDGEMENTS

The authors wish to thank Tini Bäer and Peter Overweg for assistance with the chemical analyses, prof. Ian Simmers for editing the english text, Henri Sion for drawing the figures and Romée de Vries for repeated typing of the manuscript.

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