

# Influence of rock composition on some trace metals in spring waters from high alpine watersheds

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High alpine aquifers are appropriate environments to better understand the possible influence of rocks on natural waters. Springs have been chosen in monolithological watersheds to distinguish the contribution of each type of rocks. The relationship between the major alkaline cations in solution (Ca, Na, Mg, K) and the surrounding rocks is quite well known. Less obvious is the influence of the mineralogy and geochemistry of the rocks on trace element composition of the solution. Five rock types are considered: granites, mafites, ultramafites, carbonates and gypseous-dolomitic rocks. About 300 analyses of spring water were studied. A large number of water analyses from granites, carbonates and gypseous rocks are from the Aquityp Project (Parriaux *et al.* 1990).

## Results

The main observations about trace elements are:

(1) the spring waters from high alpine watersheds are cold, oxic and neutral to basic (pH=7 to 9). The pH is not controlling the amount of metals in solution, as opposed to acid polluted waters.

(2) sulphate-rich rocks (gypseous-dolomitic) are very poor in heavy-metals trace, but waters issued from these rocks have similar metal concentrations than waters from metal-rich rocks (mafites and ultramafites).

(3) spring waters are not saturated with respect to trace metal solid phases (oxydes, hydroxydes, sulphates or carbonates). Important exceptions are first Fe-hydroxydes and second Al-hydroxydes and Si-oxydes.

Figure 1 illustrates, as a typical example, the relative abundances of trace metals in mafic rocks and in the related spring waters. In these rocks, Fe, Al, Mg and Ca are major elements. Ca and Mg are dominant cations in solution. Fe and Al are only present as trace amounts in waters. On the same figure, the main inorganic species in natural waters are shown for each element (Stumm and Morgan 1996). The distribution in fig.1 reflects the hydrolysis

behaviour of each family of elements: 1) alkaline, 2) Fe, Al, 3) Ni, Cu, Zn and Cd, 4) Mn, Ti. For other rock types, the picture does not change much.

## Alkali and alkaline earth metals: Sr, Ba, Rb

Free aquo-ions are dominant for Sr, Ba and Rb. The abundance of Sr in rocks decreases in the sequence sulphates > carbonates > silicates. The influence on the water composition is straightforward: waters from gypseous rocks have the highest contents and waters from silicated rocks the lowest.

Silicate rocks have notably higher contents for Ba and Rb than carbonates and sulphates. However, due to the low solubilities of the silicate minerals that contain Ba and Rb (K-feldspar and micas), springs in

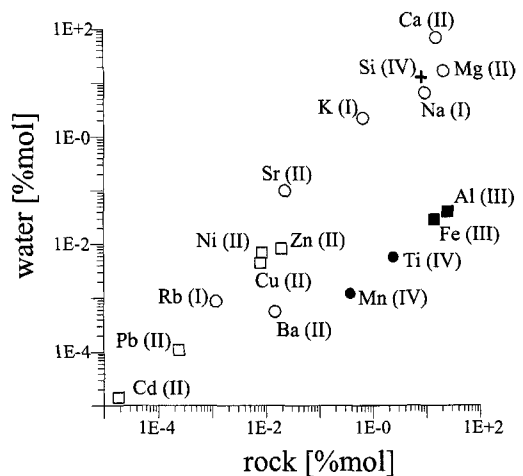


FIG. 1. Median relative content for trace and major elements in water vs rocks, from watersheds in mafic rocks. Number in ( ) is the valence of the ions in solution and the symbols represent the major inorganic species: free aquo-ions (white circles), free ions and CO<sub>3</sub>-complexes (white squares), O<sub>2</sub>-complexes (black circles), OH-complexes (black squares) and anionic hydrolyzed (crosses).

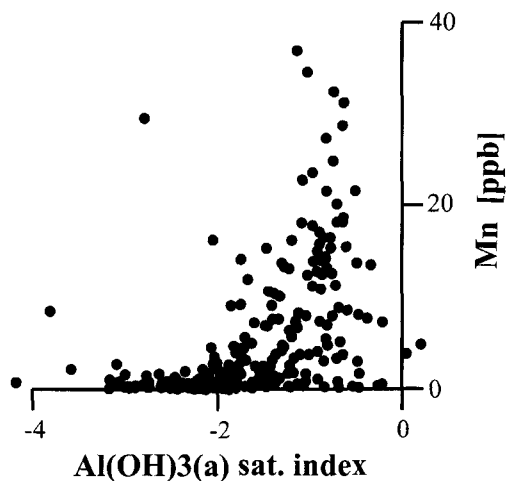


FIG. 2. Concentration of Mn in solution vs the saturation index of  $\text{Al}(\text{OH})_3(\text{a})$ .

crystalline massifs have very low concentrations in both elements. Waters from gypseous rocks are enriched in Rb and waters from carbonates in Ba, compared to waters from silicate rocks (granitic or mafic rocks).

### Fe and Al

Although Fe and Al usually form hydroxy-complexes in solution, colloidal forms are important too. About half of the samples analysed appear to be saturated or over-saturated with respect to  $\text{Fe}(\text{OH})_3$  amorphous (a). All samples are close to saturation or under-saturated with respect to  $\text{Al}(\text{OH})_3(\text{a})$ . Neoformation of clay minerals is rare in low temperature weathering processes in the Alps. The main products of such alterations are oxyhydroxides of Fe and Al, which is in agreement with the water. Fe- and Al-oxyhydroxides particles provide important surfaces for sorption of other metals (Buffle and van Leeuwen 1992).

### Ni, Cu, Zn and Cd

Metallic-oxydes or hydroxydes are strongly under-

saturated in solution (except for Al and Fe). Hence, precipitation does not appear to control the concentrations of metals in solution. Moreover, no relation seems to exist between the concentrations in rocks and in waters for non-alkaline metals.

All samples with  $\text{Ni} > 2$  ppb in solution (up to 8 ppb) are (over)saturated with respect to  $\text{Fe}(\text{OH})_3(\text{a})$ . A background value for Ni in non-polluted alpine waters could be defined at 0-2 ppb. Higher contents may be due to adsorption onto colloidal particles, mainly Fe-oxyhydroxides.

Cu, Zn and Cd display a similar relation with respect to the saturation index of  $\text{Fe}(\text{OH})_3(\text{a})$ . Typical background values are: Cu: 0-5 ppb, Zn: 0-8 ppb, Cd  $< 1$  ppb.

### Ti and Mn

Ti increases with the Fe content of waters. But interpretations are difficult because of the low abundance of Ti:  $< 1$  ppb in most solutions.

Samples with high concentrations of Mn are close to equilibrium with  $\text{Al}(\text{OH})_3(\text{a})$  (Fig.2). As for Ni and Fe, this could reflect adsorption of Mn onto Al-oxyhydroxydes colloids.

### Discussion

As far as the concentrations of non-alkaline metals in water is concerned, the abundance of these elements in the interacting rocks is of minor importance. However alkali and alkaline earth metals in solution are strongly dependent of the sulphate and carbonate content of the rocks.

Precipitation does not appear to be the mechanism that controls the concentration of metals in solution, except for Fe and Al. Sorption of metals on particles or walls seems predominant.

### References

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