

## Porewater chemistry of the Orciatico clays

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Clays are one of the favoured rock types as both host rocks and buffer backfill materials for the deep underground disposal of radioactive waste. Factors for this include their low hydraulic conductivity, high adsorption of radionuclides and their mechanical properties. It is commonly assumed that migration of fluids and solutes through clays is very slow, though direct observation of such movement is limited. Although laboratory experimental studies provide much useful information on shorter term processes, they are less suitable for addressing longer term processes relevant to performance assessment issues. However, study of natural analogues (essentially natural experiments) can give insight into processes occurring over thousands or millions of years. As part of an EC co-funded project, clay porewaters from a site near Orciatico, Tuscany, Italy have been studied, and provide information on solute transport through mudrocks.

### The Orciatico analogue

The site near the village of Orciatico has previously been the focus of research into the effects of heating upon mudrocks (Leoni *et al.*, 1986). In brief, it consists of a laccolith-shaped intrusion into Pliocene marine clays and lies on the flanks of a small hill at approximately 260 m above sea level. The intrusion is irregular in plan, but is approximately 1 km across. Preliminary geophysics, and the lack of extensive heating to the surrounding mudrocks, suggest the presence of only a limited mass of igneous material (i.e. a relatively thin laccolith).

Five boreholes were drilled by Ismes S.p.A. into the mudrocks at increasing distances from the exposed contact with the intrusion. Three of these cores were sampled and porewaters extracted by squeezing for chemical analysis. Borehole I5 (260 m elevation, 20 m depth, 40 m from the intrusion) was the only one of these boreholes to encounter igneous rock. Borehole I2 (180 m elevation, 7 m depth, ~1000 m from the intrusion) was furthest from the intrusion, and Borehole I1 (250 m elevation, 50 m depth, 150 m from the intrusion) lay between Boreholes I2 and I5.

### Extraction of porewaters and analysis

Sections of drill core were preserved on site by wrapping in foil and placing in tightly fitting plastic tubes with the ends sealed in wax. On receipt, the cores had their wrappings carefully removed before trimming and being placed in a hydraulically-driven press for several days to extract samples of porewater (Entwisle and Reeder, 1993). From an initial mudrock sample of 500–800 g, approximately 20–90 g of porewater could be recovered. These porewaters were then analysed for major and trace cations by inductively-coupled plasma optical-emission spectroscopy, for anions by ion chromatography. They were also analysed to determine their  $^1\text{H}/^2\text{H}$  and  $^{16}\text{O}/^{18}\text{O}$  ratios.

### Results and interpretation

Profiles of changing pore fluid chemistry with depth were constructed and a limited number of the more important profiles are given in Fig. 1. Several key observations can be made from these profiles:

All the present porewaters are much more dilute than the original porewater (seawater).

Analyte concentrations at the surface are much greater than at depth.

Concentration gradients appear to resemble diffusion profiles.

Conservative analytes (e.g. Na, Cl, stable isotopes) show a series of approximately parallel concentration profiles, one for each borehole. These appear to show a relationship to local topography.

More 'reactive' analytes (e.g. Ca, Mg, K, Al,  $\text{SO}_4$ , etc.) show just a single type of concentration profile and no relationship to local topography.

Two of the deeper samples from borehole I5 show significantly different porewater chemistry to their neighbours.

Porewater chemistry does not appear to show changes resulting from intrusion of the nearby laccolith.

A preliminary interpretation of these results is:

Local rainwater has infiltrated the clays to a depth

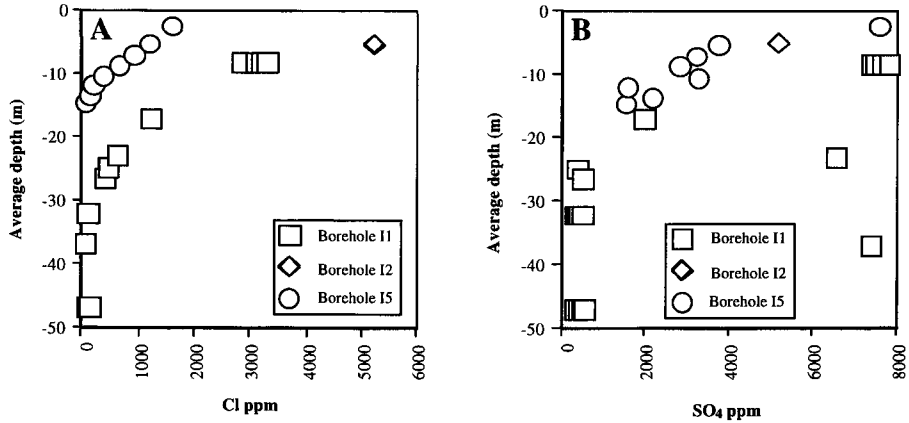


FIG. 1. Profiles of changing concentrations of: A) Cl and B) SO<sub>4</sub>.

of >50 m displacing the original saline porewater. The depth to which the fresh/saline water boundary has reached is unknown. This process has also removed any trace of changes in pore fluid chemistry as a result of heating by the intrusion.

As surface water migrates downhill, evaporation causes a gradual increase in solutes (e.g. Na, Cl) resulting in higher concentrations associated with the top of Borehole I2 compared to Borehole I5. Thus for several fixed points at the surface, diffusion into the clay would result in a series of approximately parallel concentration profiles.

Oxidation of pyrite in the clay at the surface increases acidity (and hence SO<sub>4</sub>). This happens equally for all parts of the analogue site and hence shows no relationship to topography, just a single concentration profile.

Carbonate ( $\pm$  silicate) dissolution neutralises any acidity, but causes an increase in elements such as Ca, Mg, K, Al, etc. These also show no relationship to topography, just a single concentration profile.

The unusual chemistry for two of the deeper samples in Borehole I5 may reflect pyrite-rich horizons, or more permeable regions conducting fluid from a different part of the system.

Diffusion of solutes into the clay gives rise to the observed profiles, from which it may be possible to determine transport (diffusion) properties of the bulk rock.

The derivation of bulk rock (10s of metres in size) transport properties will be of benefit in better understanding the migration of contaminants (including radionuclides) within mudrocks.

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### References

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