Use of stable chlorine isotopes to evaluate the origin of a Cl-rich plume in the Oxford Clay, England

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In low-temperature, aqueous settings, chlorine is generally a non-reactive and therefore conservative element. Other than during fractional crystallization/ dissolution of salts, significant fractionation of stable chlorine isotopes has been attributed to various solute transport processes through a fine-grained medium; in particular, ion filtration during passage through a clay (Campbell, 1985; Phillips and Bentley, 1987) and diffusion (Desaulniers *et al.*, 1986; Eggenkamp and Coleman, 1997).

To further investigate processes by which chlorine stable isotopes can be fractionated in low-temperature, fine-grained systems, we have performed analyses on groundwater and leachate samples collected from within and around a landfill in the Jurassic Oxford Clay in Bedfordshire, England. To characterise the isotopic effects of relevant processes we have conducted ion exchange/adsorption experiments in the laboratory.

Geological setting

Bedfordshire is located in central England, in an area which has a history of clay quarrying from the Oxford Clay. The landfill that is the focus of this study, Brogborough, was originally an open clay pit and became a landfill in the late 1970s. Groundwater monitoring boreholes have been in place around the landfill and in the surrounding Marston Vale area since the early 1990s. Chemical analyses from groundwaters and waste leachates (i.e. aqueous fluids collected from wells within the landfill) have been sampled over the last six years by Shanks and McEwan; stable chlorine isotope analyses obtained for this study span the period between November 1996 and January 1998.

Results

The nine leachate samples analysed have measured $\delta^{37}Cl$ values between −0.4 and 0.0‰ relative to a mean ocean chloride standard. There is no clear relationship between Cl^- concentrations and $\delta^{37}Cl$ for these samples (Fig. 1).

The groundwaters collected from boreholes located immediately around the perimeter of the landfill at Brogborough have $\delta^{37}Cl$ values between +0.4 and +1.6‰. Chlorine stable isotope compositions correlate with chloride concentrations.

Groundwater sampled further from the landfill, 0.5 km to 2 km away in the Marston Vale, have Cl isotope compositions between +0.8 and +1.1‰. The Marston Vale isotope values fall within the range of the Brogborough isotope values (Fig. 1). Both adjacent to and further away from the landfill/pit, it is the groundwaters containing higher Cl- concentrations that have the larger $\delta^{37}Cl$ values. The higher concentrations are found down-gradient from the landfill/pit, which therefore appears to be the origin of the Cl-rich plume.

Within the groundwater determinand sets, there are correlations between various solutes. Specifically, chloride concentrations are positively correlated with sodium and bromide, while calcium and magnesium are positively correlated to sulphate concentrations.

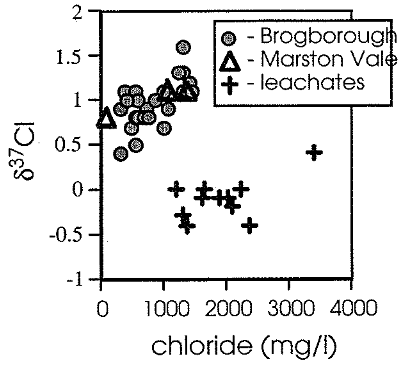

FIG. 1. Chlorine isotope values and chloride concentrations from Brogborough, Marston Vale and landfill leachates.

Both the chloride and sodium are negatively correlated to calcium, magnesium and sulphate. All correlation coefficients have values that are greater than the 99% level of significance. Additionally, chloride concentrations were plotted against millimetres of monthly rainfall. Sharp peaks of elevated chloride concentration found in some of the Marston Vale wells coincide with periods of relatively high rainfall.

Apart from sodium and chloride, no correlations were found between any of the solutes in the landfill leachate samples.

Experimentation

Measured $\delta^{37}Cl$ values from other studies range between -5 and $+2$‰ in low-temperature aqueous systems. Experimental work has shown that diffusion produces ^{37}Cl-depleted porewaters (relative to ocean chloride) by as much as -4 ‰ (Eggenkamp and Coleman, 1997), while ion filtration in a clay may produce an enriched fluid with $\delta^{37}Cl$ values up to $+1.7$‰ (Campbell, 1985).

Ion exchange experiments have been conducted, using both cation and anion exchange resins, to determine the degree to which stable chloride isotopes are fractionated. Because of the relatively small difference in atomic mass between ^{37}Cl and ^{35}Cl, cation exchange, and the subsequent adsorption/desorption of chloride to maintain a charge balance in the solution, did not produce any noticeable $^{37}Cl/^{35}Cl$ fractionation in the elutants (Loomis *et al.*, 1997). In preliminary anion exchange experiments, however, $^{37}Cl/^{35}Cl$ fractionation has been found to be quite large. A 0.5 M KCl solution was passed through a column containing an Amberlite anion exchange resin in the hydroxide form. Upon breakthrough, the isotopic composition of the initial elutant was $+4.7$‰ relative to the original KCl solution. After breakthrough, the subsequent decrease in the elutant $\delta^{37}Cl$ value matched the rate of increase in the chloride concentration.

Discussion

Both stable chlorine isotope compositions and plots of elements and element ratios from groundwater and leachate samples indicate that the groundwaters are distinctly different from the landfill leachates. If the chloride is not coming from within the landfill, then what could be its source? The fact that the groundwaters in the Cl-rich plume contain positive $\delta^{37}Cl$ values is noteworthy, because most porewaters from low-temperature sedimentary environments have negative values (Eggenkamp, 1994). Based on other studies and our recent experiments, there are three ways to produce ^{37}Cl-enriched porewaters: 1) dissolution of a ^{37}Cl-enriched salt or evaporite without diffusional transport, 2) ion filtration, and 3) anion exchange. It is difficult even to speculate on how important a process ion filtration is or was within the Oxford Clay. Anion exchange, however, can reasonably account for the elevated $\delta^{37}Cl$ values around the Brogborough landfill and in the Marston Vale groundwaters. The correlations found between various solute concentrations within the Cl-rich plume outside the landfill imply the operation of a process involving both sulphate and chloride. In the Oxford Clay this process could be the weathering of pyrite, which can produce very low pH. In the Brogborough and Marston Vale areas, extensive weathering has occurred where the Oxford Clay has been exposed at the surface. Under acidic conditions, anion exchange is facilitated between a clay and porewater. The amount of anion exchange that occurred would have been dependent upon the amount of carbonate material present in the sediment, which in turn would have controlled the extent to which the solution pH was buffered. Rainfall may also play a role, given that plots of chloride versus bromide suggest linear mixing between more dilute and more concentrated groundwaters. Together, anion exchange, the subsequent adsorption/desorption of cations to maintain charge balance between solids and solution, the saturation index with respect to gypsum, and the admixture with freshwater could account for the trends seen in the Brogborough and Marston Vale groundwaters, and the presence of the Cl-rich plume.

The results from this study to date show that stable chlorine isotopes, used in conjunction with other geochemical parameters, can provide important insights regarding the origin and transport of solutes. Continued experimentation and geochemical modelling will help to elucidate more clearly what processes produced the various geochemical trends within the Cl-rich plume and to test our hypothesis for its origin..

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