Water Rock Interaction [WRI 14]

Investigating recharge through a glacial till using sulphur and strontium isotopes: an example from East Anglia, UK

W.G. Darling\textsuperscript{a*}, D.P.F. Darbyshire\textsuperscript{b}, T.H.E. Heaton\textsuperscript{b}

\textsuperscript{a}British Geological Survey, Maclean Building, Wallingford OX10 8BB, UK
\textsuperscript{b}NERC Isotope Geosciences Laboratory, Keyworth NG12 5GG, UK

Abstract

As a result of Pleistocene glaciations, many parts of the UK have a covering of glacial sands, gravels or clays. Where such deposits overlie aquifers, recharge may be impeded. This paper describes the use of sulphur and strontium isotope ratios to determine recharge routes through a thick boulder clay (‘till’) overlying the Chalk aquifer in a part of eastern England, UK. Sulphur isotopes show that two possible sources of S may be contributing to the recharge, but strontium isotopes are more definitive, indicating most interaction is with the unweathered till.

© 2013 The Authors. Published by Elsevier B.V. Selection and/or peer-review under responsibility of the Organizing and Scientific Committee of WRI 14 – 2013

Keywords: Chalk aquifer; recharge; till; sulphur isotopes; strontium isotopes

1. Introduction

The Chalk, a very fine-grained limestone with well-developed fracture porosity, is a principal UK aquifer. In eastern England, it is typically covered by glacial deposits including sands, gravels and clays. Where there is till (boulder clay), aquifer recharge is impeded. It is important for water management that the mechanism of recharge through thick tills is well-characterised. While the basic chemistry of waters provides some evidence of the processes involved, questions remain that are more appropriate to an isotopic approach. The study reported here has been carried out in East Anglia, eastern England (Fig. 1a).

Chalk groundwaters beneath thick till have similar major ion chemistry to the overlying till porewaters in the surficial unoxidised zone [1]. These Chalk groundwaters, which have elevated Sr/Ca ratios and negligible tritium and nitrate, are interpreted as being mostly derived by slow leakage through the till. However, the presence of CFCs in the groundwaters [2] indicates some modern (rapid) recharge by flow.

* Corresponding author. Tel.: +44-(0)1491-692326; fax: +44-(0)1491-692345.
E-mail address: wgd@bgs.ac.uk.
presumably through discontinuities in the till, or via the till sheet edge [1, 2]. Accordingly, the rapid flow component of recharge should have similar isotope characteristics to the water in the shallow, oxidised till zone, while the slow flow component will have similar characteristics to the unoxidised till because there is sufficient time for interaction between recharge and porewaters in the unoxidised zone. By comparing these ‘end members’ with the Chalk groundwater it should be possible to identify which recharge route predominates. Two isotope ratios, $\delta^{34}$S and $^{87}$Sr/$^{86}$Sr, were chosen to investigate and evaluate this.

2. Results and discussion

Data have been obtained from leachates, groundwater and rock samples collected from a research borehole (CW1) drilled through about 40 m of till overlying 40 m of Chalk at Cowlinge, Suffolk, East Anglia, UK (Fig. 1b; location in Fig. 1a).

Unoxidised till water leachates have high concentrations of SO$_4$ with a distinct negative $\delta^{34}$S value between $-30$ to $-25\%$ (Fig. 1b), almost certainly derived by oxidation of reduced S in the till. Residues of leached unoxidised till samples were analysed for total S by elemental analyser, and yielded about 1% total S with a $\delta^{34}$S value close to $-30\%$, values comparable to data reported for the Kimmeridge Clay in NE England, where total S contents up to 3% (mainly pyrite) and $\delta^{34}$S values between $-35$ and $-12\%$ have been reported [3, 4]. Fractionation accompanying oxidation of reduced S to SO$_4$ is small [5]. Oxidation of reduced S with $\delta^{34}$S of $-30\%$, as found in the unoxidised tills, would therefore yield SO$_4$ with a similar $-30\%$ value. Water leachates from oxidised till tended to have lower SO$_4$ concentrations, and quite variable $\delta^{34}$S values, $-27$ to $+2\%$. However, the $\delta^{34}$S values were almost always higher than those of the unoxidised till, median water leachate $\delta^{34}$S values being about $-16\%$ in the oxidised till, and $-29\%$ in the unoxidised till. The reason for this difference is not known. If alterations occurring during the oxidation of the till included processes for SO$_4$ reaction involving kinetic isotope fractionation (e.g. most bacterial reactions), favouring reaction of $^{32}$S, the residual SO$_4$ would display an increase in $\delta^{34}$S values similar to that observed.
Alternatively, higher values in the oxidised till might simply reflect a greater proportion of \( \text{SO}_4 \) of surficial origin. Thus \( \text{SO}_4 \) from atmospheric deposition in non-coastal areas of the UK probably has \( \delta^{34}\text{S} \) values in the range +2 to +6‰ [6, 7], and \( \text{SO}_4 \) derived by oxidation of organic matter in soils may also be expected to have \( \delta^{34}\text{S} \) values between about 0 to +10‰. Water leachates from the Chalk yielded low concentrations of \( \text{SO}_4 \) with low \( \delta^{34}\text{S} \) values, from −28.1 to −19.7‰, similar to those of the overlying unoxidised tills (Fig. 1b). If reduced S with low \( \delta^{34}\text{S} \) values is present in the chalk, then its oxidation could provide the source of this \( \text{SO}_4 \) from within the chalk itself. Otherwise this \( \text{SO}_4 \) may have been derived from the overlying tills.

The \( ^{87}\text{Sr}/^{86}\text{Sr} \) values of the oxidised till leachates are significantly more radiogenic than those of the unoxidised tills (Fig. 1b). Total dissolution of the residue, after removal of the exchangeable and carbonate fractions, resulted in an \( ^{87}\text{Sr}/^{86}\text{Sr} \) ratio of 0.718616 which reflects the mean composition of the till minerals. Variation in weathering rates of minerals generally leads to differences between the Sr isotope composition of weathered material and that of the host rock. Mixing with atmospheric Sr or a component less radiogenic than the clay minerals, which dominate the till, would result in the intermediate signatures observed in the water leachates. The \( ^{87}\text{Sr}/^{86}\text{Sr} \) ratios of water leachates from the Upper Chalk decrease with increasing depth (Fig. 1b). In CW1 they reach a low of 0.708059 for the Hitch Wood hard ground at 62 m and then appear to increase slightly in the underlying Middle Chalk, probably due to the increasing non-carbonate fraction.

2.2. Acid leachates

The \( \delta^{34}\text{S} \) value of Cretaceous seawater was about +16‰, compared with +21‰ for modern seawater. A component of seawater might exist in the primary porosity of deep, poorly-flushed Chalk [8] but in the present Chalk samples the main form of ‘original’ seawater \( \text{SO}_4 \) will be that substituting for carbonate in the calcium carbonate lattice. Acid digestion of this ‘carbonate associated sulphate’ yielded \( \delta^{34}\text{S} \) values of +15.8 to +17.0‰ (Fig. 1b), consistent with a Cretaceous seawater origin. Since chalk is generally present in the till samples, it probably made the acid-leached till \( \delta^{34}\text{S} \) values higher than those of the water leachates. The acid leachates from the till yield higher Sr isotope ratios than are found within the Chalk leachates. There is a large component of chalk within the till and this may be younger than the Chalk found at greater depth in the boreholes, since comparison with the seawater curve [9] suggests an Upper Campanian age.

The acetic acid leaches of the Chalk dissolve only the carbonate fraction and the resulting \( ^{87}\text{Sr}/^{86}\text{Sr} \) ratio (Fig. 1b) should reflect the isotope signature of the seawater at the time of deposition, provided that there has been no diagenetic alteration. At 73–79 m the Cowlinge borehole penetrates the Middle Chalk [1] and the Sr isotope signature of 0.707399 for core from this depth would be consistent with an early Turonian age [9]. The seawater strontium isotope curve then rises steadily from a minimum value of 0.70728 in the late Turonian to a peak of 0.70783 at the Maastrichtian–Palaeogene boundary according to McArthur & Howarth (2004) [9].

2.3. Groundwater

Data for the till and Chalk groundwaters are plotted in Fig. 2a. The waters had \( \delta^{34}\text{S} \) values ≤ −27‰. Bearing in mind the generally high \( \text{SO}_4 \) concentrations in the unoxidised tills, any water which had interacted with them by passing through would be expected to have \( \text{SO}_4 \) with their characteristic low \( \delta^{34}\text{S} \) value of −35 to −25‰. Therefore, the Chalk groundwaters have either (a) interacted with the unoxidised till; or (b) picked up sulphate with a low \( \delta^{34}\text{S} \) value from the Chalk.

Groundwater strontium isotope signatures lie in the range 0.708076–0.708307, which is less radiogenic than in young Chalk groundwaters, although concentrations of Sr are 5–10 times higher. A plot of the \( ^{87}\text{Sr}/^{86}\text{Sr} \) ratio against depth is shown in Fig. 2b. It is apparent that, even at depth, none of the waters has acquired a chalk isotope signature as displayed by the acid leachates.

The Chalk core was leached with water for ~12 hours and because these leachates have similar isotope signatures to the waters, it suggests that reaction rapidly reaches a relatively steady state. It is possible
that over several thousand years the waters might acquire more of a Chalk signature. If it is accepted that
the older groundwaters are derived from atmospheric recharge permeating slowly through the till, then the
more significant reactions take place with the unoxidised till. Sr and SO$_4$ concentrations increase
dramatically and non-marine-derived Na is high [1], reflecting greater ion exchange.

Fig. 2. (a) plot of $\delta^{34}$S-SO$_4$ versus $^{87}$Sr/$^{86}$Sr for waters from the till and Chalk in borehole CW1, compared to those from the regional
Chalk aquifer; (b) plot of $^{87}$Sr/$^{86}$Sr versus sample depth for groundwaters from the till and Chalk in borehole CW1, compared to
those from the regional Chalk aquifer, and the acid leachates from the borehole core material. $\sigma$ errors for $^{87}$Sr/$^{86}$Sr = ± 0.000010.

3. Conclusions

Recharge to the Chalk aquifer through thick till has been investigated using S and Sr isotopes. $\delta^{34}$S has
shown that Chalk groundwaters have either interacted with unoxidised till, or picked up low-$\delta^{34}$S sulphate
from the Chalk. However, $^{87}$Sr/$^{86}$Sr shows no tendency to approach that of the Chalk derived from acid
leaching experiments, suggesting that the first option is the more probable. This implies most interaction
occurs during percolation of water through the till, in turn indicating that the slow route must very largely
dominate the recharge of the Chalk aquifer, with more rapid routes being quantitatively unimportant.

References

[2] Gooddy DC, Darling WG. Contaminant attenuation through glacial drift overlying the Chalk aquifer in southern East Anglia,
[6] Heaton THE, Sprio B, Robertson SMC. Potential canopy influences on the isotopic composition of nitrogen and sulphur in
[8] Novak M, Bottrell SH, Prechova E. Sulphur isotope inventories of atmospheric deposition, spruce forest floor and living