

$$K_i(T) = (M_i^{n_i+}) / (H^+)^{n_i}$$

Other elements (mainly in anionic form A^-) are “mobile”: their concentration is not constrained by any mass action law, and appears only in the electroneutrality equation, from which the pH of the fluid may be calculated:

$$\sum [n_i \cdot (H^+)^{n_i} \cdot K_i] / \gamma M_i - \sum [A^-] = 0$$

where γM_i is the activity coefficient of species $M_i^{n_i+}$.

On behalf of the phase rule, there are as many minerals involved as controlled elements. Knowing their dissolution constants, the temperature of the fluid and the concentrations of the free elements, it is possible to calculate the overall composition of the groundwater taking into account all the side reactions that occur in the fluid phase, like complexation of metal cations. This is possible with most geochemical codes like PHREEQE (6). Confrontation of the results with the analytical data confirms or invalidates the hypothesis on the water-rock interaction.

3. THE PECULIAR STATUS OF CARBON

Carbon deserves a special attention because the mechanism of the pCO_2 regulation in confined aquifers remains complex. In a series of sedimentary aquifers, the observed pCO_2 - temperature relationship between 10 and 200°C has been successfully explained by the equilibrium of the fluids with a mineral assemblage constituted by calcite, dolomite and a magnesium bearing aluminosilicate (7, 8). Gouze (8) also showed that additional production of CO_2 by the decomposition of organic matter, which occurs in a rather narrow temperature range (80-120°C according to Smith and Ehrenberg, 9), does not change the pCO_2 of the system as it is buffered by the set of minerals. The main problem is to identify and characterise the proper magnesium aluminosilicate, as these phases often have an uncertain stoichiometry and the range of variability of their formation constant can be of several orders of magnitude. For example published values of the formation constant of chlorite vary from $10^{-22.57}$ (10) to $10^{-16.16}$ (Michard, 11). The corresponding pCO_2 , calculated for the above mentioned buffer, lie between $10^{-3.11}$ and $10^{-1.87}$. This last value is consistent with the data we obtained for the Rupelian aquifer. However, as all the waters in this study are in a very narrow range of temperature and as no detailed mineralogical analysis of the silts is available, it is not possible to identify the peculiar Mg-Al-Si phase for this case and to constrain the set of data in this way. Therefore, due to the uncertainty of available data, the inorganic carbon content was fixed in the model.

4. MODELLING THE GROUNDWATERS AT THE MOL SITE

According to these guidelines, a modelling exercise was carried out on the waters of the Boom clay and the deep aquifers. The set of equilibrating minerals was taken according to the mineralogy of the Boom clay and the available information the Ruisbroek-Berg and Lede-Brussel sands or silts: kaolinite, calcite, dolomite, albite, microcline and chalcedony. As an example, saturation indexes for three waters are shown in Table 1.

Table 1: Logarithms of the saturation indexes with respect to the principal mineralogical phases. The sign – indicates undersaturation.

	log K	EI	Oe41C	Me20D
albite	- 19,60	0,46	0,62	0,58
microcline	- 21,60	0,78	- 1,02	0,50
calcite	- 8,47	-0,33	0,07	0,23
dolomite	- 17,02	- 0,91	- 0,05	0,42
chalcedony	- 3,71	- 0,07	0,08	0,09
kaolinite	- 37,77	1,76	1,124	0,19

Independent variables in the model are the temperature and the concentrations of the free elements Cl, S and C (inorganic). pH and concentrations of major cations and silicon are then back-calculated and compared with experimental values.

The principle of the calculation is simple. The concentration of each controlled cation can be expressed as a function of (H^+) and pCO_2 using equations (1) to (6). As the total inorganic carbon concentration is fixed, pCO_2 is also a function of (H^+) alone. [Cl] is an independent variable and so the pH results from requiring the solution to be electrically neutral and the overall composition of the solution can then be calculated. The phase rule is respected: a mineral phase is associated with each regulated element.

The examples in table 2 show a good agreement between calculated and observed values. Calculated carbon dioxide pressures amount to several millibars, which explains that the waters are subject to degassing when decompressed.

Table 2: Modelling the chemical composition of groundwaters of the Mol site. Units are mM for concentrations and °C for temperature.

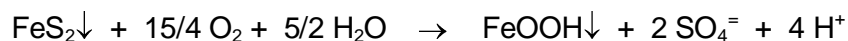
		Independent variables										
		C	Cl	S	t	pH	Na	K	Ca	Mg	Si	Alk.
Boom clay												
	Fixed	12.1	0.5	0.035	17°2							
I. W.	Meas.					8.2	12.4	0.22	0.047	0.071	0.13	12.1
	Calc.					8.54	12.4	0.20	0.047	0.120	0.16	12.3
Ruis.-Berg												
	Fixed	14.5	24.7	0.004	14°5							
Oel 41c	Meas.					7.98	35.9	0.67	0.21	0.47	0.16	14.5
	Calc.					8.16	38.0	0.57	0.13	0.37	0.14	14.8
Mee 20d												
	Fixed	13.3	92.4	4.32	21°3							
	Meas.					7.67	110	0.90	0.67	1.66	0.20	13.3
	Calc.					7.55	109.4	2.10	0.65	1.51	0.17	14.7
Lede-Brussel												
	Fixed	13.2	18.4	0.262	20°4							
Mol 15c	Meas.					8.31	30.3	0.54	0.32	0.41	0.20	13.2
	Calc.					8.08	30.9	0.55	0.13	0.33	0.17	13.5
Ste Por1b												
	Fixed	11.4	36.6	0.90	14°5							
	Meas.					8.28	47.0	0.60	0.35	0.48	0.28	11.4
	Calc.					8.06	48.0	0.72	0.22	0.62	0.14	12.0

In some of the waters of the Lede-Brussel aquifer much higher silicon concentrations than that corresponding to the solubility of chalcedony are observed; it is not well understood why a less stable form of silica is active in the deeper aquifer but this is supported by the observation of clay-opale stones known as porcelanite at the outcrops of the Lede-Brussel sands (12). Considering equilibrium with cristobalite instead of chalcedony for the Ste Por 1b water gives a calculated value of 0.33 mM, quite close to the measured concentration (see table 1).

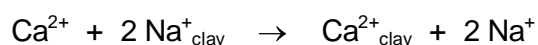
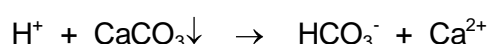
5. MODELLING OF AN OXIDISING PERTURBATION

The interstitial water of the Boom clay was sampled from two piezometers. The water from piezometer N°1 is characterised by a very low SO_4^{--} concentration (0.03 mM), whereas in piezometer N°2 it reaches

10 mM in the first few metres from the gallery. At 15 m, the concentration falls again to 0.1 mM, comparable to that measured in piezometer N°1. This perturbation observed with piezometer N°2 is certainly due to oxidation of the medium during the installation of the tubing. The first piezometer was sterilised at room temperature with formaldehyde, while the second one was sterilised by heating before insertion in the massif, which resulted in oxidation of the pyrite in contact with the hot tubing, air and water. In the pyrite-rich clay massif any oxidation results in a SO_4^{2-} enrichment of the water by the following reaction:



However, the oxidation proceeds gradually and the system is rapidly buffered: sulphate production does not exceed 15 mM and the measured alkalinity remains around 15 mM, while a strong oxidation without reequilibration of the system would produce an acid pH and a drop in the alkalinity equal to twice the sulphate increase. This reequilibration results from the dissolution of calcite and dolomite in the clay combined with ion exchange reactions between the alkaline earths and the sodium fixed on the clay surface:



Consequently, the resulting water contains sodium sulphate and bicarbonate and the pH is buffered at a value close to 8.

7. CONCLUSION

The model was also applied to water sampled from a fault at Tournemire in France (13). The considered mineralogical assemblage was: calcite, dolomite, fluorite, microcline albite, chalcedony and halloysite; the fixed parameters were pH, temperature and the concentration of chloride; for the calculations the geochemical software MINTEQA2 (14) was used. Table 3 also shows a good agreement between calculated values and analytical concentrations. This indicates that the model is not site-specific but can be used in every geological context. Only the input data : dissolution constants of the controlling minerals and values of the independent variables are site-specific.

Table 3: Chemical composition of the water from a fracture at Tournemire, France.

	Independent variables				Na	K	Ca	Mg	Al	C	F	Si
	pH	Cl	t									
Sample GE-2510		mM	°C		mM	mM	mM	mM	µM	mM	mM	mM
	Fixed	8.0	9.3	13								
	Meas.				12.6	0.14	0.37	0.29	0.14	4.4	0.23	0.11
	Calc.				13.0	0.10	0.31	0.39	0.09	6.1	0.24	0.13

Nevertheless some questions that are under investigation in our laboratory and others remain open. As mentioned before the geochemical control on inorganic carbon and its relationship with organic matter is not clear and the identification of buffering minerals can be difficult. Robustness of the model has to be tested and the description of ion exchange on clay surfaces has to be improved, as representations and data available in the literature at the present time are definitely insufficient (15), even if improvements were made in the last decade (16). It is worth reminding that it is useless to have a good model if it is not fed with good experimental data.

6. REFERENCES

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Modelling of water - rock interactions in deep groundwaters: equilibrium and perturbations

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