

4 Geochemical Modelling of Secondary Calcite Formation and Its Composition in Deep Saline Groundwaters – Case Study: Sellafield

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This section describes the work carried out for WP4 of PADAMOT by UK partners Intellisci and British Geological Survey (BGS). The work comprised the simulation of hydrogeochemical processes that are involved in the precipitation of late-stage secondary calcite. Simulations were carried out using batch-reaction modelling with the geochemical speciation and equilibrium computer program PHREEQC2 (Parkhurst and Appelo, 1999) and fully-coupled flow, transport and reaction modelling with the BGS program PRECIP (Noy, 1998) and the Universidade da Coruña program CORE^{2D} (Samper et al., 2000).

The overall purpose of doing the simulations was to mimic the geochemical reactions that might have accounted for precipitation of late-stage calcites and to study the ways that variations in the contents of the redox-sensitive trace elements Fe and Mn in the calcites are related to variations in Fe and Mn in co-existing groundwaters and thus to the redox conditions. The insights gained from this modelling should provide understanding that improves confidence in the interpretations of data acquired in WP2 of PADAMOT. Work was carried out in several stages between early-2002 and end-2004.

4.1 BACKGROUND AND OBJECTIVES

Late-stage secondary calcite as an indicator of palaeohydrogeology has been studied in PADAMOT and the preceding EQUIP project (Bath et al., 2000; Bath et al., in preparation). It has been found that various properties of secondary calcite – the distribution and paragenesis, morphology, compositional variations and isotopic compositions – are indicative of groundwater conditions when the calcite was deposited in the past. Calcite precipitates when various parameters in the chemical composition of groundwater change and affect the speciation and equilibrium so that calcite becomes oversaturated or undersaturated. In shallow ‘immature’ groundwaters, this may happen as primary minerals are altered in weathering reactions and Ca^{2+} ions are released into solution and/or as pH changes due to alteration reactions or the gain/loss of CO_2 . In deep ‘mature’ groundwaters, mixing of waters of different compositions may be a more important cause of calcite precipitation. For example, mixing of waters with different salinities may result in calcite precipitation or dissolution, even though the component waters are at equilibrium. The amounts and properties of secondary calcite thus formed would be potentially useful as palaeohydrogeological indicators.

In the first stage of this project, geochemical modelling has been carried out to investigate the reactions that might account for secondary calcite to be precipitated in both shallow and deep groundwaters. Modelling of a shallow groundwater system is described in the full report of work for WP4 by the UK partners (see Appendix B). Only the modelling of a deep groundwater system is described here, focusing on the specific example from the UK study site at Sellafield where it is believed that precipitation of calcite has occurred when fresh groundwater has flowed to depth and mixed with saline groundwater.

Groundwater compositions change with depth at Sellafield with a sharp increase in salinity occurring at about 300-350 m depth in the centre of the investigated site, where shallow circulating fresh water interfaces with deeper saline groundwater in a ‘Saline Transition Zone’

(Figure 4.1; Richards and Bath, 1997; Bath et al., 2005). It is hypothesised that dispersion and mixing of waters with differing compositions has caused the precipitation of the late stage secondary calcite at Sellafield that has been the subject of detailed studies in WP2 of PADAMOT. This modelling is a test of that hypothesis and sets out to establish a quantitative basis for interpreting the measured properties of the calcite in terms of co-existing hydrochemical conditions. Although the model is set up with data that are specific to Sellafield, the general concept of mixing between groundwaters with different salinities is typical of other sites and the model and approach have generic applicability.

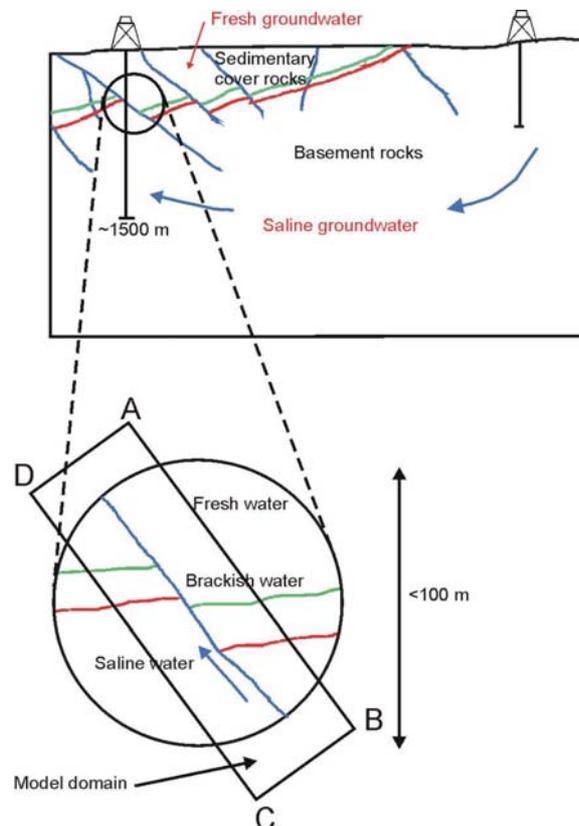


Figure 4.1. An illustration of the mixing between fresh-brackish and saline groundwaters at Sellafield which is believed to be the cause of secondary calcite formation. Sedimentary cover rocks contain fresh-brackish water and basement rocks contain saline water. Waters with different compositions mix by dispersion during groundwater movement which occurs mainly through a network of fractures.

Growth zones in secondary calcites have been detected by cathodoluminescence (CL) and by microprobe analyses in WP2 of PADAMOT. CL is promoted by Mn content and is quenched by Fe content, and its intensity is therefore indicative of Mn and Fe contents and, potentially, of palaeohydrogeological variations in redox conditions. A qualitative relationship between CL and redox fluctuations has been used in various studies (e.g. Fraser et al., 1989; Horbury and Adams, 1989; Lee and Harwood, 1989) and was proposed by Metcalfe and Moore (1997) in a contribution to the EQUIP project.

In the second part of this project, geochemical modelling has been carried out to investigate quantitatively the factors that control Fe and Mn concentrations in groundwaters. These factors are primarily the ambient redox conditions and the identity of the mineral phases containing Fe and Mn. The aim of this modelling is to obtain a more rigorous understanding of the significance of CL zoning and Fe and Mn contents of secondary calcite with respect to past redox conditions in groundwater systems. The approach described here has assumed that Fe:Mn ratios in secondary calcites are the same as Fe:Mn ratios in co-existing groundwater at the time of precipitation. It is proposed that a sound basis for palaeohydrogeological interpretation of

redox conditions is a dual approach of geochemical modelling of Fe and Mn, as developed here, and empirical correlation with other redox indicators in solid phases or fluid inclusions.

4.2 SECONDARY CALCITE GROWTH IN DEEP GROUNDWATERS

4.2.1 Modelling approach and data

Precipitation of secondary calcite has been modelled in a 1D simulation with the PRECIP code. Some of these simulations were replicated using the CORE^{2D} code as a basis for comparing performance and capabilities of the two codes. Then CORE^{2D} was used to model repeated cycles of mixing and reaction as simulations of the development of successive growth zones in calcite. The second stage of geochemical modelling involved using PHREEQC2 and PRECIP to investigate the evolution of water compositions with respect to redox, Fe and Mn thus to evaluate the redox significance of Mn and Fe variations that are indicated by cathodoluminescence and microprobe analyses of the trace element compositions of calcite growth zones.

PRECIP calculates the transport of reactive solutes along a flowpath and allows precipitation and dissolution of the rock matrix to be incorporated using kinetic rate laws, rather than the more common equilibrium formulation (Noy, 1998). This feature can be of particular importance when considering silicate reactions at low temperatures. PRECIP also incorporates the interaction between porosity changes and the groundwater flow, so that, for example, a zone of rapid precipitation may generate flows that tend to push the solutes away from it.

Hydrochemical data representing fresh and saline groundwaters were selected as reference waters from a large data set from earlier Nirex investigations at Sellafield (Nirex, 1997; Bath et al., 2004). Data were selected for depths of 357 and 543 m in Borehole 2 and are shown in Table 4.1. Measured pH data for these water samples are not reliable because contamination by alkaline drilling fluids caused quite large uncertainties in inferred in situ values, so pH was fixed at 7 in both cases and it was assumed that both waters are equilibrated with calcite. This is a reasonable assumption because the groundwaters will have evolved to equilibrium at shallow depths, probably soon after recharge.

Table 4.1. Anion and cation concentrations in Sellafield groundwaters selected for modelling. The fresh water composition is from test DET3 from Borehole 2 (357 m depth) and the saline water data are from test DET10 in Borehole 2 (543 m depth).

Reference water	A: Fresh water	B: Saline water
TDS (mg/l)	259	23060
Assumed pH (see text)	(7)	(7)
Na (mg/l)	86.6	8000
K (mg/l)	5.49	102
Ca (mg/l)	11.7	685
Mg (mg/l)	4.3	82.3
Cl (mg/l)	10	13000
SO ₄ (mg/l)	16.7	1060
Alk (mg/l as HCO ₃)	229	85.9
SiO ₂ (mg/l)	7.4	4.4

The geometrical concept of the simulation is a 1D fracture that traverses a zone of groundwater mixing (Figure 4.2). One or both of the reference groundwaters flows along the fracture, with

possibilities for dispersive mixing within the fracture and diffusive exchange with the adjacent matrix ('dual porosity' type of system). The model runs are shown in Figures 4.3 to 4.7.

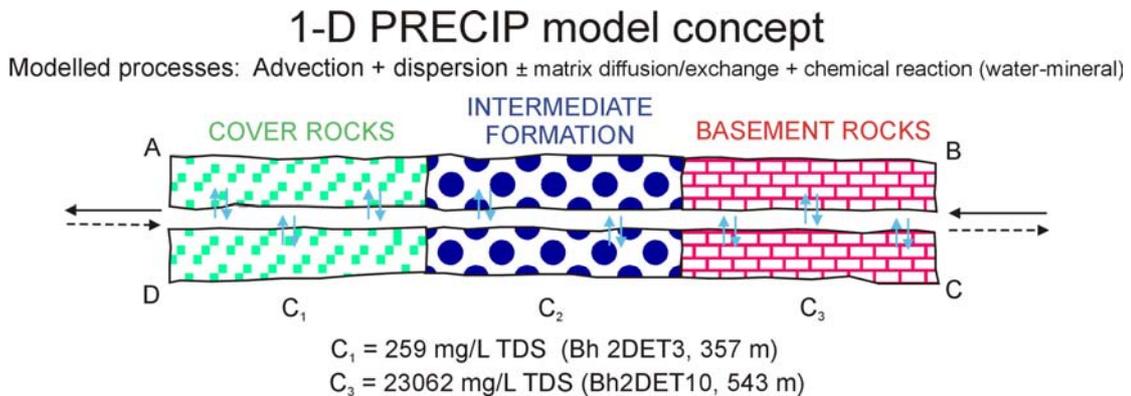


Figure 4.2. Processes and parameters for the PRECIP model of advection-diffusion-reaction in a fracture with an interface between fresh-brackish and saline groundwaters. ABCD refer to the location of this geometrical model in Figure 4.1.

4.2.2 Role of matrix diffusion

The first stage of modelling was to add the process of solute exchange by diffusion between flowing water in the fracture and stationary water in the adjacent rock matrix. These two types of water may have different compositions and thus matrix diffusion is a process that might contribute to calcite precipitation. Figure 4.3 shows calcite precipitating within a fracture as solutes diffuse from saline pore water in the matrix into flowing fresh water. This is a simple simulation of a change of groundwater conditions (e.g. a palaeohydrogeological change of the external boundary conditions that control flow) whereby fresh water invades a part of the system previously occupied by saline water and the composition of matrix pore water changes more slowly than the composition of fracture water. The model shows that the relative amount of deposited calcite decreases with distance along the fracture.

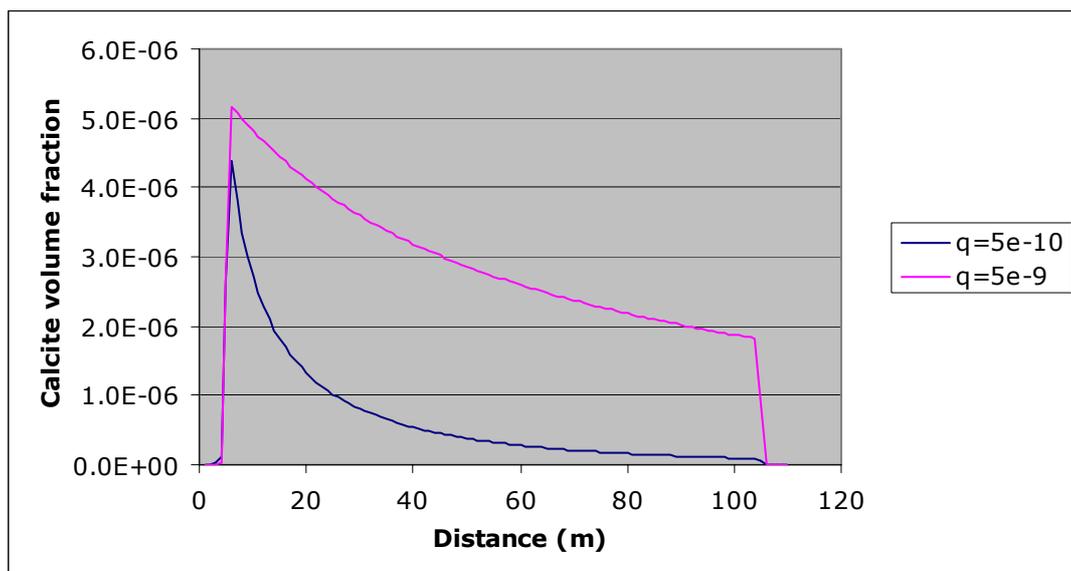


Figure 4.3. Amount and location of calcite precipitated in the fracture as reference water A (fresh) flows from left (0 m) to right (120 m) and reference water B (saline) diffuses in from the matrix. High fluxes through the fracture ($q = 5 \times 10^{-10}$ and $5 \times 10^{-9} \text{ m}^3/\text{s}$) have been used to compress the pattern of calcite precipitation over the 120 m path length.

4.2.3 Calcite precipitation in a fracture

The next stage of modelling was to simulate calcite precipitation in a fracture initially containing fresh and saline waters with a sharp interface. This represents an episode when saline water is displaced by fresh water (or vice versa), displacing the fresh-saline transition downwards. Palaeohydrogeological episodes where this might occur are injection of glacial melt water into deep saline groundwater or of pluvial meteoric water into saline groundwater under arid climate conditions. In the simplest ‘diffusion only’ case, calcite precipitates predominantly on the fresh side of the interface due to diffusion of solutes from saline water (Figure 4.4). When water also moves by advection along the fracture, solute mixing occurs by dispersion with the result that calcite precipitates along the fracture in the direction of water flow (Figures 4.5 and 4.6).

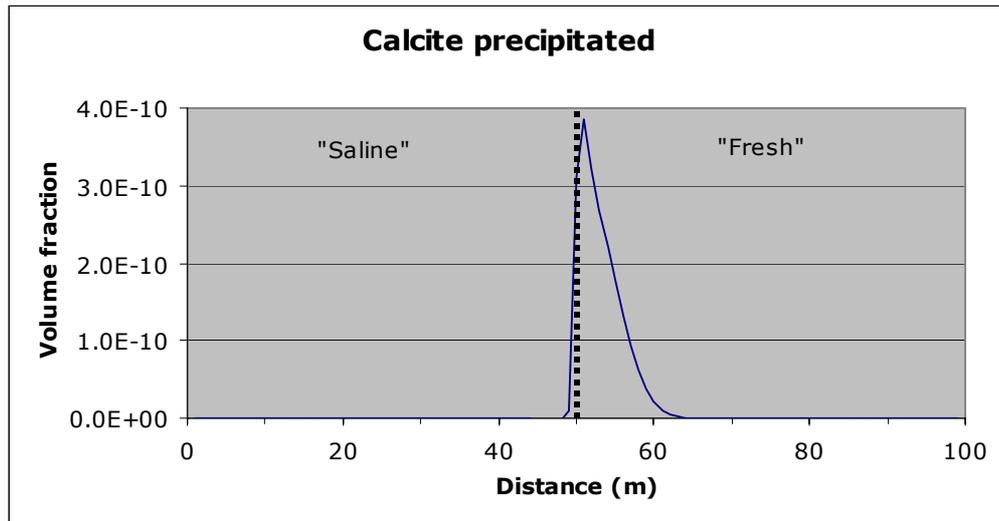


Figure 4.4. Amount of precipitated calcite in a fracture containing static water in which there is a sharp interface at 50 m between reference water A (fresh, on the right) and reference water B (saline, on the left). Calcite precipitates on the fresh water side as in-diffusion from saline water occurs and the saturation index rises above zero ($t = 100$ years).

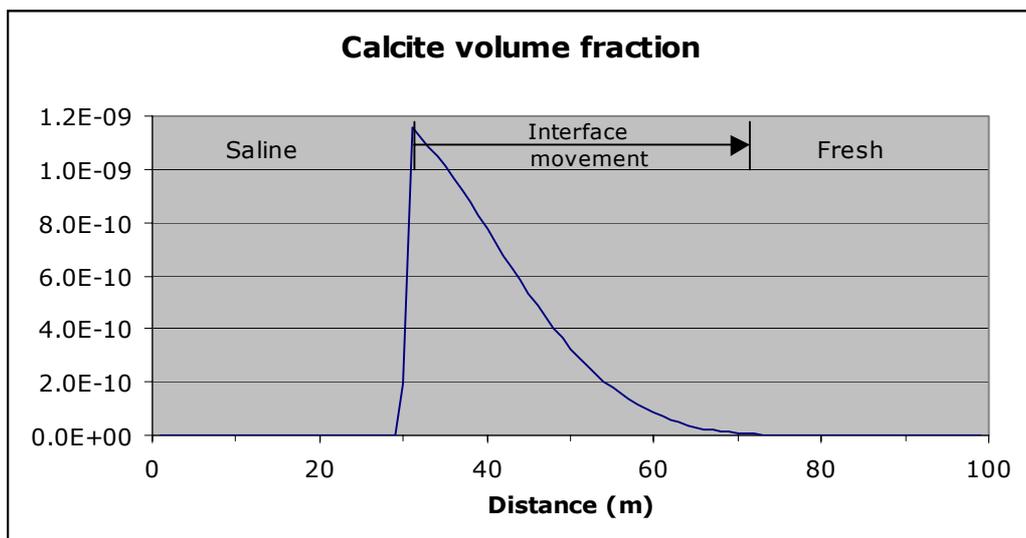


Figure 4.5. Amount of precipitated calcite in a fracture containing water in which there is a moving interface between reference water A (fresh, on the right) and reference water B (saline, on the left). The rate of movement of the interface, or velocity of water in the fracture, is of saline water intruding the fresh water zone at a rate of 40 m in 2×10^8 secs (6.3 years). In addition, there is diffusive exchange ($D_e = 3 \times 10^{-10} \text{ m}^2/\text{s}$) between fracture water and matrix water, the matrix water compositions initially having an interface as in fracture water.

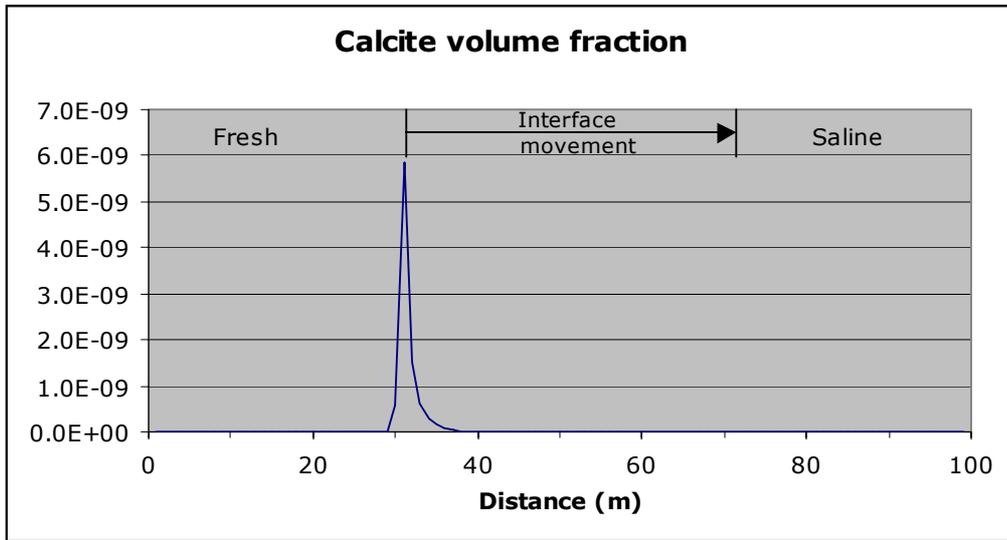


Figure 4.6. Amount of precipitated calcite in a fracture containing water in which there is a moving interface between reference water A (fresh, on the left) and reference water B (saline, on the right). The rate of movement of the interface, or velocity of water in the fracture, is of fresh water intruding saline water at a rate of 40 m in 2×10^8 secs (6.3 years). In addition, there is diffusive exchange ($D_e = 3 \times 10^{-10}$ m²/s) between fracture water and matrix water, the matrix water compositions initially having an interface as in fracture water.

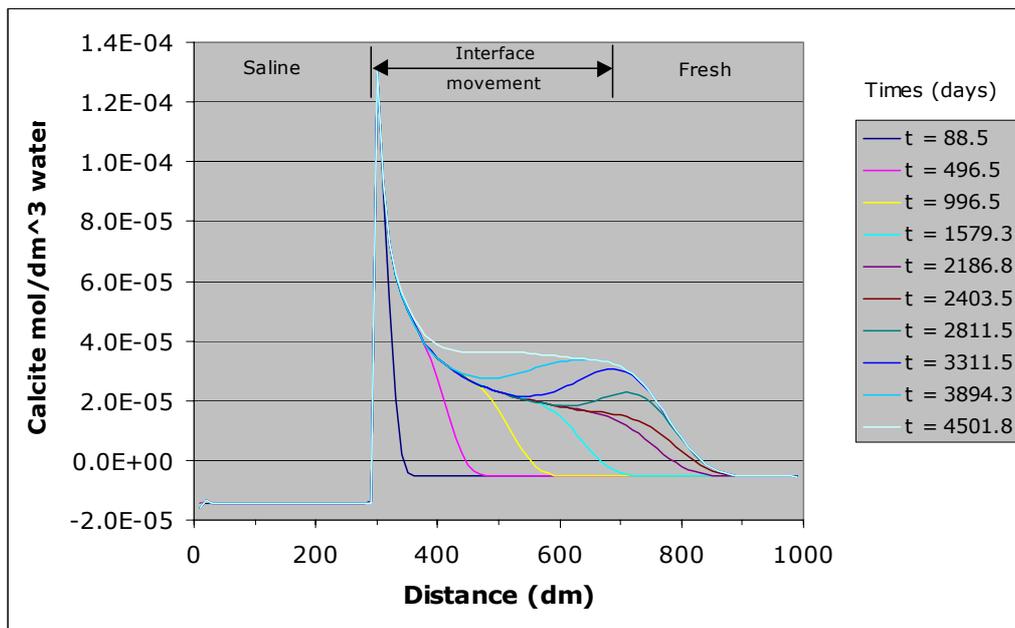


Figure 4.7. Amounts of precipitated calcite (in moles per litre of water) in a fracture containing reference water A (fresh, on the right) and reference water B (saline, on the left) with a sharp interface between them initially, and in which the position of the interface moves 400 m into the fresh water zone and then moves back to its original position, over a period of 12 years. Simulated with CORE^{2D} without matrix exchange.

CORE^{2D} was then used to model a number of oscillations of the interface between fresh and saline waters, simulating the production of discrete growth zones of calcite. Figure 4.7 shows the cumulative growth of calcite in two growth zones, corresponding to the advance and retreat respectively of a saline water front. The amounts of calcite at the end of the advance phase and

at the end of the following retreat phase are illustrated in Figure 4.8. Additional growth zones accumulate as the number of hydrochemical oscillations increases.

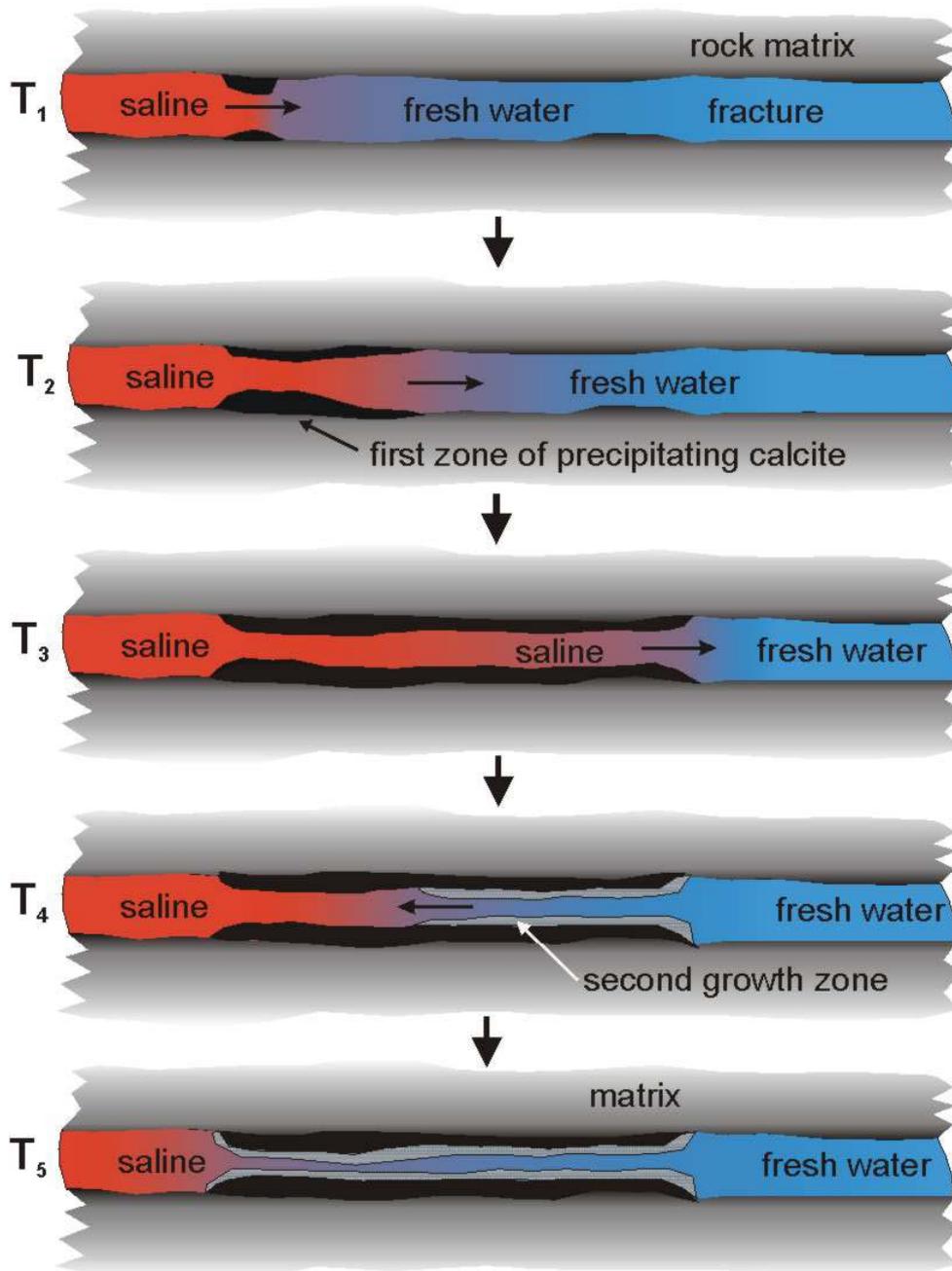


Figure 4.8. Sketch of the amounts of accumulated calcite in the first growth zone, at the end of the saline advance phase, and in the second growth zone, at the end of the saline retreat phase, of a single cycle of hydrochemical oscillation, as modelled in Figure 4.7.

4.2.4 Summary of modelling of calcite growth

The insights gained from modelling hydrochemical processes when mixing occurs in a fresh-saline groundwater transition are summarised as:

- The model is able to simulate the precipitation of secondary calcite as a result of advective-dispersive-diffusive mixing between fresh and saline groundwaters in porous matrices ('diagenetic cementation') and in fractures ('fracture calcite').

- Although it has not been explicitly modelled, calcite dissolution could also be simulated under certain conditions of advective-dispersive-diffusive mixing or by geochemical conditions such as rising P_{CO_2} or sulphide mineral oxidation.
- The amounts and distribution of precipitated calcite in a fracture depend on whether fresh water is advancing into saline water or vice versa, and also on the degree of diffusive exchange with matrix pore water solutes.
- A possible mechanism has been confirmed for the growth of zoned calcites when a groundwater system has temporally-varying water compositions due to the hydrodynamic effects of changes at external boundaries.
- This growth zoning may also be a palaeohydrogeological archive of other changes in hydrochemical conditions. The next stage of modelling simulates the distribution of Fe and Mn into secondary calcite and thus illustrates a mechanism that explains variations of cathodoluminescence between growth zones.

4.3 PAST REDOX FROM Fe AND Mn IN SECONDARY CALCITE

4.3.1 Modelling approach and data

Interpretation of Fe and Mn contents of secondary calcite in terms of redox conditions at the time of calcite growth is based on a number of assumptions about the trace element geochemistry of the calcite-water system. The background and scientific justification for these assumptions are discussed in the following paragraphs.

The first assumption is that when two trace cations such as Fe and Mn substitute into calcite, the ratio of the two cations in calcite will be very similar to the ratio in solution. This is based on the similarity of the nature of Fe and Mn solid solutions in calcite and the low abundances of Fe and Mn relative to Ca, so that the free energies of the solid solutions will be close to that of pure calcite and the activity coefficients of Fe and Mn in the crystal lattice will be very similar.

Various experimental and theoretical studies of trace element distributions between calcite and solution have been carried out. Experimental studies tend to evaluate empirical distribution coefficients, K'_d , e.g. Rimstidt et al. (1998) suggested values of about 97 for K'_d of Fe in $CaCO_3$ and 52 for K'_d of Mn in $CaCO_3$ which suggest that the Fe/Mn ratio in calcite is about 1.86 times the molar Fe/Mn ratio in solution. Theoretical studies have considered whether stoichiometric saturation is an appropriate basis for modelling the equilibrium relationship between mineral and solution. Glynn and Reardon (1990) suggest that, if stoichiometric saturation equilibrium occurs, then Fe and Mn distributions should fractionate between solution and calcite. However experimental evidence indicates that stoichiometric saturation, though it is valid for dissolution, is not an appropriate model for normal precipitation of trace elements into a solid solution (Glynn et al., 1990; Astilleras et al., 2003; Lafon, 1978). One of the reasons for this is that precipitation kinetics are faster than dissolution kinetics with less chance of conditions for reversibility and thus re-equilibration, at the mineral-solution interface. If however re-equilibration should take place, i.e. effectively a dissolution-precipitation process, then the distribution of minor elements such as Fe and Mn would be adjusted according to stoichiometric saturation.

The second assumption concerns the solid phases that control Fe and Mn in the component groundwaters prior to mixing and also during the mixing and consequent precipitation of secondary calcite. There are two alternative models for the evolution of dissolved Fe and Mn in the component groundwaters and the mixed water. One model assumes that Fe and Mn in the component waters are controlled by equilibrium with Fe- and Mn-phases and that the Fe and Mn concentrations of the mixed water are linear combinations of these concentrations. An alternative model is that Fe and/or Mn concentrations in the mixed water are re-equilibrated with

one or more secondary phases, typically pyrite, siderite and rhodochrosite. For example, it is apparent that secondary pyrite has precipitated in at least some growth zones of secondary calcite in Sellafield samples, and therefore it is possible that the co-existing Fe concentration in the mixture and thus in secondary calcite is conditioned by equilibrium with pyrite. In a palaeohydrogeological study of a shallow aquifer using CL in secondary calcite, Barnaby and Rimstidt (1989) assumed that aqueous Fe and Mn were controlled by MnO₂ and amorphous ferric oxyhydroxide and then back-calculated the free energies of formation (ΔG°_f) of the two phases so that Mn and Fe contents from CL indicated consistent redox conditions (Eh).

The modelling approach used here is to construct geochemical models that calculate Fe and Mn concentrations in component waters and in the mixed groundwater from which secondary calcite precipitates, using the programs PHREEQC and PRECIP. The modelling uses the same component water compositions from the Sellafield data set as were used in the first part of this project (Table 4.1). Prior to the model simulation of mixing, each of the component groundwaters is conditioned to calcite equilibrium and is also equilibrated with Fe- and Mn-containing phases to fix the Fe and Mn concentrations (Tables 4.2 and 4.3). In a few model runs, the pH of the fresh water component is fixed by the model so that mixing with a fresh water component with unusually low (to pH 6) or unusually high (to 8.5) pH is investigated.

In summary, these model results show that Fe concentrations in equilibrium with Fe-oxyhydroxide (Fe-ox) are insensitive to pH whereas Mn concentrations in equilibrium with MnCO₃ are more sensitive to pH (decreasing as pH increases). Overall, Fe/Mn increases in these conditions as pH increases, but it remains <1. Fe concentrations in equilibrium with Fe-oxyhydroxide decrease as pe increases, i.e. as redox becomes more oxidising. In these simulations, redox is dependent upon both Fe- and Mn phases with which solution is equilibrated: the general order of oxidising potential is MnO₂ > Fe-oxyhydroxide (more oxidising at lower pH) > FeCO₃, Fe concentrations are highest in equilibrium with FeCO₃, in which conditions redox is reducing, and in this case Fe/Mn > 1.

Table 4.2. Conditioning of fresh water component: Results of PHREEQC modelling of equilibration of reference water A (Table 4.1) with various mineral phases; the pH has also been fixed at values between 6 and 8.5 in some model runs (Eh in mV = pe x 59.1).

Equilibrium phases	pe	pH	Fe (M)	Mn (M)	Fe/Mn
Calcite, Fe-ox, MnO ₂	+8.74	7.59	2.7e-8	1.6e-6	0.016
Calcite, FeCO ₃ , MnCO ₃	-3.21	7.60	3.3e-6	2.3e-6	1.47
Calcite, Fe-ox, MnCO ₃	+1.72	7.60	5.6e-7	2.3e-6	0.25
Calcite, Fe-ox, MnCO ₃	+6.7	6	7.6e-7	6.9e-5	0.01
Calcite, Fe-ox, MnCO ₃	+5.1	6.5	6.2e-7	2.1e-5	0.03
Calcite, Fe-ox, MnCO ₃	+3.5	7	5.8e-7	7.0e-6	0.08
Calcite, Fe-ox, MnCO ₃	+2.0	7.5	5.6e-7	2.7e-6	0.21
Calcite, Fe-ox, MnCO ₃	+0.6	8	5.6e-7	1.3e-6	0.45
Calcite, Fe-ox, MnCO ₃	+0.8	8.5	5.6e-7	8.1e-7	0.70

Conditioning of the saline water component in equilibrium with calcite, FeCO₃ or pyrite, and MnCO₃ gives the range of hydrochemical conditions shown in Table 3. The Fe concentration in equilibrium with pyrite is significantly lower than that with FeCO₃ so that the Fe/Mn is also lower at <0.01, though pe is similar for FeCO₃ and pyrite redox controls. Comparison of model results in Tables 2 and 3 shows that Fe and Mn concentrations in equilibrium with FeCO₃ and

MnCO₃ are dependent on pH (i.e. higher at lower pH), although Fe/Mn remains fairly constant at 1.43.

Table 4.3 Conditioning of saline water component: Results of PHREEQC modelling of equilibration of reference water B (Table 4.1) with various mineral phases.

Equilibrium phases	pe	pH	Fe (M)	Mn (M)	Fe/Mn
Calcite, FeCO ₃ , MnCO ₃	-3.04	7.27	7.4e-5	5.2e-5	1.43
Calcite, pyrite, MnCO ₃	-3.10	7.27	2.2e-7	5.2e-5	0.0042

4.3.2 Geochemical modelling of Fe, Mn and redox

As discussed above, two different approaches were used with regard to re-equilibration of mixed water with a solid phase. In model runs with PRECIP, the Fe and Mn concentrations in the resulting mixtures are not subject to further control except for precipitation of selected minerals. Thus Fe and Mn in the mixed waters are simply linear mixtures of the concentrations in the component waters. In many of the batch mixing-reactions model runs with PHREEQC, the mixed groundwater is re-equilibrated with one or more Fe- and Mn-containing minerals, allowing both dissolution and precipitation in some runs and precipitation-only in other runs.

It is expected that pe and concentrations of Fe and Mn in a mixed groundwater will vary continuously as the mixing proportions between the component waters change. PHREEQC modelling of batch-mixing and reaction has provided some insight into the parameters in mixed waters near to each end of the mixing spectrum (i.e. at ratios of 2:8, 8:2 and 1:1). Reactions during continuous dispersive mixing have also been modelled with PRECIP and PHREEQC in 'transport mode' mode. Graphical outputs from those model runs illustrate continuous variations of pe, Fe and Mn corresponding to the zoned growth of calcite that was modelled in the first part of this project.

A large number of model simulations of mixing between these fresh and saline component waters have been carried out, using PHREEQC (in either batch mixing + reaction mode or transport + reaction mode) and PRECIP. The model conditions and constraints in each case are shown in Tables 4.4 and 4.5.

Table 4.4 Model conditions and results for simulations of mixing between fresh and saline waters using PHREEQC in batch mixing and reaction mode ('B').

Model run	Model Program	Equilibrating phases			Mixed groundwater composition			
		Fresh component	Saline component	Mixed groundwater ¹	pe	Fe (M)	Mn (M)	Fe/Mn
3c	PHREEQC/B	Fe-ox+MnCO ₃	FeCO ₃ +MnCO ₃	1:1 no equilibrating calcite or Fe & Mn phases	+0.4	3.7e-5	2.7e-5	1.37
3d&3e	PHREEQC/B	Fe-ox+MnCO ₃	FeCO ₃ +MnCO ₃	8:2 & 2:8 no equilibrating Fe & Mn phases	+1.3 & +0.4	1.5e-5 & 5.9e-5	1.2e-5 & 4.2e-5	1.28 & 1.42
3h	PHREEQC/B	Fe-ox+MnO ₂	Pyrite+MnCO ₃	8:2 Feox(P)	+3.8	6.6e-8	1.2e-5	0.0056
3i	PHREEQC/B	Fe-ox+MnO ₂	Pyrite+MnCO ₃	2:8 Pyrite(P)	+2.7	1.8e-7	4.2e-5	0.0044
3a	PHREEQC/B	FeCO ₃ +MnCO ₃	FeCO ₃ +MnCO ₃	1:1 FeCO ₃ (P&D)+MnCO ₃ (P&D)	-2.9	3.7e-5	2.4e-5	1.53
3b	PHREEQC/B	Fe-ox+MnCO ₃	FeCO ₃ +MnCO ₃	1:1 FeCO ₃ (P&D)+MnCO ₃ (P&D)	+1.0	3.7e-5	2.4e-5	1.53
3f&3g	PHREEQC/B	Fe-ox+MnO ₂	FeCO ₃ +MnCO ₃	8:2 & 2:8 Fe-ox(P&D)	+1.5 & +1.2	1.5e-5 & 5.9e-5	1.2e-5 & 4.2e-5	1.28 & 1.42
3j&3k	PHREEQC/B	Fe-ox+MnO ₂	Pyrite+MnCO ₃	8:2 & 2:8 Pyrite(P&D)+/-Fe-ox(P)	-3.1 & -3.0	6.7e-8 & 1.8e-7	1.2e-5 & 4.2e-5	0.0058 & 0.0044
3l	PHREEQC/B	Fe-ox+MnO ₂	Pyrite+MnCO ₃	2:8 Pyrite(P&D)+FeCO ₃ (P&D)	-2.8	5.8e-5	4.2e-5	1.40
6a	PHREEQC/B	Fe-ox+MnCO ₃	Pyrite+MnCO ₃	8:2 Fe-ox(P&D)+Pyrite(P&D)	-4.2	2e-3	1.2e-5	165
6b	PHREEQC/B	Fe-ox+MnCO ₃	Pyrite+MnCO ₃	2:8 FeCO ₃ (P&D)+Pyrite(P&D)	-2.8	5.9e-5	4.2e-5	1.4
6c-6h	PHREEQC/B	Fe-ox+MnCO ₃ (fixed pH 6 to 8.5)	Pyrite+MnCO ₃	8:2 Feox(P&D)+Pyrite(P&D)	-3.4 to -4.2	1.9e-2 to 1.7e-3	6.5e-5 to 1.1e-5	293 to 155
6i	PHREEQC/B	Fe-ox+MnCO ₃ (fixed pH 7.5)	Pyrite+MnCO ₃	8:2 FeCO ₃ (P&D)+Pyrite(P&D)	-2.9	1.7e-5	1.2e-5	1.42
6j-6o	PHREEQC/B	Fe-ox+MnCO ₃ (fixed pH 6 to 8.5)	Pyrite+MnCO ₃	2:8 FeCO ₃ (P&D)+Pyrite(P&D)	-2.1 to -2.9	9e-5 to 5.8e-5	5.5e-5 to 4.2e-5	1.63 to 1.38

Notes:¹ P = precipitating, D = dissolving; calcite equilibrates in all model runs; ratio, e.g. 2:8, is proportions of fresh and saline component waters in batch mixing PHREEQC model

Table 4.5 Model conditions and results for simulations of mixing between fresh and saline waters using PRECIP and PHREEQC in transport, mixing and reaction mode ('T').

Model run	Model Program	Equilibrating phases			Mixed groundwater at end of transport simulation			
		Fresh component	Saline component	Mixed groundwater ¹	pe	Fe (M)	Mn (M)	Fe/Mn
4b 14c.obs	PRECIP	Fe-ox+MnCO ₃	FeCO ₃ +MnCO ₃	no equilibrating Fe & Mn phases	-2.8			1.03
4a 14.obs	PRECIP	Fe-ox+MnCO ₃	FeCO ₃ +MnCO ₃	FeCO ₃ (P)+MnCO ₃ (P)	-2.8	1.7e-4	1.6e-4	1.03
4c 16c.obs	PRECIP	Fe-ox+MnCO ₃	Pyrite+MnCO ₃	MnCO ₃ (P)	-3.2	1e-5	1.6e-4	0.06
7a det3-10.rt2	PHREEQC/T	Fe-ox+MnCO ₃	FeCO ₃ +MnCO ₃	FeCO ₃ (P)+MnCO ₃ (P)	-2.8			1.00
7b&7c det3-10.rt4&6	PHREEQC/T	Fe-ox+MnCO ₃ (pH 8 & 6)	FeCO ₃ +MnCO ₃	FeCO ₃ (P)+MnCO ₃ (P)	-2.8			1.00
7d det3-10.rt8	PHREEQC/T	Fe-ox+MnCO ₃	Pyrite+MnCO ₃	Pyrite(P)+MnCO ₃ (P)	-3.2	3e-6	1.8e-4	0.02
7e det3-10.rt9	PHREEQC/T	Fe-ox+MnCO ₃	Pyrite+MnCO ₃	Pyrite(P)	-3.2	3e-6	1.8e-4	0.02
7f det3-10.rt10	PHREEQC/T	Fe-ox+MnCO ₃	Pyrite+Feox+MnCO ₃	Pyrite(P)+MnCO ₃ (P)	-5.1	1.1e-3	1.8e-4	6.2
7g det3-10.rt11	PHREEQC/T	Fe-ox+MnCO ₃	Pyrite+Feox+MnCO ₃	Pyrite(P)	-5.1	1.1e-3	1.8e-4	6.2
7h det3-10.rt12	PHREEQC/T	Fe-ox+MnCO ₃	Pyrite+MnCO ₃	Pyrite(P&D)	-3.2	3e-6	1.8e-4	0.016

Notes:¹ P = precipitating, D = dissolving; calcite is allowed to precipitate in all model runs.

The following paragraphs summarise the possible interpretations of low to high Fe/Mn ratios that are indicated by the modelling results in Tables 4 and 5.

Very low Fe/Mn (0.006-0.004)

Either (a) or (b):

(a) Oxidising water ($pe = +2$ to $+4$) from mixing of a fresh water with redox buffered by Fe-ox + MnO₂ with a saline water with redox buffered by pyrite. The mixed water does not re-equilibrate by dissolution, so redox is dominated by the fresh water component. Fe is very low ($\sim 10^{-7}$ M) due to precipitation of Fe-ox or pyrite. Mn is also low ($\sim 10^{-5}$ M).

(b) Reducing water ($pe = ca. -3$) from the re-equilibration of the mixed groundwater described in (a) above with pyrite which is allowed to dissolve in the model. Fe is very low, as in (a), because of very low Fe ($\sim 10^{-7}$ M) in the oxidising fresh water component and re-equilibration of the mixture with pyrite.

Moderately low Fe/Mn (0.01-0.06)

Reducing waters ($pe = -3.2$) from mixing of moderately oxidising fresh water (Fe-ox equilibrated) with reducing saline water (pyrite equilibrated). Fe is quite low (10^{-6} to 10^{-5} M) due to equilibration with pyrite in the saline component and, in some model runs, also in the mixed water. Mn is higher ($\sim 10^{-4}$ M) and is equilibrated with MnCO₃.

Fe/Mn close to unity (1.0 – 1.6)

Either (a), (b) or (c):

(a) Oxidising water ($pe = 0$ to $+1.5$) from intermediate mixing of a fresh water with redox buffered by Fe-ox with a saline water with redox buffered by siderite FeCO₃. The mixed water may or may not re-equilibrate with FeCO₃. Pyrite is not involved as a reactant mineral. Fe is moderately high at 1.5×10^{-5} M, whilst Mn is quite low at $1-4 \times 10^{-5}$ M.

(b) Reducing water ($pe = -2.8$ to -2.9) in a mixture that is dominated by a saline water with redox buffered by siderite FeCO₃. Fe is high at 3×10^{-5} to 2×10^{-4} M. Mn is between 2×10^{-5} and 2×10^{-4} M, in equilibrium with MnCO₃.

(c) Reducing water ($pe = -2.1$ to -2.9) in a mixture of a fresh water with a saline water with redox buffered by pyrite. The mixture re-equilibrates by dissolution reaction with pyrite. Fe is moderately high at $1-9 \times 10^{-5}$ M.

Moderately high Fe/Mn (~6)

Strongly reducing water ($pe = -5$) from mixing of an oxidising fresh water with a saline water buffered by equilibrium with both pyrite and Fe-ox. The mixed water is allowed to equilibrate with pyrite by precipitation only; dissolution reaction is not allowed in this model. Fe is very high at $\sim 10^{-3}$ M due to the saline component's equilibration with pyrite and Fe-ox. Mn is around 2×10^{-4} M due to equilibration of both components with MnCO₃.

Very high Fe/Mn (150-300)

Reducing water ($pe = -3.4$ to -4.2) in a mixture that is dominated by a fresh water component that is equilibrated with Fe-ox, plus a minor proportion of a saline water component that is equilibrated with pyrite. The mixed water is re-equilibrated with both Fe-ox and pyrite by dissolution reaction. Fe is very high at 2×10^{-2} to 2×10^{-3} M due to dual equilibrium with Fe-ox and pyrite. Mn is $1-7 \times 10^{-5}$ M due to equilibration with MnCO₃ in both component waters.

4.4 SUMMARY OF Fe/Mn IN CALCITE AS A REDOX INDICATOR

The interpretation and models used here have involved many simplifications and assumptions which place constraints and caveats on the validity of this approach. The basic interpretative model assumes that secondary calcite is precipitated as a result of ongoing slow dispersive mixing of groundwaters with different compositions, e.g. typified by a fresh water and a saline water. These component waters are already 'mature', i.e. they are at equilibrium with calcite and dissolved Fe and Mn are in equilibrium with corresponding oxide or carbonate phases or, for Fe, with pyrite. Two alternative geochemical conditions for the mixed groundwater are considered: either that secondary calcite forms without any re-equilibration of the mixed groundwater with Fe and Mn phases, or that the mixed groundwater re-equilibrates with co-existing Fe and Mn phases at the same time as precipitating calcite. A further basic premise is that Fe/Mn ratios in secondary calcites are identical (or at least very similar) to those in the source groundwaters.

A simple assertion for interpreting measured Fe/Mn in calcite might be that low ratios correspond to oxidising conditions whilst high ratios correspond to reducing conditions. Geochemical modelling has shown that the interpretation of redox from variations of Fe/Mn in secondary calcite is not that simple and that Fe/Mn ratios should be considered in the context of geochemical and mineralogical conditions.

Oxidising palaeo-redox conditions could be indicated by very low Fe/Mn (<0.01) or by Fe/Mn close to unity (1.0 – 1.6). The caveat on the former interpretation is that the very low ratio is preserved if the mixed groundwater re-equilibrates with available pyrite and then becomes reducing. Two caveats apply to the latter interpretation. The first is that a similar Fe/Mn ratio (i.e. ~1) can occur in reducing conditions in a mixed groundwater dominated by a component water that is equilibrated with siderite, FeCO₃. The second is that the same Fe/Mn ratio can arise if both saline component and mixture equilibrate with available pyrite. It is clear from these caveats that the possibility of reaction of a component water and/or the resulting mixed groundwater with co-existing pyrite or siderite is an important consideration. This requires knowledge of co-existing mineral paragenesis at a microscopic scale and the exercise of expert judgement in identifying the most likely water-mineral reactions.

Reducing palaeo-redox conditions could be indicated, in addition to those conditions described in the caveats in the previous paragraph, by moderately low Fe/Mn (0.01-0.06) or by moderately high (~6) and very high (150-300) Fe/Mn ratios. The latter two conditions, with high to very high Fe/Mn, arise in groundwaters where precursor components or the mixed water equilibrate with both pyrite and Fe-oxyhydroxide. This seems an unlikely condition in which both Fe^{II} and Fe^{III} minerals co-exist and react, but it is not impossible and may be sensible in groundwaters hosted by rocks with both pyrite and hematite in the mineral assemblage. The first condition, where low Fe/Mn corresponds with reducing conditions, applies where the mixed water has substantial proportions of both the oxidising fresh component (very low Fe) and the reducing pyrite-equilibrated saline component (Fe not so low but not high either). In such a mixture of comparable proportions, the pe of the saline component is sufficient to dominate the pe of the mixture whereas the Fe concentration is quite low.

4.5 CONCLUSIONS AND RECOMMENDATIONS TO R&D GROUPS AND PA GROUPS

The work described in Section 4 and in Appendix B has simulated processes that were possibly involved in the formation of secondary calcites that have been sampled and analysed in Work Package 2. Deep and shallow groundwaters in typical fractured hard rock environments have been modelled. The relationships between geochemical and hydrogeological environments are implicit in the approach to modelling, especially where coupled transport-reaction models have been used. In addition to the general geochemistry of calcite growth, specific modelling has

been carried out to study with the theory behind the interpretation of the Fe and Mn contents of secondary calcites as 'palaeo-redox' indicators. The outcomes from this are summarised in the following:

- It is a plausible hypothesis that secondary calcite in deep groundwater environments has formed due to mixing of groundwaters with varying compositions, typically showing up as varying salinities. Other factors that might also play a part are temperature fluctuation and re-mobilisation or pre-existing carbonate mineralisation. Geochemical models for the formation of calcite (and other secondary minerals) are non-unique and therefore precipitation and dissolution conditions each occupy wide ranges of parameter space.
- Growth of secondary calcite in distinct microscopic zones may be caused by hydrodynamic fluctuations in water movements and compositions plus the influence of matrix storage and exchange. The growth zones therefore are an archive of information about the ambient geochemical conditions when they were deposited. Geochemical modelling provides the framework in which the palaeohydrogeological significance of geochemical and isotopic data can be interpreted.
- A more rigorous theoretical basis for interpreting Fe and Mn contents of calcite, and thus also of cathodoluminescence has been established. The conceptual geochemical models are not unique and involve assumptions about the reactions, water mixing and pre-existing solid phases that control dissolved Fe and Mn, and about how Fe and Mn are distributed between calcite and water. The same approach could be used in principle to assess the significance of other redox- and pH-sensitive trace elements (such as Ce and U), but in reality the thermodynamic base for their calcite-solution distribution is inadequately understood.
- It is an oversimplifying interpretation to assert that low Fe/Mn corresponds always to oxidising conditions and that high Fe/Mn corresponds invariably to reducing conditions. Fe/Mn ratios and cathodoluminescence activity should be considered in the context of co-existing geochemical and mineralogical conditions. Very low Fe/Mn (<0.01) is indeed typical of a mixed groundwater between oxidising component waters, but the low Fe/Mn will have been preserved if the mixed groundwater then re-equilibrates with pyrite and becomes reducing. Moderate Fe/Mn (~1) is typical of perhaps the most usual geochemical system for deep mixed reducing groundwaters in which both saline component and mixed waters have equilibrated with pyrite. A similar condition evolves if siderite instead of pyrite is the redox buffer. High or very high (~6 up to ~300) Fe/Mn ratios may be unusual because they are characteristic of reducing groundwaters in which equilibration with both Fe-oxyhydroxide and pyrite has played a prominent role.

From these outcomes, some recommendations can be passed on to researchers and planners for site investigations:

- It is evident from quantitative modelling as well as from qualitative conceptual models of these geochemical and mineral systems that data and interpretations have substantial uncertainties and non-uniqueness. The implications need to be considered in planning research and site investigations.
- Modelling also makes it clear that robust interpretations are made possible by integration of diverse geochemical and mineralogical data. This means that a comprehensive range of sampling and analytical techniques need to be deployed to obtain distributions and paragenesis, solid solution compositions and growth zoning at microscopic scale, stable isotopic ratios, ages, trace element contents, fluid inclusion compositions, etc for secondary minerals.
- Coupled flow-transport-reaction modelling and geochemical mass budget calculations are valuable for relating geochemical changes to possible palaeohydrogeological flow conditions.

- Conceptual geochemical models for secondary calcite in shallow and deep groundwater systems are distinct, with the former involving open-system weathering in which CO₂ and other direct impacts of climate have important roles. Deep groundwaters involve groundwater mixing and closed system evolution so that the mass budgets for C and H⁺ may limit carbonates and other secondary minerals. It would be valuable in site investigations and in generic research to look more closely at the locations of these two parts of the overall groundwater system. The similarity with the biosphere-geosphere interface needs to be investigated.

The main concerns of PA teams in the context of palaeohydrogeology are with time-varying changes of the groundwater flux and flow direction, chemical environment, and other scenarios that are related to climate or other external environmental changes. The significance of modelling has to be coupled with that of the geochemical and mineralogical measurements at a particular site:

- Palaeohydrogeology provide essential support to the development of scenarios and to consideration of the range of plausible scenarios related to climate and environmental changes. Modelling of the geochemical and hydrogeological processes, especially when coupled together, indicates the potential importance of step changes and thresholds to change in chemical and hydrodynamic properties of a system that are significant to PA. Equally, the ‘asymmetry’ of past and future conditions has to be considered so that palaeohydrogeology does not necessarily define the limitations of scenarios.
- Scientific uncertainties and alternative conceptual models and interpretations are inherent in the application of palaeohydrogeology to supporting scenario developments for PA. Modelling provides a theoretical framework for understanding the scale of these uncertainties. This understanding is particularly important with respect to the interpretative models that are involved in converting proxy data to geochemical and hydrogeological properties of a system and relating these to climatic and environmental variations over time.