The Microbiology of Redox Processes – Development of a Redox Model

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The Microbiology of Redox Processes – Development of a Redox Model

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Foreword

As part of the Environment and Health Theme, the Bio-Tran project is examining microbial effects on transport processes. This report details the influences of microbial activity on redox processes in the subsurface and outlines a generic model approach for further assessing their effects.

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Summary

The work described in this report forms part of the BioTran project, which was initiated to examine the effects of microbes on transport processes, especially in the context of contaminant properties of host rocks. An understanding of these microbial processes is also relevant to other areas such as bioremediation of contaminated land, borehole and reservoir ‘bioclogging’ and microbially enhanced oil recovery. More broadly, these processes impinge on aquifer recharge, pathogen survival, and ultimately on groundwater protection. To date, the project has comprehensively reviewed the available literature and developed methodologies for experimental studies to provide information and data for existing transport models (Bateman et al., 2006; Coombs et al., 2008; West et al., 2008). This report develops this work further by examining the influences of microbial activity on redox processes in the subsurface.

Along with pH, Eh – or the extent to which a groundwater is oxidising or reducing – defines the thermodynamic stability of minerals and dissolved species and hence the solubility and transport of elements and the extent of their interactions with surfaces. Redox gradients or fronts are locations where mineral dissolution/precipitation rates may be high and may also be key locations for colloid formation or destabilisation. Chemotrophic organisations can utilise the energy of inorganic redox reactions for their life processes and hence particularly at fronts, high activity levels may be found.

This report discusses the significance of microbial catalysis in redox reactions in both near-surface and deep geological environments. In near-surface groundwaters, particularly in contaminated aquifers where microbial population densities may be high, the changes in bulk water chemistry as a result of biologically driven redox reactions can be significant. Here the micro-organisms utilise the energy from catalysed exoenergetic redox reactions, effectively coupling inorganic reactions to the production of the energy transport molecules (predominantly ATP) that drive their life processes. In such systems, profiles along the direction of flow show characteristic stepwise development of increasingly reducing conditions as the more reactive oxidants are consumed, this usually results in initial consumption of dissolved oxygen followed by nitrate, Mn(IV), Fe(III), sulphate and, finally, carbonate. For contaminated waters with high loadings of organic carbon, this serves as the predominant reductant.

In contrast, most deep geological environments, especially those being considered for applications such as waste disposal or carbon dioxide storage, are characterised by very low energy fluxes. Unlike the case of contaminated aquifers, the consequences of microbiologically mediated redox reactions in these deep environments may be subtle and build up slowly over very long periods of time. An example is discussed which provides evidence for direct involvement of microorganisms in redox reactions involving oxidation of compacted rock; the rock matrix serving as a substrate for microbial communities that are – albeit very slowly – living off the energy provided by the reactions that they catalyse.

The fundamental redox concept necessary for deep geological environments assumes that the sequence of microbial population groups is similar to that defined in shallow environments. The key difference in a deep system when compared to the near surface, is that the reductants are present in the rock and thus, rather than zones that extend over hundreds of metres or kilometres in aquifers that are defined by the kinetics of redox reactions, zones may be on the scale of mm or cm within oxidation rims of mineral grains or rock matrix and be defined by the kinetics of slow diffusive transport of dissolved oxidants. However, in order to extend the scoping calculations as illustrated in this report, it will be necessary to develop a more rigorous solute diffusion/reaction model that will individually characterise the reactions in the different redox zones. The future model would have three coupled components:
1. A solute transport module, which initially will focus on 1D diffusion from a constant or stepwise variable source but, ideally, should be expandable to 2D with the option to include advective transport

2. A redox profile generation module that identifies the most favourable redox reactions in different zones as a function of solute concentrations and available solid phases.

3. An integrated chemical / microbial reaction module that couples redox reactions with other relevant reactions (e.g. inorganic pH buffering) to quantify changes in solution and solid phases (including biomass) in particular zones. This module also tracks net changes in the porosity of the rock.

In order to support applications that can have significant environmental impacts, the model used would have to be rigorously tested. For example, the siting of a repository for radioactive waste is critical and if a deep redox front is evidence of past intrusion of oxidising water, such an observation may be sufficient to disqualify a potential site. If, on the other hand, such a redox front results from slow buffering reactions by the rock matrix, this can be an indication of a potentially very powerful far-field geosphere barrier. The model must be capable of making predictions that allow these two cases to be distinguished in an unambiguous manner.
1 Introduction

The work described in this report forms part of the BioTran project, which was initiated to examine the effects of microbes on solute transport processes, especially in the context of contaminant behaviour in the geological environment. An understanding of these microbial processes is also relevant to other areas such as bioremediation of contaminated land, borehole and reservoir ‘bioclogging’ and microbially enhanced oil recovery. More broadly, these processes impinge on aquifer recharge, pathogen survival and, ultimately, on groundwater protection. To date, the project has comprehensively reviewed the available literature and developed methodologies for experimental studies to provide information and data for existing transport models (Bateman et al., 2006; Coombs et al., 2008; West et al., 2008). This report develops this work further by examining the influences of microbial activity on redox processes in the subsurface.

In terms of understanding of geochemistry, redox is generally accepted as one of the most important system characteristics. As such, considerable weight is often placed on electrode measurements of groundwater, which produce a single redox parameter – generally presented as an Eh or pe value. On the basis of such measurements, subsurface environments are classified as being either oxidising or reducing, despite the fact that this is clearly a great over-simplification of the disequilibrium between kinetically hindered redox couples that is commonly observed in low temperature groundwaters (as highlighted by Lindberg and Runnells, 1984). This is the case even if only dissolved species are considered; disequilibria with rock minerals may be even more dramatic. Thus, even waters that are considered highly reducing, on the basis of electrode measurements and the presence of indicators such as Fe(II), H₂, CH₄, etc., may also contain significant concentrations of thermodynamic oxidants (NO₃, SO₄, CO₃, etc.) that are kinetically inert and may persist in disequilibrium for geological periods of time.

Despite the lack of the equilibrium, which is sine qua non for application of a single redox value as a system characteristic, the desire to simplify interpretation of groundwater geochemistry is such that electrode measurements are often accepted at face value and, in associated modelling, slow redox couples are simply ignored. It is not evident, however, that such a simplification is always justified even though it is tacitly assumed in most publications and rarely discussed.

Inhibited redox reactions can be readily explained by the high activation energies involved; even if the net reaction is highly exoenergetic, the energy barrier for initiation is so high that it is effectively precluded at ambient temperatures (a classic example here is the coexistence of gaseous H₂ and O₂). Nevertheless, the catalysis of such slow redox reactions by microbes is well known – particularly when the organisms utilise the energy involved to maintain their life processes (chemotrophs).

1.1 RELEVANCE OF REDOX CONDITIONS AND THE IMPORTANCE OF MECHANISTIC UNDERSTANDING

Along with pH, Eh – or the extent to which a groundwater is oxidising or reducing – defines the thermodynamic stability of minerals and dissolved species and hence the solubility and transport of elements and the extent of their interactions with surfaces. Redox gradients or fronts are locations where mineral dissolution/precipitation rates may be high and may also be key locations for colloid formation or destabilisation. Chemotrophic organisations can utilise the energy of inorganic redox reactions for their life processes and hence at fronts, high activity levels may be found. This is particularly obvious where reducing groundwaters come in contact with air, resulting in intensive growth of algal mats as can be seen in caves and mines (Coombs et al, 2008).
An understanding of the past evolution of redox conditions is essential to predict the likely locations of mineral deposits and prediction of the future development of redox is critical to determine the efficiency of many geological disposal concepts. Here “understanding” must include a consideration of kinetics for low temperature systems and hence, if microbial catalysis of specific reactions occurs, this must be explicitly considered.

For example, there is controversy over the interpretation of oxidised regions around fractures in otherwise reduced deep rocks in settings where the conventional explanation of flow of “oxidising” groundwaters is difficult to justify on the basis of hydrogeological principles. One school of thought favours perturbation scenarios that could drive oxidising water to depth (e.g. Akagawa et al., 2006, Lin et al., 2003). Alternatively, such features could represent slow microbial catalysis of the oxidation of reduced minerals by reduction of complex oxyanions.

Under normal circumstances, such academic debate would have little direct relevance to engineering projects but, in cases where sites are being considered for geological disposal of potentially hazardous waste, this becomes a critical issue that could determine the acceptance or rejection of a specific location. The fundamental question here is whether such features are indicators of a vulnerability to perturbations – the most common interpretation at present – or actually represent the consequences of long term buffering reactions involving microbial activity in a currently active flow system. The former case indicates a negative characteristic of the site while the latter could be a very positive attribute with regard to performance of the geological barrier.

Analysis of geological repository performance has, in the past, concentrated on the disposal of radioactive or chemotoxic wastes, but similar concerns could also be envisaged for the containment of other materials. For example, leakage of CO₂ from a geological storage site into a reducing environment could have serious perturbing effects e.g. mobilisation of heavy metals, arsenic and selenium, considerably degrading groundwater quality. An understanding of the vulnerability of a particular geological setting to redox reactions that are significant only when microbi tally catalysed would provide valuable input into decisions surrounding siting of storage projects.

Given this background, this report examines the microbiology of redox processes and will:

1. Describe how redox processes are influenced by microbial catalysis;
2. Illustrate how an understanding of these processes is important in understanding and interpreting information from natural analogues relevant to radioactive and chemotoxic waste disposal;
3. Define the requirements for a generic microbiological redox model.
2 Redox chemistry and the role of microbiology

In any groundwater flow system, an inventory can be defined of all species in aqueous and contacted solid phases that can participate in reactions involving transfers of electrons – i.e. with the coupling of reduction and oxidation “half reactions”:

\[ \text{A} \rightarrow \text{A}^{x+} + x \text{e}^- \]
\[ \text{B} + y \text{e}^- \rightarrow \text{B}^{y-} \]

Expressing the stoichiometry in terms of a single electron transferred, this is equivalent to oxidation of \(1/x\) moles of species A being balanced by the reduction of \(1/y\) moles of B.

In general, redox reactions involving transfer of 1 or 2 electrons (e.g. Fe(II)/Fe(III), Mn(II)/Mn(IV)) are rapid in low temperature (<50°C, say) groundwaters and proceed to thermodynamic equilibrium. In cases where a redox measurement is made with an electrode, the resultant value determined tends to reflect such couples. This contrasts with reactions that involve large numbers of electrons being transferred (e.g. \(\text{SO}_4^{2-}/\text{S}^2-, \text{NO}_3^-/\text{NH}_3, \text{CO}_3^{2-}/\text{CH}_4\)) which can be so slow that lack of equilibrium can persist over geological periods of time and no reaction with sensor electrodes occurs.

It must be emphasised that the fact that a reaction is kinetically hindered does not mean that net reaction is energetically unfavourable (Fig. 1); the high energy required to initiate reaction (which sets the kinetics) may be more than balanced by the energy than the results – again a good example would be the textbook reaction of gaseous \(\text{H}_2\) and \(\text{O}_2\). This is where microbial activity plays a key role; the ability of a very wide range of microbial groups to catalyse such reactions is well known and, indeed, leads to their operational classifications – e.g. sulphate reducers, denitrifiers, methanogens (e.g. Hunter et al., 1998 and references therein).

![Figure 1 Illustration of the activation energy (E_a) and the net free energy production (ΔG°) as a reaction proceeds](image)

In near surface groundwaters, particularly in contaminated aquifers where microbial population densities may be high, the changes in bulk water chemistry as a result of biological redox reactions can be significant. Here the micro-organisms are utilising the energy from catalysed exoenergetic redox reactions, effectively coupling inorganic reactions to the production of the energy transport molecules (predominantly Adenosine Tri Phosphate - ATP) that drive their life processes. In such systems, profiles along the direction of flow show characteristic stepwise development of increasingly reducing conditions as the more reactive oxidants are consumed (e.g. Hunter et al., 1998; Fig. 2); this usually results in initial consumption of dissolved oxygen.
followed by nitrate, Mn(IV), Fe(III), sulphate and, finally, carbonate. For contaminated waters with high loadings of organic carbon, this serves as the predominant reductant.

In deeper systems and less contaminated groundwaters, the predominant reduced species may be present in rock-forming minerals. In such a case, the extent of reaction may be greatly limited by low availability of nutrients that microbes need for growth and the rate of solute transport processes. A typical example of the latter case, when flow occurs in a fractured rock, is illustrated in Fig. 3.

It should be emphasised that, although such interpretation is consistent with the observations that active microbial populations can be found in almost all geological settings to maximum depths of at least 5 km (West and McKinley, 2002) and that oxidised features can be seen in many deep systems where the groundwater is considered to be reducing (Hofmann, 1999), microbial activity is rarely taken into account when geochemical models of such environments are developed. Instead, for cases like deep redox fronts, alternative hypotheses are developed involving a mechanism that, in the past, could have led to oxidising water penetrating to depth. This has led to development of some rather exotic scenarios – including past flows driven by retreating ice sheets, major perturbations from post-glacial marine transgressions and seismic pumping as a result of earthquakes (Fig. 4).

Figure 2 Typical sequence of microbially catalysed redox reactions in a near-surface aquifer (from Hunter et al., 1998)

Figure 3 Microbial catalysis of kinetically hindered reactions as an explanation of deep redox fronts

These two broad explanations of the redox fronts are different in terms of both the redox mechanism and the solute transport processes involved. In the former, the front may still be active, developing only at a very slow rate while the latter assumes that the redox front is a fossil – a record of past perturbation(s) preserved in the rock. Preservation could be due to either the irreversibility of the processes that produce the visual oxidised zone or blocking of access by
later reducing groundwater – either due to sealing of the entire fracture or of the pores allowing access to the matrix surrounding this feature, which may have occurred as a result of the perturbation or later as the system recovered from it.

The focus of the following sections is to examine the extent to which microbially-mediated mechanisms are supported by observational evidence and scoping calculations and then examine the consequences of such processes for various environmentally sensitive applications.

**Figure 4** Alternative hypothesis to explain observed deep redox fronts.
3 Evidence for microbial catalysis of deep redox reactions

Most deep geological environments, especially those being considered for applications such as waste disposal, are characterised by very low energy fluxes. Unlike the case of contaminated aquifers, the consequences of microbially mediated redox reactions may be subtle and build up only over very long periods of time. Consequently, evidence is needed for direct involvement of microorganisms in redox reactions involving oxidation of compact rock; the rock matrix serving as a substrate for microbial communities that are – albeit very slowly – living off the energy provided by the reactions that they catalyse. This can be achieved by examining existing studies of relevant environments. Here, a dataset from a system somewhat nearer the surface is examined: this not only allows better constrained sampling but also allows boundary conditions to be estimated more easily in order to check fundamental feasibility via scoping calculations.

The redox front used for assessing model application is described by Akagawa et al. (2006) and is illustrated in Fig. 5. This particular case has the advantages of being supported by an extensive analytical database.

Figure 5  The redox front established around a fracture in compact granitic rock analysed by Akagawa et al. (2006) (Published with permission of the Geological Society Publishing House).

Although this sharp redox front is distinguished by a marked colour change at about 15cm from the fracture plane, there is little evidence of other weathering reactions in terms of either bulk mineralogy or major elemental profiles (with the exception of some depletion of Ca within 10cm of the fracture and an increase in LOI (loss on ignition) within the visibly oxidised region).

The key trends in terms of trace redox sensitive species are illustrated in Fig. 6. Note, in particular, that total Fe and Fe(II) both show a very marked peak just within the visibly oxidised zone and that evidence of oxidation of Fe (clearly shown by the Fe (III) content) extends far into
the “reduced zone”. It is also clear that total Fe appears to be generally enriched throughout the oxidised zone.

Mn also shows a marked concentration peak, located close to the fracture surface. This contrasts to an apparent depletion in the region 5 – 15 cm from the fracture.

It is not clear, even at 25 cm from the redox front, if there may already be some evidence of Fe oxidation. In any case, around this depth there is clearly oxidation of about 50% of the total Fe. Such very high availability of Fe for oxidation may seem strange, but this is consistent with Fe being associated with minor phases rather than the bulk rock-forming minerals and other evidence for the high bioavailability of Fe from many reduced mineral phases (e.g. du Bray, 1996; Rogers and Bennett, 2004; Weisener et al., 2006). The rock furthest from the front contains predominantly Fe(II). After initial oxidation, a band from about 18-24 cm has a Fe(II)/Fe(III) ratio of about 3/2. This stoichiometry (“Fe₅O₆”) could represent either a slightly oxidised form of FeO or partial oxidation of FeO to magnetite (Fe₃O₄) or some form of ferric oxide/hydroxide.

![Figure 6 Profiles of Fe and Mn through the redox front, from Akagawa et al. (2006).](Published with permission of the Geological Society Publishing House).
When examined in detail, the Fe profile through the colour change front is rather anomalous – with an apparent peak in Fe(II)/minimum in Fe(III) just on the reducing side and the very sharp peak in Fe(III) / total Fe being 2 - 3 cm inside the oxidising zone. As this front moves, the Fe(II) would be oxidised – so that its existence is only transitory, like the secondary pyrite found at the Poços de Caldas redox fronts (West et al., 1992). If it is not an analytical artefact, this implies that some of the initially oxidised Fe(III) is reduced to Fe(II) at this location, possibly driven by the thermodynamic stability of a mineral like pyrite.

The further progress of the front is clearly associated with a significant increase in total Fe – by in the order of 0.1 - 0.2% (total mass) - which occurs immediately at the visible front, accompanied by a major increase in the proportion of Fe(III). This is compatible with oxidation of dissolved Fe(II) from groundwater occurring at this location, along with more gradual oxidation of solid phase Fe(II) – decreasing by about 0.2% over 2 cm. The most obvious oxidant here would be sulphate, although reduction of S(VI) may be incomplete (as observed at Poços de Caldas).

The step increase in total iron is noted to match well the profile of LOI (Fig. 7), indicating that either the Fe(III) product can be readily decomposed on heating (e.g. hydroxide or hydroxycarbonate) or there is also an associated build up in organic material. The presentation of this information involves normalising the changes in concentration to the “undisturbed” rock furthest from fracture (at a distance of 253 mm). The excess in concentration can then be integrated in order to form a basis for mass balance calculations (the excess in % being multiplied by the sampled thickness on the profile in mm). The tabulated data used for these and subsequent calculations (supplied by H. Yoshida) are given in Appendix 1.

Figure 7 Integrated excess of Fe(total), Fe(III) and LOI with reference to the sample at 253 mm.

There appears to be a difference in the relationship between LOI and excess Fe(III) in the visibly oxidised rock and that on the reducing side of the front. This difference is also apparent in the Fe(III)/Fe(II) ratio (Fig. 8), which is significantly less than 1 on the reducing side and either about or greater than one on the oxidising side. Considering only the oxidised side, the integrated excess Fe(III) is around 83 (% mm) whereas LOI is about 33(% mm); i.e. if this represents loss of water from hydrated ferric phases, the loss is about 40% by weight which would require about 2 molecules of water per Fe atom.

Whatever happens directly at the front, there is clearly an important mechanism that gives rise to the dramatic peak in total Fe and Fe(III) at around 13 cm. To build and maintain such a peak in
a moving front, requires either a mechanism for dissolution at the trailing edge of the feature to be coupled to precipitation at the leading edge or actual physical transport of solid phases.

Figure 8  Plot of Fe (III) / Fe (II) ratio as a function of distance from the fracture.

Behind this peak, the Fe profiles are relatively flat until a marked drop of Fe(II) and increase of Fe(III) within a few cm of the fracture surface. Nevertheless, there are indications of some fluctuations within this region, particularly when the Fe(II)/Fe(III) ratio is considered. There is certainly a danger of over-interpreting a single profile, but there could be areas with more reduced Fe around 4 and 10 cm from the fracture. It is thus possible that the redox front may have more complex structure in this zone, possibly associated with various Fe reactions with partially reduced S-species (c.f. roll fronts (e.g. Fig. 15 in Hofmann, 1999) and discussion of S redox states in West et al., 1992). Indeed, banded structures (Liesegang Bands) are often found in diffusion-dominated redox fronts but, in this case, a simple explanation in terms of solubility limits being exceeded during counter-diffusion of solute (e.g. Hofmann, 1999; section 10.1) seems unlikely.

The final main characteristic of the redox profile is the marked Mn peak near the fracture, which appears inversely correlated with the decrease in Fe(II) in this area.

In order to be more quantitative, global constraints set by mass balances need to be established. To simplify conversion between different units, the profile will be normalised to a 1cm$^2$ cross-section with an assumed constant density of 2.7 g cm$^{-3}$ and porosity of 1% and concentrations given in molar units.

For example, the total Fe increase in the visibly oxidised zone is about 0.1% total mass over 15 cm (actually 22 % mm from the data in Appendix 1); i.e. $0.022 \times 2.7 / 160 = 3.7 \times 10^{-4}$ moles of Fe$_2$O$_3$ or about $7 \times 10^{-4}$ moles of Fe if this is considered to represent an integrated supply of dissolved Fe(II) from groundwater.

In the absence of water chemistry from this specific location, a Tono water chemistry derived from granite under mildly reducing conditions will be used (analysis 106 from borehole DH5; Iwatsuki et al., 2001; NB with a regional uplift rate in the order of 0.1–0.3 mm y$^{-1}$, the depth at the time of fracture formation would be 80–240 m deeper than at present). Some key characteristics are summarised in Table 1.

Note in particular in Table 1 that, if the Fe content is appropriate (it seems reasonable), then this immediately implies that the redox front is an old feature as it clearly can only remove a small fraction of the groundwater inventory. If the fracture was 1 mm wide with a flow velocity of 10
m y\(^{-1}\), the water flux per cm would correspond to 0.1 L y\(^{-1}\). Clearly the entire flux cannot be depleted with Fe by the single cm\(^2\) area considered, but total depletion might be assumed over a distance of several 10s to 100s of metres – hence the fractional loss would be somewhere in the order of 0.1 – 0.01%. For 0.1% depletion of Fe, the observed Fe enrichment would require in the order of 3.5 Ma (assuming the redox front forms on both sides of the fracture). In fact, the fracture is estimated to be about 0.8 Ma old. The calculation is only order of magnitude estimation, but is probably consistent with the front being a feature that has been developing since the fracture formed. The “scaling factor” implied here is that the influx of Fe has been the equivalent to the content of 175 litres of groundwater.

Table 1  Tono Groundwater chemistry (analysis 106 from borehole DH5) (Iwatsuki et al., 2001).

<table>
<thead>
<tr>
<th>Parameter</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth</td>
<td>324-331 mbgl</td>
</tr>
<tr>
<td>Temperature</td>
<td>19°C</td>
</tr>
<tr>
<td>Eh</td>
<td>-16 mV (DO bdl)</td>
</tr>
<tr>
<td>pH</td>
<td>7.8</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.01 ppm – 2x10(^{-7}) M</td>
</tr>
<tr>
<td>Sulphate</td>
<td>8 ppm – 8 x10(^{-5}) M</td>
</tr>
<tr>
<td>Carbonate</td>
<td>80 ppm – 1 x10(^{-3}) M</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>0.24 ppm – 4 x10(^{-6}) M</td>
</tr>
</tbody>
</table>

Such a simple scoping calculation puts constraints on the possible mechanisms that can be invoked to front development due to flows of oxidising water. Seismic pumping, in particular, is a transient phenomenon and would seem incapable of generation of the required groundwater fluxes. If groundwater saturated with dissolved oxygen was assumed to be input to the system (in the order of 2x10\(^{-4}\) moles L\(^{-1}\) of O\(_2\)), even though a credible mechanism is difficult to imagine, the extent of oxidation might be explained by rather small fluxes. However, here the supply of Fe is problematic because of the extremely low solubility of Fe under oxidising conditions (typically 1x10\(^{-11}\) to 1x10\(^{-11}\) M). The calculated excess Fe (7 x10\(^{-4}\)moles cm\(^{-2}\)) would require the integrated input from at least 7x10\(^{3}\) L of water; with the minimum fractional depletion of 0.1%, this is equivalent to a flux of 7x10\(^{10}\) L or, for the assumed fracture flow values, an integration time of 7x10\(^{11}\) years! Although the order of magnitude data are inherently uncertain, it is very obvious that oxygenated water cannot explain the Fe excess observed.

In addition to the externally supplied Fe, there is significant oxidation of Fe(II) present initially in the rock to Fe(III); the integrated conversion of Fe(II) is about 80 % mm, equivalent to 3x10\(^{-3}\) moles. The major oxidants in the reference groundwater are clearly sulphate and carbonate. Using the scaling factor of 175 L of water (very simplistic, as the fluxes into the rock will actually be driven by concentration gradients), there is clearly more than enough sulphate (by a factor of about 40) to balance all Fe oxidation as complete reduction of sulphate consumes 8 electrons, as opposed to the single electron supplied by Fe(II) oxidation. This is compatible with the proposal above (and the common observation) that sulphate reduction is incomplete.

Nitrate concentrations are much lower; the scaling of 175 L (very conservative here due to the much smaller penetration depth) would yield about 4x10\(^{5}\) moles. Interestingly, Mn enrichment near the fracture wall amounts to about 5x10\(^{5}\) moles – a number in the right order of magnitude for Mn oxidation to be coupled to the more energetically favourable reaction with nitrate, given the 2 electron oxidation of Mn and the consumption of up to 8 electrons during nitrate reduction.
The simple mass balance calculations can be extended to examine the energy fluxes for microbial growth provided. For example, representing the oxidation of ferrous iron as:

\[
2 \text{FeO} + \text{SO}_4^{2-} + 3 \text{H}_2\text{O} = 2 \text{Fe(OH)}_3 + \text{SO}_3^{2-}
\]  

(1)

\[\Delta G^\circ_r = -158 \text{kJ/mol} \] for all reactants in their standard states (i.e. the reaction is exoenergetic).

For solutes, the activity corrections (effectively representing their concentrations in solution) are important; in this case the correction is: \(RT \log_{10} \log(\alpha_{\text{sulphite}} / \alpha_{\text{sulphate}})\), with \(RT \log_{10} = 5.7 \text{kJ}\) and, at the low concentrations involved, the activities of sulphate and sulphite being effectively equivalent to their concentrations.

If the concentrations of sulphate and sulphite are similar, the correction can be ignored, giving the estimated energy production of 79 kJ/mol of Fe oxidised. The oxidation of \(3 \times 10^{-3}\) moles thus yields about 0.24 kJ. Note that the BGSE model (Baker et al., 1998) uses the conversion of 90 kJ as the energy required to maintain 1g of biomass for 1 year; hence 0.24 kJ is equivalent to 2.6 mg biomass production and maintenance for a year. If microbial activity has been constant over the time since fracture formation, as is implied by the Fe enrichment data, the average production would be in the order of \(3 \times 10^{-9}\) g or a population of about \(2 \times 10^4\) cells per reaction column (using the mass to population conversion from BGSE). If the additional Fe found in the visibly oxidised zone is actually input entirely as Fe(II) – this would increase the available energy/resulting biomass by about 20%.

Although this is an extremely low total population, if active growth occurs only in the vicinity of active oxidation (i.e. concentrated around the Fe peak) and the pore space is very limited, such numbers are not unreasonable. For example, although the data are acknowledged to be rather crude, epifluorescence microscopy counts on core samples from redox fronts at the Osamu Utsumi mine at Poços de Caldas yielded cell numbers in the order of \(10^2 - 10^4\) g\(^{-1}\) rock (West et al., 1992).

Note that this is only one representation of the partial reduction of sulphate. At Poços, for example, there was indication that colloidal elemental sulphur could play an important role. Here the reaction could be written:

\[
6 \text{FeO} + \text{SO}_4^{2-} + 8 \text{H}_2\text{O} + 2 \text{H}^+ = 6 \text{Fe(OH)}_3 + \text{S}(0)
\]  

(2)

For comparison, the oxidation of Fe(II) catalysed by methanogens could be represented as:

\[
8 \text{FeO} + \text{CO}_3^{2-} + 7 \text{H}_2\text{O} = 8 \text{FeOOH} + \text{CH}_4 + 2\text{OH}^-
\]  

(3)

The fermentation of S(0) to produce secondary pyrite on the reducing side of the front could be:

\[
2 \text{FeOOH} + 5 \text{S}(0) + 2 \text{H}_2\text{O} = 2 \text{FeS}_2 + 3\text{SO}_2^{2-} + 6\text{H}^+
\]  

(4)

While, for the oxidation of Mn by denitrifiers, the reaction could be:

\[
\text{MnO} + \text{NO}_3^{2-} + 2 \text{H}_2\text{O} = \text{MnO}_2 + \text{NH}_3 + 2\text{OH}^-
\]  

(5)

Here, however, the free energy of reaction will, in all cases, be sensitive to pH. Although, as a first estimate, a constant initial pH around 8 might be assumed, local production or consumption of protons can give rise to significant changes, particularly if the reactions occur within microbial membranes or biofilms. This is particularly complicated for the case of sulphate reduction, where a very wide range of intermediate S oxidation states between +VI and −II may play a role (cf West et al., 1990 and references therein).

In summary, considering only the strongest oxidants in a nominally reducing water (nitrate and sulphate), the system as indicated in the middle of Fig. 9 could arise – nitrate reducing organisms couple the reduction of N(V) to N(0) (nitrogen gas) or N(-III) (ammonia) to the oxidation of accessible reductants (e.g. Mn(II), Fe(II)) in both groundwater and rock. In this relatively oxidising environment, any sulphide minerals present may also be oxidised to form additional sulphate (which could involve specific S-oxidising bacteria) and also cause a decrease in pH.
Figure 9  Representations of the development of redox front with consideration of the potential role of microbial catalysis of specific redox reactions. Top: starting conditions, middle: reduction of nitrate and sulphate only, bottom: more complex situation with partial S reduction and methanogenesis.
After nitrate is consumed, a further group of organisms dominate under the more reducing conditions under which sulphate can be reduced. Here not only sulphate from groundwater, but also that produced by the previous oxidation of sulphides can be utilised. The reductants in the rock that could be oxidised here include Fe(II) and Mn(II). Note that, as both these elements are relatively soluble in reduced form, such consumption may drive diffusion profiles that lead to depletion of these elements from the reduced side of the front.

In order to examine the behaviour of specific elements, however, the particular complexity of the utilisation of sulphate by microbial populations needs to be taken into account. This has been shown to be important already in natural analogue redox front studies (e.g. West et al., 1990, 1992), where “sulphur bacteria” appear to be associated with pyrite oxidation on the oxidising side of the front, Fe-oxyhydroxide precipitation at the front (in association with Fe-precipitating bacteria) and formation of secondary pyrite on the reducing side of the front (Fig. 9, lower). The initial step of sulphate reduction may thus only involve 2 or 3 electrons (e.g. S(VI) to S(IV) or S(III)) and not only oxidise reduced metals, but also partially oxidise sulphide (e.g. S(-II) to S(0) – colloidal S).

The partially oxidised S species can then be “fermented” by a further microbial group, to result in the secondary pyrite production – possibly coupled to oxidation of methane. The methane is, itself, generated by methanogens under even more reducing conditions. In this case, reduction of carbonate is coupled to oxidation of Fe(II).

Microbes may be directly involved in the precipitation of secondary minerals or may simply provide local microcosms in which such formation is encouraged. In both cases, depletion of the precipitating element from solution can facilitate its diffusive transport to the zone within the redox profile where the microbes involved are most active.

Thus, this conceptual model seems to explain the main observed features of this observed redox front.

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1 Obviously, the degree of oxidation will depend on the precise form of Fe and Mn. For example, reduced Fe in biotite is relatively inactive under low temperature oxidising conditions.
4 Requirements for the development of a redox model for deep geological environments

4.1 THE CONCEPTUAL MODEL

The fundamental redox model assumes that the sequence of microbial population groups is similar to that illustrated above in Fig. 9. The key processes occurring in each of the zones is summarised in Table 2.

Table 2 Reactions associated with particular microbial groups.

<table>
<thead>
<tr>
<th>Microbial group</th>
<th>Reduction</th>
<th>Oxidation</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-reducers</td>
<td>N(V) -&gt; N(0), N(-III)</td>
<td>Mn(II) -&gt; Mn(IV)</td>
<td>Possibly also S-oxidisers (S(-II), S(0) -&gt; S(VI))</td>
</tr>
<tr>
<td>S-reducers</td>
<td>S(VI) -&gt; S(IV), (III), ...</td>
<td>Fe(II) -&gt; Fe(III)</td>
<td>Possibly also partial S-oxidation (S(-II) -&gt; S(0)) Mn(II) solubilised</td>
</tr>
<tr>
<td>Fe-precipitators</td>
<td>Heterotrophs?</td>
<td></td>
<td>Associated with main population of S bacteria on oxidising side of visible redox front</td>
</tr>
<tr>
<td>S-fermentors</td>
<td>(S(0) – S(III)) -&gt; S(-II) + (S(IV) – S(VI))</td>
<td></td>
<td>Possibly also methane oxidation</td>
</tr>
<tr>
<td>Methanogens</td>
<td>C(IV) -&gt; C(-IV)</td>
<td>Fe(II) -&gt; Fe(III)</td>
<td>Occurs on the reducing side of the visible redox front</td>
</tr>
</tbody>
</table>

It should be noted that the strict separation of oxidation and reduction reactions is idealised as, in reality, mixed populations of microbes may form communities with these chemolithotrophs probably supporting a range of heterotrophic organisms (indicated above only for potential iron-precipitating microorganisms).

In the case where the redox front develops in a diffusion-dominated environment, the backdiffusion of the products of redox reactions can be an important source of energy and contribute towards nutrient recycling. Nevertheless, to ensure that energy-accounting is rigorous, it is important to quantify all fluxes between reaction zones. In addition to redox-active solutes, production or consumption of solid-phase materials and changes in water chemistry – in particular pH – must be included in the assessment.

In summary, the model for each particular zone can be represented as in Fig. 10. The supply of reactants to the zone is defined by the flux of dissolved species from neighbouring zones as driven by concentration gradients plus the introduction of new solid phases by the movement of the leading edge of the zone. Similarly, products may be lost by back diffusion or the movement of the trailing edge of the zone. Note that elements directly associated with biomass may be transported along with the movement (taxis) of individual microbes.
4.2 FURTHER REQUIREMENTS OF THE MODEL

4.2.1 Other inorganic reactions

Apart from determining constraints on growth as established by available nutrients or energy sources, changes in solute concentration (which will depend on porosity) must be determined in order to calculate diffusive fluxes. Although not shown in Figure 10, it may also be necessary to include inorganic reactions that may affect labile components (although it is assumed that major rock weathering does not occur, some particular fast reactions may be significant - e.g. those buffering pH changes).

![Figure 10](image)

**Figure 10** Simple representation of the conceptual model for reactions within a specific zone of the redox front characterised by a particular microbial community.

Although the information on major element profiles reported by Akagawa et al. (2006) is, as noted above in section 3, consistent with the idea of a continuous, microbially-catalysed redox front, there are further data that could be used to test this concept. Such testing could involve either examining the ability of the model developed to explain other observations or, more powerfully, documenting blind predictions from the model that could be tested by further measurements.

An example of the former could involve the U data (Fig. 11) for the granite redox profile. The observed peak of U on the reducing side of the visible redox front is consistent with U being associated with the formation of secondary pyrite – as was observed at Poços de Caldas (West et al., 1990; 1992). It is noticeable, however, that there has been a net loss of U from the rock; if concentrations are again normalised to the U in the furthest rock sample (Fig 12), the integral removal of U corresponds to about 17% of the inventory in this profile. By comparison, although the Th profile shows major fluctuations, the net loss of this element is less than 1% of its inventory.

As a reality check, the integrated U loss can be back-calculated into a flux into water advecting through the fracture in the inverse of the Fe gain calculation presented above. The integral loss of 490 ppm mm\(^{-2}\) is equivalent to 0.13 mg U, adding 0.26 mg (from the 2 sides of the fracture) to the effective flux of water (3.5 x10\(^5\) L) past the profile. The net increase in U concentration
would thus be around 0.7 ng L\(^{-1}\) (ppt) – which seems rather high compared to the concentrations typical of such waters (about 20 ppt – JNC, 2000). It is noticeable, however, that (unlike total Fe, for example) the concentration of U in rock varies significantly between the deeper samples. If U loss is normalised to the second-deepest sample, this would reduce the integral loss by almost an order of magnitude (just over 2% overall), which may be more consistent with the assumption that the flux through a 1 cm\(^2\) area should be small relative to measured groundwater concentrations.

Figure 11 Profiles of U and Cs (from Akagawa et al., 2006). (Published with permission of the Geological Society Publishing House).
Figure 12 Profiles of excess U and Th (see text for discussion).

This situation would, however, give rise to further tests of the model – which would be more rigorous, in that the predictions are made blind. For example, it is expected that U isotopic measurements would be consistent with U around the peak corresponding to continuous mobilisation with little direct loss over a timespan in the order of $8 \times 10^5$ y, while the U nearer the fracture would be expected to have a signature representing continuous U loss (see e.g. Mazurek et al., 1996). At the peak, the U would not be associated with Fe(III) oxyhydroxides – but rather secondary pyrite.

Figure 13 Micrograph of “Fe precipitates” in granite pore spaces (Akagawa et al., 2006). (Published with permission of the Geological Society Publishing House).

The form of biogenic pyrite and associated mineralisation (e.g. of U) can be quite characteristic – with framboidal or nodular forms being common. Indeed, the micrograph of “Fe precipitates” presented by Akagawa et al., (2006; Fig. 13) could possibly represent framboidal pyrite that has been oxidised during the preparation of thin sections. This interpretation could be readily tested on samples specially selected and prepared to prevent such oxidation.

Indeed, if the existence of secondary pyrite is confirmed on the reducing side of the front, measurement of stable S isotope ratios in groundwater sulphate, secondary pyrite and any traces of primary pyrite that might be found in unaltered rock would allow a very rigorous test of the
assumed key role of microbial redox catalysis as resulting isotope fractionations are characteristic and unambiguous (e.g. West et al., 1990, 1992 and references therein).

4.2.2 Diffusion into the rock matrix

Another prediction of the model is that the diffusion into the rock matrix is currently ongoing and that this does not represent a sealed fossil system. This could be tested by measuring natural series isotope profiles – particularly of shorter-lived isotopes (e.g. $^{226}$Ra and daughters) – which can provide unambiguous evidence of solute accessibility to the rock matrix.

4.2.3 Role of microbes in formation of deep redox fronts

One other aspect of the model that can be tested – although probably only rather indirectly – would be the assumed role of methanogens in the formation of the “deep” redox front, beyond the visibly oxidised zone. A process of this type would not produce measurable methane in pore fluids, but the integrated accumulation of methane in old crystalline waters may be measurable and isotopically distinct from methane that could arise from other sources (e.g. waters that have flowed through sediments).

4.2.4 Long-term changes in groundwater chemistry

Finally, it is important to check for indicators of possible changes to the ambient groundwater chemistry that would have to be taken into account if a more quantitative model was being developed. Over the period in the order of 0.8 Ma since the fracture formed, uplift may have been significant; the range of 0.1–0.3 mm y$^{-1}$ being typical for Japan (Sasao et al., 2006) which corresponds to a total of 80–240 m. Although, in general, the greater depth of the fracture during its earlier history might strengthen the arguments that the feature does not simply represent surface oxidation, there is also the possibility that waters may have been more saline in the past. In particular, past marine transgressions might have both increased the flux of water but also provided a source with significantly higher oxidant concentration (e.g. sulphate in sea water is around 2700 ppm – over 300 times higher than the reference water considered).

It should be emphasised that, although a period of marine water supply in the past could provide the required flux of oxidant to generate the redox front over a much shorter period, this mechanism fails to explain other characteristics of the profile – in particular the observed excess Fe in the visibly oxidised zone. Indeed, extended marine periods make interpretation of the Fe profile very difficult, as concentrations of Fe are very low in sea water – typically around 3.4 ppb, almost 2 orders of magnitude lower than the concentration assumed in the reference water.

Nevertheless, it may be noted that the profile may preserve fossil indicators of past marine transgression events. One possibility here is iodine, which has been observed to be characteristically high in marine sediments and relatively immobile if fixed by microbial activity (e.g. McKinley et al., 1984). In this case, the extended periods of marine conditions have occurred in the past, high I levels may be found in the areas of higher microbial activity – e.g. around the main Fe peak.

4.2.5 Relevance to transport models

The very simple scoping calculations outlined above simply indicate that the microbial catalysis of the development of a redox front under apparently reducing conditions (i.e. anoxic water which may be considered to be reducing on the basis of electrode measurements) is energetically feasible and that the resultant populations are, in general terms, compatible with those measured under conditions with stronger evidence of a biological role. To go further, however, the different redox reactions that could occur in different zones need to be determined which, as noted above, needs the associated development of a transport model that will allow concentration
of dissolved species to be determined (not only redox active species, but also H⁺/OH⁻ to allow variations in pH to be assessed).

The transport model can probably be represented as 1D diffusion in this case, with either a constant or stepwise variable boundary condition of water chemistry at the fracture surface (the latter being particularly important if there are indications of past marine transients). To identify the redox reactions occurring in particular zones, redox half-reactions can be specified as functions of pH and the concentration of key reactants (e.g. Fig. 14). Note, for example, that the figure indicates that methanogenesis as a result of coupling carbonate reduction to Fe(II) oxidation becomes energetically feasible only at higher pH values. Such analysis allows the energetics constraining microbial growth to be better defined.

Figure 14 Example of the pH sensitivity of some redox half reactions. The potential free energy available by combining a reduction (in blue) with an oxidation (in red) can be read off in units of kJ / mole of electrons transferred (see McKinley et al., 1997 for further explanation).

4.2.6 Conversion factors

The current conversion factors of available energy into biomass/microbial populations is extremely simplistic and could, in principle, be improved by considering possible energy penalties associated with accessing both nutrients and redox active species – particularly those associated with solid phases. Nevertheless, this is a secondary goal for this particular application as, here, it is necessary only to show that the redox-sensitive element profiles and indicators of microbial activity are internally consistent.

4.2.7 Other applications

The model can, as indicated in the previous section, be tested further by expanding the data on the system studied by Akagawa et al. (2006). Additionally, this model should be generally applicable to any low temperature microbiially catalysed redox front – e.g. as found also around fractures in sedimentary rocks (e.g. Mazurek et al., 1996).
For a new case, if the boundary conditions in terms of age of the fracture, water flux/chemistry and chemistry/mineralogy of the undisturbed rock are defined, the model could be used in a fully predictive mode – allowing it to be rigorously tested.

4.3 REDOX MODEL SPECIFICATION

The primary goal of a new model is to extend the scoping calculations outlined in the previous section by developing a more rigorous solute diffusion/reaction model that will individually characterise reactions in different redox zones. This would need to be complemented by extending the database on the analogue system to test more rigorously the applicability of the model. If, as is common in such cases, the model is then shown to be inconsistent with the extended dataset, possible modifications/improvements could then be considered. In any case, if a compatible model can be demonstrated, it could then be further tested with independent analogue data from other relevant redox profiles.

The future model would have 3 coupled components:

1. A solute transport module, which initially will focus on 1D diffusion from a constant or stepwise variable source but, ideally, should be expandable to 2D with the option to include advective transport

2. A redox profile generation module that identifies the most favourable redox reactions in different zones as a function of solute concentrations and available solid phases.

3. An integrated chemical / microbial reaction module that couples redox reactions with other relevant reactions (e.g. inorganic pH buffering) to quantify changes in solution and solid phases (including biomass) in particular zones. This module also tracks net changes in the porosity of the rock.

Fundamentally, the model is similar to past simulations of the thermodynamic constraints on microbial activity but it would aim to be much more realistic in terms of determining the processes associated with individual redox reactions. This contrasts with past models, which only considered a conservative assessment of maximum possible microbial perturbation of the system and thus greatly simplified the representation of the energy sources to the key chemolithotrophic populations.

In order to support applications that can have significant environmental impacts, the model used would have to be rigorously tested. For example, siting of a repository for radioactive waste is very important and if a deep redox front is evidence of past intrusion of oxidising water, such an observation may be sufficient to disqualify a potential site. If, on the other hand, such a redox front results from slow buffering reactions by the rock matrix, this can be an indication of a potentially very powerful far-field geosphere barrier. The model must be capable of making predictions that allow these two cases to be distinguished in an unambiguous manner.

Natural analogue cases will allow model predictions to be tested against observations – in terms of both redox-sensitive element profiles and secondary indicators of microbial activities. As the availability of sample material and the time available for analysis and interpretation may be greater in the analogue case than in an actual site, this can form a basis for establishing priorities for the parameters that, in practice, are the best indicators of the stability or otherwise of a particular hydrogeochemical system.
5 Conclusions

This report has discussed the significance of microbial catalysis in redox reactions in both near-surface and deep geological environments. In near-surface groundwaters, particularly in contaminated aquifers where microbial population densities may be high, the changes in bulk water chemistry as a result of biological redox reactions can be significant. Here the microorganisms are utilising the energy from catalysed exoenergetic redox reactions, effectively coupling inorganic reactions to the production of the energy transport molecules (predominantly ATP) that drive their life processes. In such systems, profiles along the direction of flow show characteristic stepwise development of increasingly reducing conditions as the more reactive oxidants are consumed (e.g. Chapelle, 1993), this usually results in initial consumption of dissolved oxygen followed by nitrate, Mn(IV), Fe(III), sulphate and, finally, carbonate. For contaminated waters with high loadings of organic carbon, this serves as the predominant reductant (e.g. Hunter et al., 1998).

In contrast, most deep geological environments, especially those being considered for applications such as waste disposal or carbon dioxide storage, are characterised by very low energy fluxes. Unlike the case of contaminated aquifers, the consequences of microbially mediated redox reactions in these deep environments may be subtle and build up only over very long periods. An example is discussed which provides evidence for direct involvement of microorganisms in redox reactions involving oxidation of compact rock; the rock matrix serving as a substrate for microbial communities that are – albeit very slowly – living off the energy provided by the reactions that they catalyse.

The fundamental redox concept necessary for deep geological environments assumes that the sequence of microbial population groups is similar to that defined in shallow environments (Hunter et al, 1998). The key difference in a deep system when compared to the near surface, is that the reductants are present in the rock and thus, rather than zones that extend over hundreds of metres or kilometres in aquifers that are defined by the kinetics of redox reactions, zones may be on the scale of mm or cm within oxidation rims of mineral grains or rock matrix and be defined by the kinetics of slow diffusive transport of dissolved oxidants. However, in order to extend scoping calculations (as illustrated in this report) it will be necessary to develop a more rigorous solute diffusion/reaction model that will individually characterise reactions in different redox zones. The future model would have 3 coupled components:

1. A solute transport module, which initially will focus on 1D diffusion from a constant or stepwise variable source but, ideally, should be expandable to 2D with the option to include advective transport
2. A redox profile generation module that identifies the most favourable redox reactions in different zones as a function of solute concentrations and available solid phases.
3. An integrated chemical / microbial reaction module that couples redox reactions with other relevant reactions (e.g. inorganic pH buffering) to quantify changes in solution and solid phases (including biomass) in particular zones. This module also tracks net changes in the porosity of the rock.

In order to support applications that can have significant environmental impacts, the model used would have to be rigorously tested. For example, siting of a repository for radioactive waste is very important and if a deep redox front is evidence of past intrusion of oxidising water, such an observation may be sufficient to disqualify a potential site. If, on the other hand, such a redox front results from slow buffering reactions by the rock matrix, this can be an indication of a potentially very powerful far-field geosphere barrier. The model must be capable of making predictions that allow these two cases to be distinguished in an unambiguous manner.
Appendix 1  Selected analytical data for the profile analysed by Akagawa et al., 2006 (supplied by H. Yoshida).

<table>
<thead>
<tr>
<th>Distance (mm)</th>
<th>T-Fe2O3 (%)</th>
<th>S (%*mm)</th>
<th>Fe2O3 (%)</th>
<th>S (%*mm)</th>
<th>FeO (%)</th>
<th>S (%*mm)</th>
<th>Fe2O3/FeO</th>
<th>MnO (%)</th>
<th>S (%*mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA1-1 0.00</td>
<td>0.925</td>
<td>-0.62</td>
<td>0.78</td>
<td>6.40</td>
<td>0.15</td>
<td>-6.90</td>
<td>5.20</td>
<td>0.133</td>
<td>1.07</td>
</tr>
<tr>
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<td>1.16</td>
<td>0.71</td>
<td>4.56</td>
<td>0.42</td>
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<td>1.69</td>
<td>0.031</td>
<td>0.04</td>
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<td>0.65</td>
<td>5.10</td>
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<td>-4.40</td>
<td>1.63</td>
<td>0.049</td>
<td>0.23</td>
</tr>
<tr>
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<td>1.64</td>
<td>0.65</td>
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<td>-3.87</td>
<td>1.63</td>
<td>0.022</td>
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</tr>
<tr>
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</tr>
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<td>0.89</td>
<td>0.71</td>
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<td>0.43</td>
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<td>0.020</td>
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<tr>
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<td>1.23</td>
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Spreadsheet used for calculations: \( \Sigma \) is the integrated concentration over the separation between two samples normalised to the concentration at 253 mm. \( \Sigma' \) is the same integration, except normalised to the concentration at 234 mm (for U only). \( S1 \) is the integrated normalised content of the profile, while \( S2 \) gives the integrated initial content of the column (assuming that the 253 mm sample is representative) and the net excess in the column as a percentage of this value. \( S3 \) gives the integrated excess (normalised to 253 mm) for samples 1-20, i.e. in the visibly oxidised zone.
References

British Geological Survey holds most of the references listed below, and copies may be obtained via the library service subject to copyright legislation (contact libuser@bgs.ac.uk for details). The library catalogue is available at: http://geolib.bgs.ac.uk.


