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# The importance of conceptual models in the reactive transport simulation of oxygen ingress in sparsely fractured crystalline rock

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ABSTRACT

Redox evolution in sparsely fractured crystalline rocks is a key, and largely unresolved, issue when assessing the geochemical suitability of deep geological repositories for nuclear waste. Redox zonation created by the influx of oxygenated waters has previously been simulated using reactive transport models that have incorporated a variety of processes, resulting in predictions for the depth of oxygen penetration that may vary greatly. An assessment and direct comparison of the various underlying conceptual models are therefore needed. In this work a reactive transport model that considers multiple processes in an integrated manner is used to investigate the ingress of oxygen for both single fracture and fracture zone scenarios. It is shown that the depth of dissolved oxygen migration is greatly influenced by the *a priori* assumptions that are made in the conceptual models. For example, the ability of oxygen to access and react with minerals in the rock matrix may be of paramount importance for single fracture conceptual models. For fracture zone systems, the abundance and reactivity of minerals within the fractures and thin matrix slabs between the fractures appear to provide key controls on $O_2$ attenuation. The findings point to the need for improved understanding of the coupling between the key transport-reaction feedbacks to determine which conceptual models are most suitable and to provide guidance for which parameters should be targeted in field and laboratory investigations.



## 1. Introduction

Several countries are currently investigating the suitability of deep granitic rock formations for hosting repositories for used nuclear fuel. One of the many technical issues that arises is the geochemical stability of these rock environments over extended periods of time (e.g. tens to hundreds of thousands of years) which may encompass major changes in surface boundary conditions due to, for example, glaciation–deglaciation cycles. Considerable attention has been paid to the potential for dissolved oxygen ($O_2$) to invade the subsurface and create oxidizing conditions in the vicinity of proposed repositories (e.g. Glynn et al., 1999; Guimerà et al., 1999; Puigdomenech et al., 2001; Spiessl et al., 2008). The presence of dissolved oxygen may promote corrosion of emplaced waste containers (Glynn et al., 1999), accelerate the instability of some of the engineered barriers (McMurry, 2000), and in the event of repository failure, increase the mobility of radionuclides and metals (Glynn et al., 1999; McMurry, 2000; Puigdomenech et al., 2001).

The ability of granitic rocks, which are typically fractured and contain preferential groundwater flow paths, to mitigate dissolved $O_2$ ingress can be assessed using a number of approaches, including paleohydrogeological studies, natural analog investigations, and reactive transport simulations. These methods of assessment have their related advantages and disadvantages, for example, paleohydrogeological studies may be hampered by a series of issues including those related to obtaining an adequate spatial distribution of solid-phase mineralogical and compositional data (e.g. Glynn et al., 1999), especially if this information is to be obtained along a single

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fracture or fracture network. In addition, uncertainties regarding the magnitude and chemical composition of past groundwater flow in fractures or fracture zones are substantial. Reactive transport models are typically an integral component of such studies because they can aid with the interpretation of paleohydrogeological information, and they provide one of the few means for determining the influence of parameter variability and process significance on the evolution of redox zonation (e.g. Guimerà et al., 2006; Spiessl et al., 2008).

As with any complex system, the conceptual models that are used for reactive transport simulation of redox evolution in fractured crystalline rocks contain simplifying assumptions related to the flow system and to the reaction and transport processes. In many instances the conceptual model for reactive transport is an *a priori* conjecture which is not assessed as part of studies that are focussed on, for example, determining the impact of parameter uncertainty. Table 1 presents a brief comparison of several recent conceptual models for the system under consideration. The models can be broadly categorized as:

I. Equivalent porous medium (EPM) models for the fracture and/or fracture zone (e.g. Glynn et al., 1999),
II. Discrete fracture models with reactive infill or coatings and no interaction with the adjacent rock matrix (e.g. Sidborn and Neretnieks 2008), and
III. Fracture–matrix models in which the fracture and/or matrix may contain reactive minerals (e.g. Sidborn and Neretnieks 2008; Spiessl et al. 2008).

Many recent conceptual models have only considered the presence of one mineral in one location (e.g. infill, coating, or primary matrix mineral). Microbially mediated reactions may also be included in such models and there is field evidence to support a role for microbial $O_2$ uptake near fractures (e.g. Puigdomenech et al., 2001); however, as noted by Sidborn and Neretnieks (2008), microbes are likely to be present only in fractures due to the very small micropores in a granitic rock matrix.

A key question which has arisen when selecting a conceptual model is the accessibility of reduced Fe(II) minerals in intact rock; the very low porosity and potential lack of connectivity in crystalline rock suggests that the effectiveness of molecular diffusion in these formations may be limited. It has proven difficult, for example, to use methods such as X-ray absorption imaging to quantify porosity and diffusion coefficients in samples of unaltered granodiorite because of the very low porosity on the order of 0.5% (Altman et al., 2004). On the other hand, effective diffusion coefficients for intact granitic rocks from the Canadian Shield have been determined *in situ* by Vilks et al. (2004a) and found to be on the order of $10^{-12}$ to $10^{-13}$ $m^2/s$. Because these experiments were conducted in drilled boreholes around which stress redistribution is expected (Vilks et al., 2004a), there remains some uncertainty regarding the applicability of the data for simulating diffusion of $O_2$ from deep natural fractures. In addition, when comparing *in situ* and laboratory-derived effective diffusion coefficients for rocks deeper than 240 m, Vilks et al. (2004b) noted that laboratory results for iodide diffusion in core samples were higher than *in situ* values from boreholes by a factor of 1 to 15. Alteration due to weathering reactions may also affect diffusive solute migration in crystalline rock systems (Vilks et al., 2004a; Altman et al., 2004), leaving some uncertainty on the actual magnitude of the effective diffusion coefficients.

The influence of choosing different conceptual models for simulating the reactive transport of oxygen in sparsely fractured granitic rock has received relatively little attention. Guimerà et al. (2006) simulated oxygen ingress for two conceptual models, including one that represented only a fracture (i.e. no fracture–matrix interaction) containing Fe-bearing minerals, and one representing the intact rock matrix in which biotite was the principal mineral providing reducing capacity. Not surprisingly, very little transport of oxygen was observed for the intact rock model because of the much lower hydraulic conductivity and flow velocity when compared to the fracture model (Guimerà et al., 2006). Sidborn and Neretnieks (2008) developed a series of analytical expressions to compare the depth of penetration of dissolved oxygen in a single fracture when oxygen reacts with: a) only the fracture wall coatings, b) only the fracture infill minerals, or c) matrix minerals after diffusion of oxygen from a nonreactive fracture. They predict that after 10,000 years of oxygen ingress these three conceptual models may lead to transport distances in single fractures that range from 100 to 1500 m (Sidborn and Neretnieks, 2008). Spiessl et al. (2008) have considered both single-fracture and fracture-zone conceptual models in their investigation of parameter uncertainty; however, these two models were very

**Table 1**
Summary of the key features of recent conceptual models for simulation of oxygen transport and reaction in fractured crystalline rocks.

| Conceptual model | Physical characteristics | Matrix diffusion into adjacent matrix? | $O_2$ reacts with | Example |
|---|---|---|---|---|
| Matrix-skin-reaction | Open fracture and a fixed width of the rock matrix are considered together as one reaction zone | Not beyond the finite matrix zone considered | Biotite in rock matrix | Glynn et al. (1999) |
| Single fracture with infill | Fracture has infill and a porosity less than 1.0 | No | Annite (as biotite Fe-end member) in the fracture infill | Guimerà et al. (2006) |
| Single fracture with coatings | Open fracture with fracture wall coatings | No | Biotite/chlorite as wall coating | Sidborn and Neretnieks (2008) |
| Single fracture with adjacent rock matrix | Open fracture with infinitely wide, adjacent rock matrix | Yes | Biotite as a matrix mineral | Sidborn and Neretnieks (2008) |
| Single fracture and adjacent rock matrix | Open fracture with coating and a wide adjacent rock matrix | Yes | Chlorite in fracture and biotite and pyrite in matrix | Spiessl et al. (2008) |
| Fracture zone and adjacent rock matrix | Highly fractured zone with a wide adjacent rock matrix | Yes | As above | Spiessl et al. (2008) |