# Life and death of chemical reaction fronts – a field, experimental and numerical study

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***In this exciting and innovative project, you will explore reaction front dynamics – a feature that is ubiquitous in the natural world and of high importance to questions of high societal impact including ore deposit generation, nuclear waste disposal safety and $CO_2$ sequestration. In this project you will get to the bottom of the feedbacks between different processes occurring during reaction front progression and/or stagnation. As such you will focus on the evolution of fluid transport to and from reaction sites. This transport depends on a balance between transport-enabling reaction steps such as dissolution and pore formation and transport-inhibiting reaction steps such as recrystallization and mineral precipitation. In this project, you will link experimental and theoretical studies of reaction fronts and compare results to reaction fronts in nature.***

In the geosphere, fluid-mediated mineral reactions are of pivotal importance in governing the redistribution of elements and isotopes. Incomplete elemental redistribution is preserved in the rock record in the form of geochemical reaction fronts, the boundaries between reacted and unreacted material. Such fronts control geochemical exchange between the hydrosphere and the geosphere, the formation of mineral deposits, and migration of aqueous fluids and melt in the lithosphere. Associated mineralogical changes can dramatically change the physicochemical properties of Earth materials affecting their flow properties (rheology), strength, porosity and permeability. Recent experimental work has shown that reaction rates of chemical fronts are likely controlled by the transport of elements contradicting previous assumptions of dissolution/precipitation-controlled reaction rates. Understanding the dynamics of progression and stagnation of reactive fronts is therefore one of the most important challenges in geoscience.

We have chosen dolomitisation, the secondary replacement of calcite ($CaCO_3$) by dolomite ($CaMg[CO_3]_2$), as our case study system. This reaction is readily accessible to low/moderate temperature experimentation, and can therefore be used to infer process in many other mineralogical settings. In addition, it is one of the most volumetrically important carbonate metasomatic processes, with dolomite hosting numerous ore deposits. The project will develop a process-oriented, parameterized toolbox for numerical modelling that describes the evolution of metasomatic reaction fronts on a grain scale. The results will be a radical change in our ability to reliably predict the complex interplay between the highly dynamic processes (nucleation, recrystallization, transport) controlling element fluxes and will have impact on several areas of science and industry including studies of crustal rheology, hydrocarbon reservoirs and, mineral deposits.

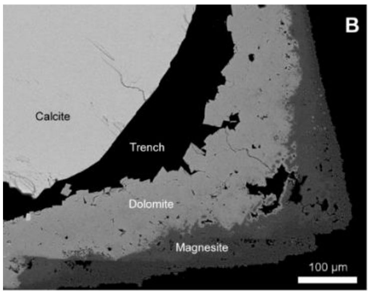

*Figure 1: Termination of dolomite body on the North Wales Platform. A) m-scale stratabound termination of dolomite (brown) against limestone (white) as indicated by arrows. People for scale. Box is enlarged in B, indicating sharp, non-facies selective termination at dm-scale, potentially related to local permeability variations, such as fractures (notebook = 20 cm). C) BSE image of an experiment of carbonate replacement: cross section of the reacted crystal shows a doubled reaction rim replacing the former calcite crystal.*

The main aim is to develop a theoretical framework to predict the progression and stagnation of chemical fronts, by quantitatively describing the coupling and feedback between element transport including element fluxes and fluid/elemental pathways, mineral reaction, recrystallization, evolution of fluid pathways, and their associated rates. To achieve this, we need to relate nucleation and growth processes within an evolving reaction front to the local composition of pore fluids within a known rock fabric as the transport properties of these systems are intimately linked to the dynamic evolution of fluid pathways. Specifically, the project aims to answer the following three questions:

***How does fluid composition and rock texture influence reaction affinity, nucleation and growth kinetics at the chemical front?*** An answer to this question will allow us to predict reaction front progression based on an assumed or known fluid and/or reactant.
***What is the temporal and spatial link between pore type, connectivity and reaction progression?*** Answering this question will allow us to predict reaction front progression as a function of permeability and develop a numerical protocol to predict chemical front behaviour in space and time. This will be particularly important for economic prospectivity that is reliant upon knowledge of the spatial distribution of porosity such as hydrocarbon and ore exploration.
***What are the parameters controlling chemical front progression and/or stagnation and do these parameters vary under different conditions of temperature, prior permeability or rock texture?*** An answer to this question will inform and enable reliable large scale chemical transport models to be universally applied to reactive transport processes in many socio-economically and geodynamically important settings.

## Objectives:

For the present study, we have chosen to focus on dolomitisation, i.e. a carbonate replacement system. Our group has not only been conducting experiments in carbonate systems for several years building substantial expertise in sample preparation, reaction rates, and analytical methods, but also performed numerical simulation focussing on the processes involved. The project has three objectives:

O 1: Experimentally quantifying the evolution of reaction fronts during dolomite replacement in single and polygrain samples to measurable physio-chemical parameters such as flow-rate, permeability, grain size, fluid chemistry, and temperature controlling nucleation and growth rates.
O 2: Detailed parameterization of natural and experimental carbonate replacement domains.
O 3: Development of a numerical model that predicts the evolution of a dolomitisation front based on feedbacks between permeability development, reaction and chemical transport, to allow upscaling and harmonisation of results from 1 and 2.

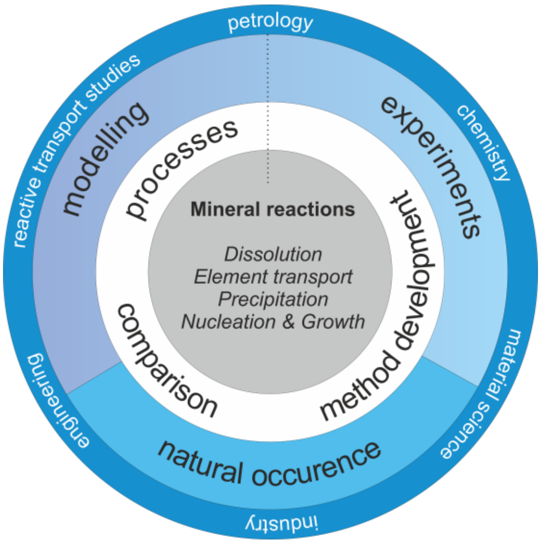

Figure 2: Schematic illustration showing the different processes controlling mineral reactions. The project will integrate advances in method development, process evaluation and comparison between model predictions and natural field data.

To achieve these goals, we focus on the micron to cm-scale, combining 3 integrated approaches (Fig. 2):

1) Experimental quantification of the diffusive, advective and reactive parameters controlling the spatial and temporal evolution of a reaction front in natural carbonate rocks.
2) Numerical simulations of reaction front dynamics
3) Collection of detailed data from the field focussing on well-exposed dolomite-limestone reaction fronts (e.g. North Wales Platform, Fig. 1)

To characterize the samples (both experimental and natural) and fluid pathways you will use 4D state-of-the-art analytical and visualisation techniques. Evolution of permeabilities will be monitored during the flow-through experiments using a custom-made permeameter. The formation of secondary porosity will be quantified (SEM, µ-CT) and linked to quantitative physicochemical analysis of both fluid and solid phases (ICP-MS/TIMS – fluid chemistry including isotopes, NanoSIMS – isotope tracers, EBSD – grain size and EMPA – solid chemistry). Comparison of results with natural dolomitisation fronts will provide natural evidence of the character of reaction fronts and facilitate upscaling of experimental data to reactive transport models. Data from outcrops of reaction fronts and from samples taken from this front will also ground truth model output and provide support for code refinement such that existing numerical codes can be upgraded to realistically simulate reaction front progression from mm to cm scale.

## Potential for high impact outcome

Fluid-rock interaction is fundamental to chemical segregation in the Earth crust, including the formation of ore deposits, the creation of porosity essential for petroleum reservoirs, and chemical exchange between the hydrosphere and geosphere. Replacement of limestone by dolomite and dolomite by magnesite have been reported widely in natural systems and are commonly associated with the interaction of the parent rock with magnesium-bearing solutions such as seawater or hydrothermal fluids. Whilst combined outcrop, laboratory and reactive transport studies have significantly improved our understanding of the governing processes of dolomitisation in recent years, the factors controlling the position and properties of the replacement front remain poorly described and understood. In particular, it is unclear what controls the size and geometry of dolomite bodies and, in particular, which mechanisms govern their spatial termination. We anticipate the project generating several papers for submission to high impact interdisciplinary and disciplinary journals.

## Training

The student will work under the supervision of Dr Thomas Mueller and Prof Sandra Piazolo within the Institute of Geophysics and Tectonics. This project provides a high level of specialist scientific training in: (i) experimental petrology (ii) cutting-edge geochemical analytical approaches (iii) numerical modelling (iv) integrated textural-metamorphic reconstruction, (v) advanced field data analysis. Co-supervision will involve regular meetings between all partners, use of Leeds analytical facilities including the state of the art TIMS, FE-SEM, EPMA, Cohen laboratories and extended visits for the student to the NERC Isotope Geosciences Laboratory. The successful PhD student will be part of a team of undergraduate and graduate students working on similar problems and/or using the same techniques. The student will have access to a broad spectrum of training workshops run by the Faculty, including numerical modelling, managing your degree, and preparing for your viva (http://www.emeskillstraining.leeds.ac.uk/).