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Control of serpentinisation rate by reaction-induced cracking

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ABSTRACT

Serpentinisation of mantle rocks requires the generation and maintenance of transport pathways for water. The solid volume increase during serpentinisation can lead to stress build-up and trigger cracking, which ease fluid penetration into the rock. The quantitative effect of this reaction-induced cracking mechanism on reactive surface generation is poorly constrained, thus hampering our ability to predict serpentinisation rate in geological environments. Here we use a combined approach with numerical modelling and observations in natural samples to provide estimates of serpentinisation rate at mid-ocean ridges. We develop a micromechanical model to quantify the propagation of serpentinisation-induced cracks in olivine. The maximum crystallisation pressure deduced from thermodynamic calculations reaches several hundreds of megapascals but does not necessary lead to crack propagation if the olivine grain is subjected to high compressive stresses. The micromechanical model is then coupled to a simple geometrical model to predict reactive surface area formation during grain splitting, and thus bulk reaction rate. Our model reproduces quantitatively experimental kinetic data and the typical mesh texture formed during serpentinisation. We also compare the model results with olivine grain size distribution data obtained on natural serpentinised peridotites from the Marum ophiolite and the Papuan ultramafic belt (Papua New Guinea). The natural serpentinised peridotites show an increase of the number of olivine grains for a decrease of the mean grain size by one order of magnitude as reaction progresses from 5 to 40%. These results are in agreement with our model predictions, suggesting that reaction-induced cracking controls the serpentinisation rate. We use our model to estimate that, at mid-ocean ridges, serpentinisation occurs up to 12 km depth and reaction-induced cracking reduces the characteristic time of serpentinisation by one order of magnitude, down to values comprised between 10 and 1000 yr. The increase of effective pressure with depth also prevents cracking, which positions the peak in serpentinisation rate at shallower depths, 4 km above previous predictions.

1. Introduction

Olivine is the main constituent of upper mantle rocks. Under hydrothermal conditions olivine reacts with water to form serpentine and brucite, which are hydrous phases. This replacement reaction, commonly termed serpentinisation, is promoted by tectonic deformation exposing mantle rocks (peridotites) on the Earth's surface at mid-ocean ridges and in ophiolites. The serpentinisation of olivine modifies mantle rocks rheology (Escartín et al., 2001), geochemical water cycle (Rüpke et al., 2004) and the thermal structure of the lithosphere (Allen and Seyfried, 2004). Moreover, the iron contained in olivine can be partly oxidized to form magnetite and hydrogen (Moody, 1976), with first-order consequences for the formation of extremely reducing environment (Frost, 1985) and the magnetic signal recorded in the oceanic lithosphere (Toft et al., 1990; Sleep et al., 2004).

All these changes in physico-chemical properties associated with serpentinisation depend on the reaction rate. Replacement reactions such as serpentinisation can be decomposed in four successive steps: (1) transport of fluids to olivine, (2) olivine dissolution, (3) transport of aqueous species and (4) precipitation of serpentine. Hydrothermal experiments on olivine powders have shown that dissolution and precipitation (steps 2 and 4) are fast compared to the transport of fluid and aqueous species (steps 1 and 3). The transport steps are thus controlling the reaction rate (Martin and Fyfe, 1970; Wegner and Ernst, 1983; Seyfried et al., 2007; Malvoisin et al., 2012). Diffusion at grain junctions is slower than olivine dissolution at temperature below 350 °C (Malvoisin and Brunet, 2014). Therefore, fractures are the main fluid pathways involved during serpentinisation. Because the solid volume

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increases by approximately 50 % during serpentinisation, fractures can be clogged be reaction products, inducing a decrease in peridotite permeability (Macdonald and Fyfe, 1985; Hövelmann et al., 2012; Godard et al., 2013; Farough et al., 2016). However, this clogging is not complete, as shown by the preservation of a porosity of several percent in natural serpentinised peridotites (Tutolo et al., 2016). At the kilometre to the metre scale, fracture networks are mainly formed by tectonic deformation (Tucholke and Lin, 1994; Tauzin et al., 2017). By contrast, at the grain scale, thermal contraction, stress build-up due to the reaction, and preferential dissolution along sub-grain boundaries and other flaws (Malvoisin et al., 2012; Plümper et al., 2012; Klein et al., 2015; Lisabeth et al., 2017) are the main processes invoked for the generation of the observed mesh textures, characterised by polygonal olivine grains surrounded by serpentine veins (Wicks and Whittaker, 1977). Thermal cracking is associated with fast tectonic exhumation and associated temperature decrease in peridotites (Boudier et al., 2010). Demartin et al. (2004) provided a micro-mechanical model and experimental constraints for thermal cracking in peridotites. In addition to thermal effects, the positive solid volume change during serpentinisation also generates stresses (i.e., crystallisation pressure) sufficient to fracture the rock (Macdonald and Fyfe, 1985; Iyer et al., 2008; Kelemen and Matter, 2008; Jamtveit et al., 2009). It is still not clear if fluid pathways generation in natural samples is controlled by thermal or reaction-induced cracking. Based on evidences of hierarchical fracturing in orthopyroxenite dykes from Leka ophiolite (Norway), Iyer et al. (2008) proposed that reaction-induced fracturing is the main process forming fluid pathways during serpentinisation while Boudier et al. (2010) used olivine preferred orientation to show that thermal contraction controls cracking in peridotites from Oman. Rouméjon and Cannat (2014) proposed a mixed scenario for serpentinised peridotites from mid-ocean ridges with microfractures formed by thermal cracking serving as a basis for fracture network densification by reaction-induced cracking. However, quantitative estimates of the influence of the two fracturing processes on reactive surface area generation are still lacking to predict their influence on serpentinisation rate.

The crystallisation pressure has been extensively studied at ambient temperature for monophasic systems such as ice or salts through experimental and theoretical works (e.g., Steiger, 2005). The proposed theory is based on the presence of a constantly renewed nanometre scale liquid film at the rock surface to both supply ions for crystal growth and allow the crystal to perform mechanical work (e.g. Røyne et al., 2011). The simplest way to model reaction-induced cracking is to relate directly fracturing to the reaction progress, typically by using a critical stress criterion for fracture opening. This approach allows to investigate qualitatively the influence of reaction-induced fracturing on reaction front propagation (Rudge et al., 2010) and on the generated fracture patterns (e.g. Jamtveit et al., 2009; Kelemen and Hirth, 2012; Plümper et al., 2012). Despite the overall success of these models in reproducing the phenomenological features associated with reaction-induced fracturing, quantitative comparisons of model outputs with both texture evolution and bulk reaction rate are still missing.

Here, we propose to bridge this gap by developing a grain-scale model accounting for the feedbacks between reaction kinetics, crystallisation pressure and fracture mechanics. Our micromechanical approach minimizes the use of phenomenological parameters and allows to make actual predictions of bulk reaction rate and texture evolution, which are compared to published experimental data (Malvoisin et al., 2012) and to new measurements on peridotites from the Marum ophiolite and the Papuan ultramafic belt (Papua New Guinea) serpentinised at low temperature (Kaczmarek et al., 2015).

2. Observations in natural samples

2.1. Image analysis of variably serpentinised peridotites

Here we aim to investigate mineralogical processes occurring during serpentinisation in natural samples, and extract the evolution of grain size, shape and number density as a function of reaction progress. We use ophiolitic samples from the Marum ophiolite and the Papuan ultramafic belt (PUB; Papua New Guinea) including pristine, moderately and extensively serpentinised peridotites, with reaction progress ranging from only a few percents up to more than 95%. The ophiolite was obducted during the convergence between the Australian and the Pacific plates (Lus et al., 2004) and subsequently serpentinised during its exposure at the surface.

Fifteen samples of variably serpentinised peridotites from the Marum ophiolite and the PUB are selected for petrological study and image analysis (Table S1). Mineral chemistry and back-scattered electron (BSE) images are performed with a Tescan Mira LMU (JEOL) field-emission scanning electron microscope operated at 20 kV and 23 mm working distance and equipped with an EDS detector from Oxford Instrument at the University of Lausanne. Serpentine mineralogy is characterised by Raman microspectrometry using a Horiba LabRAM HR800 microspectrometre equipped with a 532.1 nm laser at the University of Lausanne. In each sample, we use optical microscopy observations to select one to four olivine-rich and pyroxene-free zones, ranging from 2.3 to 11.7 mm in size, for image analysis. This results in a total of 37 zones containing one or several olivine crystals fragmented by micro-cracks. Each of these zones is mapped by acquiring between 18 and 464 BSE images (depending on the size of the zone). For each zone, BSE images are then stitched together to reconstruct a mosaic image with a resolution ranging between 0.54 and 0.67 μm per pixel (Fig. S1 a and d). We use a gray scale criterion and dilation/erosion techniques to automatically attribute each pixel to either (1) olivine, (2) serpentine and/or brucite, or (3) other phases (e.g., magnetite, spinel or epoxy). The measured surface area of serpentine is converted into an amount of reacted olivine by using the olivine/(serpentine + brucite) volumetric ratio (0.68), allowing us to obtain the reaction progress.

Binary images are then produced with olivine pixels only (Fig. S1 b and d) and then segmented in order to associate pixels from the same grain (Fig. S1 c and f). Finally, bounding rectangles with the minimal surface area are adjusted to each grain contour in order to retrieve grain size and orientation (Fig. S1 c and f). Olivine grains smaller than 5 μm are not considered for statistical analysis due to the lack of resolution below this size. The final number of grains identified in each zone is between 287 and 36,537 (Table S1) which is above the limit of approximately 200 grain sections necessary for statistical analysis (Malvoisin et al., 2012). In the following, the grain size refers to the mean of the sizes of the long and short sides of the minimal bounding rectangle. Grain orientation refers to the angle between the horizontal and the side of the bounding rectangle crossing the first quadrant of the unit circle (0 to 90°). For statistical analysis on grain orientation, groups of grains with close crystallographic orientations are defined by using polarised light microscopy with which grains associated to the same primary olivine crystal have similar optical properties. For each of these groups, angle mean values and standard deviations are determined by using circular statistics (Fisher, 1993).

2.2. Morphological properties of residual olivine grains

The natural samples from the PUB are dunites, while peridotite samples from the Marum ophiolite are dunite, harzburgite and