

Non-stoichiometric hydroxycarbonate solid solutions as reaction products of serpentine carbonation

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INTRODUCTION

The natural carbonation of near-surface or exposed masses of serpentinite rock has recently been under scientific scrutiny as a potential means of enhanced atmospheric CO₂ sequestration and storage. An extensive monographic review of the geochemical and mineralogical aspects involved of this fluid-rock interaction can be consulted in Kelemen et al. (2011). One of the troublesome issues affecting the accuracy of hydrogeochemical models employed in the quantitative prediction of sequestration rates, and ultimately the overall process effectiveness, stems from the assumption of reactions leading to the formation of pure, stoichiometric mineral products. In the present study, we provide microanalytical and spectroscopic evidence supporting the formation of non-stoichiometric Ca- and Mg-hydroxycarbonates, as primary carbonation products found in serpentinites belonging to the Samail ophiolite, in the Sultanate of Oman.

SAMPLING AND EXPERIMENTAL METHODS

The sampling area lies in the vicinity of Buwah village, in northeastern Oman, where the Samail ophiolite outcrops. The collected carbonate samples occur within veins crosscutting, tectonized and highly serpentinized harzburgite. These carbonate-bearing veins are hosted along major fractures and shear zones, locally reaching 1.5 to 2 m in width, and can be traced for several meters along strike. These structures form a dense network of interconnecting and crosscutting veinlets, occasionally coalescing into small stockworks. Polished thin-sections of sampled carbonates were studied under a polarized-light petrographic microscope and later analyzed using SEM-EDS and confocal Raman spectroscopy.

RESULTS AND DISCUSSION

Fig. 1 displays a backscattered-electrons (BSE) micrograph depicting an example of a serpentinite lithoclast with a replacing corona of a different mineralogical nature. Microanalysis performed in the latter reveals a composition containing both Ca and Mg in non-stoichiometric amounts (at.% 8.8 and 11.26, respectively). Slight compositional heterogeneities can be discerned in the BSE image of the rim; however, these do not correspond to any significant variation in the analytical results. The Raman spectra acquired in these alteration coronas display bands compatible with reference information regarding magnesite (Borromeo et al., 2016) at ~ 330 , 730-740, 1090-1098 cm⁻¹. However, these coexist with other conspicuous peaks at ~ 640 , 820, 1000 cm⁻¹, and, most notoriously, several peaks at wavenumbers above 1100 cm⁻¹, denoting the vibrational modes of OH groups within the shift interval in the 2700-3115 cm⁻¹. The coupling of analytical and spectroscopic data points towards a non-stoichiometric Ca and Mg hydroxycarbonate solid solution phase as the primary product of serpentinite carbonation. Furthermore, the appearance of additional spectral vibrational modes suggests a symmetry lower than the typical trigonal carbonate structure. Beyond the alteration corona, the lower-contrast, i.e. darker colored material in Fig.1, revealed a nearly pure composition in Mg (Ca ~ 1 at.%) and a Raman spectrum depicting a series of peaks at ~ 215 , 330, 735, 1094

cm^{-1} compatible with reference information (Borrromeo et al., 2016) concerning the vibrational modes of magnesite (MgCO_3).

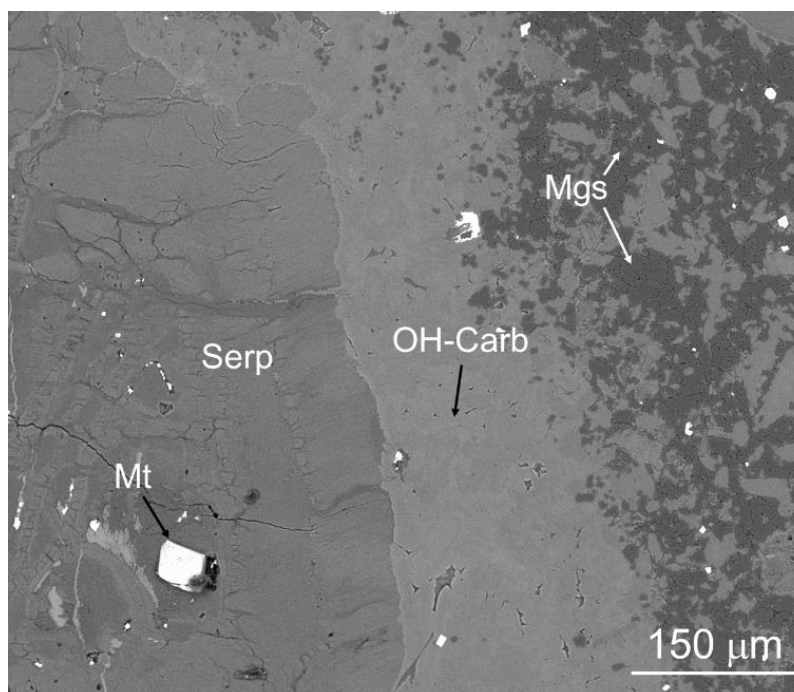


Fig 1. BSE micrograph depicting a reaction rim in a carbonatized serpentinite lithoclast. Mt = magnetite, Serp = serpentinite, OH-Carb = hydroxycarbonate solid solution, Mgs = magnesite.

The textures shown in Fig. 1 point towards the formation of magnesite latter in the reaction pathway, as it appears to be replacing the primary hydroxycarbonate solid solution.

CONCLUSIONS

The data gathered in this study suggest that the occurrence of non-stoichiometric reaction products in serpentinite carbonation has been highly underestimated. In fact, the primary products of serpentinite carbonation observed in samples from the Samail ophiolite consist of Ca-Mg hydroxycarbonate solid solutions, with magnesite forming later in the alteration sequence. These observations strongly recommend further research concerning the kinetics and thermodynamics features of solid solution-aqueous solution systems in the context of ophiolite weathering mechanisms.

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