Surface-specific measurements of olivine dissolution by phase-shift interferometry

HELEN E. KING1,*, HISAO SATOH2,3, KATSUO TSUKAMOTO3 AND ANDREW PUTNIS1

1Institut für Mineralogie, University of Münster, Corrensstrasse 24, 48149 Münster, Germany
2Department of Earth and Planetary Materials Science, Graduate School of Science, Tohoku University, Aramaki, Aoba, Sendai, Sendai 980-8578, Japan
3Mitsubishi Materials Corporation, 1002-14, Mukohyama, Naka 311-0102, Japan

ABSTRACT

Natural olivine dissolution and replacement often occurs preferentially along specific crystallographic planes. Thus, olivine reactivity at specific surfaces was examined in situ using phase-shift interferometry, which has a detection limit <10⁻⁵ m/s, by dissolving two smoothed olivine crystal faces and a third sample corresponding to a surface that was generated by preferential dissolution along structural defects. The experiments were conducted at 22 °C and ambient pressure in 0.1 M NaCl solutions that were acidified to pHs between 1 and 4 using 0.1 M HCl. These experiments show that olivine dissolution can vary from one surface to another as well as in different areas of the same surface that have similar characteristics. The fastest vertical retreat occurred at the surfaces related to defects. However, only vertical advancement was observed at pH 1 on this surface consistent with the observation of isolated islands on the surface during atomic force microscopy investigations after the experiment. Raman analysis of the precipitated phase showed that it was not one of the thermodynamically stable phases expected from PHREEQC modeling. However, the correlation between the siloxane ring peak of amorphous silica with a similar peak in the precipitate spectrum, in conjunction with previous experimental and natural observations, indicates that the precipitate was a Si-enriched amorphous phase. Therefore, precipitation can facilitate the further dissolution of olivine on this surface as long as it does not completely armor the surface. Precipitate formation on surfaces associated with outcropping defects supports the natural observations of preferential dissolution and serpentinitization along these defects implying that the fast dissolution of these surfaces will play a critical role during olivine replacement. In addition, comparison with flow-through experiments indicates that outflow fluid chemistry may provide an incomplete picture of processes occurring during olivine dissolution.

Keywords: Interferometry, dissolution, precipitation, olivine

INTRODUCTION

Olivine has recently been recognized as a key mineral for many environmental remediation schemes such as acid mine drainage (Kleiv and Thornhill 2008), CO₂ (Jarvis et al. 2009), and sulfur sequestration (Rappold and Lackner 2010). In addition, the natural reaction of olivine with fluids plays an important role in acidic fluid neutralization (Varekamp et al. 2009) and its reaction with seawater to produce serpentine minerals has important consequences for the rheology and geochemistry of the oceanic lithosphere (Escartin et al. 1997; Bach and Früh-Green 2010). Although extensive research has been conducted into olivine reactivity most olivine dissolution experiments are limited to flow-through experiments that use ground olivine (e.g., Oelkers 2001; Pokrovsky and Schott 2000). However, there is evidence that in nature olivine dissolution occurs preferentially along specific crystallographic planes. For example, olivine that has undergone mantle flow has an anisotropy that causes parting along specific directions enabling the (010) surface to become accessible to fluids (Boudier et al. 2010). In experiments, dissolution of ground olivine also produces surface features that are attributed to preferential dissolution at dislocations and different cleavage planes (Grandstaff 1978). Awad et al. (2000) studied dissolution at the (010), (100), and (001) surfaces of olivine and showed that preferential dissolution occurred at the (010) surface. However, the experiments of Awad et al. (2000) were conducted by cutting and mechanically polishing an oriented olivine crystal and measuring the crystal size periodically to determine the dissolution rate. Previous work on calcite dissolution indicates that this method of sample preparation can increase the dissolution rate due to the formation of defects associated with mechanical grinding (Macinnis and Brantley 1992).

To explore the dependence of crystallographic orientation on olivine dissolution we have performed in situ measurements using phase-shift interferometry (PSI) experiments on three distinct olivine surfaces. The results of this study advances our understanding of preferential olivine dissolution as well as the concomitant precipitation of new phases that also occurred during our experiments and have been observed in nature (Boudier et al. 2010) and previous experimental investigations (Davis et al. 2009; King et al. 2010).