

Kinetic modeling of olivine carbonation reaction: study of the rate dependence on temperature and $p\text{CO}_2$ in open and closed systems

GIUSEPPE D. SALDI^{1*}, DAMIEN DAVAL^{1,2}

AND KEVIN G. KNAUSS¹,

¹Lawrence Berkeley National Laboratory, Berkeley, CA, edsaldi@lbl.gov (* presenting author); ddaval@lbl.gov; kgkanuss@lbl.gov

²LHyGeS, CNRS UMR 7517, Strasbourg, France

Although both olivine dissolution and magnesite precipitation rates have been studied and modeled over a significant range of temperatures and aqueous chemical compositions, the mechanisms of the process that combines these two reactions have not been adequately described from a kinetic standpoint.

It was shown that the formation of a silica passivating layer at the interface between pristine olivine and aqueous solution can significantly slow down or even stop the dissolution of this mineral, thus hindering the attainment of the conditions necessary to initiate the carbonation reaction [1, 2]. Recent experimental measurements also indicate that magnesite precipitation can be the rate limiting step to forsterite carbonation in some other conditions [3].

To improve the understanding of mineral carbonation processes and provide new data that can contribute to its kinetic description we conducted a series of experiments in pure water from 90 to 180 °C, at a $p\text{CO}_2$ of 100 and 200 bar, using both the well characterized San Carlos olivine and a pure synthetic forsterite sample. Batch experiments were performed in flexible Au bags whereas steady-state carbonation rates were investigated at 150 °C by means of a mixed-flow Ti-reactor. The study of the chemistry of aqueous solution and the analysis of reacted olivine samples by XRD, SEM-EDX and Rockeval 6 allowed us to describe quantitatively the carbonation reaction as a function of $p\text{CO}_2$ and temperature. All experiments were characterized by the ubiquitous presence of a silica-rich layer at the olivine-aqueous solution interface. The nature of this layer changes as a function of temperature, and can lead to increasing rates of carbonation as magnesite precipitation rates increase with increasing temperature.

Comparison between the results obtained from two one-month-long batch and mixed-flow reactor experiments at 150 °C show that the extent of carbonation is limited by the saturation with respect to a silica polymorph, and possibly by the formation of secondary Mg-silicates. In the closed system, olivine to magnesite conversion rates are <1 %, whereas the extent of carbonation are significantly higher in the open system (8-9 % at least) and magnesite precipitation was found to be the rate limiting step of the reaction in this latter case.

The role of Fe in the passivating properties of the silica layer and its incorporation into the carbonate phase under reducing conditions is also being studied and some experimental results will be presented.

[1] Bearat et al. (2006) *Environ. Sci. Technol.* **40**, 4802-4808. [2] Daval et al. (2011) *Chem. Geol.* **284**, 193-209. [3] Saldi et al. (2012) *Geochim. Cosmochim. Acta*, doi:10.1016/j.gca.2011.12.005.

High precision 4-isotope Sulfur measurements using the CAMECA IMS 1280-HR

P. PERES, F. FERNANDES, M. SCHUHMACHER, P. SALIOT*

CAMECA, 29 quai des Grésillons, 92622 Gennevilliers Cedex, France, peres@cameca.com

Secondary Ion Mass Spectrometry (SIMS) technique provides direct in situ measurement of elemental and isotopic composition in selected μm -size areas of the sample. The CAMECA IMS 1280-HR is an ultra high sensitivity ion microprobe that delivers unequalled analytical performance for a wide range of SIMS applications: isotope ratio measurements, geochronology applications (U-Pb dating in Zircon), trace element analyses, particle screening measurements,...

Conventional Sulfur isotope studies focus on the two most abundant isotopes ^{32}S and ^{34}S . However, there has been an increasing interest in the minor ^{33}S (~0.7%) and ^{36}S (~0.02%) isotopes since mass independent fractionation effects have been discovered [1-3].

This paper presents 4-isotope Sulfur data obtained on standard and unknown pyrite samples. Measurements have been performed using a small $10\mu\text{m}$ Cs^+ beam spot, and high mass resolution conditions (~4,500) to resolve the hydride mass interferences. The four S isotopes have been collected simultaneously: ^{32}S , ^{33}S and ^{34}S on Faraday Cup detectors, and the low abundance ^{36}S (intensity ca. 2×10^5 c/s) on an Electron Multiplier. The EM yield drift has been automatically monitored and corrected using a proprietary algorithm. More than 100 spot analyses have been performed in fully automated mode, with an analysis time of 4 minute/spot.

Data on the standard sample show that a precision < 0.2 permil (1SD) can be achieved for $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ (and $\Delta^{33}\text{S}$). An excellent precision, < 0.3 permil (1SD), is also obtained for $\delta^{36}\text{S}$ (Figure 1) and $\Delta^{36}\text{S}$.

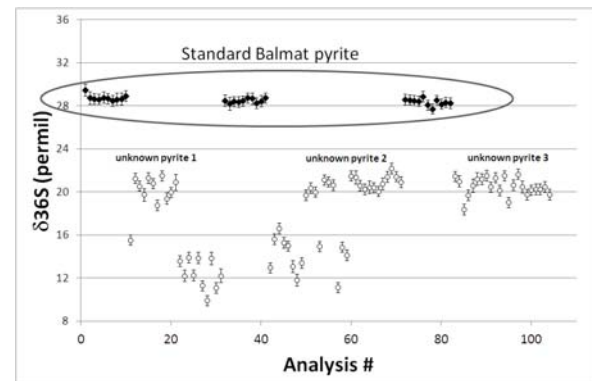


Figure 1: $\delta^{36}\text{S}$ data on standard and unknown pyrite samples.

This measurement protocol with multicollection configuration FC-FC-FC-EM allows to work with good spatial resolution (spot size ~ $10\mu\text{m}$) and yields excellent precision for all Sulfur isotopes, including for the lowest abundance ^{36}S .

[1] Kamber and Whitehouse (2007) *Geobiology* **5**, 5-17.
[2] Williford et al. (2011) *GCA* **75**, 5686-5705.
[3] Whitehouse (2011) *Goldschmidt 2011 abstract*, 2155.