

³⁷Ar diffusion in pyroxene: Implications for thermochronometry and mantle degassing

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The kinetics of argon diffusion in pyroxenes is critical to several problems in the Earth and planetary sciences. Pyroxenes are among the most abundant minerals in the Earth's upper mantle and are thought to be important carriers of radiogenic ⁴⁰Ar (⁴⁰Ar*) [e.g., 1]. Additionally, pyroxenes commonly contain >10% the total ⁴⁰Ar* within many meteorites, and therefore hold great potential for quantifying thermal events on meteorites and their parent bodies. Nonetheless, pyroxenes have not been thoroughly studied with respect to Ar diffusion kinetics. We conducted detailed, feedback-controlled laser heating diffusion experiments using synthetic Ar isotopes in gem-quality clinopyroxene (CPX) and orthopyroxene (OPX) crystals, which yielded activation energies (E_a) of >300 kJ/mol (>70 kcal/mol), positively correlated with $\ln(D_0/a^2)$, which varies between 5 and 25. These E_a 's are an order of magnitude larger than previously reported values obtained with a different experimental approach [1].

Our data indicate that Ar diffusion within pyroxenes is strongly temperature dependent and insignificant at low to moderate temperatures (<1000 °C). At higher temperatures ⁴⁰Ar diffusion is rapid and may proceed more quickly from pyroxenes than it does from glass or plagioclase (i.e., above the temperature at which their extrapolated Ar Arrhenius relationships intersect). Thus, very brief, high-temperature shock heating events may preferentially degas pyroxene without significantly resetting glass or plagioclase age spectra. In this way diffusive ⁴⁰Ar distributions observed within pyroxenes in meteorites can provide critical information about the timing and nature of shock events on Mars, the Moon, and other meteorite parent bodies. Subsequent low-T phenomena should minimally obscure these features.

Regarding mantle degassing, our observed kinetics suggest that diffusive equilibration through 0.1-0.5 mm pyroxene grains occurs in minutes to hours at basaltic melt generation temperatures (~1300 °C), and is therefore unlikely to inhibit mantle degassing as has been previously inferred [1].

[1] Watson *et al.* (2007) *Nature* **449**, 299–304.

Zinc removal by sulfate-reducing bacteria: Implications for acid mine drainage treatment

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Some passive treatment systems of acid mine drainage (AMD) developed in the Iberian Pyrite Belt (IPB) showed a complete removal of Fe and Al [1] in highly polluted acidic discharges (3200 mg/L SO₄, 440 mg/L Zn, 330 mg/L Fe, 100 mg/L Al) [2]. They consist of an aeration dam followed by two reactive tanks filled with limestone. However, treatment processes using limestone display deficiencies in the removal of divalent metals, mainly Zn. The main aim of this study was to demonstrate the effectiveness of a biological treatment with sulfate-reducing bacteria (SRB) of effluents with high sulfate and zinc concentrations. To date, SRB were mainly isolated from anaerobic environments showing maximum Zn tolerance level of 150 mg/L [3]. In this work, SRB were isolated successfully from three samples: two of them from IPB mining districts in which Zn concentrations are reported to be toxic to these microbes [3] -Cueva de la Mora (CM) and Mina Esperanza (ME) with 400 and 95 mg/L Zn, respectively-; and the other from sewage sludge (SS), where the existence of SRB has been widely observed. Later, the isolated-SRB were subjected to [Zn] = 250 mg/L for 7 weeks in a growth medium (MTM; [4]).

Results showed that after 5, 5 and 6 weeks for SS, ME and CM experiments, respectively: (1) sulfate was reduced to sulfite and then to sulfide and concentrations in solution decreased; (2) subsequently Zn concentrations decreased from 250 mg/L to values below detection limit; (3) both decreases were consistent with the precipitation of newly- formed wurtzite (ZnS) identify by XRD and SEM-EDS; and (4) SRB tolerated high Zn concentrations as showed by the most probable number method (average [SRB] increased from 9.6·10³ to 1.3·10⁶ CFU/mL). In conclusion, we propose to design a two-steps passive system -alkaline (limestone) and biological (SRB)- as a treatment strategy for AMD at abandoned IPB mining environments.

[1] Macías *et al.* (2009) *GCA* **73**, A811. [2] Caraballo *et al.* (2009) *Appl. Geochem.* **24**, 2301–2311. [3] Martins *et al.* (2009) *J. Hazard. Mater.* **166**, 706–713. [4] Sani *et al.* (2001) *Advances Environ. Res.* **5**, 269–276.