Measuring mineral dissolution kinetics using an automated flow-through module

B. De Baere[*], K.U. Mayer and R. Francois

Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia, Vancouver BC, Canada V6T 1Z4 (*correspondence: bdebaere@eos.ubc.ca)

We have developed a purpose-built flow-through dissolution sample introduction module. Until now, this experimental set-up has been used to carry out sequential leaching [1]. The application we present here is the quantification of mineral dissolution rate constants.

As a proof of concept study, we measured the dissolution kinetics of the mineral calcite. Individual calcite fragments from Chihuahua, Mexico were gradually dissolved using a leaching sequence covering pH 2-6 (using time-dependent proportions of DIW to HNO_3). The effluent was sent to an Agilent 7700 ICP-MS and analysed for $^{43,44}Ca$.

In parallel, we developed a simple geochemical reactive transport model in PHREEQC based on the forward rate equations as published by Plummer et al.. [2]. Surface area was estimated from the geometric surface area of the fragment. In order to optimize the forward model dissolution rate constants to best reflect the experimental data, PEST software (model-independent parameter estimation) was used to run a reverse model in a weighted least squares sense.

We are able to generate optimized dissolution rate constants ($k_1 = 1.18 \times 10^{-6}$ and $k_3 = 8.73 \times 10^{-11}$ moles cm^{-2} sec^{-1}, correlation coefficient between optimized model and experimental data $R^2 = 0.998$) which are within an order of magnitude or less of previously published studies [3, 4].

The key benefits of this newly developed technique include (1) time efficiency – in this study a typical leaching sequence lasted ~ 100 minutes; (2) extensive data coverage (here, n = 2000) which is of particular value to optimize the fit between model and data; and (3) automation – the entire leaching sequence is fully programmed. This approach has thus the potential to rapidly generate a large database of dissolution rate constants for a wide range of minerals.

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Can diffusion cause discrepant Lu-Hf isochrons in meteorites?

V. Debaille[*,1], Q.-Z. Yin[2] and Y. Amelin[3]

[1]Lab. G-Time, Université Libre de Bruxelles, Belgium (*correspondance: vinciane.debaille@ulb.ac.be)
[2]Dept. of Geology, University of California in Davis, USA (qyin@acdavis.edu)
[3]Research School of Earth Sciences, Australian National University, Australia (yuri.amelin@anu.edu.au)

The ^{176}Lu-^{176}Hf isotopic system, widely used for dating cosmochemical and geological processes, still suffers from two uncertainties. First, Lu-Hf isochrons for some early Solar System materials have excess slope of unknown nature. Second, unlike the well constrained Sm/Nd value to within 2% for chondritic uniform reservoir (CHUR), the Lu/Hf ratios in chondrites vary up to 18% [1], hence questioning the CHUR value for Lu/Hf. Even the 3% dispersion of Lu/Hf ratios [2] among the chondrites of low metamorphic grade, is greater than the dispersion of Sm/Nd among all studied chondrites. In order to better understand the Lu-Hf systematic of chondrites, we analyzed mineral fractions from the Richardton H5 chondrite to construct an internal Lu-Hf isochron, and set up a model to evaluate the role of diffusion in perturbing the Lu-Hf system.

The isochron yields an age of 4647±210 millions years (Ma) (MSWD= 9.4). Low precision is caused by relatively small spread the $^{176}Lu/^{177}Hf$ ratios from 0.02 to 0.05. Combining this study with the phosphate fractions measured in [3] yields a slope of 0.08855±0.00072, translating to a ^{176}Lu decay constant of 1.862±0.016 x 10^{-11} year^{-1}, in agreement with the terrestrial value of 1.867±0.008 x 10^{-11} year^{-1} [4]. Richardton phosphates show an extreme variation of the $^{176}Lu/^{177}Hf$ ratios from 0.8 to 143 [3], identifying phosphates as a major host of Lu. This is critical as apatite has substantially higher diffusion rates of REE [5] than most silicate minerals that comprise meteorites.

The model shows that preferential diffusion of Lu compared to Hf from apatite to other minerals can produce apparent older isochron, and that among parameters that influence the rate of diffusion, the temperature seems the main factor influencing the disturbance. This suggests, similarly to [2], that only type 3 chondrites with lowest metamorphic grade should be used to determine the Lu decay constant and the CHUR values.

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