

Experimental study of the kinetics of CO₂-sequestration by olivines and Hawaiian picrites

LIN QIU^{1*}, ZHENGRONG WANG¹, SHUN-ICHIRO KARATO¹, JAY J. AGUE¹, MICHAEL ORISTAGLIO¹, EDWARD BOLTON¹, AND DAVID BERCOVICI¹

¹Department of Geology and Geophysics, Yale University, New Haven, CT, USA

*presenting author: lin.qiu@yale.edu

Mafic/ultramafic rocks have been suggested as promising candidates to store anthropogenic CO₂ permanently. In this study, we employed an experimental approach to quantitatively evaluate the carbonation reaction kinetics as CO₂-rich fluids react with olivine (Fo₉₀) and high-Mg basalts (Hawaiian picrites).

Gem-quality olivine grains, olivine powders (10-20µm) and basalt powders (10-40µm) reacted with CO₂-containing solutions (e.g., 1M and 3M NaHCO₃ solution) in gold capsules placed in a hydrothermal autoclave over durations of 1-7 days at 200 °C and 150 bar. Dissolution experiments for these samples have also been carried out at three pH values (4.1, 6.9 and 9.3) to understand dissolution kinetics. After completion of experiments, gold capsules were checked for leaks, experimental run products were examined using SEM and electron microprobe, and the solution was analysed for alkalinity and major and trace element compositions at Yale University.

Our preliminary results show that carbonation rates of olivines and basalts are a function of the chemistry of the solution (e.g., concentration of NaHCO₃), the grain size, the mineralogy of the solid, and the duration of the experiments. We find that carbonation rates increase with increasing concentration of NaHCO₃ and decreasing grain size, but decrease with time. For example, an increase of NaHCO₃ concentration from 1M to 3M raises the carbonation rate for olivine grain by a factor of 6, and the carbonation rate for 10- 40µm olivine powders with 1M NaHCO₃ solution is an order of magnitude greater than that for single olivine grains. Carbonation rates of olivine and basalts in the first day are significantly higher than that of the subsequent days and slow down after 3-days of reaction. A dissolution and precipitation model is formulated to quantitatively simulate this process.

The clumped isotope geothermometer in soil and paleosol carbonate

JAY QUADE^{1*}, JOHN EILER², MATHEIU DAERON³, AND DAN BREECKER⁴

¹University of Arizona, Geosciences, quadej@email.arizona.edu (* presenting author)

²California Institute of Technology, Geological and Planetary Sciences, eiler@gps.caltech.edu

³CNRS, Science du Climat et de l'Environnement, mathieu.daron@gmail.com

⁴University of Texas at Austin, Geological Sciences, breecker@jsg.utexas.edu

We studied both modern soils and buried paleosols in order to understand the relationship of temperature estimated from clumped isotopes in carbonates (T^{°C}_{clumped}) to actual surface and burial temperatures. Carbonates from modern soils in a broad range of climates were sampled from Arizona, Nevada, Tibet, and India. T^{°C}_{clumped} obtained from these soils shows that soil carbonate only forms in the very warmest months of the year, largely in the afternoon, and probably in response to intense soil dewatering. The highest T^{°C}_{clumped} obtained from modern soil carbonate are <40°C. On average, T^{°C}_{clumped} significantly exceeds mean annual temperature by 10-15°C due to (1) summertime bias in soil carbonate formation, and (2) sensible heating of soil. Secondary controls on T^{°C}_{clumped} are site aspect, but especially soil depth and shading.

Site mean annual temperature (MAT) across 0-30°C is highly correlated with T^{°C}_{clumped} from soils, following the equation:

$$\text{MAT}(\text{°C}) = 1.20 * \text{T}^{\text{°C}}_{\text{effective air T from clumped}} - 21.72 \quad (r^2=0.92) \quad (1)$$

where T^{°C}_{effective air T from clumped} is the effective air temperature at the site estimated from T^{°C}_{clumped}. The effective air temperature represents the air temperature required to account for the T^{°C}_{clumped} at each modern soil site. The highly correlated relationship in equation (1) permits mean annual temperature in the past to be reconstructed from T^{°C}_{clumped} in paleosol carbonate, though it should be noted that soil carbonates appear to principally reflect warm season temperatures and so the proxy might be more precisely used as a measure of warm season climate or, in combination with other mean annual temperature proxies, of seasonality.

We also measured T^{°C}_{clumped} from long sequences of deeply buried (≤5 km) paleosol carbonate in the Himalayan foreland in order to evaluate potential diagenetic resetting. We found that paleosol carbonate faithfully records soil T^{°C}_{clumped} down to 3-4 km burial depth, or ~100°C. Deeper than this and above this