

How surface heterogeneity impacts reaction rates in carbonate rocks

SIMON EMMANUEL^{1*} AND YAEL LEVENSON¹

¹The Hebrew University of Jerusalem, Jerusalem, Israel,
(simonem@cc.huji.ac.il)(* presenting author)

Due to the ubiquitous nature of calcite in natural systems, much research has focused on determining the reaction kinetics of calcite dissolution. However, the empirical rate laws derived in such studies assume that the reactivity of calcite crystals typically used in laboratory experiments is the same as the reactivity of natural carbonate surfaces that have been exposed to fluid during diagenesis. In this study, we demonstrate that the difference between polished calcite surfaces and naturally-aged calcite surfaces is significant. Atomic force microscopy (AFM) measurements show that the rate of calcite dissolution within micron-size pores of a limestone sample is much lower than the rate of dissolution in the surrounding calcite surface. In addition, we use numerical simulations to show that this difference cannot be explained using a diffusion - surface reaction model. Instead, we attribute the heterogeneous reaction rates to the high density of tiny asperities on the polished surface surrounding the pore which increase the overall reactivity of the surface. We suggest that the range of reaction rates we observe could be representative of real geological systems, helping to explain the widely reported discrepancy between laboratory and field rates. The implications for weathering, dissolution in carbonate reservoirs, and carbon sequestration are also discussed.

Tracking stable CO₂ isotopes with laser spectroscopy at Jungfrauoch

LUKAS EMMENEGGER, BÉLA TUZSONAND,
PATRICK STURM AND STEPHAN HENNE

Empa, Laboratory for Air Pollution / Environmental
Technology, CH-8600 Dübendorf, Switzerland
(lukas.emmenegger@empa.ch)

Isotope ratios of trace gases contain highly valuable information about their sources, sinks and transport processes from the local to the global scale. While isotope ratio mass spectrometry (IRMS) has been the method of choice, laser spectroscopy is rapidly gaining importance because it can deliver real-time data with unprecedented temporal resolution at moderate cost and instrument size.

We employ a quantum cascade laser absorption spectrometer (QCLAS) and perform continuous monitoring of the stable CO₂ isotopes in the free troposphere since December 2008 at the High Altitude Research Station Jungfrauoch (3580 m a.s.l.), Switzerland [1]. The instrument is based on differential absorption technique in the 4.3 μm spectral range. Being a fully cryogen-free setup, it is well suited for unattended field applications, delivering both δ¹³C and δ¹⁸O of CO₂ at atmospheric abundance with a precision of 0.02 ‰ for both δ¹³C and δ¹⁸O-CO₂ at 10 minutes integration time [2].

The high temporal resolution of the δ¹³C time series allows the detection of pollution events and the application of the Keeling plot method for source signature identification. Backward Lagrangian particle dispersion simulations are used to determine the spatial origin of these CO₂ emission sources. Furthermore, the long data series permits the analysis of yearly, seasonal and daily patterns. Footprint clustering shows significantly different wintertime δ¹³C and δ¹⁸O-CO₂ values depending on the origin and surface residence time of the air masses.

We present the development of the instrumental set-up, the improvements of the most critical parts and the resulting performance. Then, we discuss methodologies for calibration and data treatment and illustrate the advantages of measuring high time resolution isotopic signatures of CO₂ in the atmosphere with exemplary results.

[1] Tuzson, B. *et al.*, ACP, 2011, 11, 1685–1696. [2] Sturm, P. *et al.*, AMTD, 6, 423–459, 2013.