

^{PS}In-Situ, Micron-Scale Analyses of Carbonate $\delta^{13}\text{C}$ by SIMS: A Method for Identifying Carbonate Cements that Form in Response to CO_2 Injection at the Illinois Basin Decatur Project Site*

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Abstract

This work demonstrates the utility of in situ carbon and oxygen isotope microanalysis ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) by secondary ion mass spectrometry (SIMS) in carbon sequestration research. A desirable long-term consequence of CO_2 -injection into underground rock formations at prospective storage sites (such as deep saline sandstone aquifers capped by impermeable strata) is the precipitation of carbonate mineral cements, the isotopic fingerprinting of which is a central theme here. More specifically, we focus on the unique advantage of the SIMS technique, which lies in the capability of analyzing very small sample volumes that are otherwise inaccessible to sampling techniques in conventional isotope ratio mass spectrometry (IRMS). For example, single carbonate crystallites as small as 3-10 μm across can be readily analyzed by SIMS with sub per-mil accuracy and precision. Importantly, the ability to perform micrometer-scale measurements in situ from either thin sections or 1-inch (25 mm) diameter polished core plugs preserves the petrographic context of measured carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values.

An important aspect of analytical methods-advancement is the continued development of reference materials that will allow for correcting SIMS-specific sample matrix effects in a wider range of Ca-Mg-Fe-carbonate compositions. At present, routine analyses can be performed on the end-members calcite (and aragonite), siderite and magnesite, as well as on the spectrum of compositions that fall along the dolomite-to-ankerite solid solution series (Śliwiński, et al., 2016a, 2016b).

At the Illinois Basin Decatur Project (IBDP) demonstration site (Leetaru et al., 2009; Leetaru and Freiburg, 2014), it is estimated that at least 10-20% of the introduced CO_2 may be consumed, and thus permanently stored, via the precipitation of Ca-Mg-Fe-carbonates (e.g. Liu et al., 2011; Carroll et al., 2013). We provide here a preliminary characterization of the pre-injection mineralogy and isotopic fingerprints ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of carbonate cements in the Mt. Simon Sandstone reservoir and the overlying shaly caprock (the Eau Claire Formation). By drawing upon published data on ambient reservoir conditions and the C-isotope composition of the injected CO_2 , we also make simple predictions about the possible $\delta^{13}\text{C}$ signatures of different carbonate cement types that may form in response to imposed CO_2 storage.

Carbonate cements are generally abundant (although somewhat heterogeneously distributed) within the diverse suite of lithofacies that comprise the Eau Claire (Neufelder et al., 2012; Śliwiński et al., 2016). Cement mineralogy is predominantly dolomite-ankerite, calcite and subordinate siderite to Mg-siderite. Volumetrically significant occurrences also locally occupy the pore space of the upper Mt. Simon near contact with the overlying caprock (Hoholick et al., 1984; Fishman, 1997; Bowen et al., 2011; Denny et al., 2015). Limited analyses indicate that carbonate minerals (calcite, dolomite) are also present in mudstone/shale interbeds at depth in the general vicinity of the CO₂ injection zone within the lower Mt. Simon (e.g. see Table 8.3 in Finley, 2005). These clay mineral-rich interbeds are considered to be the first reactive environments that will be encountered by the emplaced CO₂ plume as it buoyantly rises through the reservoir, and are estimated to have the same capacity for sequestering carbon by mineral-trapping reactions as the basal Eau Claire shale (Finley, 2005). Characterization could include isotopic fingerprinting studies of carbonates from these intervals in core material recovered from: (1) wells drilled at the IBDP site prior to CO₂-injection (2011-2014), and (2) future coring efforts during the now on-going, post-injection monitoring phase of the project.

Comparative studies of pre- and post-injection samples could aid in ground-truthing and/or refining reactive flow and transport models that attempt to: (1) predict the rate of mineral-trapping reactions, (2) to delimit the likely spatial distribution of reaction products (carbonate cements), and (3) to estimate the fraction of the CO₂ introduced into the reservoir/caprock system that will likely become permanently immobilized in mineral form (Liu et al., 2011). Whereas the CO₂ injection zone is situated within the lower Mt. Simon Sandstone at the IBDP site, injection was also planned into the upper portion of this reservoir unit at the nearby site of the FutureGen 2.0 project (now defunded; e.g. Bonneville et al., 2013).

We identify some areas of current research interest where in situ isotope microanalysis by SIMS could provide unique insights to investigations concerned with understanding how CO₂ will interact with geological reservoirs and caprocks under engineered storage conditions. It is likely that studies of natural CO₂ accumulations - regarded as analogues to engineered CO₂ storage - could find the micrometer-scale spatial resolution afforded by the SIMS technique particularly advantageous.

Research efforts directed at natural analogues seek to quantify the rate and extent of CO₂ trapping via precipitation of carbonate mineral cements (i.e., 'carbon mineralization' or 'mineral-trapping'), and by so doing to make quantitative predictions about the probable long-term fate of CO₂ in a prospective reservoir. Stable carbon and oxygen isotope analyses are an important component of this line of research, as they provide a means by which to distinguish different carbonate cement populations within the pore space of a reservoir or caprock unit (e.g. CO₂-charge-related cements vs. those that may have formed during earlier stages of sediment alteration). However, clear interpretations of conventional isotopic data (sampling typically at the 100-1000 µm³ scale) will be hindered in situations where it is not possible to mechanically or chemically separate (due to small crystal size) different carbonate cement generations. This, specifically, is where in situ analysis by the SIMS technique has a unique advantage (routine in situ sampling at the 1-10 µm scale).

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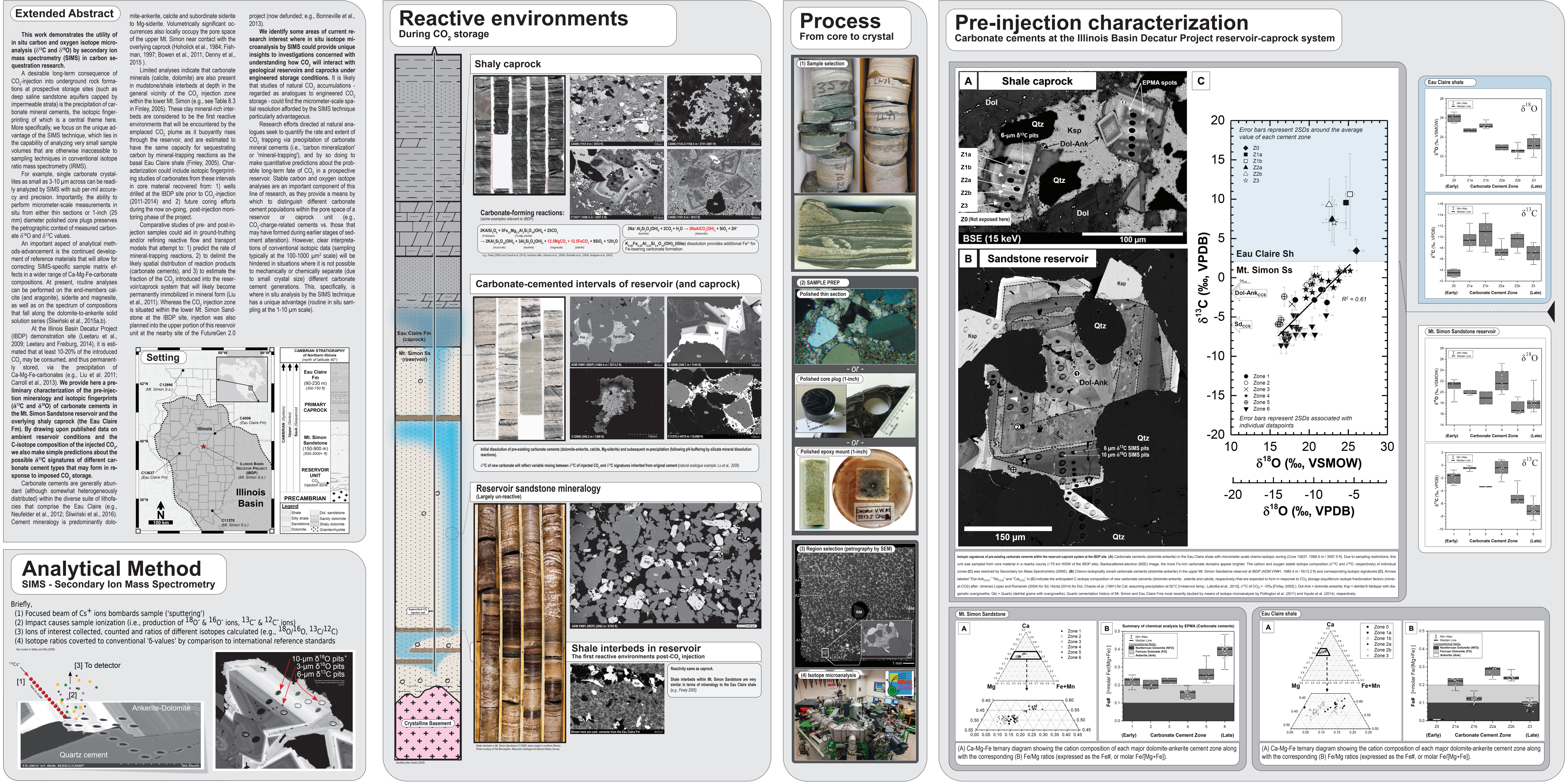
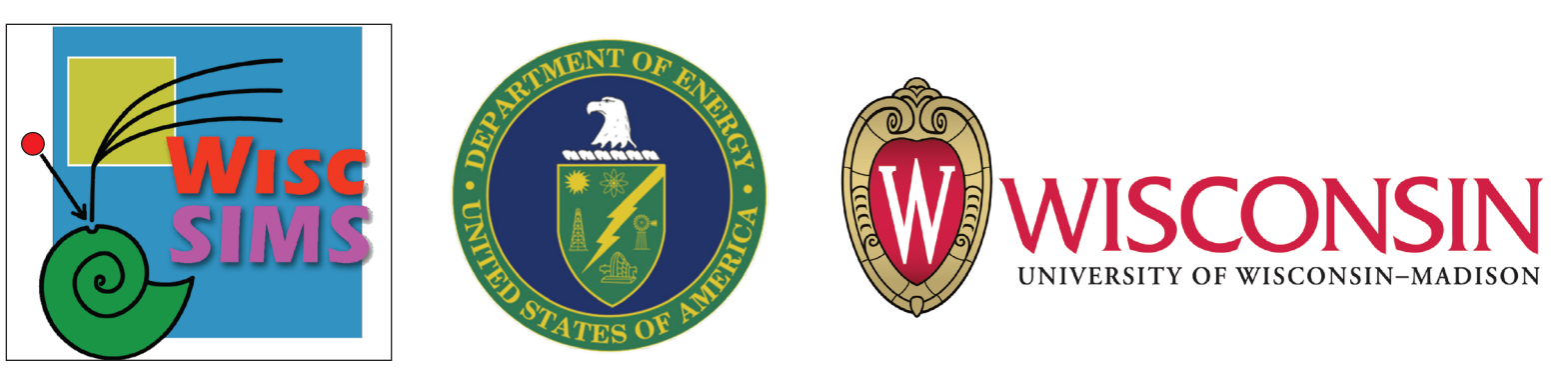
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