Measurement of the reactive surface area relevant to CO₂ mineralization in a reservoir sandstone

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Introduction

The accessible surface area of reactive minerals considered in reactive transport models are needed to multiply rate constants associated with the reactive minerals, since the latter are typically normalized to a unit surface area. An experimental approach is developed and applied in this study that enables the measurement of the surface area of each reactive mineral located within the connected pore network of a sandstone from a carbon sequestration pilot site in Cranfield, Mississippi [1]. Several analytical techniques are used that probe the sample at different scales and dimensions, including X-ray based micro-tomography (u-CT), Energy Dispersive X-ray Spectroscopy-Scanning Electron Microscopy (SEM-EDX), Backscattered Electron Microscopy (BSE-SEM), and Focus Ion Beam-Scanning Electron Microscopy (FIB-SEM). In contrast to the methods commonly employed to measure mineral surface areas, our approach accounts for the fraction of the mineral surface that is accessible to transport. Our method thus may help minimize the discrepancy often observed in the literature between the rates predicted by models and those measured in the field, and could be used in reactive transport models that would accurately predict the fate of CO_2 in the deep subsurface.



Figure 1: Mineral accessibility mapping

Results and Conclusion

The accessible surface area of each reactive mineral present in the sandstone is inferred, in m^2/g , by multiplying the fraction of each reactive mineral next to the connected pore network, measured in 2D (Figure 1), with the surface area of the connected pore network in the rock, which is measured in 3D from u-CT tomography images.

The characterization approach employed in this study is suitable for mapping the mineral distribution and pore structure found in a reservoir sandstone currently being considered as a sequestration site. Our approach could be also employed to characterize the physical and chemical properties of the rock after CO_2 injection. This would be useful in determining where precisely carbon dioxide is trapped in the rock and in identifying the CO_2 sequestration mechanisms.

[1] Landrot et al. (2012) Chem. Geol. in review

The density, thermal expansion and compressibility of FeO in model basalts (An-Di-Hd) and a lunar basalt: Fe²⁺ in 6-fold coordination

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FeO is an important component in both terrestrial and lunar basalts and yet its partial molar volume at one bar is not well known because of the difficulty of performing double-bob density measurements under reducing conditions. Moreover, there is growing evidence from spectroscopic studies that Fe²⁺ occurs in 4, 5, and 6-fold coordination in silicate melts, and it is expected that its partial molar properties will vary accordingly. We have conducted both density and relaxed sound speed measurements under reducing conditions on four liquids in the An-Di-Hd (CaAl2Si2O8-CaMgSi₂O₆-CaFeSi₂O₆) system: (1) Di-Hd (50:50), (2) An-Hd (50:50), (3) An-Di-Hd (33:33:33) and (4) Hd (100), as well as a lunar basalt. All the multi-component (model basalts and lunar basalt) liquid density data were combined with published density data on SiO₂-Al₂O₃-CaO-MgO-K₂O-Na₂O liquids (Lange, 1997), and CaO-Al₂O₃-TiO₂-SiO₂ liquids (Lange and Carmichael, 1987) in a fit to a linear volume equation; the results lead to a partial molar volume for FeO = 12.2 (\pm 0.1) and TiO₂ = 23.9 (\pm 0.1) cm³/mol at 1723 K, and dV/dT for FeO = 3.45 (\pm 0.62) 10⁻³ and TiO₂ = 3.88 (\pm 1.43) 10^{-3} cm³/mol-K. The partial molar volume for FeO is similar to that for crystalline FeO at 298 K (halite structure; 12.06 cm³/mol), which suggests an average Fe^{2+} coordination of ~6 in these model basalt and lunar basalt compositions. In contrast, the fitted partial molar volume of FeO in pure hedenbergite liquid is 14.6 ± 0.3 at 1723 K, which is consistent with an average Fe²⁺ coordination of 4.3 derived from EXAFS spectroscopy (Rossano, 2000). Similarly, the compressibility data for the three model basalt and lunar basalt liquids were combined with compressibility data on SiO₂-Al₂O₃-CaO-MgO liquids (Ai and Lange, 2008) and new sound speed data on CaO-MgO-TiO₂-SiO₂ liquids in a fit to an ideal mixing model for melt compressibility; the results lead to a partial molar compressibility ($\pm 1 \sigma$) for FeO = 3.25 (± 0.15) 10⁻² and TiO₂ = 8.67 (\pm 0.06) 10⁻² GPa⁻¹ at 1723 K. In contrast, the compressibility of FeO in pure hedenbergite liquid is significantly larger than that in the basalts: 6.3 (\pm 0.2) 10⁻² GPa⁻¹. When these results are combined with density and sound speed data on CaO-FeO-SiO₂ liquids at one bar (Guo et al., 2009), a systematic and linear variation between the partial molar volume and compressibility of the FeO component is obtained, which appears to track changes in the average Fe²⁺ coordination in these liquids. Therefore, the three most important conclusions of this study are: (1) ideal mixing of volume and compressibility does not occur for all FeO-bearing liquids, owing to changes in Fe²⁺ coordination, (2) the partial molar volume and compressibility of FeO varies linearly and systematically with Fe²⁺ coordination, and (3) ideal mixing of volume and compressibility does occur among the three multicomponent An-Di-Hd liquids and extends to lunar basalt compositions, presumably because of a common, average Fe^{2+} coordination of ~6.