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Effect of quartz overgrowth precipitation on the multiscale porosity of sandstone: A (U)SANS and imaging analysis

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Abstract

We have performed a series of experiments to understand the effects of quartz overgrowths on nanometer to centimeter scale pore structures of sandstones. Blocks from two samples of St. Peter Sandstone with different initial porosities (5.8% and 18.3%) were reacted from 3 days to 7.5 months at 100 and 200 °C in aqueous solutions supersaturated with respect to quartz by reaction with amorphous silica. Porosity in the resultant samples was analyzed using small and ultrasmall angle neutron scattering and scanning electron microscope/backscattered electron (SEM/BSE)-based image-scale processing techniques.

Significant changes were observed in the multiscale pore structures. By 3 days much of the overgrowth in the low-porosity sample dissolved away. The reason for this is uncertain, but the overgrowths can be clearly distinguished from the original core grains in the BSE images. At longer times the larger pores are observed to fill with plate-like precipitates. As with the unreacted sandstones, porosity is a step function of size. Grain boundaries are typically fractal, but no evidence of mass fractal or fuzzy interface behavior was observed suggesting a structural difference between chemical and clastic sediments. After the initial loss of the overgrowths, image scale porosity (>∼1 cm) decreases with time. Submicron porosity (typically ∼25% of the total) is relatively constant or slightly decreasing in absolute terms, but the percent change is significant. Fractal dimensions decrease at larger scales, and increase at smaller scales with increased precipitation.

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1. INTRODUCTION

The microstructure and evolution of porosity in time and space play a critical role in many geologic processes, including the migration and retention of water, gas and hydrocarbons, the evolution of hydrothermal systems,

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weathering, diagenesis and metamorphism, as well as technological processes such as CO_2 sequestration, shale gas and secondary oil recovery. The size, distribution and connectivity of these confined geometries collectively dictate how fluids migrate into and through these micro- and nanoenvironments, wet and react with mineral surfaces. To properly interpret the time–temperature–pressure history of a geological system the physical and chemical "fingerprints" of this evolution in the rock should be interrogated from the nanoscale to the macroscale.

In many sandstones formation of pore-filling overgrowths plays a critical role in the modification of porosity at all scales. However, the effect of pore scale and substrate composition on pore filling processes remains unclear. It has been suggested, on the basis of observations of pore-filling in sandstones (Putnis and Mauthe, 2001; Emmanuel and Berkowitz, 2007; Emmanuel and Ague, 2009; Emmanuel et al., 2010; Cook et al., 2011; Anovitz et al., 2013a), that solubility increases in small pores due to interfacial energy effects, and that larger pores, therefore, fill first. However, preliminary data also suggest that the interaction between precipitate and substrate (e.g., calcite growth in controlled pore glass (CPG), functionalized CPG or limestone, Stack et al., 2014), varying geochemical parameters (pressure, temperature, compositions, etc., Wang et al., 2013) and nonuniformity in the flow field (Noiriel et al., 2012; Molins et al., 2012) can dramatically affect pore filling (Stack et al., 2014). Ising models suggest that the optimum pore size for precipitation may depend on saturation state and pore geometry (Hedges and Whitelam, 2012, 2013). It is evident that precipitation in porous media is a complex process that is still poorly understood. In addition, available analysis (Anovitz et al., 2013a) suggests that the surface fractal dimension is pore-size dependent. This, in turn, would suggest a size-dependent variation in the number density of available nucleation sites. In-situ observations of nucleation and precipitation reactions, correlated with their rates, may help identify fundamental principles governing the precipitation process.

Annealing processes during precipitation and recrystallization can also play an important role in the evolution of pore structure. Wong et al. (1986) noted that if the fluid is "clean" (i.e., pure water), roughness is controlled by the competition between thermal fluctuations and surface tension. This is analogous to the roughening of domains walls in the pure Ising model, which predicts a transition temperature (T_r) above which roughening occurs even under equilibrium conditions (cf. Chui and Weeks, 1981; Barabási and Stanley, 1995). Random contamination of growth sites by impurities in pore fluids can lower T_r, analogous to results obtained from random-field Ising models (Wong, 1985), and the roughening of domain walls by thermal fluctuations in the atomistic nonequilibrium model (Barabási and Stanley, 1995). Similarly, Cohen (1987) noted that sedimentary rocks appear to behave in a manner significantly different from that expected for sintered material, including formation of fractally rough grain boundaries. He suggests this "anti-sintering" behavior is caused by reduction of grain/pore free energy due to interaction with pore waters. A similar effect was observed by Anovitz et al. (2009) in contact metamorphosed Hueco limestone.

The purpose of this paper, therefore, is to investigate controls on pore-scale precipitation-dissolution processes under experimentally controlled conditions. To do so we have taken samples of the relatively pure St. Peter Sandstone of different initial porosity and exposed them under static, externally buffered conditions, to quartz-oversaturated solutions at 100 and 200 °C for periods ranging from 3 days to 7.5 months. Although a great deal is known about the factors that control the dissolution and precipitation rates of quartz (cf. Dove and Rimstidt, 1994; Dove, 1999; Dove et al., 2005, 2008), we here interrogate how these depend on, and affect the pore structure of, the matrix in which precipitation occurs. We have, therefore, experimentally grown quartz overgrowths in a sandstone matrix, and used a combination of small and ultra-small angle neutron scattering and electron imaging techniques to examine qualitatively and quantitatively the processes by which quartz precipitation occurs.

2. EXPERIMENTAL TECHNIQUES

2.1. Starting materials

Starting materials consisted of two samples of St. Peter sandstone from southwestern Wisconsin: 04Wi17b and 05Wi30 (Kelly et al., 2007; Anovitz et al., 2013a). These were chosen for their markedly varied initial porosities, with 04Wi17b containing only about 4.8% porosity, and 05Wi30 containing 25.8% initial porosity, the difference being due to the presence of substantial, optically continuous silica overgrowths in the former. Both were otherwise nearly pure quartz arenites, containing only very small amounts of calcite and iron-oxide. In both cases the experimental samples were cut from small samples of the initial rock ($<\sim 1\ in^3$) with no obvious inhomogeneities to assure that the starting samples for each experiment were as consistent as possible. Further descriptions of the origin and chemistry of these samples are provided by Kelly et al. (2007) and Anovitz et al. (2013a).

For these experiments a starting solution was required: (1) that was oversaturated with respect to the solubility of quartz, (2) that contained a significant quantity of dissolved silica, and (3) in which the solubility was relatively independent of temperature. As the solubility of silica in water is essentially independent of pH at low pH values, this meant a high-pH solution was required. The solubility of quartz and amorphous silica over a range of NaOH concentrations was calculated from the data of Wesolowski et al. (2004). At concentrations between about 0.1 and 0.5 molal NaOH, the solubilities of both amorphous silica and quartz are nearly temperature-independent. As a higher NaOH concentration increases the silica solubility we selected one near the upper limit of this range for our experiments.

To make the starting solution we placed 3.19 g of Cab-o-Sil fumed silica, 78.0447 g of $H_2{}^{18}O$, and 21.9540 g of D_2O (isotopic results will not be presented here) in a quartz-glass liner into a 300 cm^3, bolt-closure pressure vessel. As both the liner and the Cab-o-Sil were composed of amorphous