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# Dissolution and crystallization in confinement

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Confined fluids are a critical phase in a variety of geological systems. Transport and deformation-processes in most water-bearing rocks are mediated through small fluid pores, films or channels that are confined by the surrounding mineral grains. The nature of the grain-grain interface is crucial because it is the place where the dissolution and crystallization of the mineral and the transport of solutes to the surrounding pore space occurs. The exact nature of the grain-grain interface is under debate.

Recently several new experimental techniques have been used to study the confined fluid properties [1-3] or the grain interface structure [4-5]. In order to understand dissolution and crystallization in confinement it is necessary to understand the interplay between the confined fluid properties and the structure of the solid surface arising from instabilities in the growth/dissolution processes.

I review different experimental methods that may be employed for such studies and outline development and preliminary results from two techniques: X-ray reflectivity and optical interferometry.

#### References

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# The gypsum/anhydrite transition: A source of water during diagenesis?

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It has been established [1] that the gypsum/anhydrite transition, accompanied by release of 480 kg of water per m<sup>3</sup> of gypsum, occurs below 60°C at a pressures up to 50 MPa. Models [2,3] show that within a normal range of geothermal gradients and sediment types, the transition should be complete in most sedimentary basins by the time that gypsum has been buried under approximately 400 m of rock and sediment. Nevertheless, the geochemical and structural relations in the evaporite-detached Nuncios Fold Complex (NFC) of the Sierra Madre Oriental, Mexico [4], are best explained by late, deep expulsion of water accompanying the gypsum-anhydrite transition.

Within the NFC, fluid-rock interaction was compartmentalized within two geochemically distinct hydrostratigraphic units (HU) during folding. The lower HU, presumably once buried beneath approximately 5 km of vounger carbonate rock, has undergone extensive oxygen isotope exchange at about 200 °C with an aqueous solution having a  $\delta^{18}O_{VSMOW}$  of ~10%. Based on evidence from oxygen and strontium isotope relations and stratigraphy, the basal, 1000m-thick evaporite sequence, dominated by anhydrite, was a principal source of the geochemically distinct fluids that exchanged with rocks of the lower HU. In the upper HU, carbonates dominated fluid geochemistry. The migration of high-pressure fluids from the lower unit into the upper unit was possible only during increased deformation associated with late-stage fold tightening.

During the gypsum-anhydrite transition the  $\Delta V_{solid}$  decreases by 39%, whereas the water generated occupies 49% of the original volume [2]. Thus, overall, anhydrite-water occupies about 10% more space than the parent gypsum. If the transition occurs at a relatively shallow depth in a subsiding basin, is it possible that an appreciable part of the water generated remains in pore spaces produced by the  $\Delta V$  of the solid phases? If this water of dehydration remained trapped in the lower HU of the NFC during burial, it might produce precisely the isotopic relations we have observed. If viable, the same process might also have helped produce modern overpressured fluids common in the subsurface of the US Gulf Coast and elsewhere, and it might bear on structural deformation of rocks associated with bedded evaporites [5].

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