



Experimental Measurements of Micron-thick Interphase Thermodynamics along a Water-Rock Interface

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Water-rock interaction determines how the geochemical cycles evolve from Earth surface to the deep interior, related to the fluxes, time, and reactivity between fluid phases and solids. Thus, quantifying mass balances from the global scale to the local one, for understanding planetary geodynamics as well as optimizing geothermal doublets, require understanding how the driving force is controlled between solids and dissolved phases [1, 2]. As a consequence, water-rock budget has a major role to drive the porosity accessible to flow. The standard approach is to consider the chemical potentials of the bulk phases assuming the interface to be infinitely thin and therefore thermodynamically negligible, except with highly divided materials and/or super-confined solutions. Our work is based on previous investigations evidencing the formation of an interphase layer/domain, up to one micron thick, having distinct thermodynamic features with respect to the bulk phase properties [3].

Herein, diffraction limited FTIR micro-spectroscopy in transmission mode, based on confocal microscope coupled to broadband supercontinuum laser or synchrotron beam, was employed as an energetic probe to monitor the thermodynamic characteristics of liquid water as a function of beam location in a synthetic fluid inclusion (one pore micro-scale closed cavity). FTIR hyperspectral data was recorded to illustrate distance-dependent vibrational energy (absorption signatures) at room and homogenization temperatures. The vibrational energy was transformed to Gibbs free energy using a partition function [4].

The results showed that Gibbs free energy changes by 600 to 1000 J/mol up to 1 μm far from the water-quartz interface. This variation indicates a significant change in the chemical reactivity of liquid water over a thick domain, rather defining an "interphase" instead of an "interface." We observed that the thermodynamic property of this interphase domain has a thermal dependency, and by increasing the temperature the chemical potential has a higher value. The Gibbs free energy variation with T can be interpreted by either an enthalpic or an entropic contribution, or a combination of both. This surprising discovery calls for a shift in the paradigm of the bulk phases dominance in water-rock interaction.

References

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