

Influences of the quartz host mineral on the Raman spectra of H₂O and aqueous salt bearing fluid inclusions

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Raman Spectroscopy offers a powerful tool for the investigations of aqueous phases in fluid inclusions and can provide insights of vibrational modes of different species. The water stretching vibrations between 2800 up to 3800cm⁻¹ are the most informative signals for the investigation of fluids. This region shows one broad signal, which is a complex profile of overlapping bands. Dissolved electrolytes, which are present as simple ions are not Raman active but they can influence the characteristic Raman bands of the aqueous solution. The shape of the Raman contour shows a systematic change in dependence of the amount of dissolved anions and cations in the solution. The intensity in the front area of the water peak is decreasing to smaller values and a peakshift to higher wavenumbers could be observed. For this reason the Raman spectra of the stretching region of liquid water is often used to determine the salinity of fluid inclusions.

The Raman spectra of liquids were studied in synthetic H₂O and aqueous salt bearing fluid inclusions in quartz. The inclusions were synthesized at 600°C and various pressures in our laboratory. The Raman spectrum of H₂O is substantially different between a drop of water and a fluid inclusion. The spectrum of fluid phases in inclusions is not only defined by the fluid phase itself. The host mineral can influence the signal dramatically and modify the shape of the Raman bands due to polarization of the laser beam. In birefringent minerals such as quartz the spectra is strongly influenced by the crystallographic orientation of the host. Other modifications on the spectra are caused at the quartz- fluid inclusions interface depending on the angle of the surface of the inclusion wall. These phenomena may cause erroneous estimations of the salinity of fluid inclusions. We have qualified and quantified the variability of the Raman spectra due to these polarization effects in quartz.

Slow reaction rates, disequilibrium, and excess Argon: Teaching some bad dogs new tricks

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Geochemical, petrological, and geochronological interpretations about the evolving earth require assumptions about the poorly constrained rates of fundamental geologic processes. Among these processes are chemical reactions - whose rates determine whether systems reach equilibrium, and chemical transport mechanisms - whose rates control the lengthscale of equilibrium as well as important boundary conditions in models of isotopic closure. Here, I describe ways in which we can make use of otherwise problematic field situations where, 1) the equilibrium assumption, and 2) the standard model for isotopic closure, break down.

Models of reactive-transport within layered rock systems can be used to exploit fluid-rock disequilibrium to quantify reaction kinetics attending metamorphism. This method, involving Sr-isotopic diffusion and exchange is reviewed, as well as the fundamental result of its first application which suggests natural metamorphic reactions rates are many orders of magnitude slower than required for equilibrium to be maintained in most systems [1]. Such slow time-integrated reaction rates, corroborated by several other field based observations, mean that the petrologic evolution of the crust cannot a priori be assumed to follow equilibrium based predictions [2]. Quantification of reaction rates, coupled with equilibrium models, permits more accurate modeling of dynamic natural systems.

Excess argon, the result of a violation of the standard closure model, is a frequent annoyance in Ar/Ar thermochronology. Most important in the development of excess argon is the breakdown of the "zero-concentration boundary condition" assumption. Two system parameters ultimately control this: 1) the transmissive timescale, which is the time required for Ar-40 to escape from the local rock system, and 2) the total local sink capacity, which is the degree to which other local phases (minerals, fluids, and even grain boundaries [3]) may take in (i.e. partition) the Ar-40 relative to the mineral of thermochronologic interest. Numerical modeling of diffusive transport and exchange has yielded an empirical analytical equation which predicts the amount of excess argon in any phase in a system as a function of these two parameters [4]. With this quantitative model, it is possible to use this measureable quantity (excess Ar) as a tracer of transport, timescales, and cooling in its own right.

References

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