

## Non-Complexing Anions for Raman Microprobes under Hydrothermal Conditions

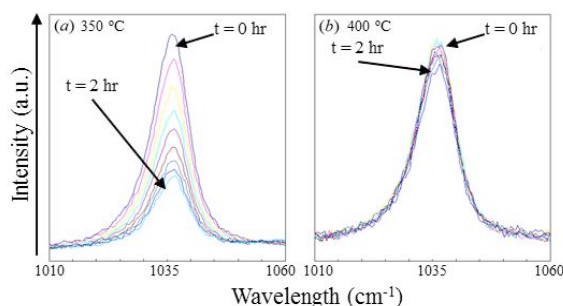
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Small scale techniques based on the use of diamond anvil cells (DAC) and capillary cells (“high pressure optical cells”, HPOC) are being increasingly employed to study subcritical and supercritical solutions using Raman spectroscopy [1]. Quantitative Raman measurements to determine thermodynamic properties and structural information often require the use of internal reference standards. These must be soluble, non-complexing and stable under hydrothermal conditions. The species used for this purpose at ambient conditions are bisulfate ( $\text{HSO}_4^-$ ), perchlorate ( $\text{ClO}_4^-$ ), perhenate ( $\text{ReO}_4^-$ ), and triflate ( $\text{CF}_3\text{SO}_3^-$ ).

This paper reports the thermal stability of these internal standards as a function of pH up to 420 °C and 30 MPa. Time-dependent reduced isotropic Raman spectra were obtained using a custom-made LabRamHR 800 spectrometer with quartz HPOC capillary cells at 30 MPa. Typical spectra are shown in Figure 1. In neutral solutions, perchlorate, perhenate and triflate are stable up to 140 °C, 200°C and 400°C, respectively. Simple rate equations, criteria for selecting reference anions, and measurement practices for quantitative hydrothermal studies in Raman microprobes are presented.

Figure 1. Raman spectra showing 0.1 m  $\text{CF}_3\text{SO}_3^-$  decomposition: a) 350°C pH 2 and b) 400°C neutral conditions.



[1] I.M. Cho, R.C. Burruss, W. Lu (2005), in *Adv. in High-Press. Technol. Geophys. Appl.*, J. Chen, Y. Wang, T.S. Duffy, G. Shen, L.F. Dobrzhinetskaya, Eds., Chap. 24, pp. 475-485.

## Quantifying the open-system behavior of cosmogenic noble gases in quartz

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Simultaneous production and diffusion of cosmogenic noble gases in minerals at the Earth's surface offers a potentially powerful tool for reconstructing past Earth surface temperatures. In order to utilize this open-system behavior for paleothermometry, knowledge of both the production rate and diffusion kinetics of a particular cosmogenic nuclide-mineral pair is required. We investigated the diffusion kinetics of  $^3\text{He}$  and  $^{21}\text{Ne}$  in quartz through a series of stepwise heating and degassing experiments. Natural and synthetic quartz samples were irradiated with protons to produce uniform distributions of  $^3\text{He}$  and  $^{21}\text{Ne}$  through similar nuclear transmutations as those induced by cosmic rays. Single grains of irradiated natural quartz exhibit two stages of linear Arrhenius behavior for both He and Ne diffusion: one at low temperatures and for gas release fractions of  $\sim 75\%$ , and one at high temperatures for the remaining  $\sim 25\%$ . We interpret these two Arrhenian arrays to represent multiple diffusion domain-type behavior in quartz and will discuss the physical meaning of such domains through ongoing experiments on synthetic and natural quartz. Comparison of degassing experiments on vein quartz from the Transantarctic Mountains, conducted using both cosmogenic  $^3\text{He}$  from a several-hundred grain aliquot and proton-induced  $^3\text{He}$  from a single grain, demonstrates the following: (i)  $<6\%$  of the cosmogenic  $^3\text{He}$  produced within the low retentivity domain is retained at subzero temperatures over several Myr of exposure, while (ii)  $>90\%$  of  $^3\text{He}$  is retained within the high retentivity domain. A simple exposure history for this sample using a two-domain diffusion model suggests a maximum effective exposure temperature of  $-14^\circ\text{C}$ , although  $^{10}\text{Be}$  and  $^{21}\text{Ne}$  measurements suggest a more complicated history involving both burial and exposure. In contrast, the measured diffusion parameters for Ne from all experiments suggest quantitative retention in quartz over millions of years and at effective exposure temperatures less than  $45^\circ\text{C}$ . The ratio of cosmogenic  $^3\text{He}$  to  $^{21}\text{Ne}$  in quartz may therefore be useful for studying the temperatures of surface processes in polar environments.