

## Potential concentration measurements of $\text{HCO}_3^-$ and pH estimates in natural fluid inclusions by Raman spectroscopy: a case study from Libcice Gold Deposit

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Unusual fluid inclusion composition has been reported earlier at the Libcice orogenic gold deposit. (Zacharias, 2002 and Hrstka et al., 2011). Bicarbonate( $\text{HCO}_3^-$ )-rich  $\text{H}_2\text{O}-\text{CO}_2$  fluids (with minor amounts of  $\text{CH}_4-\text{N}_2-\text{H}_2\text{S}-\text{C}_2\text{H}_6$ ) and  $\text{H}_2\text{O}$  fluids were recorded by this earlier study. Based on the high variability of FIA and expected variable  $\text{HCO}_3^-$  content these fluids has been identified as ideal candidate for  $\text{HCO}_3^-$  quantification in natural fluid inclusions. Quantitative calculations of the concentration of Raman active ions such as:  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4$ ,  $\text{PO}_4^{3-}$ , and  $\text{HS}^-$ , can lead us to important information about pH,  $f_{\text{O}_2}$ ,  $f_{\text{S}}$  fugacity as well as other parameters of the paleofluid (Dubessy et al., 1989, 2008). The concentration of  $\text{SO}_4$ ;  $\text{HS}^-$  polyatomic species in natural paleofluids was measured and quantified for some species (Dubessy et al., 2002), but not many data have been reported for the  $\text{HCO}_3^-$ .

This study reports on high temperature Raman measurements made in order to confirm the abnormally high concentrations of bicarbonate in Libcice paleofluids and also on the first attempts to validate the individual Raman peaks for future quantitative analysis of  $\text{HCO}_3^-$  in aqueous-carbonic paleofluids. The pH calculation in quartz hosted natural fluid inclusions based on the pH controlled equilibria of ( $\text{HCO}_3^-$ )/( $\text{CO}_3^{2-}$ ) (with main Raman peaks at about  $1017\text{ cm}^{-1}$  and  $1064\text{ cm}^{-1}$ , respectively) were also evaluated. The high concentration of  $\text{HCO}_3^-$  in the fluids was confirmed by the presence of a peak at  $1014\text{ cm}^{-1}$  and at  $1360\text{ cm}^{-1}$  even at the temperatures above total homogenization). Proportions of the IR peak integrated areas were measured in order to receive the relative concentration of  $\text{HCO}_3^-$  in the aqueous solution.

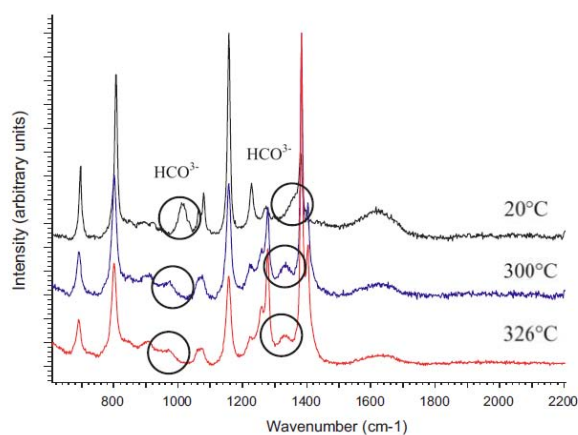


Fig. 1. Example Raman spectra of bicarbonate-rich aqueous phase present in  $\text{H}_2\text{O}-\text{CO}_2$  fluid inclusions at variable temperatures. Two major areas used for  $\text{HCO}_3^-$  identification and quantification are highlighted. Note the Raman peak shift with temperature.

For the low temperature measurements the peak area ratio was suggested as the most practical to estimate concentrations, whereas the peak height ratio seems more applicable for temperatures above  $100\text{ }^\circ\text{C}$ . The spectrum of quartz matrix and the possibility of spectral subtraction of quartz from the inclusion spectra were tested to overcome the peak overlap of quartz and  $\text{CO}_3^{2-}$  at around  $1066\text{ cm}^{-1}$ . Based on our results, the Libcice paleofluids were estimated to pH 7 - 8.5. The extremely high variation in relative peak intensity of the monitored part of quartz spectrum was confirmed even within a single grain. Other peak parameters were tested to establish the best potential calibration strategies for quantitative Raman measurement of bicarbonate in natural fluid inclusions both at room and at elevated temperatures. This research is important for the future pH calculation development and high

temperature Raman spectroscopic study of fluid inclusions/paleofluids.

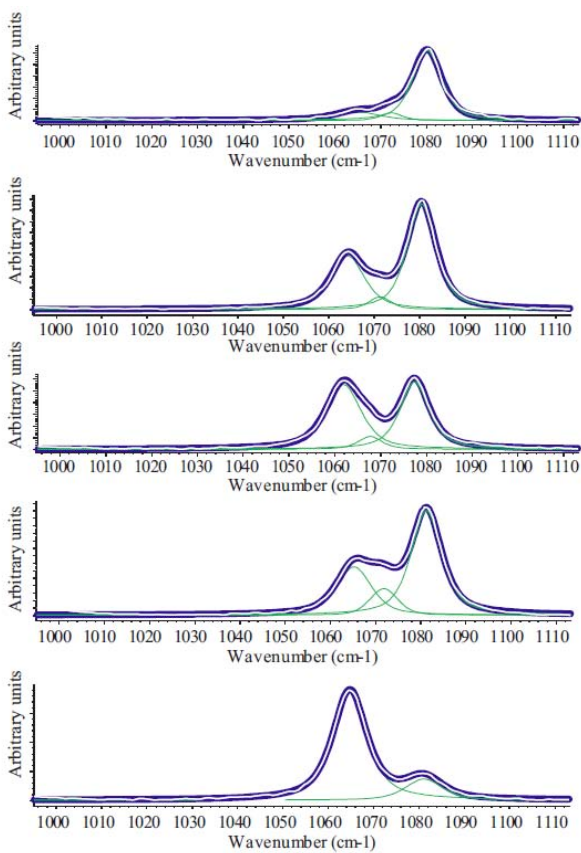


Fig. 2. Example Raman spectra of the quartz matrix showing variation in the region of interest for  $\text{CO}_3^{2-}$  quantification and potential pH calculation of paleofluids. Note the presence of variable matrix peak intensities in the area of  $1064 \text{ cm}^{-1}$  which is also an area of major  $\text{CO}_3^{2-}$  peak.

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