THE ACCURACY OF CA/NA RATIO AND SALINITY DETERMINATION USING MICROTHERMOMETRY OF HIGH-SALINITY FLUID INCLUSIONS IN DIAGENETIC MINERALS: A STUDY USING SYNTHETIC FLUID INCLUSIONS.

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Introduction

During the last decade, highly sensitive and precise analytical methods for the analysis of fluid inclusions in various minerals such as miniaturised crush-leach, Laser Ablation Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS), Laser Ablation Optical Emission Spectrometry (LA-OES) and synchrotron X-ray fluorescence microanalysis (SXFMA) have been developed (Banks, Yardley, 1992; Günther et al., 1998; Fabre et al., 1999; Ryan et al., 2001). These non-absolute analytical techniques are able to analyse major, minor and trace element ratios in fluid inclusions. Quantification of the absolute concentrations of these elements in the inclusions, or in other words, reconstructing the fluid composition from which the minerals formed, requires that the concentration of at least one element is known. This element can then be applied as internal standard for the quantification of other analysed ions. For this purpose, microthermometry can be used. However, interpretation of microthermometric data involves phase diagrams of simple systems and one should to have an idea about the accuracy of such an approach. We evaluated this method of fluid composition reconstruction for the case of sedimentary, Zn-Pb mineralising fluids, using synthetic fluid inclusions.

Methodology for the reconstruction of the fluid composition

The method outlined below was first applied by Weisbrod and Poty (1975) and have been used widely when ratios of cations present in the fluid inclusions are measured (e.g. Shepherd et al., 1985; Everett et al., 1999). The method is based on the fact that different salts have varying effects on the freezing point depression of pure H_2O. Previous workers argued that this depression is similar for 1 mole NaCl or KCl, but 1 mole $CaCl_2$ or $MgCl_2$ give the same depression as ~1.5 mole NaCl. However, using the improved regression equations of Oakes et al. (1990) and Dubois and Marignac (1997) for the freezing point depression of H_2O-$CaCl_2$ and H_2O-$MgCl_2$, respectively, 1 mole of $CaCl_2$ or $MgCl_2$ seems to have a similar effect as 2 moles of NaCl, rather that 1.5 moles. If it is assumed that all salts present are chlorides and that the effects of the individual salts are cumulative, then the following equation is valid:

$$\frac{eq.wt\%NaCl}{M_{NaCl}} = n_{NaCl} + \theta_{KCl} n_{KCl} + \theta_{CaCl_2} n_{CaCl_2} + \theta_{MgCl_2} n_{MgCl_2} + \ldots \qquad (1)$$

where M is the molecular mass, n_{salt} stands for the number of moles of the salt in 100g solution and θ_{salt} is the effect of the salt on the freezing point depression relative to the effect of NaCl (1 for KCl and 2 for $CaCl_2$ and $MgCl_2$). The left hand term in equation (1) represents the hypothetical number of moles of NaCl that is necessary to explain the observed freezing point depression of the saline inclusion. Since salts other than NaCl, KCl, $CaCl_2$ and $MgCl_2$ are present only in minor and trace amounts in most natural saline fluid inclusions, these salts can often be neglected in the right hand term of equation (1). The elemental ratios can be related with the actual number of moles of NaCl per 100g of solution present in the fluid inclusions:

$$n_{KCl} = n_{NaCl} \times \left(\frac{K}{Na}\right) \qquad (2)$$

$$n_{CaCl_2} = n_{NaCl} \times \left(\frac{Ca}{Na}\right) \qquad (3)$$

$$n_{MgCl_2} = n_{NaCl} \times \left(\frac{Mg}{Na}\right) \qquad (4)$$

By substituting (2) to (4) in (1), we get:

$$\frac{eq.wt\%NaCl}{M_{NaCl}} = n_{NaCl}\left[1 + \left(\frac{K}{Na}\right) + 2 \times \left(\frac{Ca}{Na}\right) + 2 \times \left(\frac{Mg}{Na}\right)\right] \qquad (5)$$

In equation (5), the number of moles NaCl is the only unknown. The concentration of the other minor and major elements analysed can readily be obtained from the elemental ratios.

Application to synthetic inclusions

Synthetic fluid inclusions in quartz were prepared which contained 30 026 ppm Na, 27107 ppm Ca, 4487 ppm K, 977 ppm Mg, 101 180 ppm Cl and 1597 ppm Br. Their composition falls in the ranges for that of oil-field brines and Zn-Pb mineralising fluids in carbonate-hosted Zn-Pb deposits. During cryogenic experiments, they show a melting behaviour typical as decribed for the H_2O-NaCl-$CaCl_2$ system. First melting was observed at temperatures between -51 and -48°C. Hydrohalite melted at -25.2 to -26.4 °C and Tm(ice) varied between -12.2 and -12.8°C. Modelling of the microthermometric data (Tm(hh) and Tm(ice)) of fluid inclusions in these samples using CalcicBrine 1.5 (Naden, 1996) demonstrates that the molar Ca/Na ratio can be determined with very good accuracy. The mean modelled Ca/Na ratio is 0.53, identical to the nominal ratio. The relative standard deviation on the ratio determinations is ~ 5%. The modelled total salinity (NaCl+$CaCl_2$) is 16.4 ± 0.3 wt% which is higher than the *true* NaCl+$CaCl_2$ (15.1 wt%), but identical to the actual total salinity (NaCl+$CaCl_2$+KCl+$MgCl_2$). These results suggest that the melting behaviour of fluid inclusions with a composition typical for those found in MVT-mineralisation can be accurately modelled by the H_2O-NaCl-$CaCl_2$ system.

Reconstruction of the fluid composition using the microthermometrical data, interpretation in an H_2O-NaCl system (Bodnar, 1993) and applying the method outlined above demonstrates an accuracy within ~1% of the nominal concentration of the salts. The results show that a combination of microthermometry and bulk or microanalytical techniques can precisely reconstruct the composition of highly saline, Ca-Na-Cl rich fluid inclusions.

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