THERMODYNAMIC CALCULATION OF SOLUTE CONCENTRATIONS IN FLUID INCLUSIONS BASED ON ELEMENT RATIOS AND MICROTHERMOMETRIC DATA

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Recent improvements in chemical analysis of fluid inclusions, using techniques such as LA-ICP-MS, PIXE, SXRF and LIBS for individual inclusions, and crush–leach analysis for bulk samples), now permit *concentration ratios* of solute elements to be determined with high accuracy. In order to apply these results to geochemical problems of hydrothermal processes, the element ratios must be converted to *absolute concentrations* in the inclusions. Approaches to this conversion problem have remained very approximate so far, and have not kept pace with the improved quality of the raw analytical data.

A strategy to obtain the absolute concentrations is to combine the element ratios with an indicator of the colligative properties of the analysed fluid inclusions, such as the melting temperature of solid daughter phases (e.g. ice, hydrohalite, halite, gas-hydrate clathrates, etc.) [1,2]. Melting temperatures can be measured by routine microthermometry to an accuracy of better than 0.2°C, thus providing a sensitive measure of bulk salinity. Traditionally in the fluid inclusion literature, the observed depression of melting points is expressed in terms of *equivalent* NaCl concentration. However, it is widely recognised that the presence of solutes other than NaCl can strongly influence the melting temperatures of daughter crystals, and hence influence estimates of bulk salinity. Previous methods to correct for these effects [1,2,3] have been restricted to very simple chemical systems (ternary or quaternary). Thus, while the problem for real, multicomponent inclusions has long been recognised, it has remained unsolved.

We have developed a thermodynamic procedure, named MELTDOWN, to calculate the absolute solute concentrations in multicomponent electrolyte solutions from input element ratios and microthermometric determinations of final-melting temperatures of daughter crystals, T_m(solid), such as ice and various salts. Equilibria are calculated using the algorithm of Mironenko et al. [4], which employs the Gibbs free energy minimization method and applies Pitzer's model to calculate the activity of water and the solute activity coefficients. The thermodynamic database of Spencer et al. [5] is used for the system Na-K-Ca-Mg-Cl-SO$_4$-H$_2$O over the temperature range –60°C to 25°C, and the database of Greenberg and Møller [6] is used for the system Na-K-Ca-Cl-SO$_4$-H$_2$O for phase transitions from 0°C to 250°C. The databases contain parameters for calculating constants of chemical reactions (lgK) and Pitzer parameters ($\beta_{ca}^{(0)}, \beta_{ca}^{(1)}, \beta_{ca}^{(2)}, C_{ca}^{\phi}, \theta_{cc'}, \theta_{aa'}, \psi_{cc'a}, \psi_{aa'c}$), at various temperatures.

Accordingly, the MELTDOWN model can calculate chemical equilibria for the Na-K-Ca-Cl-SO$_4$-H$_2$O system within the temperature range –60°C to +250°C. Although the databases yield very similar results between 0°C and 25°C, they use different polynomials to describe the mutually adjustable Pitzer parameters and solubility products as a function of temperature, and are consequently inconsistent with each other. Our model therefore switches automatically from one database to another, depending on the current temperature.

Calculations are first performed at T_m(solid), with pressure specified by the presence of vapour. Element concentration-ratios are fixed at the analytical values and the absolute concentrations are initially set at very low values. Two calculation pathways are followed, depending on which solid is the last to melt in the inclusions: 1) If ice melts last, the amount of water in the model aqueous solution is progressively reduced at T_m(ice), and at each step a test is made for equilibrium with ice; 2) If a salt is the last solid to melt, the concentration of the solutes in the model solution are progressively increased until saturation is reached at T_m(salt). In both cases, once the equilibrium concentrations of the solutes have been found, the temperature is progressively decreased down the liquidus of the system, and the solution is repeatedly tested for saturation with respect to other solid phases, until the eutectic temperature is found. The temperature step is 0.01°C and the concentration step is 0.005m. The result of these computations is the desired bulk composition of the fluid inclusion, plus a list of the expected phase transitions at temperatures below the input T_m(solid). This list allows the results for specific fluid inclusions to be checked for consistency against all the melting temperatures observable during microthermometry. Providing the calculations are accurate, any inconsistencies should alert the

researcher to missed elements in the inclusion analyses, to misinterpretations of the identity of the solid phases, or to metastable phenomena.

The MELTDOWN model has been verified with experimentally studied Na-K-Ca-Mg-Cl-SO$_4$-H$_2$O (sea water) and NaCl-CaCl$_2$-H$_2$O systems. Comparisons of experimental and calculated data are presented in Tables 1 and 2.

Table 1.

Temperature (°C) of first appearance of solids upon chilling of seawater

Solid	Experiment.	Model [5]	MELTDOWN model
Ice	-1.921 [7]	-1.924	-1.921
Mirabilite	-8.2 [8]	-5.90	-5.87
Hydrohalite	-22.9 [8]	-22.84	-22.87
Sylvite	-36 [8]	-34.25	-34.3
MgCl$_2$·12H$_2$O	-36 [8]	-36.82	-36.82
Antarcticite	-54 [8]	-53.64	-53.73

Table 2.

Experimental [3] and calculated (MELTDOWN) total salinities (wt%) at various NaCl/(NaCl+CaCl$_2$) weight ratios for experimentally measured ice-melting temperatures

NaCl/(NaCl+CaCl$_2$) 0.796			NaCl/(NaCl+CaCl$_2$) 0.593			NaCl/(NaCl+CaCl$_2$) 0.169		
T_m(ice) (°C)	wt% exptl.	wt% calculated	T_m(ice) (°C)	wt% exptl.	wt% calculated	T_m(ice) (°C)	wt% exptl.	wt% calculated
-6.12	9.57	9.57	-9.10	13.10	13.15	-19.99	20.86	21.09
-14.19	17.79	17.77	-15.14	18.36	18.34	-28.02	24.54	24.77
-20.05	21.99	21.88	-23.28	23.43	23.27	-34.03	26.75	26.92

In order to treat a wider range of inclusions the model must be extended with respect to both the number of components (especially those with low eutectic temperatures, such as Li) and the range of melting temperatures (above 250°C and below –60°C). This requires retrieval of Pitzer parameters from available experimental data on binary and ternary systems.

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