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Articles

Comment

Comment on "Effect of the vapor phase on the salinity of halite-bearing aqueous fluid inclusions estimated from the halite dissolution temperature", by M. Steele-MacInnis and R.J. Bodnar

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Abstract

Recently Steele-MacInnis and Bodnar reported an experimental study on the estimation of the salinity of halite bearing fluid inclusions from dissolution temperatures of halite crystals, in the presence and absence of a vapour phase Steele-Mac-Innis and Bodnar (2013). The authors present new purely empirical equations to calculate fluid inclusion bulk salinity, which is mainly determined by dissolution temperature of halite ($SLV \rightarrow LV$) with a minor correction due to presence of a vapour phase at higher temperatures, similar to the study of Bakker (2012). The experimental approach in their work is inappropriate, it does not provide experimental data, and it does not illustrate an estimate of uncertainty, accuracy and precision of the results. The mathematical modelling with purely empirical best-fit equations is insufficient, and partly erroneous. Comparison with the model from Bakker (2012) results in highly incorrect, inconsistent and imprecise statements about the quality of the results from Bakker (2012). Furthermore, the authors use "supplementary data" to continue a discussion without peer-review.
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1. SLV CURVE: EXPERIMENTAL METHOD AND RESULTS

Steele-MacInnis and Bodnar (2013) present results of experiments that repeat those of Sterner et al. (1988), to test the reproducibility and reliability of the *SLV* curve properties in the H$_2$O–NaCl system. The experimental method to synthesize highly saline fluid inclusions is based on loading separately known masses of H$_2$O and NaCl in capsules that also contain quartz cores with microcracks, which will subsequently heal at high temperatures and pressure and which will form numerous fluid inclusions. Crack-healing processes are instantaneously and may already occur during loading and unloading of experiments, i.e. at temperatures and pressures that may differ from the intended experimental conditions. Moreover, crack healing may occur before the separate loaded phases homogenize in one highly saline brine. Consequently, a variety of densities and salinities may occur in a fluid inclusion assemblage. Table 2 in Steele-MacInnis and Bodnar (2013) illustrates experimental conditions, average dissolution temperatures and average homogenization temperatures, but lacks uncertainty analyses. Proper experimental data are not presented. The average values are based on the measurements of an undefined number of fluid inclusions (between 5 and 15). Steele-MacInnis and Bodnar (2013) indicate that they measured a variation of 0.5 °C in T_m ($SLV \rightarrow LV$) and 5 °C variation in T_h ($LV \rightarrow L$), and classify this variation as a normal range, which is irrelevant to the accuracy of the

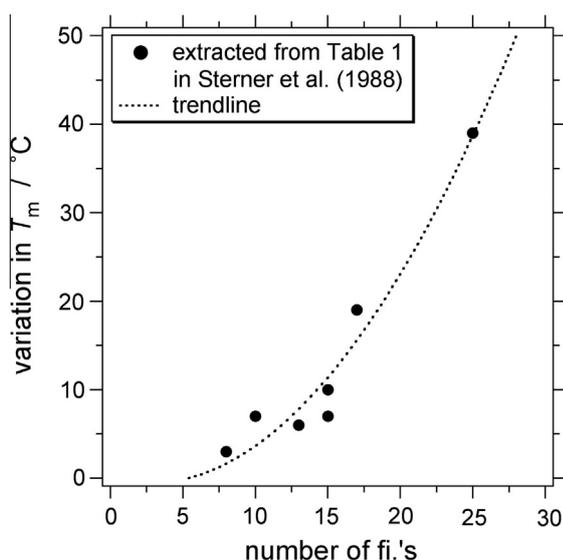[*] Tel.: +43 38424026211.
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Fig. 1. Variation in T_m values in binary H$_2$O–NaCl-rich inclusions as a function of the number fluid inclusions measured in one sample, according to the experimental data from Sterner et al. (1988).

results. Variations in temperatures are regarded as "random errors" which do not exceed ±1 °C (Steele-MacInnis and Bodnar, 2013), however these numbers highly underestimate the illustrated variation in homogenization temperatures. Experimental work in our laboratory has revealed a much larger variation in dissolution temperatures of halite if a larger population of highly saline synthetic fluid inclusions is taken into account. This is consistent with the experimental work from Sterner et al. (1988), and can be deduced from their Table 1 (Fig. 1). The variation is about 3 °C if only 8 inclusions are measured, whereas a variation of 30 °C is reached if at least 25 inclusions are measured. The experimental technique and the experimental laboratory used by Sterner et al. (1988) and those used by Steele-MacInnis and Bodnar (2013) are the same, therefore, the variation and uncertainty must be similar, although this information cannot be deduced from the manuscript. Consequently, the presented average values in their Table 2 cannot be scrutinized on reliability, and do not contribute to a better-defined *SLV* curve in binary H$_2$O–NaCl solutions. A larger variation in microthermometric data is suggested in paragraph 3.1 by mentioning that they selected only "eight synthetic fluid inclusion samples that showed <50 °C difference ...".

2. VOLUMETRIC PROPERTIES

The volumetric properties (φ^{vap}) of these inclusions at T_m were only approximately analyzed in Steele-MacInnis and Bodnar (2013) by comparison with the appearance diagram of hypothetical spherical and flat circular fluid inclusions in Roedder (1984). Bakker and Diamond (2006) have already illustrated that this approximate method is highly inaccurate, and can be greatly improved by using a spindle stage and two-dimensional images of a specific fluid inclusion.

3. EFFECT OF THE VAPOUR PHASE: EXPERIMENTAL METHOD AND RESULTS

Bodnar (1994) illustrated microthermometric data for fluid inclusions with a 40 mass% NaCl solution, which homogenize by vapour phase disappearance (Table 2 in Bodnar, 1994). Similar to Tables 2 and 3 in Steele-MacInnis and Bodnar (2013), only average values are given, and the absence of proper experimental data does not allow an estimation of the uncertainty and reliability of these numbers. Steele-MacInnis and Bodnar (2013) used the "bracketing approach" to overcome difficulties in loading an exact composition into capsules before experimentation. Each experiment was performed twice, with a slightly higher and lower concentration of NaCl. Table 3 in Steele-MacInnis and Bodnar (2013) does not provide verifiable results and information about both types of experiments, but gives an average value of dissolution and homogenization temperatures without an indication of any variation and without the number of inclusions that are measured. Most of the experiments presented in Table 3 in Steele-MacInnis and Bodnar (2013) are performed within the β-quartz stability field. The effect of the α–β phase change in quartz on the properties of fluid inclusions has not yet been systematically studied, although in each experiment this boundary is crossed twice. Decrepitation experiments at room pressures (e.g. Hladky and Wilkins, 1987) clearly indicate a "peak noise" at the α–β phase change ($\approx$ 572 °C) that may correspond to a massive irreversible decrepitation of all fluid inclusions in a quartz sample. Recent experiments by Doppler et al. (2013) have indicated that fluid inclusions are affected by the α–β phase change at higher experimental temperatures and pressures.

4. MATHEMATICAL MODELLING

Purely empirical model of binary H$_2$O–NaCl solution according to Driesner and Heinrich (2007) and Driesner (2007) can be applied to predict most fluid properties. They clearly define boundary conditions for purely empirical equations that allow a complete interpretation of the H$_2$O–NaCl system along the *SLV* curve. However, Steele-MacInnis and Bodnar (2013) prefer to use new purely empirical fits of liquid and vapour density along the *SLV* curve, based on tabled values in Driesner and Heinrich (2007), and they prefer to use the correlation from Sterner et al. (1988) to calculate the salinity along the *SLV* curve. The purely empirical fitting in Steele-MacInnis and Bodnar (2013) is based on a simple polynomial fitting of parameters, without the obvious limitation of phase boundaries, and it results, therefore, occasionally in highly inaccurate numbers. Moreover, a purely empirical fit to numbers resulting from the model of Driesner and Heinrich (2007) is in principle a double fitting procedure, that result in less accurate numbers if the complexity of the second fitting equation is less than the first.

The mathematical approach in Steele-MacInnis and Bodnar (2013) compares bulk densities that are estimated at T_m (at an arbitrary selected salinity) with bulk densities that are estimated at T_h. They claim that this equation calculates the density of a liquid phase throughout the region of liquid–vapour coexistence, independent of pressure. However, this equation can only reproduce liquid densities at the SLV curve (c.f. Driesner, 2007). Consequently, the mathematical approach, as illustrated in Fig. 3 in Steele-MacInnis and Bodnar (2013), must result in erroneous numbers.

A third stage of purely empirical fitting is applied in Eq. 3 in Steele-MacInnis and Bodnar (2013), that relates directly the volume fraction of liquid (φ^{liq}) at T_m with dissolution and homogenization temperatures. The parameters involved in this stage are obtained from the previously mentioned mathematical approach. It must be noted that the uncertainty and unreliability of numbers increase in each additional stage of purely empirical fitting procedures.

The combination of Eqs. 1, 2, and 3 in Steele-MacInnis and Bodnar (2013) results in an "easy-to-use" method that can be incorporated in simple spreadsheet-based programs, unlike highly complex thermodynamic models. The reliability of these equations is highly questionable according to the previously mentioned considerations, and the application of simple equations is always limited within thermodynamics. They usually cannot be used to predict the fluid properties of an entire fluid system, and may lead to highly inaccurate numbers if boundary conditions are not well defined.

5. *VX* DIAGRAM

The Vx diagram of the binary H_2O–NaCl system from Bakker (2012) is argued by Steele-MacInnis and Bodnar (2013) to include conditions that are not relevant to fluid inclusion studies. First, homogenization temperatures are not included in the Vx diagram of Fig. 9 in Bakker (2012), because they would exceed the limits of heating stages, but volume fraction of the vapour bubble is selected instead as a second constraint. Second, the considerations of Steele-MacInnis and Bodnar (2013) exclude the possibility to entrap a vapour-like fluid at higher temperature and pressure, because homogenization conditions would exceed the stability conditions of minerals. In addition, they proclaim that heterogeneous trapping does not give information about trapping condition of fluid inclusions (paragraph 4.2 in Steele-MacInnis and Bodnar, 2013). These are major mistakes in understanding trapping conditions of fluid inclusions, and possible post-entrapment modifications of fluid inclusions. It is general knowledge that trapping conditions can be directly obtained from homogenization conditions of coexisting liquid-rich and vapour-rich fluid inclusions (e.g. Diamond, 2003). The occurrence of heterogeneous trapping in nature is more common than illustrated in most fluid inclusion research, because the presence of multiple components in a pore fluid system result in a huge fluid-immiscibility field, up to high temperatures and pressures. The phase diagram illustrated in Fig. 9 in Bakker (2012) is not "misleading" (paragraph 4.2 in Steele-MacInnis and Bodnar, 2013) but illustrates fluid

properties in a wide range of conditions according to the equation of state from Anderko and Pitzer (1993). Natural fluid conditions cannot be deduced from this diagram, but it includes all possible fluid properties that can be calculated with this equation of state, either at experimental laboratory conditions or in natural rock.

6. COMPARISON BETWEEN MODELS AND EXPERIMENTAL DATA

An objective comparison with thermodynamic models (e.g. Anderko and Pitzer, 1993; Bakker, 2012) and purely empirical models (Driesner and Heinrich, 2007; Driesner, 2007) is not given in the paper of Steele-MacInnis and Bodnar (2013). Moreover, experimental data other than their fluid inclusion data are not used in this study to illustrate the accuracy of their model. A contradiction in statements about the accuracy of the model according to Bakker (2012) is given in paragraph 3 and 4 in Steele-MacInnis and Bodnar (2013): "consistency" and "systematically inconsistent", respectively. The uncertainties and incomplete fluid inclusion data in their purely empirical model does not allow any judgement about the quality of other models.

The model according to Bakker (2012) is further discussed in "supplementary data", which does not contain complementary data, such as extended data sets, or a more detailed description of the method, but is composed of an unreviewed discussion. Moreover, it contains a Vx diagram without tick marks that cannot be used or directly compared with other Vx diagrams such as presented in Bakker (2012).

7. SUPERIORITY OF THERMODYNAMIC MODELLING

Fundamental thermodynamic principles account for all the phenomena that can be observed in fluid inclusions, and they regulate the appearance of purely empirical mathematical equations that mirrors the relationship between thermodynamic parameters within a relative small range of conditions. These principles can be applied to the entire binary H_2O–NaCl system, but are completely ignored in the considerations of Steele-MacInnis and Bodnar (2013). A major advantage of thermodynamic modelling is that it may include more fluid components, such as KCl, CO_2 and CH_4, whereas purely empirical equations are highly restricted to only a small part of the available data in the binary H_2O–NaCl system. Thermodynamical modelling is, therefore, more reliable for the analysis of natural fluid inclusion systems, that usually contain a large variety of components.

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