The relationship between salinity, dissolution temperatures of halite, and volume fraction of the vapour phase in the binary H_2O-NaCl system

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Phase transitions observed in fluid inclusions during microthermometrical experiments can only be interpret in terms of composition and density if adequate and accurate equations, either empirical or theoretical, of the fluid that is trapped are available. The equations should be able to reproduce experimental properties of the specific fluid systems, moreover, they should be able to produce "reasonable" interpolated and extrapolated data.
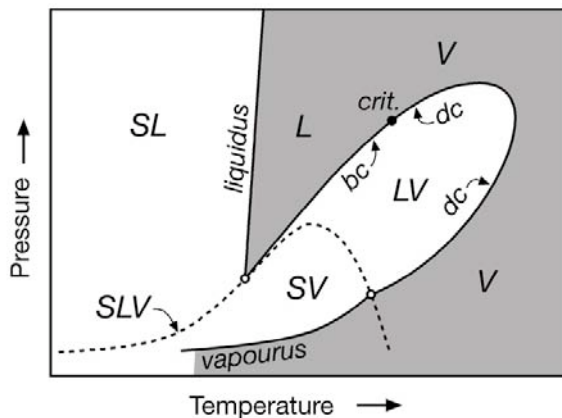

Fig. 1. Schematical isopleth of the H_2O-NaCl system illustrating a variety of phase assemblages. The shaded area contains a homogeneous fluid.

Dissolution of halite crystals in a brine occurs along the liquidus of this binary system (Fig. 1). The liquidus shifts to higher temperatures if the bulk salinity increases. The "starting point" of the liquidus is located on the SLV curve (halite + brine + vapour), and it extends to high pressures in a relatively small temperature interval. The dissolution of halite crystals in fluid inclusions can occur in two differently developing phase assemblages upon heating:

1. SLV → SL → L
2. SLV → LV → L (or V)

The first type of dissolution occurs on the liquidus, the second type of dissolution occurs on the SLV curve, and not on the liquidus. In principle, the dissolution temperature of both types cannot be used to calculate salinities directly. According to equilibrium thermodynamics, two parameters (or variables) have to be estimated or measured to define binary systems in inclusions, such as H_2O-NaCl. In practise, the nearly pressure-independent extension of the liquidus allows an approximate estimation of salinity with the definition of the SLV curve for type 1 dissolution. The intersections of isochores within the immiscibility field and the SLV curve (which mark the dissolution temperature of halite, Fig.2) are occasionally close to the "starting point" of the liquidus, therefore, the salinity is also approximately estimated by the definition of the SLV curve for type 2 dissolution.
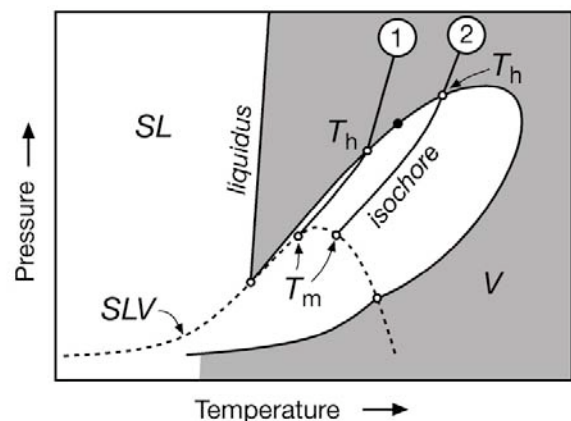

Fig. 2. Schematical isochores in a H_2O-NaCl system illustrating total homogenization (T_h) in to the liquid phase (1) and in to the vapour phase (2). T_m indicates dissolution temperatures of halite.

Figure 2 illustrates that the dissolution temperature of halite can be substantial higher for inclusions with lower bulk densities and the same bulk salinity, and thereby violating the above

mentioned simplification for type 2 dissolution. In other words, the size of the vapour bubble is also a factor that defines the bulk salinity of a fluid inclusion that reveals a total homogenization temperature that is higher then the dissolution temperature of halite (type 2, Fig. 3).
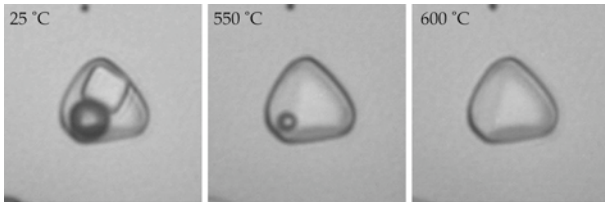

Fig.3. Microthermometrical heating experiment of a highly saline fluid inclusion of type 2 dissolution.

An equation of state for the H_2O-NaCl system according to Anderko & Pitzer (1993) is the only equation that can be used to calculate an isochore within the immiscibility field of a system with specific bulk salinity. It can, therefore, be used to calculate the intersection conditions of the SLV curve and variable bulk densities (Fig.4).
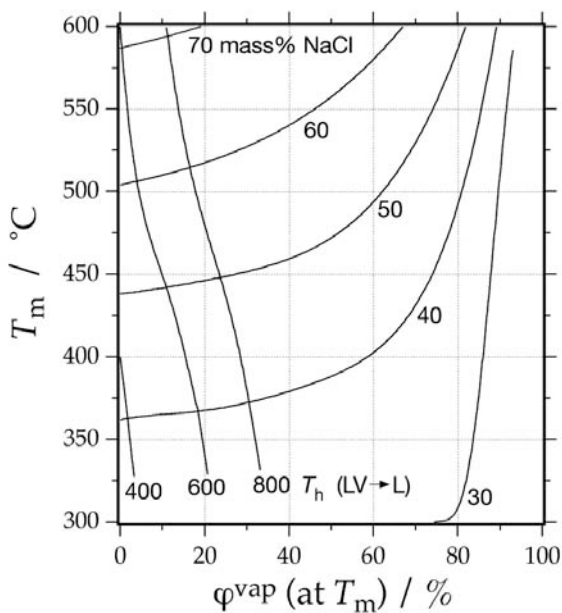

Fig.4. Relationship between T_m of halite (SLV→LV) and the volume fraction of the vapour bubble at T_m. at selected salinities. Nearly vertical curves represent equal total homogenization temperatures (LV→L) in ˚C.

Figure 4 is calculated with the software "LonerAP" which is part of the package FLUIDS (Bakker, 2003). The temperature limits in Figure 4 are in principle the limitation of the heating-freezing stage (i.e. 600 ˚C). Moreover, microthermometry above 600 ˚C may result in decrepitation of fluid inclusions because internal pressures may reach values above 100 MPa. Therefore, the estimation of vapour bubble volume fractions according to the method of Bakker & Diamond (2006) or a simplified estimation of volume fractions directly from area fractions at the temperature of dissolution of halite is a reliable method to obtain bulk salinities

The equation of state from Anderko & Pitzer (1993) is based on experimental data of vapour-liquid equilibria and density data in the homogeneous liquid region. In addition, the activity of NaCl along the liquidus is also included in modelling this fluid system. The properties of the SLV-curve are approximately reproduced with this equation of state, with a maximum relative deviation of 5% from experimentally obtained values. Below 300 ˚C, this equation of state cannot be applied, which is according to the temperature limits indication of the original paper. At lower salinities, below about 35 mass% NaCl, isochores in the immiscibility field are nearly parallel to the temperature-pressure conditions of the SLV-curve, which prevents the estimation of a straight-forward relationship between T_h and T_m.

Combining the equation of state for the H_2O-NaCl system from Anderko & Pitzer (1993) and knowledge about the SLV curve allows the determination of both bulk salinity and density of a fluid entrapped in inclusions, and can be used to estimate isochores within and outside the immiscibility field of the system. This equation of state can also be used for the ternary H_2O-NaCl-KCl system.

REFERENCES

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