

FLUID INCLUSION LIQUID-VAPOUR HOMOGENIZATION IN THE VICINITY OF THE DENSITY MAXIMUM OF AQUEOUS SOLUTIONS

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Introduction

Recent advances in fluid inclusion analysis make it possible to measure liquid-vapour homogenization temperatures (T_h) of initially metastable monophasic liquid inclusions by using single ultra-short laser pulses to induce vapour bubble nucleation (Krüger et al., 2007). Fig.1 presents a phase diagram of water calculated from the IAPWS 95 formulation (Wagner and Pruß, 2002), including the stability field of the metastable liquid. The line of Temperatures of Maximum Density (TMD) intersects the liquid vapour curve at 4.0 °C and has a negative slope in P-T space. The diagram illustrates that high-density isochores pass through a pressure minimum at the intersection point with the TMD line and that some of them return to positive pressures intersecting the (metastable) liquid-vapour curve again at low temperatures. This retrograde liquid-vapour homogenisation (T_{hr}) occurs upon cooling and can be observed in inclusions where $T_{hr} > T_{n,ice}$ (the temperature of ice nucleation). Theoretically T_h and T_{hr} represent the same fluid density; at 4.0 °C (the TMD), the values of T_h and T_{hr} become equal. In the case of fluid inclusions, which are not strictly isochoric, the temperature dependent volume change of the host mineral, however, is expected to shift T_{hr} to higher values, resulting in a seeming increase of the TMD.

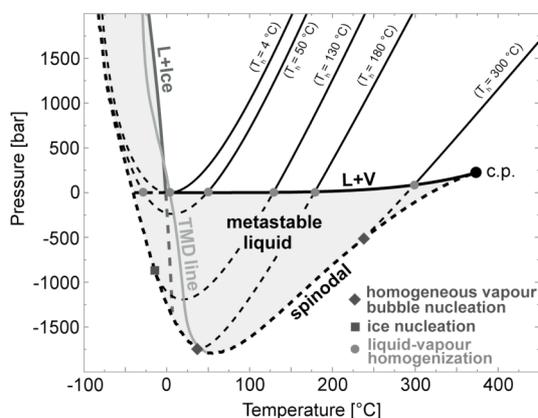


Figure 1. Phase diagram of water calculated from the IAPWS 95 formulation

Theoretical modelling

The aim of the present study was to quantify the effect of the volume change of different host minerals on the fluid density and thus on T_{hr} . As a basis for the modelling we used the IAPWS 95 formulation to calculate “true” isochores for pure water. We then applied a correction to account for the volume change of the host mineral by using thermal volume expansion coefficients (α) for calcite, quartz and gypsum. Thereby T_h was chosen as a starting point for the volume/density correction (cf. Fig. 2). Thermal expansion coefficients were fitted either directly from experimental data by Rao et al. (1969) for calcite and by Schofield et al. (1996) for gypsum or from volume data recommended by the *Thermophysical Properties of Matter Database (TPMD)* (Touloukian et al., 1977) for quartz and calcite and by the *High Temperature Materials–Mechanical, Electronic and Thermophysical Properties Information Analysis Center (HTMIAC)* (Desai, 1990) for quartz. In the case of calcite, α values have to be extrapolated to temperatures below 20 °C.

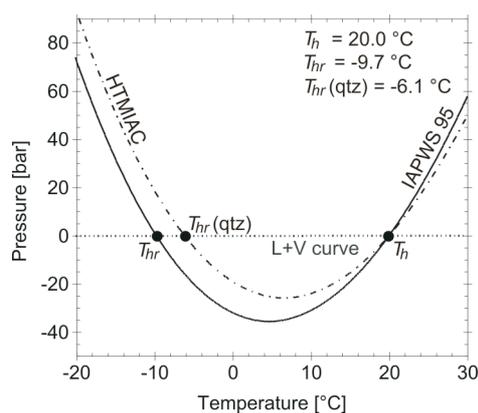


Figure 2. Shift of T_{hr} resulting from the volume change of the quartz host (α values from HTMIAC)

Results

Fig. 3 shows the shift of the T_h - T_{hr} curve for pure water (IAPWS 95 formulation) depending on the host mineral. The temperature where T_h is equal to T_{hr} increases from 4.0 °C

to 4.7-5.1 °C in calcite, to 5.9-6.1 °C in quartz and to 8.3 °C in gypsum and hence suggests a seeming increase of the TMD.

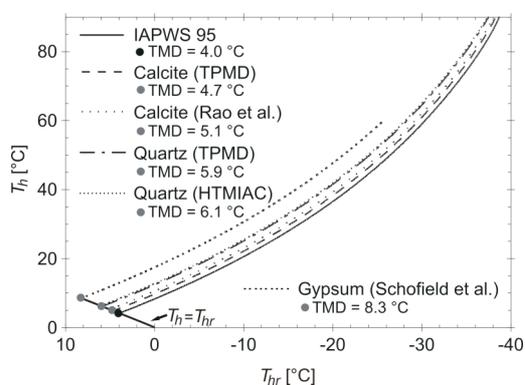


Figure 3. T_h - T_{hr} curves for different host minerals suggesting a seeming shift of the TMD of pure water.

Application to natural fluid inclusions

Natural fluids usually contain some salt and can often be approximated by gas-free aqueous NaCl solutions. In order to apply the T_h - T_{hr} curves for pure water to salt solutions we assume that the curves are simply shifted by translational displacement depending on the decrease of the TMD with increasing salinity (cf. *Int. Crit. Tables*), but do not change their shape.

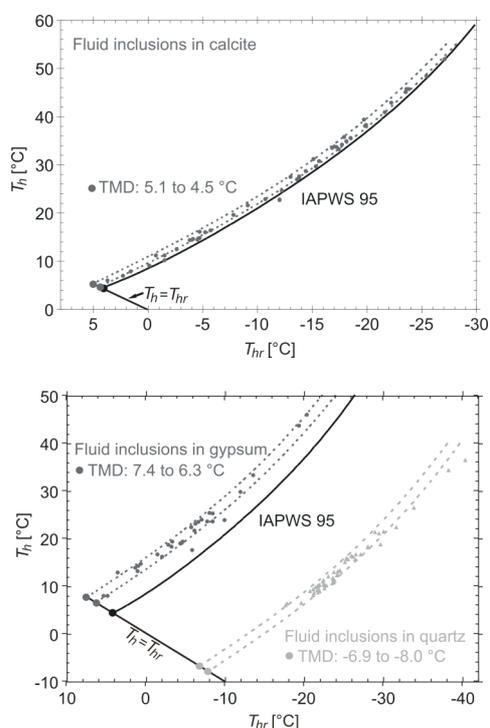


Figure 4. T_h - T_{hr} plots from natural fluid inclusions in calcite, gypsum and quartz.

Fig. 4 shows three examples of natural fluid inclusions in calcite, gypsum and quartz. In the calcite sample the TMD seemingly ranges between 5.1 and 4.5 °C and corresponds to a salinity of the solution between 0.0 and 0.36 wt% NaCl_{equiv}, which is in agreement with measured ice melting temperatures (T_{mice}) between 0.0 and -0.2 °C. In the gypsum sample the T_h - T_{hr} data display a shift of the TMD from seeming 8.3 °C to 7.5 - 6.3 °C corresponding to a salinity of 0.40 - 0.88 wt% NaCl_{equiv}. T_{mice} values of these inclusions, however, range from 0.4 to 0.7 °C and thus indicate slightly higher salinities (0.7 - 1.2 wt% NaCl_{equiv}). Finally, in the quartz sample the inclusions display a shift of the TMD in the range of 13.0 to 14.1 °C corresponding to a salinity of 5.3 - 5.7 wt% NaCl_{equiv}, i.e. T_{mice} values between -3.2 and -3.5 °C. In fact, the measured T_{mice} values typically range between -3.5 and -4.1 °C and thus indicate higher salinities as well.

Conclusion

The present study shows that the temperature dependant volume changes of the fluid inclusion host minerals cause a significant shift of the T_h - T_{hr} curves and a seeming increase of the TMD of aqueous solutions. The relatively poor consistency of the salinities derived from the TMD values and the T_{mice} indicates that either our assumption of a pure translational displacement of the T_h - T_{hr} curves or the simplifying assumption of a NaCl solution might be incorrect. Further investigations will be necessary to better understand the relation between the TMD and T_{mice} of aqueous salt solutions.

References

- Krüger, Y., Stoller, P., Rička, J., Frenz, *Eur. J. Mineral.* 19, 693-706 (2007)
- Wagner, W., Pruß, A. *J. Phys. Chem. Ref. Data.* 31, 387-535 (2002)
- Rao, K.V.K., Naidu, S.V.N., Murthy, K.S., *J. Phys. Chem. Solids.* 29, 245-248 (1968)
- Schofield, P.F., Knight, K.S., Stretton, I.C., *Am. Mineral.* 81, 847-851 (1996)
- Touloukian, Y.S., Kirby, R.K., Taylor, R.E., Lee, T.Y.R. *Thermophysical Properties of Matter*, Vol. 13, 350-357 and 637-640 (1977)
- Desai, P.D. HTMIAC Special Report, 40 (1990)
- International Critical Tables*, Eds. E.W. Washburn, New York, N. Y. (1933)