## **GEOCHEMICAL PHENOMENA AT NEGATIVE PRESSURES**

Shmulovich K.I. (IEM RAS), Mercury L. (Orsay, France)

kiril@iem.ac.ru; mercury@geol.u-psud.fr

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Certain liquids can be put under a metastable superheated state: these are liquids under tension, or equivalently liquids at "negative pressure". This peculiar state can exist in isolated clusters of intergranular fluid, and/or in fluid inclusions cooled below the equilibrium curve L-V without gas nucleation, and/or in soil water trapped inside thin capillaries, and/or at the focus point of shock waves in a liquid medium. Negative pressure has geochemical significance in fluid inclusions and soil capillaries, but experimental data for solution under tension are very scarce [1]. Published data [2,3] are essentially based on extrapolating the equation of state (EoS), calibrated at positive pressures in stable conditions. Only the EoS of pure water was partly calibrated at P < 0 (-100 MPa) by speed of sound measured by Brillouin spectroscopy [4].

In synthetic fluid inclusions (SFI), large values of negative pressures (down to -120, -130 MPa) can be obtained easily enough with pure water and salt solutions [1,5]. However, pressure of the trapped liquid is not measured but is estimated either by extrapolation of the EoS at negative pressure (pure water), or by linear extrapolation of isochoric lines from the stable domain (positive pressures) to the metastable one (salt solutions). Fig.1 presents our estimations of pressure after measurements of Th – temperatures of homogenization of the SFI (the reaction  $L+V \rightarrow L$ ), and Tn – temperatures of vapour phase nucleation (L $\rightarrow$ L+V). These SFI were trapped in quartz matrix crystal at 400°C and 0.5 GPa, and Th is around 150°C. If there is a Th-Tn difference above several degrees centigrade, the steep slope of isochors for water and aqueous solutions leads to create "tension" in the liquids (negative pressures). As shown by fig. 1, the spread of pressures for one population of SFI is large. For example, for pure water inclusions, the estimated pressures range from -30 MPa to -120 MPa. The reasons of such a scope are not clear now: possibly it results from a change of the SFI volumes (not isochoric) or a nucleation of the vapour phase either in homogeneous mode or in heterogeneous mode depending on the internal surface state or on presence of impurities in the trapped fluids. SFI containing solutions of NaCl (2 and 4 m) and CsCl 4 m exhibited smaller interval of (Th-Tn) variations and consequently minor spread in pressures. The values of Th are very well reproducible either for different SFI in the same population as for the same inclusion but at different position of the sample in the cooling-heating stage ("Linkam"). The values of Tn are only reproducible for the same inclusion.



Fig.1. Results of calculation for pressures in SFI at Tn. Some published values are shown as well

Special measurements were done to estimate the feed-back of the thermal gradient of the "Linkam" stage on Th and Tn. The same inclusions were measured at "normal" position and after an upside down rotation. The influence of the heating rate was studied as well with 20°, 10°, 5° and 2° per minute values. Change of 7-8°C are thus recorded for total differences (Th-Tn) around 50°C and more. The maximal values (Th-Tn) were close to 65°C, but for many small inclusions the reaction  $L\rightarrow L+V$  (defining Tn) was not observed. These inclusions are homogeneous at any temperatures up to the destruction of the samples. As seen on fig.1 the experimental points are positioned on the same isochors (except CsCl solutions) and consequently the small homogeneous inclusions must be positioned below, on the same isochor than the inclusions with measured Th and Tn. This means that much more negative pressures takes place at cooling in the small inclusions, perhaps tension close to the spinodal. The L-V spinodal on fig.1 is the curve limiting the area of mechanical stability for the liquid phase: along this curve  $(\delta V/\delta P)_T=0$ .

The similar effects of homogeneous nucleation are observed in natural samples, but the density in the inclusions is often unknown.

A graphical example for estimating the negative pressure using the slope of the increasing tension in the liquid phase on cooling can be drawn, using a large fluid inclusion (near 100 microns) in quartz with 4 m NaCl solution. The inclusion was sintered at 500°C and 500 MPa during 2 weeks.

The temperature of homogenization for the inclusion (Th= $221^{\circ}$ C) corresponds to density of water 0.839 g/ccm. The Th is very well reproducible at +/- 1°C. The extrapolation of the EoS of NaCl solutions in the metastable region has not been tested, and so we use pure water EoS.

For salt solutions the slope of isochor will be steeper than for water, but isochors have a small curvature and these simplifications partly compensate each other.



Fig.2. Estimation of negative pressure at Tn= 170°C for inclusion with Th=221°C (see film)

The process of vapour nucleation was video recorded (see http://www.iem.ac.ru//staff/kiril). Nothing happened when inclusion was cooled from 230°C to 171°C with 5°/min rate, and the steady state at 171°C corresponds to around -81 MPa.

After short next cooling, at 169.6°C, a brutal and intense boiling was observed in the inclusion. The density increased by jump from 0.839 (metastable fluid density) to 0.897 g/cc (density of liquid on the L-V curve at Tn), i.e. density increased by 7 %. It is a very large value for low compressible liquid and in the stable state area, an increasing 120 MPa pressure is required to produce a similar density change. Retrograde boiling in homogeneous isochoric system graphically demonstrates the rate of increasing tension in the liquid before phase transition (nucleation). Formation of many gas bubbles in the inclusion supports the idea of homogeneous nucleation but a triggering of the nucleation by sound waves emitted during the first vapour bubbles appearance is possible as well.

## References

- 1. Green I.L., Durben D.J., Wolf G.H., Angell C.A. Water and solutions at negative pressure: Raman Spectroscopic study to -80 megapascals // Science. 1990. V. 249. PP. 649-652.
- 2. *Mercury L., Azarouval M., Zeyen H., Tardy Y.* Thermodynamic properties of solutions in metastable systems under negative or positive pressures // Geochim. Cosmoch. Acta. 2003. V. 67. N. 10. PP. 1769-1785.
- 3. *Mercury L., Tardy Y.* Negative pressure of stretched liquid water: Geochemistry of soil capillaries // Geochim .Cosmoch. Acta. 2001. V. 65. N. 20. PP. 3391-3408.
- 4. *Alvarenga A.D., Grimsditch M., Bodnar R.J.* Elastic properties of water under negative pressures // J. Chem. Phys. 1993. V. 98. N. 11. PP. 8392-8396.
- 5. Zheng Q., Durben D.J., Wolf G.H., Angell C.A. Liquid at large negative pressures: water at the homogeneous nucleation limit // Science. 1991. V. 254. PP. 829-832.
- 6. *Roedder E.* Metastable superheated ice in liquid-water inclusions under high negative pressure // Science. 1967. V. 155. PP. 1413-1417.

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