MITT.ÖSTERR.MINER.GES. 146 (2001)

MELTING PROPERTIES OF ICE III, (V), VI AND THEIR ISOCHORIC GRADIENT OF WATER UP TO 20 KBAR AND 300°C – A REVIEW OF LITERATURE DATA

by

P. W. Mirwald

Institute of Mineralogy and Petrography
University of Innsbruck, Innrain 52, A-6020 Innsbruck

A reexamination of literature data on the melting of ice I-VII and the PVT-behavior of water the range of -20 to 300°C and 1 to 20 Kbar has been conducted.
The basic data for the melting of different ice-modifiactions has been produced by TAMMANN (1900) and BRIDGMAN (1912 a,b; 1935; 1937) which only have been been modified in slight details by later workers (PETRENKO & WHITNORTH, 1999). As to the reevaluation of the PVT-behavior of water the NBA Steam tables served for this study beeing augmented by some low temperature data by BRIDGMANN (1912a,b).
Starting point of this study was the reexamination of the melting of ice of which the P-T phase diagram is displayed in Fig. 3. While ice I, V and VII show a fairly regular melting behaviour the melting curves of ice II and VI exhibit an abnormally curved course with a "kink" at 2.3 and at 8.3 kbar. From a phase theoretical point of view this insinuated a more complex situation between solid, melting and liquid than previously assumed.
The inspection of the PVT-data of water revealed some irregularities when plotted in isothermal and isobaric sections respectively. The compression and thermal expansion of materials, expressed by its coefficients dV/dP_T and dV/dT_P, are related to the isochoric gradient by the expression $dV/dT_P/ dV/dP_T = - dP/dT_V$. The isochoric gradients were calculated for the above outlined P-T-frame. Some examples of the gradient curves plotted versus pressure and temperature respectively are displayed in Fig. 1 and 2.
The data reveal systematic changes in slope what may be interpreted as irregular and/or discontinuous volume behaviour of water. In addition, for a more precise determination of the P-T-position of slope changes the derivative have been used in some cases.
The results derived from the isochoric gradient curves have been incorporated in Fig. 3. They reveal a systematic volume/density variation of over the P-T-range reviewed what enables to construct a tentative pattern of P-T regions of different volume behaviour of water.
Generally, three major regimes (I, II, III) may be distinguished within the P-T-range studied. They are separated by two "boundaries" starting off at the "kink" in the melting curve of ice II and VI. These boundaries are in principle little pressure dependent exhibiting an average slope in the range of 25 to 35 bars/K. A further boundary of rather isothermal character is likely in the temperature range between 60 - 100°C which seems to subdivide the two lower pressure regions I and II. Generally, the available data do not allow a precise allocation of the boundaries so far.

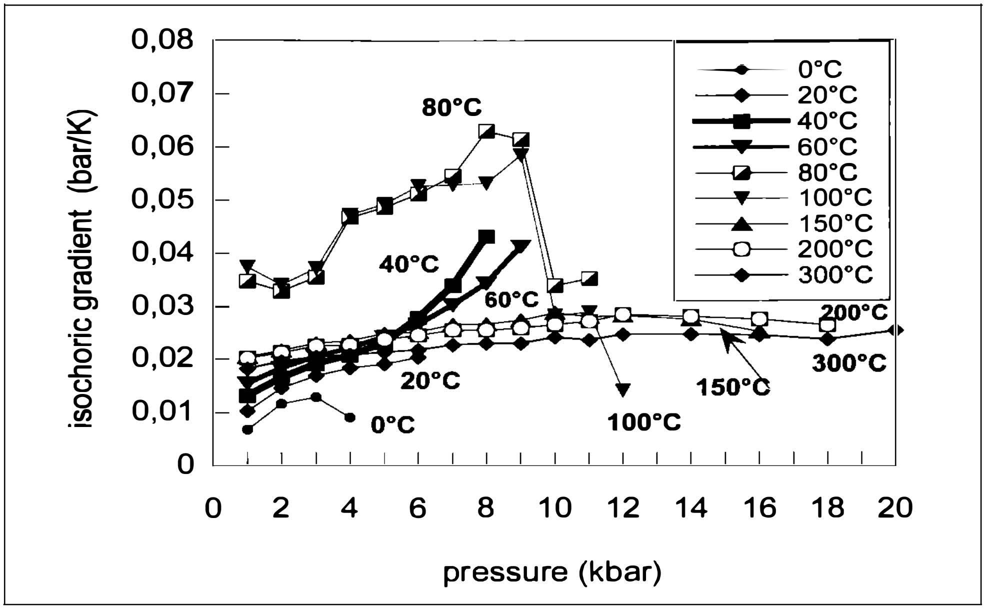

Fig. 1

Isobares of the isochoric gradient of water plotted versus pressure between 1 and 18 kb (cf. fig. 3: T isoch/p).

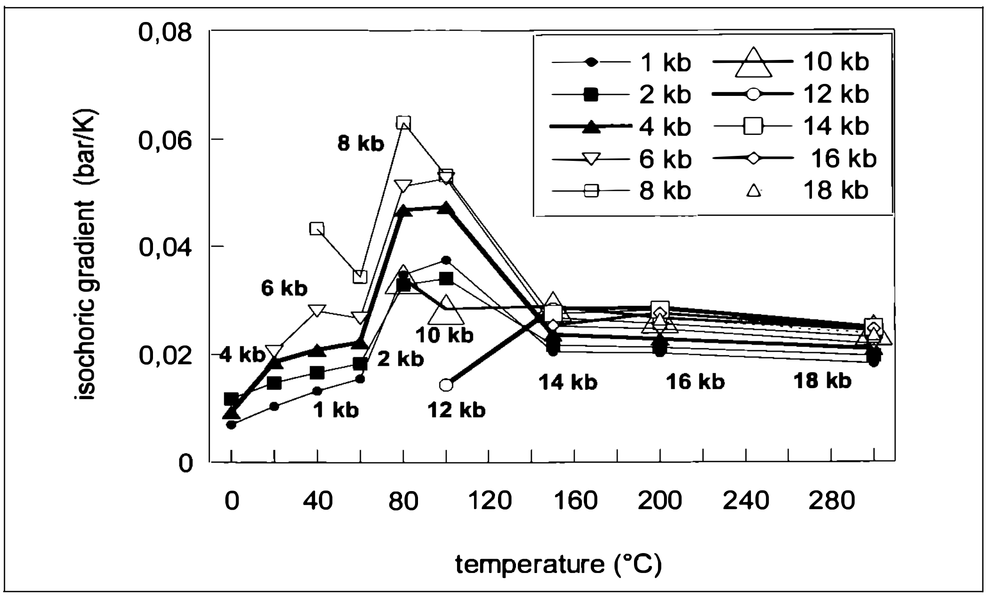

Fig. 2

Isotherms of the isochoric gradient of water plotted versus temperature between 0 and 300°C (cf. fig. 3: T isoc/t).

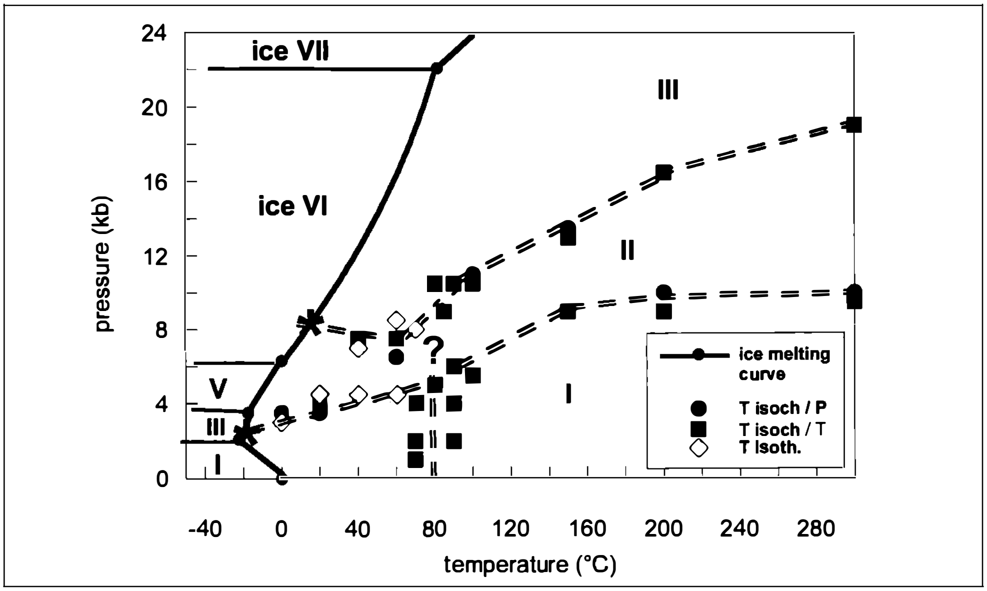

Fig. 3
Phase diagram of H_2O; the melting curve of ice I, III, V, VI, VII and a tentative outline of P-T-regimes of different behaviour of the specific volume of water (dashed double lines). Symbols: T isoch/t: and T isoch/p taken from isochoric gradient curves, see fig.1 and 2; T isoch: data taken from isothermal compression curves; stars: "kinks" in the melting curve of ice III and VI.

The finding of different P-T regimes for the specific volume behaviour of water insinuates different structural states. Possibly, this might also explain the often observed discontinuous solution rate behaviour of minerals in the temperature range 50 to 100°C, e.g. ANDERSON et al., (1991). A similar assumption might be valid for high P-T solution data e.g. by BECKER et al. (1985) and MANNING (1994), which indicate, at 700°C a first discontinuous rate change at 10 kbar and a second one at 19 kbar. If this proves true the slope of boundary I/II and II/III would significantly decrease.

For verification of these assumptions and for a more precise determination of the "boundaries" which separate the different P-T-regimes specific experiments are in progress.

Literature

ANDERSON, CASTET, SCHOTT & MESNER (1991): Geochim. Cosmochim. Acta 55, 1769-1779.

BECHER, CEMIC & LANGER (1983): Geochim. Cosmochim. Acta, 47, 1573-1578.

BRIDGMAN (1912a): Proc. Am. Acad. Arts Sciences, 47, 441-558.

BRIDGMAN (1912b): Proc. Am. Acad. Arts Sciences, 48, 310-362.

BRIDGMAN (1935): J. Phys. Chem. 3, 597-605.

BRIDGMAN (1937): J. Phys. Chem. 5, 964-966.

HAAR, GALLAGHER & KELL (1984): NBS/NRC Steam Tables, Mc-Graw-Hill Book Comp., 1984.

MANNING (1994): Geochim. Cosmochim. Acta 58, 4831-4839.

PETRENKO & WHITNORTH (1999): Physics of Ice, Oxford Univ. Press, 1999.

TAMMANN (1900): Ann. Phys., Ser. 4, 2, 1-31.