

Synthetic fluid inclusions in natural quartz. II. Application to PVT studies

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Abstract—Synthetic fluid inclusions have been used to determine volumetric properties of H₂O and a 20 wt.% KCl solution from 300–700°C and 1–3 kb. Comparison of results obtained for H₂O with previously published data indicates that the synthetic fluid inclusion technique provides PVT data that are within a few percent of those obtained from conventional PVT studies. This technique thus provides a fast, relatively simple means of determining PVT properties of many fluids of geologic interest.

INTRODUCTION

VOLUMETRIC (PVT) DATA for fluids are required to interpret and understand results of experimental and laboratory studies related to various geologic processes. Unfortunately, these data are extremely sparse, and the only fluids of geologic interest for which PVT data are available over a wide range of temperatures and pressures are H₂O, CO₂ and H₂O–NaCl. The lack of available PVT data for fluids of more complex compositions may be attributed to the difficulty, length of time and special equipment required to obtain such data using conventional experimental approaches.

Recently, STERNER and BODNAR (1984) described a technique for trapping representative samples of fluids at elevated temperatures and pressures which involves healing fractures in inclusion-free natural quartz to form synthetic fluid inclusions. Based on a comparison of available phase equilibria and PVT data with results of microthermometric analyses of these synthetic inclusions, these workers showed that the fluids in the inclusions had the same density and composition as the parent solution from which they were trapped. As a result of this observation, STERNER and BODNAR (1984) suggested that synthetic fluid inclusions could be used to determine phase equilibrium and PVT properties of a variety of fluids of geologic interest easily and over a wide range of temperatures, pressures and compositions.

In this paper we describe in detail the procedure for determining PVT properties of fluids using the synthetic fluid inclusion technique. In order to verify the validity of this technique, we have determined the specific volume of H₂O over the range 300–700°C and 1–3 kb using synthetic fluid inclusions, and have compared these data to previously published results obtained using standard experimental techniques. We

then applied the same procedures to determine PVT properties of a 20 wt.% KCl solution over this same temperature and pressure range.

EXPERIMENTAL PROCEDURE

The experimental procedures used to produce synthetic fluid inclusions have been described in detail previously (STERNER and BODNAR, 1984) and, therefore, are only briefly summarized here. Quartz cores approximately 4.5 mm in diameter and 1–2 cm in length were cut from inclusion-free Brazilian quartz and fractured using a thermal-shock technique. The cleaned, dried, fractured cores were placed into 5 mm diameter platinum capsules along with the appropriate fluid (either pure H₂O or a 20 wt.% KCl solution), sealed with an arc-welder, and placed into cold-seal type pressure vessels. Fifteen samples of each composition (H₂O and 20 wt.% KCl) were run for 10 days at various temperatures and pressures ranging from 300–700°C and 1–3 kb.

After quenching and removing the quartz cores from the capsules, the cores were cut into approximately 1 mm thick disks, polished on both sides, and homogenization temperatures of the inclusions determined on a Fluid, Inc. adapted USGS-type heating/freezing stage. Approximately 10 inclusions were measured in each sample and the temperatures are thought to be accurate to ±2°C based on previous calibration of the stage.

RESULTS

H₂O

Results of 150 pure H₂O fluid inclusion homogenization temperature determinations from fourteen samples are summarized on Table 1. Also shown on Table 1 are experimental conditions, calculated specific volumes of the inclusions and percent deviation of these values from the data of BURNHAM *et al.* (1969a). The data for one sample, run at 700°C and 1 kb, are not included in Table 1. Inclusions in this sample all homogenized at 374 ± 1°C, some to the vapor phase and others by critical behavior. Because the specific volume varies greatly with small changes in temperature near the critical point, this range in homogenization temperatures, and mode of homogenization, resulted in a wide range of calculated specific volumes (from ~3.2–4.0 cm³ · g⁻¹). This sample was, therefore,

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TABLE 1. Specific Volumes of H₂O Obtained From Synthetic Inclusions

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|-----|---|-------------|------------|-------|-------|-------|-------|
| 300 | 1 | 224.0-227.6 | 226.6 (10) | 1.202 | 1.207 | 1.213 | -0.53 |
| 400 | 1 | 300.6-301.8 | 301.1 (13) | 1.408 | 1.417 | 1.446 | -2.08 |
| 500 | 1 | 353.5-355.5 | 354.4 (10) | 1.799 | 1.819 | 1.894 | -4.08 |
| 600 | 1 | 372.2-374.5 | 373.3 (10) | 2.620 | 2.694 | 2.667 | 0.98 |
| 300 | 2 | 174.7-176.7 | 176.0 (10) | 1.123 | 1.129 | 1.134 | -0.49 |
| 400 | 2 | 248.4-251.8 | 250.2 (10) | 1.252 | 1.263 | 1.265 | -0.18 |
| 500 | 2 | 303.7-305.0 | 304.2 (10) | 1.421 | 1.442 | 1.450 | -0.60 |
| 600 | 2 | 338.6-339.9 | 339.2 (12) | 1.631 | 1.672 | 1.703 | -1.84 |
| 700 | 2 | 361.3-361.8 | 361.5 (10) | 1.924 | 1.979 | 2.012 | -1.66 |
| 300 | 3 | 135.6-137.1 | 136.1 (15) | 1.076 | 1.084 | 1.078 | 0.51 |
| 400 | 3 | 209.2-211.9 | 210.7 (10) | 1.174 | 1.186 | 1.176 | 0.84 |
| 500 | 3 | 262.2-263.7 | 263.0 (10) | 1.283 | 1.304 | 1.299 | 0.34 |
| 600 | 3 | 304.0-304.6 | 304.4 (10) | 1.422 | 1.450 | 1.451 | -0.08 |
| 700 | 3 | 330.9-332.4 | 331.1 (10) | 1.568 | 1.617 | 1.627 | -0.64 |

- (1) Formation temperature (°C)
 (2) Formation pressure (kb)
 (3) Range of measured homogenization temperatures (°C)
 (4) Average homogenization temperature (°C) and number of measurements (in parenthesis)
 (5) Uncorrected specific volume of H₂O (cm³·g⁻¹) obtained from average homogenization temperature and data of Keenan *et al.* (1978)
 (6) Specific volume of H₂O corrected for thermal expansion of quartz (data from Skinner, 1966)
 (7) Specific volume of H₂O at formation temperature and pressure (from Burnham *et al.*, 1969a)
 (8) Percent deviation between corrected specific volume and data of Burnham *et al.* (1969a)

not suitable for PVT determinations. It should be noted, however, that even though the precision of the calculated specific volume is very poor, the predicted specific volume at formation conditions (3.543 cm³·g⁻¹; BURNHAM *et al.*, 1969a) is within the range of calculated values.

The specific volume of H₂O in the inclusions at homogenization was obtained from the measured homogenization temperature and data for the specific volume of H₂O along the liquid-vapor curve (KEENAN *et al.*, 1978). These values are listed in Table 1 (column 5). If the inclusions were trapped along the liquid-vapor curve, or if it is assumed that, once formed, inclusions represent constant-volume (isochoric) systems, as is the case in most fluid inclusion studies, this value would then correspond to the actual specific volume of H₂O at formation conditions.

To a first approximation, the assumption that fluid inclusions represent isochoric systems is valid and introduces only negligible errors into the interpretation of heating/freezing data on inclusions. In actuality, however, the inclusion volume does change in response to a variety of external conditions, including temperature, pressure and dissolution of material from the inclusion walls, as described by ROEDDER and BODNAR (1980) and BODNAR and BETHKE (1984). Volume changes produced by pressure (more specifically, the internal pressure of the inclusion) and dissolution of material from the inclusion walls are extremely small for most inclusions in most minerals and can generally be ignored. The effect of temperature, however, is considerably greater, and the uncorrected specific volumes obtained here (Table 1, column 5) have, therefore, been corrected for the thermal expansion of quartz to obtain a better approximation of the specific volume of H₂O at trapping conditions. The corrected specific volumes

were obtained by determining the percent volume increase in quartz that would occur during heating from the homogenization temperature to the formation temperature using the data of SKINNER (1966). In these calculations, the coefficient of thermal expansion of quartz was assumed to be independent of pressure. The uncorrected specific volumes obtained from the measured homogenization temperatures were then increased by an amount equal to the percent increase in the volume of quartz upon heating from the homogenization temperature to the formation temperature. The magnitude of this correction ranged from ~0.4–3.1 percent of the uncorrected specific volume. These corrected specific volumes are listed in Table 1 (column 6) and are plotted on Fig. 1.

In order to compare the results obtained here with previously published data, specific volumes of H₂O as a function of temperature along the 1, 2 and 3 kb isobars reported by BURNHAM *et al.* (1969a) have also been plotted on Fig. 1. Although there is some scatter, the agreement between the two data sets appears to be good. A more rigorous comparison of the data is presented in Fig. 2, in which the percent deviation between the two data sets is shown in histogram form; the data are also listed in Table 1 (column 8). As shown on Fig. 2, ten of the fourteen corrected specific volume determinations obtained from synthetic inclusions agree with the data of BURNHAM *et al.* (1969a) within ±1 percent. These results suggest that the synthetic fluid inclusion technique does provide a reasonable approximation of the PVT properties of H₂O.

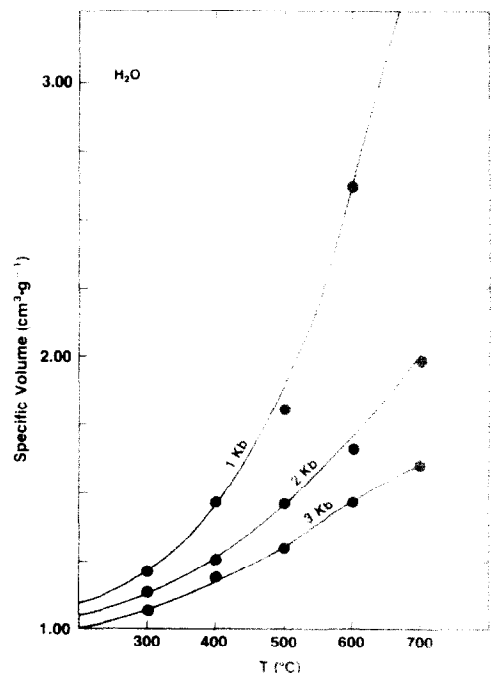


FIG. 1. Specific volume of H₂O determined using synthetic fluid inclusions (dots). Also shown for comparison is the variation in specific volume of H₂O as a function of temperature along the 1, 2 and 3 kb isobars from BURNHAM *et al.* (1969a). Data are also listed in Table 1 (column 6).

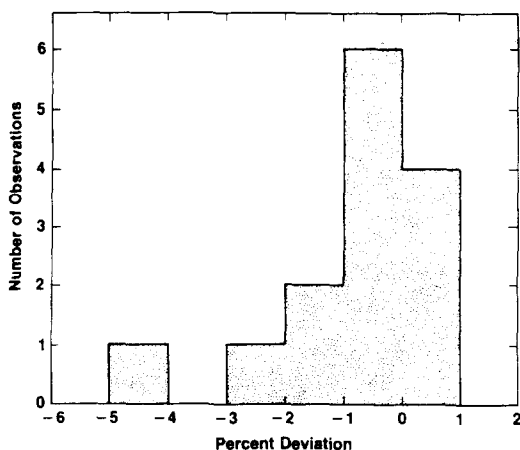


FIG. 2. Percent deviation between specific volumes of H₂O obtained from synthetic fluid inclusions and values reported by BURNHAM *et al.* (1969a). Data are also listed in Table 1 (column 8).

Possible causes for the discrepancies between the calculated and predicted specific volumes shown on Fig. 2 include (1) errors in homogenization temperature determinations, (2) errors in PVT data used to calculate specific volumes and, (3) inadequately controlled experimental conditions. Errors in homogenization temperature determinations ($\pm 2^\circ\text{C}$) and uncertainties in the PVT data (0.1–0.3%; BURNHAM *et al.*, 1969a) alone cannot totally account for these discrepancies, suggesting that at least a portion of the difference results from inadequately controlled experimental conditions. For the experimental orientation used in this study, BOETCHER and KERRICK (1971) report that temperatures may be in error by $\pm 5^\circ\text{C}$ or more, depending upon depth of immersion of the pressure vessel in the furnace; pressure measurements are probably only accurate to approximately ± 25 bars. Uncertainties of these magnitudes are sufficient to account for the differences between predicted and calculated values and are thought to be the main cause of these differences.

20 wt.% KCl solution

Having shown that synthetic fluid inclusions may be used to obtain a good approximation of the PVT properties of H₂O and assuming that this technique is valid for fluids of other compositions, we have used synthetic inclusions to determine the density¹ of a 20 wt.% KCl solution over the range 300–700°C and 1–3 kb. Experimental conditions, measured homogenization temperatures and calculated densities obtained from fourteen samples are listed in Table 2. One sample, run at 700°C and 1 kb, was found to contain co-existing vapor-rich and liquid-rich sylvite-bearing in-

clusions, indicating that the inclusions were formed in the two-fluid-phase field. Thus, this sample could not be used to determine PVT properties. However, these inclusion types may be used to determine phase equilibrium properties, as has been described previously (BODNAR and STERNER, 1984; BODNAR *et al.*, 1985).

Uncorrected densities (Table 2, column 5) were obtained from measured homogenization temperatures and data for densities of vapor-saturated 20 wt.% KCl solutions (KHAIBULLIN and BORISOV, 1966). These values were then corrected for the volume increase produced by the thermal expansion of quartz, as described above, to obtain corrected densities at the temperature and pressure of formation (Table 2, column 6). The corrected densities have been plotted on Fig. 3 and “best-fit” curves drawn through the data points to show the change in density as a function of temperature along the 1, 2 and 3 kb isobars. Also shown on Fig. 3 are vapor-saturated densities from KHAIBULLIN and BORISOV (1966) and four data points from EGOROV *et al.* (1976) for a 20 wt.% KCl solution at 1000 kg·cm⁻² (~ 981 bars). Although the pressures are slightly different, there is good agreement between our results and those of EGOROV *et al.* (1976). Unfortunately, owing to lack of other data for 20 wt.% KCl solutions in this temperature and pressure range, a rigorous evaluation of the accuracy of our results is not possible.

The data shown on Fig. 3 have been used to construct the more commonly used isoplethal *P-T* projection showing various isochores for a 20 wt.% KCl solution (Fig. 4). Densities and vapor-pressures along the liquid-vapor curve are from KHAIBULLIN and BORISOV (1966), and the liquid-vapor curve has been extrapolated to 700°C based on our earlier observation that the sample run at 700°C and 1 kb was below the

TABLE 2. Densities of 20 wt.% KCl Solutions Obtained from Synthetic Fluid Inclusions

| | 1 | 2 | 3 | 4 | 5 | 6 |
|-----|---|-------------|------------|---|-------|-------|
| 300 | 1 | 230.8–232.8 | 232.0 (12) | | 0.988 | 0.985 |
| 400 | 1 | 312.3–316.1 | 314.1 (10) | | 0.906 | 0.901 |
| 500 | 1 | 394.4–399.1 | 395.9 (10) | | 0.814 | 0.807 |
| 600 | 1 | 494.3–499.2 | 496.8 (10) | | 0.675 | 0.663 |
| 300 | 2 | 184.9–186.2 | 185.7 (11) | | 1.031 | 1.025 |
| 400 | 2 | 256.9–258.2 | 257.5 (10) | | 0.963 | 0.955 |
| 500 | 2 | 328.2–329.8 | 329.0 (10) | | 0.895 | 0.884 |
| 600 | 2 | 386.3–387.5 | 386.8 (10) | | 0.828 | 0.808 |
| 700 | 2 | 436.4–440.4 | 437.9 (10) | | 0.766 | 0.749 |
| 300 | 3 | 139.1–143.2 | 142.3 (20) | | 1.067 | 1.059 |
| 400 | 3 | 220.1–220.8 | 220.5 (10) | | 0.999 | 0.989 |
| 500 | 3 | 275.0–279.8 | 277.8 (10) | | 0.942 | 0.927 |
| 600 | 3 | 334.6–335.9 | 335.2 (11) | | 0.884 | 0.860 |
| 700 | 3 | 374.5–377.2 | 376.0 (10) | | 0.840 | 0.817 |

- (1) Formation temperature ($^\circ\text{C}$)
- (2) Formation pressure (kb)
- (3) Range of measured homogenization temperatures ($^\circ\text{C}$)
- (4) Average homogenization temperature ($^\circ\text{C}$) and number of measurements (in parentheses)
- (5) Uncorrected density ($\text{g}\cdot\text{cm}^{-3}$) obtained from average homogenization temperature and data of Khaibullin and Borisov (1966)
- (6) Density of 20 wt.% KCl solution corrected for thermal expansion of quartz (data from Skinner, 1966)

¹ PVT data for 20 wt.% KCl solutions have been presented as densities, rather than specific volumes, to facilitate comparison with the published data of KHAIBULLIN and BORISOV (1966) and EGOROV *et al.* (1976), which are also presented as densities.

liquid-vapor curve, *i.e.*, in the two-phase field. The isochores shown on Fig. 4 represent best-fit straight lines through four data points; in actuality the isochores should be very slightly concave upwards in this temperature and pressure region based on a comparison with PVT properties of H₂O-NaCl solutions (POTTER and BROWN, 1977; HILBERT, 1979). As a result, the pressure one would determine at the highest pressures shown on Fig. 4 (3 kb) would be too low for a given temperature by approximately 50–100 bars.

SUMMARY

Our results indicate that synthetic fluid inclusions provide a reasonably good approximation (within a few percent) of volumetric properties of fluids of geologic interest. Although the data lack the accuracy and precision of PVT data obtained using more conventional techniques, this shortcoming is more than compensated for by the speed and relative ease with which the data are obtained. Most importantly, perhaps, the synthetic fluid inclusion technique requires none of the specialized, highly-sophisticated equipment necessary to obtain such information using standard experimental techniques (*c.f.*, BURNHAM *et al.*, 1969b). All that is required are high temperature-high pressure vessels, which are common in many research laboratories, and a fluid inclusion heating/freezing stage.

In order to obtain actual densities or specific volumes of the fluids, as we have done here, volumetric data

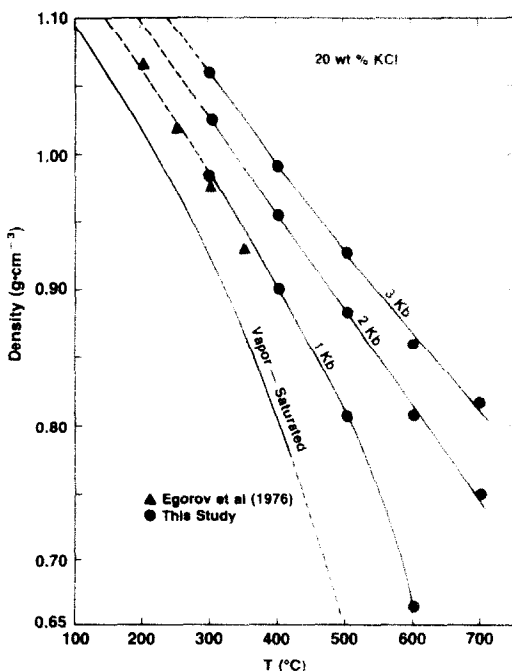


FIG. 3. Density of 20 wt.% KCl solutions as a function of temperature at 1, 2 and 3 kb determined from synthetic fluid inclusions. Also shown are densities of vapor-saturated 20 wt.% KCl solutions from KHAIBULLIN and BORISOV (1966) and four data points at 1000 kg · cm⁻² from EGOROV *et al.* (1976). Data are also listed in Table 2.

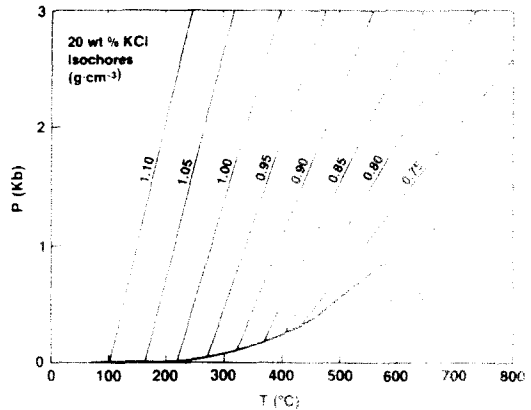


FIG. 4. Pressure-temperature (isoplethal) projection showing isochores (g · cm⁻³) of 20 wt.% KCl solutions determined from synthetic fluid inclusions. Densities and vapor pressures along the liquid-vapor curve are from KHAIBULLIN and BORISOV (1966). Extrapolation of liquid-vapor curve to 700°C is based on observations of this study (see text for explanation).

along the liquid-vapor curve are required for the fluid of interest. Fortunately, experimental data are available for many fluids of geologic interest (see, for example, POTTER *et al.*, 1975), and for those fluid compositions for which data are not available, adequate theoretical models exist which closely approximate PVT properties along the vapor-saturation curve (*e.g.* POTTER and HAAS, 1978; CONNOLLY and BODNAR, 1983). Even if experimental or theoretical data are unavailable for a particular fluid composition, the *P-T* trend of the isochore (of unknown value) may still be obtained from synthetic inclusions. For many applications, particularly for interpreting fluid inclusion heating/freezing data, it is the path of the isochore in *P-T* space that is important, and not necessarily the value of the isochore.

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REFERENCES

- BODNAR R. J. and BETHKE P. M. (1984) Systematics of stretching of fluid inclusions I: Fluorite and sphalerite at one atmosphere confining pressure. *Econ. Geol.* **79**, 141–161.
- BODNAR R. J. and STERNER S. M. (1984) Application of synthetic fluid inclusions to phase equilibria studies [abstr.] *EOS* **65**, 292.
- BODNAR R. J., BURNHAM C. W. and STERNER S. M. (1985) Synthetic fluid inclusions in natural quartz. III. Determination of phase equilibrium properties in the system H₂O-NaCl to 1000°C and 1500 bars. *Geochim. Cosmochim. Acta* **49**, 1855–1867.
- BOETTCHER A. L. and KERRICK D. M. (1971) Temperature

- calibration in cold-seal pressure vessels. In *Research Techniques for High Pressure and High Temperature* (ed. G. C. ULMER) pp. 179–193. Springer-Verlag, New York.
- BURNHAM C. W., HOLLOWAY J. R. and DAVIS N. F. (1969a) Thermodynamic properties of water to 1000°C and 10,000 bars. *Geol. Soc. Amer. Spec. Paper No. 132*, 96 p.
- BURNHAM C. W., HOLLOWAY J. R. and DAVIS N. F. (1969b) The specific volume of water in the range 1000 to 8900 bars, 20° to 900°C. *Amer. J. Sci.* **267-A**, 70–95.
- CONNOLLY J. A. D. and BODNAR R. J. (1983) A modified Redlich-Kwong equation of state for H₂O-CO₂ mixtures: Application to fluid inclusion studies [abstr.]. *EOS* **64**, 350.
- EGOROV V. YA., ZAREMBO V. I. and FEDOROV M. K. (1976) PVTX relations in the system KCl-H₂O at temperatures up to 350°C and pressures up to 1500 kg/cm². *J. Applied Chem. USSR* **49**, 119–121.
- HILBERT R. (1979) PVT-Daten von Wasser and von wässrigen Natriumchlorid-Lösungen bis 873K, 4000 Bar und 25 Gewichtsprozent NaCl. Diss.-Ing. University of Karlsruhe, 212 p. (in German).
- KEENAN J. H., KEYES F. G., HILL P. G. and MOORE J. G. (1978) *Thermodynamic Properties of Water, Including Vapor, Liquid, and Solid Phases (S. I. Units)*. John Wiley and Sons, New York, 156 p.
- KHAIBULLIN I. K. and BORISOV N. M. (1966) Experimental investigation of the thermal properties of aqueous and vapor solutions of sodium and potassium chlorides at phase equilibrium. *High Temperature* **4**, 489–494.
- POTTER R. W. II and BROWN D. L. (1977) The volumetric properties of aqueous sodium chloride solutions from 0° to 500°C at pressures up to 2000 bars based on a regression of available data in the literature. *U. S. Geol. Surv. Bull.* **1421-C**, 36 p.
- POTTER R. W. II and HAAS J. R., JR. (1978) Models for calculating density and vapor pressure of geothermal brines. *U. S. Geol. Surv. J. Res.* **6**, 247–257.
- POTTER R. W. II, SHAW D. R. and HAAS J. R., JR. (1975) Annotated bibliography of studies on the density and other volumetric properties for major components in geothermal waters 1928–74. *U.S. Geol. Surv. Bull.* **1417**, 78 p.
- ROEDDER E. and BODNAR R. J. (1980) Geologic pressure determinations from fluid inclusion studies. *Ann. Review Earth Planet. Sci.* **8**, 263–301.
- SKINNER B. J. (1966) Thermal expansion. In *Handbook of Physical Constants*, Revised Edn. (ed. S. P. CLARK) *Geol. Soc. Amer. Mem.* **97**, 75–96.
- STERNER S. M. and BODNAR R. J. (1984) Synthetic fluid inclusions in natural quartz I. Compositional types synthesized and applications to experimental geochemistry. *Geochim. Cosmochim. Acta* **48**, 2659–2668.