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Note

EXPERIMENTAL PROCEDURES FOR DETERMINING PRECISE INVERSION TEMPERATURES OF QUARTZ CRYSTALS

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The high–low inversion of natural quartz crystals may occur within the temperature interval 500–578°C [1]. Several authors have shown how this variation may be used as a valuable petrogentic indicator, as can the shape of the recorded differential inversion deflection curve [1–9].

In a recent attempt to apply this technique to suites of metamorphosed rocks from the South Pacific, it was found that direct application of the experimental procedures, such as given by Smykatz-Kloss [1,7], gave an unacceptable level of precision using the conventional DTA instrumentation available to the authors. Variations in the determined inversion temperatures of splits from the same sample could be as great as ±1.5°C for inversion temperatures (t_i) > 570°C. There appeared to be little possibility of obtaining the ±0.3°C level of precision cited by Smykatz-Kloss [7].

Rigorous standardisation of procedure was employed to minimise influences on the results by factors related to sample preparation and equipment. In particular, a series of experimental runs were made using a number of internal and external standards (K_2SO_4, Na_3AlF_6, Ag_2SO_4, Na_2MoO_4) and four coarsely crystalline quartz samples, chosen for homogeneity of character. These showed that the main cause of discordant results were instrumentally produced variations in the heating rate ($\phi = dT/dt$) between, but not within, successive runs.

In the procedure outlined by Smykatz-Kloss [1,7], an internal standard of pure, water-free K_2SO_4 is blended with quartz. This permits direct comparison to be made between the inversion temperatures of the two substances; that for K_2SO_4 occurring at 583.5°C. Although Smykatz-Kloss stresses the need for careful and frequent calibration of DTA apparatus [1,7], it was found that the calibration of the available, relatively simple instruments, which sufficed for general thermal analytical runs over wide temperature ranges at heating rates $\geqslant 10°C\ min^{-1}$, were quite insufficient at low heating rates and high recording chart speeds. These latter were deliberately used over the measured inversion temperature range to gain maximum information from the peak shapes recorded in each run [5]. Even small variations in

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ϕ proved sufficient to produce large differences in the linear spacings between the inversion peaks of quartz and K_2SO_4. These differences, in turn, produced the low precision between sequential runs on identical samples.

It thus appeared that suitably precise determinations of the inversion temperatures could be made only with instruments that are sufficiently sophisticated to ensure that deviations of $\phi \leqslant 1.5\%$ or, alternatively, where special arrangements can be made to measure the inversion peak temperature differences independently of heating rate. (cf. Keith and Tuttle's [9] acceptance of levels of precision (t_i) ± 5–15°C for some of their quartz determinations and the use by Smykatz-Kloss [7] of a privately built DTA apparatus [10] to explore the precision and accuracy of his determinations.)

An alternative approach suggested itself from the results of the series of experimental runs mentioned above. This involved using the machine's program controller simply to produce a linear heating rate while employing two or more standards with thermal activity in the range 500–600°C to determine the actual heating rate. To this end, additional determinations were made using combinations of single and mixed internal and external (reference) standards. Problems arose with sintering reactions between some of the blends of chemicals used, precluding the use of one or two likely looking solutions. Best results were achieved using a procedure which retained Smykatz-Kloss' quartz plus K_2SO_4 mix in one crucible while using Na_3AlF_6 (cryolite) with or without ignited alumina in the reference container. This simple approach appears to permit application of the quartz inversion temperature technique by petrologists possessed of relatively unsophisticated DTA apparatus.

INSTRUMENTATION AND CONDITIONS

Shimadzu DT-2B thermal analyzer; 4 Pt–Pt_{90}/Rh_{10} thermocouples 0.5 mm OD arranged at 90°; Pt/Rh crucibles 6 mm OD ×17 mm set in a beryllia holder.

Furnace atmosphere: air, no turbulence.

Reference sample: 100 mg Na_3AlF_6 (cryolite), 75–150 μm, loose packed, or 75 mg Na_3AlF_6 + 50 mg Al_2O_3, 75–150 μm, loose packed.

Quartz sample: 100 mg quartz, hand-ground in an agate mortar, 75–150 μm + 25 mg anhydrous, pure K_2SO_4, loose packed.

PID programmed heating rate from 500 to 590°C: 5°C min^{-1} (actual heating rates varied from 3.8 to 5.3°C min^{-1} between different runs).

Chart speed over the measured temperature range: 10 mm min^{-1}. Sensitivity over the same range ± 10 μV.

Experience showed that best results were obtained by pre-heating the tubular furnace to 500°C before introducing either sample. Determinations were then made so as to include the inversion temperatures of each of the three materials for both rising and falling furnace temperatures. The peak temperatures, as shown on the recorded chart, could then be projected onto a constructed baseline linking the true characteristic reaction temperature, or initial temperature of the Na_3AlF_6 inversion, with the final temperature of the K_2SO_4 inversion. The linear distance between these projected peak temperatures was then measured and direct proportion used to calculate the temperature of the quartz peak relative to the 20.8°C spacing of Na_3AlF_6 and K_2SO_4 peaks; the Na_3AlF_6 inversion being taken at 562.7 ± 0.3°C.

Precision of the method proved to be ±0.3°C provided that the heating rates used in a suite of different runs differed by less than 10%. Larger variations in ϕ gave erratic results which are presumed to arise from enhancement of variations in the differential heat conductivity of the different reactants used. The heating rates were calculated directly from the temperature line on the chart or from the 20.8°C linear spacing of the inversion peaks of the two standards.

Faust [11] gives the heat of reaction for the quartz inversion as 3.1 cal g^{-1}, considerably less than that for either K_2SO_4 or Na_3AlF_6, but the present authors have been able to confirm Smykatz-Kloss' observation that with ΔT^0 between 0.3 and 2°C it is possible to obtain a distinct signal with only 10% quartz in a 100-mg sample.

Throughout this work the authors have been acutely aware of the need for international standards in the area of mineral thermal analysis particularly to permit interlaboratory correlation and to allow for the important provisos spelt out by Smykatz-Kloss [7, p. VII]. Typical results obtained in the present work were: rock-crystal, Sri Lanka, 572.4°C; granite, Stewart Is (New Zealand), 572.3°C; rose quartz, New York (U.S.A.), 572.0°C; amethystine quartz vein, Tokatea (N.Z.), 571.6°C; garnet schist, South Island (N.Z.), 571.3°C; granite, Devon (U.K.), 567.6°C.

REFERENCES

1 W. Smykatz-Kloss, Thermal Analysis, Vol. 3, Proc. 3rd ICTA, Davos, 1971, Birkhaeuser Verlag, Basel, 1972, p. 637.
2 P. Kresten, Stockholm Contrib. Geol., 23 (1971) 91.
3 P. Kresten, Linseis J., 1 (1971) 6.
4 W. Smykatz-Kloss, Contrib. Mineral. Petrol., 26 (1970) 20.
5 W. Smykatz-Kloss, Contrib. Mineral. Petrol., 36 (1972) 1.
6 W. Smykatz-Kloss, Oberrheinische Geol. Abh., 21 (1972) 75.
7 W. Smykatz-Kloss, Differential Thermal Analysis: Application and Results in Mineralogy, Springer-Verlag, Berlin, 1974, p. 185.
8 O.F. Tuttle, Am. Mineral., 34 (1949) 723.
9 M.L. Keith and O.F. Tuttle, Am. J. Sci., Bowen vol., (1952) 208.
10 F. Lippmann, Keram. Z. (Lübek), 11 (1959) 475, 524, 570.
11 G.T. Faust, Am. Mineral., 33 (1948) 337.