Journal of Thermal Analysis, Vol. 42 (1994) 85-97

Dedicated to Professor Lisa Heller-Kallai on the occasion of her 65th birthday

THE DETERMINATION OF AUTHIGENIC QUARTZ IN POROUS SEDIMENTARY ROCKS BY MEANS OF DIFFERENTIAL SCANNING CALORIMETRY

W. Smykatz-Kloss and W. Klinke

Mineralogical Institute of the University, D-76128 Karlsruhe, Germany

Abstract

The DSC method is used to characterize diagenetic transformations of porous sedimentary rocks by measuring the reversible high-low inversion of quartz crystals. For this, ten specimens of authigenic quartz from cavities in sand- and limestones have been studied, avoiding any influence of mechanical treatment on the inversion behaviour. The method shows to be very sensitive in determining disordered parts of quartz crystals, using the interrelationship between the degree of structural disorder and the decrease of the inversion temperature. The application of the method for the purpose of prospection for hydrocarbons, sulfides or phosphates is shortly discussed.

Keywords: diagenesis for sandstones, DSC, quartz crystals

Introduction

The high-low inversion of quartz crystals has interested geoscientists for many years since the days of the famous Le Chatelier (1887). There is still some confusion in regard to the character of this transition, whether it is a true lambda transition, an equilibrium phase transition or not (e.g. see Keith and Tuttle 1952; Buerger 1960; Sosman 1965; Moore 1992). In any case: the inversion is reversible, it is occurring again and again when heating and cooling quartz crystals for several times, and the temperature of it may be quite typical for the processes of formation, metamorphism or diagenesis of quartz-bearing rocks (Tuttle 1949; Keith and Tuttle 1952; Lameyre *et al.* 1968; Smykatz-Kloss 1970, 1974; Kresten 1971; Giret *et al.* 1972; Moore 1992). In recent papers it is stressed that the conditions of analysis and – mainly – preparation (grinding!) may influence the inversion behaviour, mainly the shape of the (DTA, DSC) effect and the temperature of inversion (ti), e.g. Moore and Rose (1973); Moore (1986, 1988); Steinike *et al.* (1987). And it is well known that the inversion be-

0368–4466/94/ $ 4.00

John Wiley & Sons, Limited
Chichester

haviour of microcrystalline quartz may be quite different from that of macrocrystalline quartz (Flörke 1962; Buurman and van der Plas 1971; Smykatz-Kloss 1972, 1974; Moore 1992). This may be due to the increasing degree of structural disorder with decreasing grain size (Smykatz-Kloss 1972; Graetsch *et al.* 1987) and to the influence of small amounts of impurities, mainly of water (Wiedemann and Smykatz-Kloss 1981; Smykatz-Kloss 1984; Graetsch *et al.* 1987; Moore 1992). Generally, the high-low inversion of quartz occurs at 573±1°C. Only in the case of high structural disorder the (reversible) temperature of inversion may be lowered down to 500°C or even to 400°C (Smykatz-Kloss 1972; Moore 1992). That is the case for many quartz samples from sediments or soils (Smykatz-Kloss 1970, 1972, 1974; Buurman and van der Plas 1971), which are characterised by small crystal size and by numerous impurities and inclusions as well. Mainly different amounts of water may be enriched at the intergrowth interfaces of microcrystalline silica modifications (Graetsch *et al.* 1987). That means, it is often possible to determine several inversion effects for the same siliceous rock, e.g. for a sandstone: one very sharp and intensive effect around 573°C (which mirrors the conditions of formation of the primarily igneous crystals) and one or more broad but less intensive effects due to diagenetic processes.

Purpose of study

Diagenetic transformations of porous sedimentary rocks (sandstones, limestones) change mainly the physical properties of these rocks, e.g. the porosity, permeability, hardness, compaction etc. Generally, the porosity of these rocks decrease by precipitation of minerals from circulating pore solutions (quartz, carbonates, clay minerals, sulphates, phosphates). But certain environments may lead to higher dissolution of primary minerals. Thus, the effect of volatiles originating from the pyrolysis of clay minerals (kaolinite, smectite) which may occur in or near coal seams may enhance the dissolution of carbonates (Heller-Kallai *et al.* 1987; Heller-Kallai and Mackenzie 1987). Increased solubility of quartz in water due to complexing by organic compounds has been observed by Bennett and Siegel (1987), – the organics were produced by the biodegradation of petroleum and consist largely of a complex mixture of organic acids having close to neutral *pH* (Bennett and Siegel 1987). Regarding the diagenetic processes in sandstones, the interrelation between increased quartz dissolution and the abundance of organic volatiles or fluids (hydrocarbons, crude oil) may be of interest for the prospection of oil and gas: The pore fluids saturated in silica may migrate to higher levels in the sandstones, mix with descending waters and – after the change (decrease) in *pH* – lead to intensive precipitation of silica in these higher horizons. Thus, intensive neoformation of authigenic silica minerals in sandstones may be an important hint to the abundance of hydrocarbons in deeper horizons. This authigenic silica will mainly alter to microcrystalline quartz (chalcedony or chert) filling the cavities and pores between the coarser quartz grains of the sandstones or small fissures and veins cutting the sedimentary rocks.

The purpose of this study is the thermal analytical characterization and determination of these authigenic microcrystalline quartz crystals in porous sedimentary rocks (lime- and sandstones) and by this a contribution to the mineralogical prospection for hydrocarbons in sedimentary host rocks.

Samples and method of analysis

Ten specimens of authigenic quartz from cavities in sand- and limestones have been chosen for this study. The locations and short descriptions of the samples are given in Table 1. In detail, five milky quartz crystals (3 from cavities in limestones, 2 from small fissures in sandstones), three bituminous quartz crystals from limestones, one 'lawn quartz' (Rasenquartz) crystal from a small vein in Bunter sandstone and one carneol sample (= fossil soil) from Rotliegend sandstone have been studied. All localities are situated in Baden-Württemberg.

To avoid any influence of mechanical treatment on the inversion behaviour of these quartz crystals, all specimens were analysed without any crushing or preparation. The whole crystals (weight: between 10 and 14 mg, see Table 2) were put into the DSC crucible and heated up to 700°C, then cooled again to room temperature. The cooling curve was taken to be sure that all endothermic effects occurring on heating were truely reversible. Only those effects which occurred as exothermic effects in the cooling curves were considered.

The study of the high-low quartz inversion up to now has been done mainly by differential thermal analysis (DTA, e.g. Keith and Tuttle 1952, Flörke 1962, Kneller *et al.* 1968, Lameyre *et al.* 1968, Smykatz-Kloss 1970, 1972, 1974, 1984, Kresten 1971, Giret *et al.* 1972, Moore 1986, 1988, 1992). The comparison of DTA results with thermosonimetry showed the structural transformations of silica (and carbonate) minerals to be much more complicated than hitherto referred (Lönvik and Smykatz-Kloss 1984). That means, in some cases DTA may not be sensitive enough to observe all transition effects. One reason may be the comparably large sample amount used in DTA runs (see Moore 1992).

Therefore, in this study a DSC equipment was used (DUPONT-1090). The analyses were made in the Institute of Mineralogy (Crystallographic Dept.) of

Table 1 Studied specimens of authigenic quartz crystals from limestones and sandstones

Specimen No.	Locality	Occurrence, type	Description
30	Enzberg	cavity in 'Muschelkalk'	milky qu.
32	Herrenberg	cavity in (mo-2)	milky, 5 mm ø crystals
55	Magstadt	cavity in (mo-3)	milky, 5 mm ø crystals
72	Neubulach	vein quartz in Bunter sandstone	'Rasenqu.', 2 cm ø
74	Bruchsal	cavity in (mo-3)	bituminous q., 1 mm ø
77	Bruchsal	cavity in (mo-3)	bituminous, 20 mm ø
78	Dietlingen	cavity in (mo-3)	stinking qu.
91	Renningen	weathered from sandstone	milky qu.
94	Heimsheim	weathered from sandstone	milky, 5 mm ø
102	Schramberg	carneol (Rotliegend)	microcrystalline, red

Table 2 Inversion effects of sedimentary quartz crystals (the main effect is underlined)

Sample No.	Type	Host rock	Sample amount/ mg	Authigenic inversion effects (±1°C)				'Primary'qu. effects (±0.5°C)
30	milky qu.	limestone	12.1	502	525	540	570.0	
32	milky qu.	limestone	12.4			552		
55	milky qu.	limestone	13.5		522	541	567.0	571.0
72	lawn qu.	sandstone	12.4	542	557	564	568.0	572.2
74	bituminous qu.	limestone	11.2	512	523	541	570.0	
77	bituminous qu.	limestone	10.5		530	541	563.0	571.5
78	bituminous qu.	limestone	12.0	518		539	565.5	570.0
91	milky vein qu.	sandstone	10.8					571.5
94	milky vein qu.	sandstone	12.4	520		540	568.5	570.5
102	microcryst. carneol	Rotliegend sandstone	10.5		523	540		571.0

the University of Heidelberg, Germany (courtesy of Prof. W. Eysel). DTA analyses of the same samples made by our NETSCH-STK 409 microanalyzer gave comparable but less sensitive results. The DSC runs were done with a heating rate of 10 deg·min^{-1} in a DSC cell 910; crucibles: aluminium pans (reference pan: empty); thermocouples: chromel-alumel; furnace atmosphere: inert gas flow of 50 ml Ar/min. To improve the accuracy of the temperature determination K_2SO_4 was added to the sample as an internal standard (showing an inversion peak at 583°C). By this, the accuracy of (peak-) temperature measurement was ±0.5°C for sharp and intensive effects (e.g. the 'igneous' quartz inversion around 573°C and the K_2SO_4 inversion) resp. ±1°C for less intensive and broad effects.

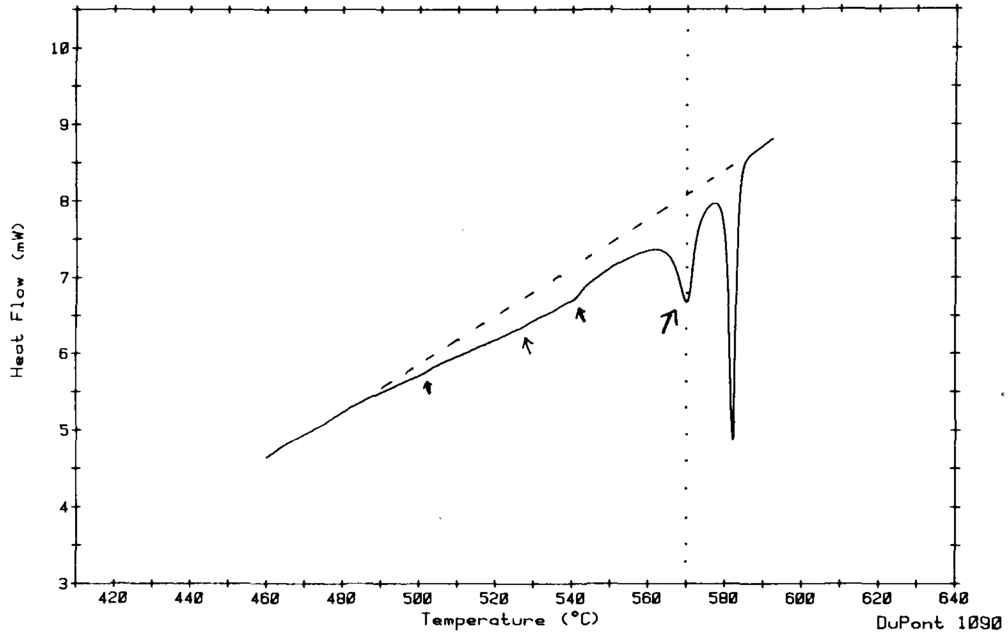

Fig. 1 DSC curve of sample No. 30 (authigenic quartz crystal from a cavity in limestone, Enzberg). The arrows point to inversion effects of diagenetic quartz

Results

Table 2 contains the results of the present study, Figs 1–10 show the DSC curves of the analyzed samples.

With the exception of the milky vein quartz (No. 91) all samples show inversion effects below 570°C, due to disordered parts of the studied quartz specimens. In general, these inversion effects at low temperatures which reflect the inversion behaviour of the authigenic part of the crystals (overgrowths, pore and

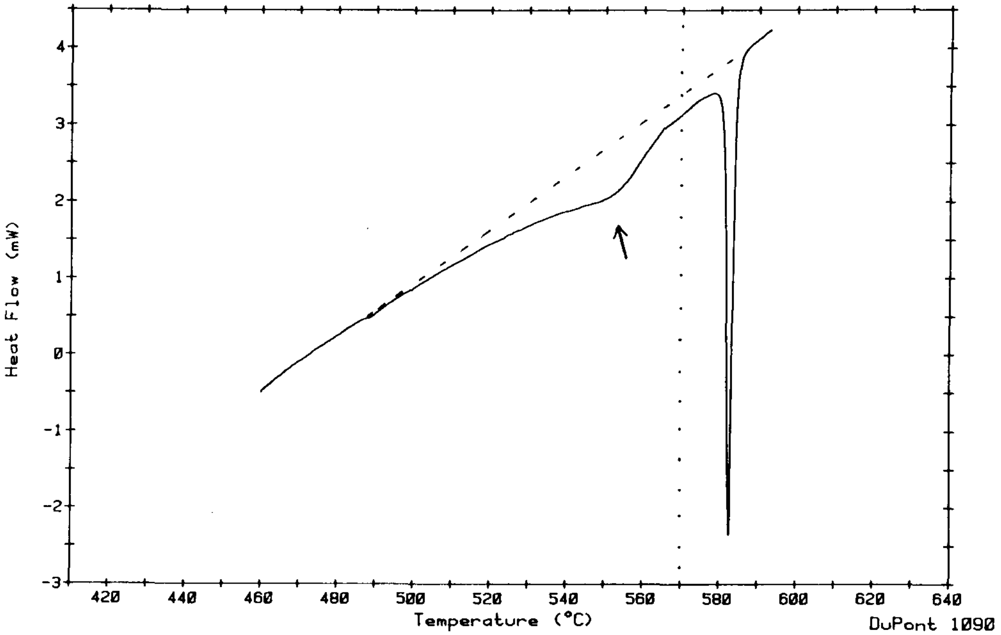

Fig. 2 DSC curve of sample No. 32 (authigenic quartz crystal from limestone). The sharp endotherm is caused by the K_2SO_4 standard (585°C)

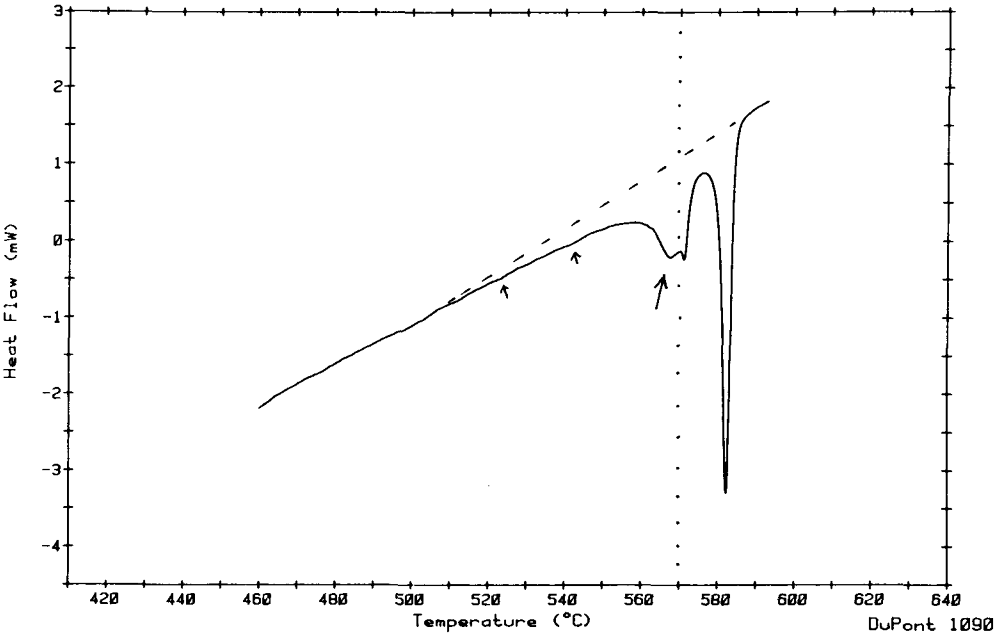

Fig. 3 DSC curve of sample No. 55 (authigenic quartz from limestone)

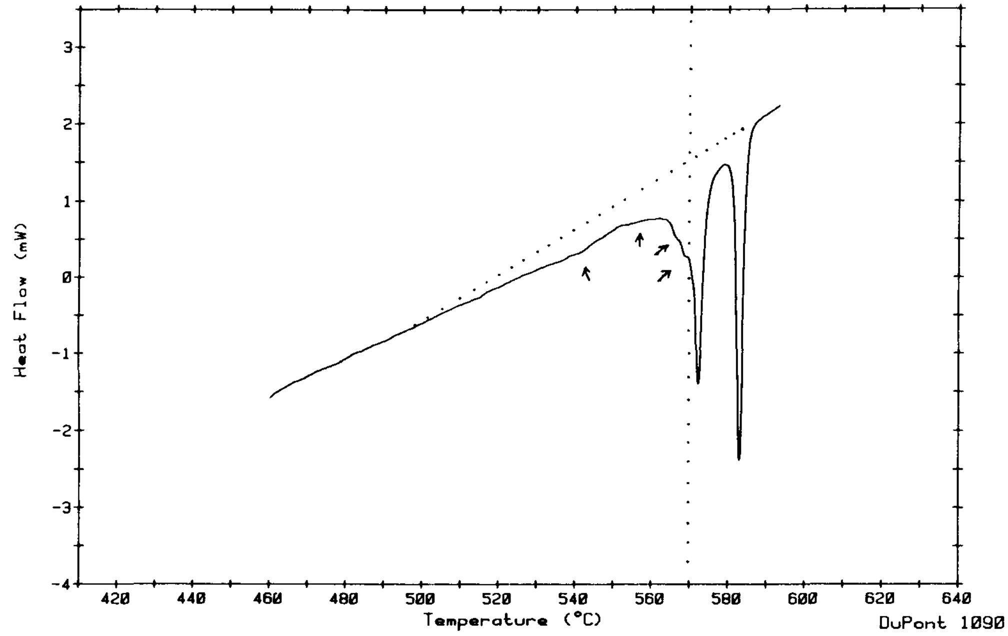

Fig. 4 DSC curve of sample No. 72 (vein quartz in Bunter sandstone)

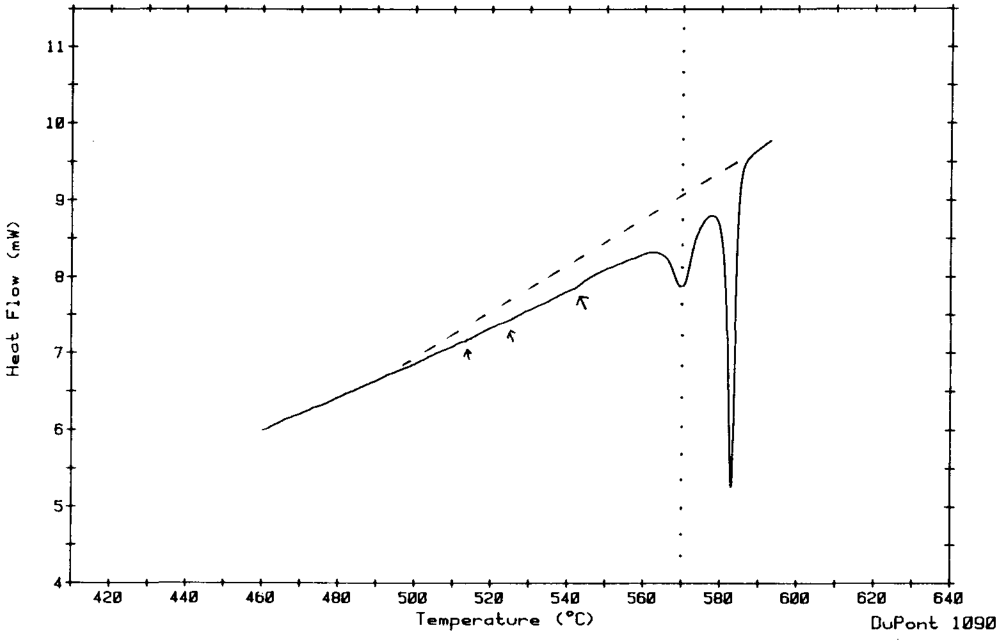

Fig. 5 DSC curve of sample No. 74 (from cavity in mo-3 from limestone)

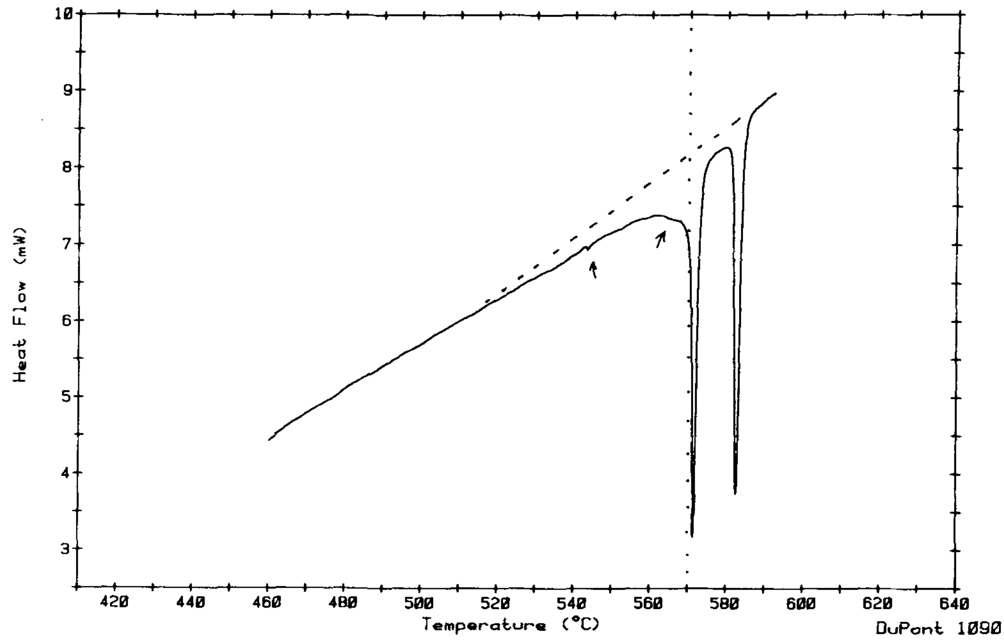

Fig. 6 DSC curve of sample No. 77 (quartz from cavity in limestone; same locality as 74)

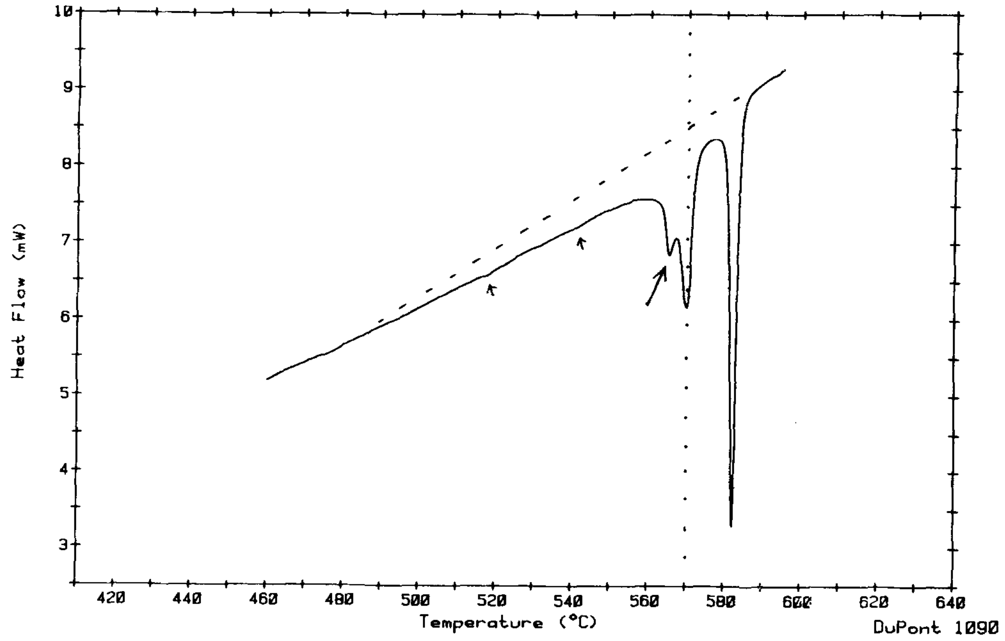

Fig. 7 DSC curve of sample No. 78 (weathered quartz from limestone, Dietlingen)

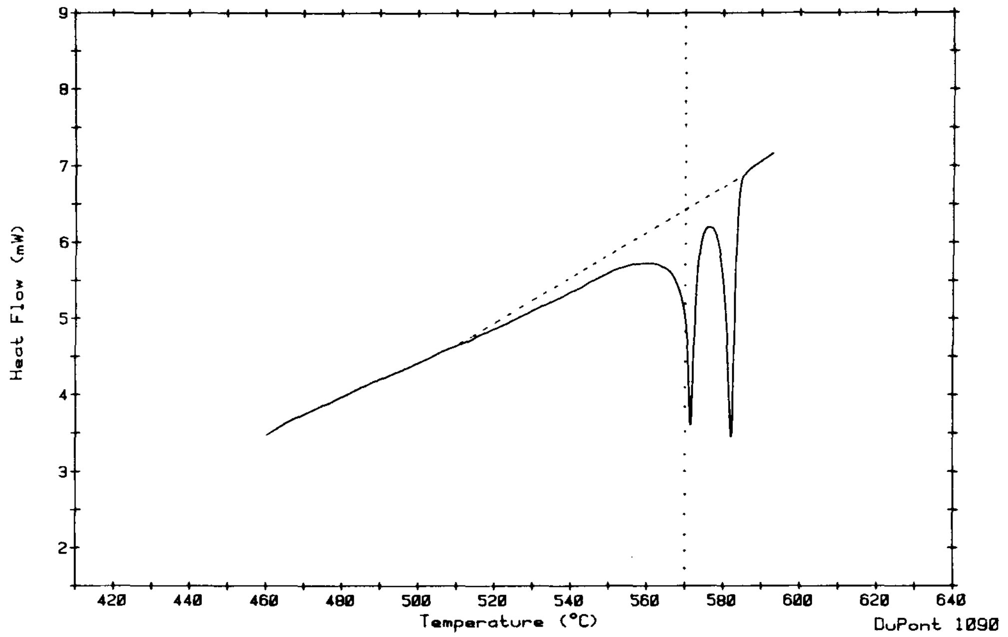

Fig. 8 DSC curve of sample No. 91 (vein quartz from sandstone)

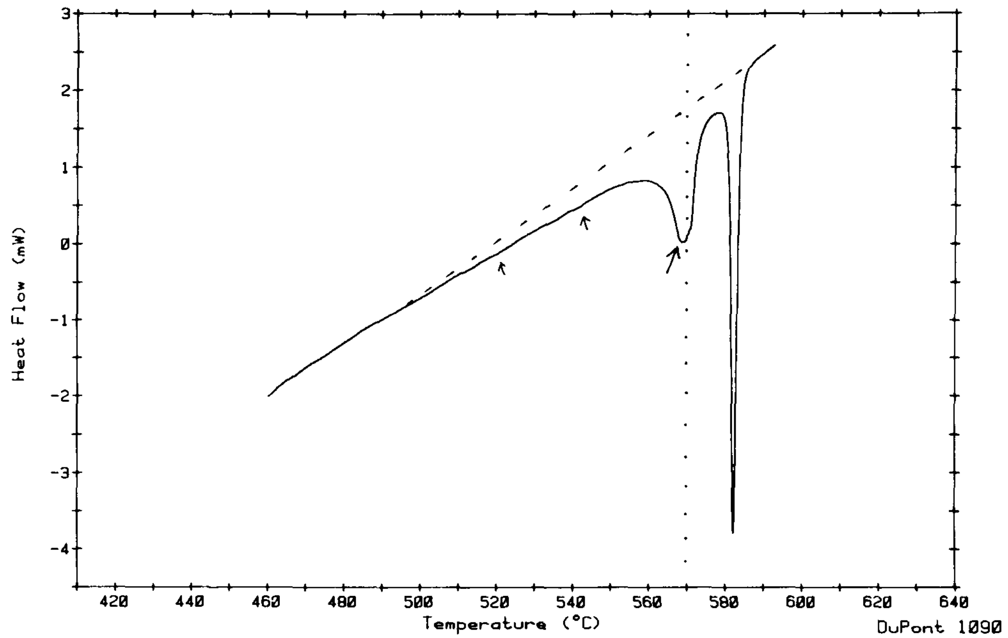

Fig. 9 DSC curve of sample No. 94 (vein quartz from sandstone)

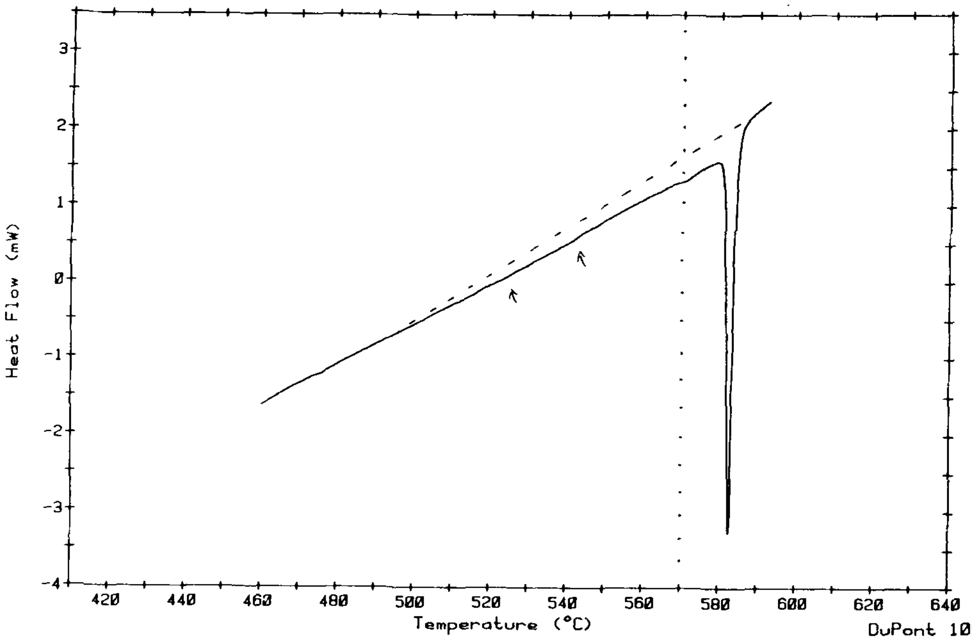

Fig. 10 DSC curve of sample No. 102 (microcrystalline quartz from the Carneol horizon in Rotliegend sandstone). All curves from first heating

vein fillings) are of low intensity: a broad effect covering the temperature range between 500 and 570°C with only weak shoulders instead of pronounced endothermic peaks shows to be very typical. But there are several exceptions (samples No. 30, 32, 55, 74, 78, 94) which exhibit the main effect in the low-temperature (= authigenic) region (Figs 1, 2, 3, 5, 7, 9). Only the microcrystalline carneol sample (No. 102, Fig. 10) does not show a distinct and clear inversion peak.

The authigenic quartz crystals from limestones (No. 30, 32, 55, 74 and 78) exhibit their main inversion effect at low temperatures, while most of the sandstone quartz crystals show the main effect at temperatures above 570°C (due to impurities of 'igneous', primary quartz crystals?).

Summary and discussion

The DSC method shows to be very sensitive in determining disordered parts of quartz crystals, using the known interrelationship (Flörke 1962, Buurman and van der Plas 1971, Smykatz-Kloss 1972, 1974, Moore and Rose 1973) between the degree of structural disorder and decrease of the inversion temperature. The method enables the study of very small amounts of samples (e.g.10–15 mg), thus enabling the determination of only small parts of disordered (= diagenetic) quartz in samples which consist mainly of ordered (detrital, igneous, 'primary') quartz. From the 10 analyzed quartz crystals from cavities and fissures in limestone and sandstone one sample (e.g. No. 91, the 'milky vein quartz') should have been formed in an environment offering higher formation energies, that means by precipitation from hydrothermal solutions. Four samples (No. 30, 32, 55 and 74) – all occurring in cavities of limestones – seem to be true diagenetic formations. The bituminous 'stinking' quartz (No. 78), which exhibits the larger part being formed authigenically, another bituminous quartz (No. 77) and the remaining quartz crystals from sandstones show at least both, one part being primary, one part having been formed during diagenesis. The estimation of the peak areas may give the (semi-) quantitative relations between primary and secondary quartz of the same sample. To apply the method in the outlined investigations (see 2.), e.g. for the purpose of prospection for hydrocarbons (or, possibly, for sulfides or phosphates) in deeper horizons of sedimentary rocks, some more investigations seem to be necessary, which may be encouraged by the presented results.

* * *

The authors are grateful to Prof. Dr. W. Eysel and Dr. Maltry (Mineralogical Inst., Heidelberg) for providing the DSC curves, to Mrs. M. Tannhäuser for preparing the manuscript and to two anonymous reviewers for valuable suggestions.

References

1 H. Le Chatelier, Bull. Soc. Franc. Minéral. Cryst., 10 (1887) 204.
2 M. L. Keith and O. F. Tuttle, Amer. J. Sci., (1952) 208.
3 M. J. Buerger, Crystal Structure Analysis. Wiley & Sons, New York 1960.
4 R. B. Sosman, The Phases of Silica. Rutgers Univ. Press, New Brunswick/N. J. 1965.
5 G. S. M. Moore, special reprint from Hatfield ICTA-Conf., 1992.
6 O. F. Tuttle, Am. Mineralogist, 34 (1949) 723.
7 J. Lameyre, C. Levy and J. Mergoil, Bull. Soc. Franc. Minéral. Cryst., 91 (1968) 172.
8 W. Smykatz-Kloss, Contrib. Mineral. Petrol., 26 (1970) 20.
9 W. Smykatz-Kloss, Differential Thermal Analysis. Application and Results in Mineralogy. K. Springer, Berlin 1974.
10 P. Kresten, Contrib. Geol., 23 (1971) 91.
11 A. Giret, J. Lameyre, C. Levy and C. Marion, C. R. Acad. Sci. Paris, 275 (1972) 161,
12 G. S. M. Moore and H. E. Rose, Nature, 242 (1973) 187.
13 G. S. M. Moore, Phase Transitions, 7 (1986) 25.
14 G. S. M. Moore, Thermochim. Acta, 126 (1988) 365.
15 U. Steinike, D.-C. Uecker, K. Sigrist, W. Plötner and T. Köhler, Cryst. Res. Technol., 22 (1987) 1255.
16 O. W. Flörke, Chemie der Erde, 22 (1962) 91.
17 P. Buurman and L. van der Plas, Geol. Mijnbouw, 50 (1971) 9.

18 W. Smykatz-Kloss, Contrib. Mineral. Petrol., 36 (1972) 1.
19 H. Graetsch, O. W. Flörke and G. Miehe, Phys. Chem. Minerals, 14 (1987) 249.
20 L. Heller-Kallai, I. Miloslavski and Z. Aizenshtat, Clay Minerals, 22 (1987) 339.
21 L. Heller-Kallai and R. C. Mackenzie, Clay Minerals, 22 (1987) 349.
22 P. Bennett and D. I. Siegel, Nature, 326 (1987) 684.
23 W. A. Kneller, H. F. Kriege, E. L. Saxer, J. T. Wilbrand and T. J. Rohrbacher, The Properties and Recognition of Deleterious Cherts which occur in Aggregates used by Ohio Concrete Products. Res. Found. Ohio, Aggr. Group Geol. Dept. Univ. Toledo, 1968.
24 W. Smykatz-Kloss, 'Purity Determinations by Thermal Methods' (Eds.: Blaine, R. L. & Schoff, C. K.) ASTM-STP 838, (1984) 121–137.
25 K. Lönvik and W. Smykatz-Kloss, Thermochim. Acta 72 (1984) 159.

Zusammenfassung — In der vorliegenden Studie wird die DSC-Methode zur Charakterisierung diagenetischer Umwaldlungen von porösen Sedimentgesteinen herangezogen. Hierfür werden die reversiblen Inversioneffekte von zehn authigenen Quarzen aus Hohlräumen in Sandsteinen und Kalken gemessen, wobei eine Beeinflussung des Inversionsverhaltens durch mechanische Beanspruchung vermieden wird. Die Methode erweist als sehr empfindlich bei der Bestimmung fehlgeordneter Quartzanteile, indem der Zusammenhang zwischen dem Fehlordnungsgrad und der Erniedrigung der Inversionstemperatur ausgenützt wird. Die Anwendung der Methode für die Prospektion auf Kohlenwasserstoffe, Sulfide oder Phosphate wird kurtz diskutiert.