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*Dedicated to Dr. Robert Mackenzie on the occasion of his 75th birthday*

# THE HIGH-LOW QUARTZ INVERSION
## Key to the petrogenesis of quartz-bearing rocks

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## Abstract

The paper reviews studies on possible applications of the high-low quartz inversion in petrology. Since the first suggestions of Fenner and Tuttle, nearly fifty papers have dealt with the subject, including ten by the present authors. The detailed discussion of the preparative and instrumental factors which may influence the quartz inversion behaviour reveals that the DTA (DSC) runs have to be made under highly standardized conditions to permit measurement of the 'material inherent factors' (mainly crystal physical factors) which cause variations in shape and temperatures. The most striking variations in shape and temperatures of the inversion effect (e.g. including temperatures more than 70°C lower than the 'textbook value' of 573°C for the quartz inversion) are observed for microcrystalline quartz crystals. The literature and the authors' own investigation demonstrate that the most interesting field of application of the method is that of authigenic quartz formation in sediments and soils. The characterization of metamorphic quartz is more complicated. Four fields of study are chosen to demonstrate the possible application of the quartz inversion characterization for petrogenetic interpretations: (1) the differentiation between authigenic and inherited quartz crystals in sediments, (2) the characterization of the contact-metamorphic aureoles around granites, (3) special regional-metamorphic terrains and (4) (from a few so far unpublished studies) the differentiation between sedimentary and soil silcretes.

**Keywords:** chalcedony, crystalline disorder, DSC, DTA, high-low quartz inversion, silcretes

## 1. Introduction

The high-low inversion of the very common mineral quartz, $SiO_2$, has concerned generations of mineralogists. When Tuttle (1949) published his observation that this inversion can differ by up to 2°C from the 'textbook value' (573°C, where the two modifications, high quartz and low quartz, are in thermodynamic equilibrium), and that this variable temperature may be a geologic thermometer, he followed suggestions made by Fenner (1913) [1]. The reproducible high-low inversion of quartz crystals normally occurs at this temperature of 573°C, i.e. it does so for a well-ordered and well-crystallized specimen. Berkelhamer (1944) [2] found that the endothermic inversion effect in the heating curves differed in shape for coarse and fine fractions. Faust (1948) [3] determined the heat of reaction as 3.1 cal $g^{-1}$ ($\rightarrow$12.98 J $g^{-1}$) and recommended both the temperature of inversion (i.e. 573°C) and $\Delta H$ (i.e. 3.1 cal $g^{-1}$) for use in calibration in thermal analysis. Keith and Tuttle

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(1952) [5], Nagasawa (1953) [6] and Tuttle and Keith (1954) [7] then published data from detailed rock studies by means of differential thermal analysis, DTA. Nagasawa [6] investigated 20 vein quartz crystals from Japan and reported remarkable shape variations of the inversion effect (e.g. Fig. 1), which he attributed to the heterogeneity of the specimen with regard to the inversion temperature. In fact, his DTA curves mirror the variation in the inversion temperature (Fig. 1, Table 1). Nagasawa [6] studied the effects of heating rate (see section 4.1.10) and particle size (section 4.1.2). Keith and Tuttle [5] and Tuttle and Keith [7] applied the method to granite studies and reported the first large variations in quartz inversion temperatures.

## 2. Variations in quartz inversion temperatures

Fifteen years then passed before (nearly spontaneously at several localities) geoscientists started to measure the inversion of some hundreds of quartz crystals

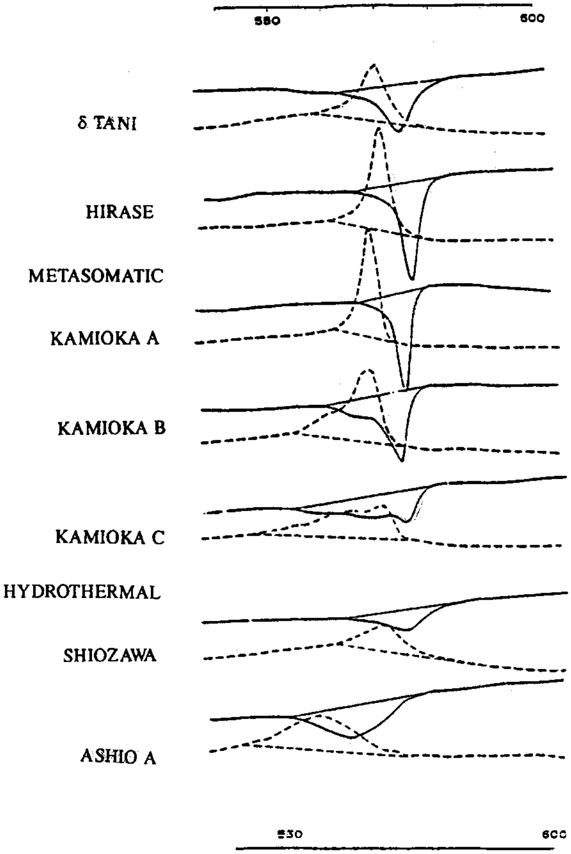

**Fig. 1** DTA curves of 7 vein quartz crystals from Japan (from Nagasawa [6]); endothermic effects down, exothermic up. Heating and (dashed lines) cooling curves

**Table 1**

| $T_i$/°C [±°C deviation] | | Sample description | | Reference |
|---|---|---|---|---|
| (a) min. | (b) max. | (a) | (b) | |
| "Variation of 1.9°C" | | | | [4] Tuttle 1949 |
| 563 | 574 | Japanese vein quartz | | [6] Nagasawa 1953 |
| 538 | 575 | sediment | granite | [7] Tuttle and Keith 1954 |
| 565 [±2°] | 574[±0.5°] | authigenic in limestone | hydrothermal vein | [10] Smykatz-Kloss 1969 |
| 532 [±2°] | 575 [±0.5°] | concretionary in slates | igneous | [11] Smykatz-Kloss 1970 |
| 570 | 574.8 | geode in quartzite | amphibolite | [22] Kresten 1971 |
| 553 [±2.5°] | 573 [±2.5°] | meta-quartzite | pegmatite | [23] Kresten 1971 |
| 518 [±2°] | 574 [±1°] | chrysoprase, Silesia | agate, Pfalz | [13] Smykatz-Kloss 1972 |
| | | microcrystalline quartz crystals | | |
| 532 [±3°] | 575 [±0.5°] | vein quartz crystals, Black Forest | | [14] Smykatz-Kloss 1972 |
| 571.3 [±0.2°] | 574 [±0.2°] | contact aureoles: hornfels and granite | | [25] Giret et al. 1972 |
| 525 [±5°] | 545 [±5°] | vein quartz crystals, Scotland | | [24] Robertson[1] 1973 |
| 567.6 [±0.3°] | 572.4 [±0.3°] | granite | rock crystal | [26] Rogers and Howett 1985 |
| 569.6 [±0.35°] | 572.4 [±0.35°] | quartz from geothermal field, N. Z. | | [27] Lisk *et al.* 1991 |
| 502 [±3°] | 572.2 [±0.3°] | cavity in "Muschelkalk" | sandstone | [28] Smykatz-Kloss and Klinke[2] 1994 |

[1] measurement by thermosonimetry, operator: Dr. K. Lönvik, Trondheim, Norway.

[2] measured by DSC, all other measurements by DTA.

from various rocks and soils. The method used was DTA. Panov *et al.* [8], Lameyre *et al.* [9], the present authors [10–15], Kresten [22, 23], Giret *et al.* [25] and Moore and Rose [18] published many data during the following seven years (1967–1974). Despite some results differing in detail, from all these papers it became clear that the inversion effect of natural quartz crystals can occur over a range of temperature of more than 70°C, with variations in peak shape and peak intensity as well. Table 1 presents some data from the literature.

## 3. Inversion effect for microcrystalline quartz crystals

The most striking effects were found for microcrystalline and for some authigenic quartz crystals from sediments and soils (e.g. see Fig. 2). Berkelhamer [2], Nagasawa [6], Flörke [31], Midgley [29], Kneller *et al.* [32], Warne [33], Buurman and van der Plas [34] and Smykatz-Kloss [11, 13] observed broad effects of low intensity and very often a series of flat, overlapping endotherms (on heating) with several peaks between ~500 and ~570°C (e.g. Fig. 2). McDowell and Vose [30] described 'a sluggish thermal response'. Smykatz-Kloss and Klinke [28] investigated microcrystalline carneol from Permian sandstones and found only broad endotherms of very low intensity (see section 5.4 and Fig. 14). Evidently, the temperature of the quartz inversion is dependent on the grain size; very fine-grained

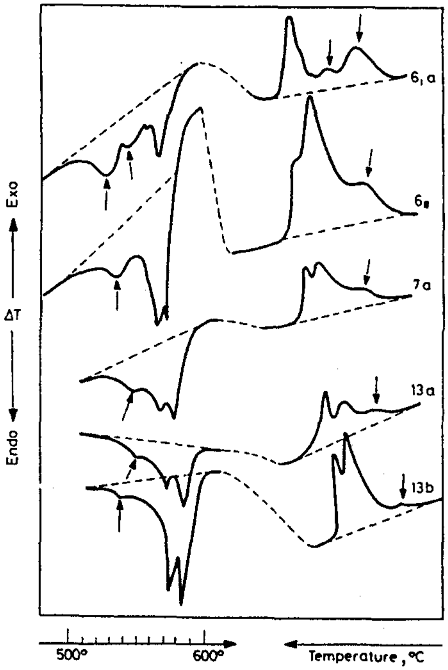

Fig. 2 DTA curves (first heating and cooling) of some quartz crystals formed by sedimentary processes; the endothermic effect which occurs at the highest temperature is due to the inversion of the internal standard $K_2SO_4$ (=583°C) (from Smykatz-Kloss [15, 16])

(micro- to cryptocrystalline) crystals include a high degree of structural disorder due to the comparatively large surface (Flörke [31]).

## 4. Factors influencing the inversion effect

### *4.1 Preparative and instrumental factors*

Most of the cited papers include investigations on the different factors which may influence the structural disorder of quartz crystals and/or the data from thermal analysis. Especially the studies of Nagasawa [6], Tuttle and Keith [7], Smykatz-Kloss [11, 13, 15], Moore [17–20], Steinike *et al.* [21], Mackenzie and Milne [35], Bayliss [37], Hofmann and Rothe [36], Heide [43], Wendlandt [38] and recently Lisk *et al.* [27] were concerned with the influence of different factors on the inversion behaviour of quartz crystals.

### 4.1.1 Grinding

The effect of grinding has been studied by Mackenzie and Milne [35], Hofmann and Rothe [36], Moore [17, 19, 20], Moore and Rose [18] and Lisk *et al.* [27]. Some hours of grinding in an agate mortar led to the complete destruction of mica structures [35]. Hofmann and Rothe [36] and Moore and Rose [18] noted that excessive grinding can reduce the long-range structure of quartz. Even crushing during sample preparation markedly affects the degree of disorder in the quartz lattice [27].

### 4.1.2 Sample size and particle size

The sample size (amount of sample) does not influence the temperatures of structural transformations (inversions) [13, 15, 18, 25]. Only the peak area, which is proportional to the heat of reaction [15, 22, 38, 43, 49], mirrors different amounts of quartz in heated samples (compare with Fig. 8).

The particle size (grain size), however, has to be considered. This is extremely important for natural very fine-grained (microcrystalline; section 3) and for extremely fine-ground specimens as well (section 4.1.1). Nagasawa [6] observed 'a smaller amplitude in the finer fractions', and Bayliss [37] found decreasing peak temperatures with decreasing particle size, 'but only in the finest fractions' [37]. Figure 3 illustrates the interrelation between 'sample particles size' and inversion temperatures as reported in [26].

### 4.1.3 Packing density

A strong packing density reduces the porosity of a sample. This may have some influence in thermal reactions where fluids or gases are involved as reaction products (e.g. during dehydration, dehydroxylation or degassing processes), but not for structural transformations.

### 4.1.4 Sample arrangement

The sample should be in direct contact with the thermocouples for optimal results to be attained [15]. Where this is impossible because of the furnace or crucible

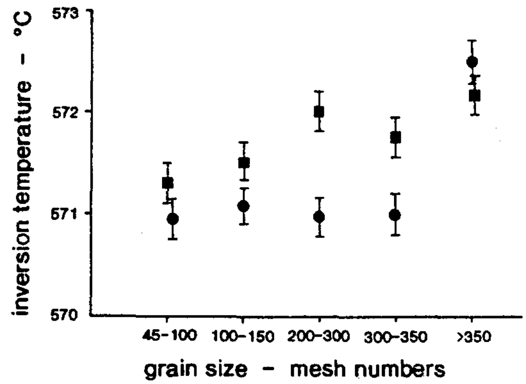

**Fig. 3** Variation in α-β inversion temperature with sample particle size for two quartz samples. The abscissa scala is arbitrary (from Rodgers and Howett [26])

design, the sample should be arranged as near as possible to the thermocouples. Both the sample and the reference material should be arranged symmetrically in the centre of the furnace to avoid a shifting of the baseline in the resulting DTA diagram [15, 43].

### 4.1.5 Reference material

The best reference material is always a substance which exhibits very similar chemical and physical properties to those of the studied sample in order to avoid differences in heat capacity and heat flow [15]. For the proper measurement of quartz inversion temperatures, Rodgers and Howett [26] recommend the use of ignited alumina ($Al_2O_3$)+cryolite ($Na_3AlF_6$) as an 'internal temperature standard' (compare section 4.3.1). The amount of reference material should be nearly the same as the amount of sample [15].

### 4.1.6 Gas adsorption

Stahl [39] reported that adsorbed gases influence the polymorphic α ↔ β quartz transformation, e.g. the size and the shape of the effect. Smykatz-Kloss and Klinke [28] discussed the influence of hydrocarbons on the formation of authigenic quartz in sediments.

### 4.1.7 Furnace atmosphere

The influence of the furnace atmosphere is of some importance as concerns measurements on Fe-, Mn-, C- and S-bearing specimens, e.g. for oxidates and redusates [15, 16]. In quartz inversion determinations, the choice of a reducing furnace atmosphere (e.g. $N_2$ or Ar) may be of great advantage for sediments rich in these elements.

### 4.1.8 Thermocouples

Ni-constantan thermocouples are quite suitable for the temperature range relevant in quartz inversion studies. However, thermocouples of $Pt\text{-}Pt_{90}Rh_{10}$ are generally used because of the larger range of temperatures at which these elements can be applied. Different thermocouples may influence the amplitude of thermal effects, but not the temperatures.

### 4.1.9 Crucibles

The quartz inversion effect is relatively weak (e.g. 12.98 J $g^{-1}$). This means that heat-conducting materials (e.g. metals) are to be preferred over insulating materials (e.g. ceramics) for the crucibles: in cases of overlapping and 'broad' effects, crucibles made from metals lead to a better separation of several effects which overlap partly, but the intensity ($\Delta T$) is larger in ceramic crucibles [15, 43].

### 4.1.10 Heating rate

This factor has a great influence. Nagasawa [6], Smykatz-Kloss [15], Wendlandt [38], Dodd and Tonge [40], Heide [43] and others reported increasing peak temperatures with increasing heating rate (which is to be expected in dynamic heating methods such as DTA, DSC, TS, etc.). Only Lisk *et al.* [27] have observed a decrease in measured peak temperatures with increasing heating rate. This contrasts with all other reports. Lisk *et al.* [27] explain the observed effect by the complicated nature of the quartz inversion, 'in which both homogenization of defect structures and the decrepitation of fluid inclusions within the quartz grains are believed to have assisted in triggering the structural changes' [27]. Rodgers and Howett [26] stress that the heating rate in quartz inversion determinations should be linear in the range between 500 and 600°C. They recommend blending both of the quartz sample (with $K_2SO_4$) and of the inert material (with cryolite) to obtain a nearly linear heating rate [26].

### 4.1.11 Repetition of runs

In studies of the possible influence of the repetition of runs, Nagasawa [6] and Smykatz-Kloss [15] found no marked difference on repeated heating and cooling. This is to be expected for polymorphic phase transitions such as $\alpha \leftrightarrow \beta$ quartz inversion.

### 4.1.12 Other influences

Rodgers and Howett [26] found that preheating of the furnace up to 500 °C before the insertion of either sample improved the linearity of the heating rate and the intensity of the endothermic inversion effect. Smykatz-Kloss and Klinke [28] recommended the analysis of all quartz specimens without any crushing or special preparation, to avoid any influence of mechanical treatment on the inversion behaviour, and also suggested the use of not more than 10–15 mg of sample.

## *4.2 Material inherent factors*

As regards the use of variable inversion temperatures of quartz crystals for petrogenetic purposes, the 'preparative and instrumental factors' and their influence on the inversion behaviour of quartz crystals should be well known. Only when it is possible to ignore them (see section 4.3) can the material inherent factors such as the crystal chemical composition ad the crystal physical properties, including special petrologic factors (rock pressure, and partial pressure of fluids or gases), be estimated and applied to reconstruct the origin and environment of (trans)formation of quartz-bearing rocks.

### 4.2.1 Crystal chemical composition

Tuttle [4], Keith and Tuttle [5] and Tuttle and Keith [7] believed that 'crystal chemical differences' were responsible for the observed variations in the quartz inversion temperatures. For synthetic quartz crystals, this has been stressed by Sabatier and Wyart [41] ('les conditions chimiques de cristallisation étaient déterminantes'). However, all the following authors reported that the influence of the chemical milieu on the quartz inversion behaviour was quite low. This statement (e.g. Smykatz-Kloss [13, 15, 16] or Kresten [22]) seems quite reasonable: quartz belongs among the very pure minerals, exhibiting not more than 0.3 weight% of impurities in total [15, 22, 32]. The impurities consist of low amounts of water (fluid inclusions), some ions dissolved in the fluids ($Na^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$, $SO_4^{2-}$ and $HCO_3^-$ ) and very low amounts of cations substituting the $Si^{4+}$ (mainly $Al^{3+}$, $Fe^{3+}$, $Na^+$, $Li^+$, $H^+$ and $Ti^{4+}$ [15, 22, 32]).

### 4.2.2 Crystal physical properties

'Crystal physical factors' are thought to be much more responsible than chemical impurities for the variation in (quartz) inversion behaviour [2, 13, 15, 18, 22, 26, 27, 30, 31, 35–37, 42]. This may be deduced from the results of grinding experiments [see section 4.1.1] and from theoretical considerations [15, 25, 31, 36]. Mechanical treatment (e.g. crushing or grinding) weakens the bonding forces in a crystal lattice, thereby lowering the energy necessary for structural transformations. Mechanical treatment creates structurally disordered parts, 'domains' where the structural transformation (e.g. the low-high quartz inversion) will occur somewhat earlier than in less disordered domains. The result is a broadening and flattening of the inversion effect in the DTA (DSC or TS) curve. This is observed for many microcrystalline specimens, and for artificially crushed quartz crystals. With increasing time of grinding (or with increasing intensity of grinding), the inversion effects become smaller and smaller [17–20] and finally disappear completely [17, 35]: the material has increasingly lost its crystalline character until it has become amorphous.

Additional to this damage to the crystal lattice, a decrease in particle size (grain size) implies an increase of disorder due to the larger surface [31].

Crystal physical effects in nature will be caused by all processes which result in any kind of pressure (stress or strain). This may start with syngenetic processes during the transport of rocks or rock particles, and during crystallization from melts or solutions. It will be continued during diagenesis, weathering and metamorphism (see section 5.3). The interdependence between the metamorphism and structural disorder of (quartz) crystals, however, is more complicated: metamorphic processes may involve recrystallizations and retrograde transformations, which may 'overprint' and change the original (or older) crystalline character of quartz (and its inversion behaviour). This is broadly discussed by Smykatz-Kloss [13, 15], Kresten [22, 23], Giret *et al.* [25], Rodgers and Howett [45] or Lisk *et al.* [46].

A measure of the degree of crystal structural disorder of minerals which involve a displacive transformation (a reversible high-low temperature inversion) is the hysteresis between the temperature of inversion on heating and that on cooling [15, 42]. With increasing degree of disorder, the hysteresis effect becomes larger and larger. Smykatz-Kloss and Schultz [42] studied the inversion behaviour of synthetic cristobalites. Well-ordered cristobalite (tetragonal $SiO_2$) inverts at 270±2°C into a high-temperature modification [15, 42]. With increasing temperature of synthesis, the following changes in cristobalite inversion properties have been observed:

(a) the character of the inversion effect changes from several, small, very broad and overlapping endotherms of low intensity ('domains') to one single and clear peak;

(b) the effect becomes continuously clearer and sharper;

(c) the temperature of inversion increases from ~100–150°C (temperature of synthesis: 300°C) to 243.5±0.5°C (temperature of synthesis: 600°C).

The accompanying X-ray diffractograms revealed that the degree of crystal structural order progressively improved.

Low temperatures of synthesis, and consequently low temperatures of formation, imply a higher degree of structural disorder for growing crystals: the lower the temperature of formation, the higher will be the defect character of quartz crystals. The growing crystals include strange particles (solid inclusions), solutions and strange ions: low-temperature (i.e. low-energy) formations include a high(er) degree of disorder than in crystals formed in high-energy environments (e.g. igneous or metamorphic). Consequently, quartz crystals formed in low-energy environments (e.g. authigenic sediments and soils; some low-temperature veins) should exhibit less intensive inversion effects (as compared with igneous crystals), including inversion temperatures of less than 570°C [13, 15, 16, 22–25, 31, 46].

### *4.3 Consequences as concerns optimal measurement of quartz inversion temperatures*

The consequences of the above discussion are that optimal determination of quartz inversion temperatures, i.e. the true characterization of 'material inherent factors', demands that the conditions of preparation and analysis will be standardized as much as possible [15, 22, 25–27, 45, 46]. If the conditions of analysis applied are (slightly) different from those recommended by one of the authors [15], at least the possible difference from the 'true', material inherent inversion character should be estimated and considered. The intensive studies of Rodgers and co-workers [26, 27, 45, 46] on the experimental procedures for determining precise inversion temperatures of quartz crystals culminated in the statement [27] that 'the present results emphasize, yet again, the need to standardize rigorously procedures used in TA, particularly where recorded data are to be compared between samples, operators, instruments and laboratories'. We fully agree with this.

In standardized DTA runs, the accuracy and reproducibility of the determination of the inversion temperature of well-ordered quartz crystals have proved to be ±0.3–0.5°C [11–15] (compare with Table 1). For badly-ordered (microcrystalline) crystals, the accuracy has been reported as ±2–3°C [13, 14, 23]. These values can be markedly improved by using internal standards [13–15, 25–28, 45, 46]. Suitable for this are the substances cryolite, $Na_3AlF_6$ (inversion temperature: 562.7°C [15]), and especially $K_2SO_4$ (inversion temperature: 583.5°C [15]). By application of these internal standards (their inversion temperatures occur quite near to the $T_i$ of quartz!), an accuracy of ±0.35°C [27], ±0.3°C [15, 26, 28] and ±0.2°C [25], respectively, has been obtained.

Most of the mentioned inversion studies have been made by means of DTA. For special purposes, a different method such as thermosonimetry (TS) or differential scanning calorimetry (DSC) is quite recommendable. In TS curves, overlapping inversion effects will be much better resolved than in DTA [24, 44], but the accuracy of temperature measurement may be lower than in DTA. DSC has proved very accurate and sensitive, including a good resolution of overlapping effects [28] (see section 5.1).

## 5. Petrological application of quartz inversion studies

Following the suggestions of Tuttle [4], Nagasawa [6] and Keith and Tuttle [7], several authors attempted to apply the method for petrogenetic purposes [8–16, 22–28, 44–46]. Some examples given below may illustrate the possibilities of the method's petrogenetic application. They include a few so far unpublished results from recent studies on microcrystalline soil formations (silcretes; see section 5.4).

### *5.1 Differentiation between quartz crystals of sedimentary and igneous origin*

The first mention of differences between the inversion behaviour of 'high-temperature deposits' and 'low-temperature deposits' was made by Nagasawa [6]. Studying 21 vein quartz crystals from Japan, he found that the DTA curves of these crystals exhibited considerable variations in shape, which he attributed to the mixture of different quartz components: 'Quartz from high-temperature deposits shows simple and sharp curves and quartz from low-temperature deposits shows broad or flat curves' [6]. Nagasawa [6] did not mention that the DTA curves in his paper also displayed some pronounced differences in the inversion temperatures (Fig. 1 and Table 1).

Some 15 years later, one of the present authors studied authigenic quartz crystals from limestones in Germany [10] and found the inversion temperature of the quartz crystals from one limestone occurrence (from Suttrop in Westphalie) to be above 571°C, and that from another occurrence (Dietlingen in Badenia) to be below

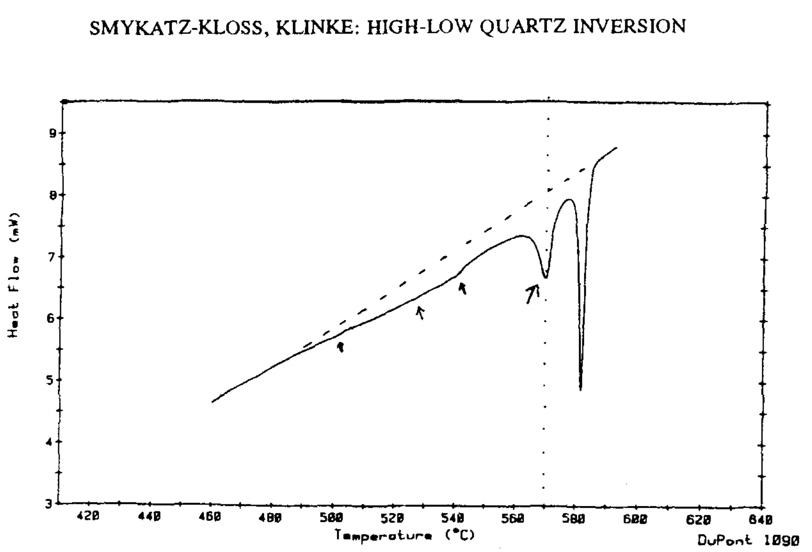

**Fig. 4** DSC curve of sample No. 30 (authigenic quartz crystal from a cavity in limestone, Enzberg). The arrows point to inversion effects of diagenetic quartz. The endothermic effect at 583°C mirrors the inversion temperature of the internal standard ($K_2SO_4$) (from Smykatz-Kloss and Klinke [28])

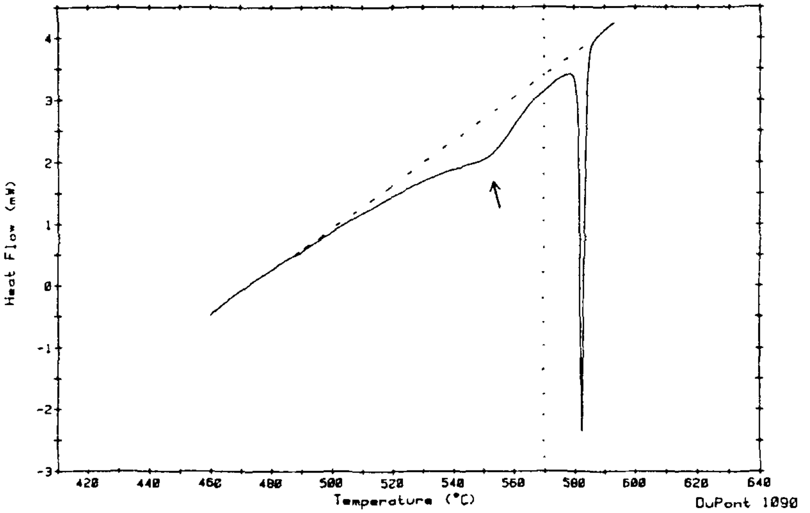

**Fig. 5** DSC curve of sample No. 32 (authigenic quartz crystal from limestone). The sharp endotherm is caused by the $K_2SO_4$ standard (from Smykatz-Kloss and Klinke [28])

571°C [10]. Additional optical investigations made it probable that the Suttrop quartz crystals (exhibiting inclusions of anhydrite and some sulfides) had been formed from hydrothermal solutions, while the Dietlingen crystals were true authigenic formations from sedimentary pore solutions [10]. From studies of more than 300 quartz crystals [10–15], it was suggested that this temperature of 571°C

(±0.3°C) was a 'true borderline' between hydrothermal (igneous) and sedimentary formations [15]:

$$T_{i(\text{sedim.})} < 571°\text{C} < T_{i(\text{igneous})}$$

Figures 4–7 show DSC curves of four authigenic quartz crystals in limestones. Only one of these four crystals (No. 32; see Fig. 5) seems to be a true authigenic quartz, having been formed from sedimentary pore solutions and showing a broad inversion effect lower than 571°C. The three other crystals (Nos 30, 55 and 78; see

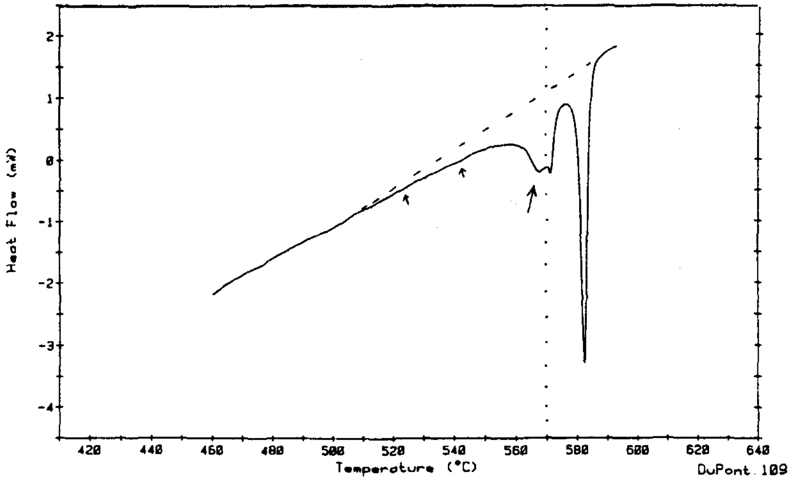

**Fig. 6** DSC curve of sample No. 55 (authigenic quartz from limestone) (from Smykatz-Kloss and Klinke [28])

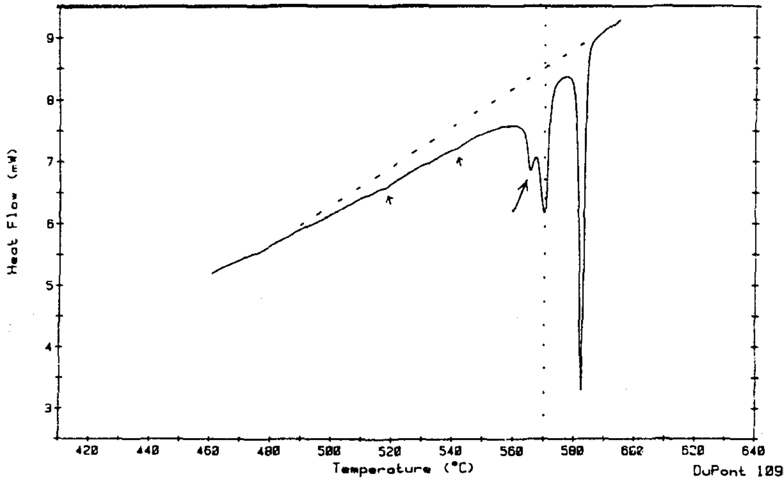

**Fig. 7** DSC curve of sample No. 78 (weathered quartz from limestone, Dietlingen) (from Smykatz-Kloss and Klinke [28])

Figs 4, 6 and 7, respectively) consist of authigenic (the broad effects below 571°C, marked with arrows) and 'detritic' (hydrothermal or igneous) portions. Included is the DSC curve of the Dietlingen quartz (Fig. 7, see above): older DTA curves [10] showed this quartz to be pure authigenic; the DSC method may be more sensitive and better resolving than DTA.

Lisk *et al.* [46] studied quartz crystals from the Broadlands-Ohaaki geothermal field in New Zealand and found similar relations, i.e. 'slightly but consistently higher values for hydrothermal than for primary quartz' [46]. They correlated these differences with the permeability of the primary sediments for the geothermal waters: 'The data may reflect differences in relative permeability with zones of higher primary permeability corresponding to zones whose quartz has higher inversion temperatures' [46].

### *5.2 Quartz crystals from contact-metamorphic aureoles*

Giret *et al.* [25] studied quartz crystals from granites (Fig. 8, left and bottom right) and from the contact-metamorphic aureole around these granites (Fig. 8, top right). In their highly standardized differential thermal analyses (with $K_2SO_4$ as an internal standard), an accuracy of ±0.2°C was achieved in the determination of the inversion temperatures (this is the highest reported accuracy in all the cited papers). From Fig. 8, it can be seen that the hornfels (2; directly at the granite contact) exhibits quartz crystals with higher inversion temperatures than the host rock (1, top right), which is outcropping at a distance of some meters. The heat of the crystal-

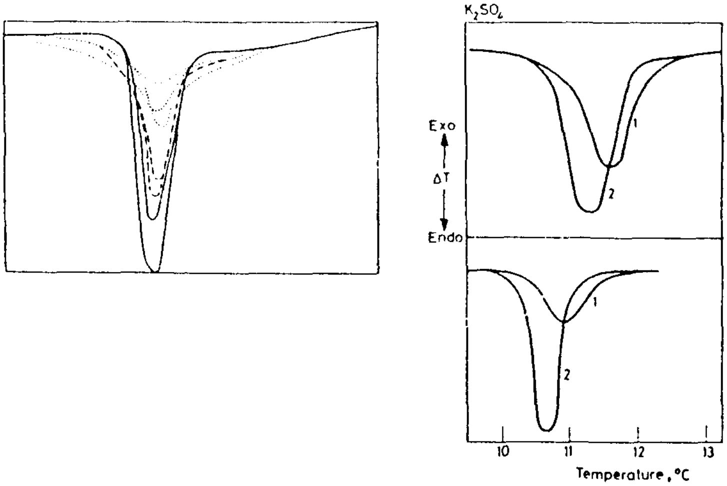

**Fig. 8** DTA curves of the low-high quartz inversion; left: some quartz crystals from different specimens of the same granite massive (the samples contain different amounts of quartz); right, top: comparison of quartz from a (meta)sedimentary rock (quartzite, arkose) with that from a contact-metamorphic hornfels of the same massive; the quartz crystals of both massive are clearly to be differentiated by means of their inversion temperatures (from Giret *et al.* [42]); right, top: 1 = quartzite, 2 = hornfels; right, base: 1 and 2 = quartz from two granites

lizing granite has led to the recrystallization of the surrounding rock by transforming it into the contact-metamorphic hornfels. Evidently, this process has improved the quartz inversion temperatures of the hornfels [25].

### *5.3 Study of regional-metamorphic rocks*

The inversion behaviour of quartz crystals from regional-metamorphic rocks seems to be much more complicated than that of sedimentary, igneous or contact-metamorphic rocks [9, 11, 15, 22, 23, 45]. The data mirror the complex pressure-temperature history of these rocks. Retrogressive processes may overprint older high-grade influences [15, 45]. As regards the 'borderline temperature' of 571°C (see section 5.1), the $T_i$ of metamorphic quartz crystals may occur on either side of this 'line' [15]. A real impression of these complex interrelations between the p-T

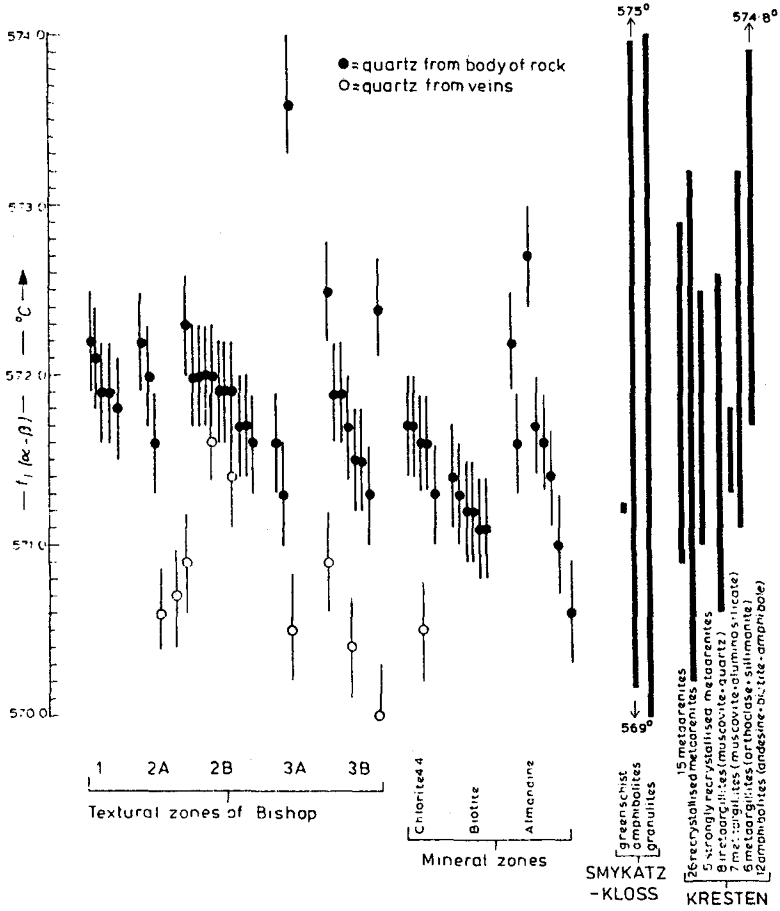

**Fig. 9** DTA ($\alpha$-$\beta$) inversion temperatures of quartz rock samples of the Haast Schist Belt and Torlesse Supergroup, compared with data from Smykatz-Kloss [1971, 1974) and Kresten (1971a, b) (from Rodgers and Howett [45])

history and the quartz inversion temperatures is offered by the study of Rodgers and Howett [45] (Fig. 9). They state that 'quartz crystals from progressively metamorphosed greenschist facies rocks show a slight decrease in their $T_i$ with increasing mineralogical grade. But the pattern is confused by retrogressive metamorphism' [45]. Rodgers and Howett [45] investigated the quartz crystals from metamorphic rocks and from veins cutting through these rocks, and always found lower inversion temperatures for the vein quartz crystals (Fig. 9).

Smykatz-Kloss [15] observed differences for the quartz crystals of a metamorphic profile in the Beaume valley (Cevennes, France): $T_i$ increased slightly with increasing metamorphic grade (mainly with increasing temperature), but only within the greenschist facies rocks. Then, with the beginning of the cordierite-amphibolite facies, the inversion temperature abruptly decreased. Within the amphibolite facies, $T_i$ increased with increasing metamorphic temperatures again [15]. Evidently, the increase in $T_i$ was caused by a certain recrystallization.

Kresten [22, 23] studied the metamorphic rocks in the Västervik area in Sweden. He found that the quartz inversion temperatures were directly proportional to the temperature of formation and to the partial pressure of $H_2O$, and indirectly proportional to the total pressure [22]. For migmatites and associated rocks, he reported inversion temperatures between 553 and 573°C, and observed a continuously increasing quartz inversion temperature with the metamorphic grade, exhibiting increasing inversion temperatures for the sequence metasediment – metasediment+'granitic block' – schlieric neosome – homophanic neosome [23]. Kresten explained the increase in $T_i$ with increasing migmatization in terms of processes of recrystallization.

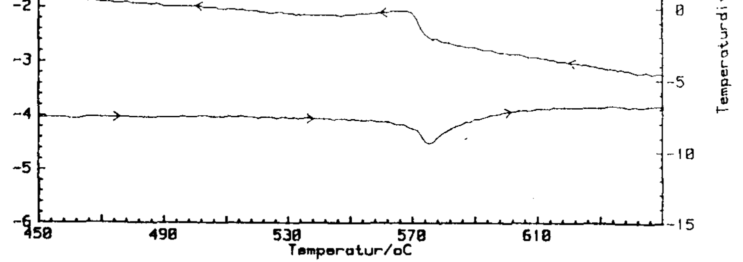

Fig. 10 DTA curves (heating+cooling) and simultaneous TG curves of allochthonous silcrete PLK-II/2 from the Cape Province (for localities of samples for Figs 10–13, see Joachim [47])

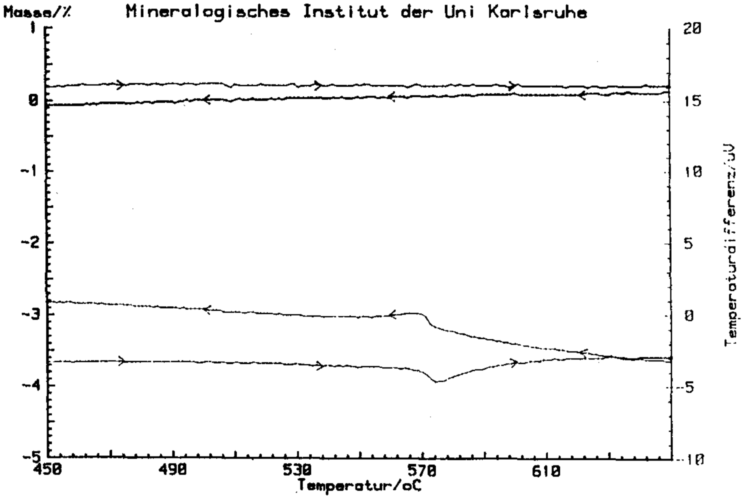

Fig. 11 DTA and TG curves of allochthonous Caura silcrete (W-Australia)

## 5.4 *Quartz crystals from silcretes*

Silcretes belong among the duricrusts and are (a) true soil formations formed from oscillating soil waters *in situ* on top of siliceous host rocks ('autochthonous silcretes') or (b) allochthonous formations from sedimentary or weathering solutions in alkaline playa lakes (Joachim [47], Smykatz-Kloss *et al.* [48]). Mineralogically, they consist of all kinds of microcrystalline silica minerals (opal-A, opal-CT, microcrystalline quartz = mainly chalcedony), and kaolin minerals ± goethite or other Fe-minerals). Four examples are shown in Figs 10–13, two from each type. The allochthonous, kaolin-free silcretes (PLK-II and the Caura silcrete) display

**Table 2** Inversion data on quartz crystals from silcretes

| Sample | Silcrete type | $T_i$ (heating)/°C |  | $\Delta T$/°C | Hysteresis/°C |
|---|---|---|---|---|---|
|  |  | (±0.5) | (±5) |  | ($T_{i\,heating} - T_{i\,cooling}$) |
| FG II-H | in situ |  | 500 | 0.15 | –55 |
| Fe-bearing Silcrete | in situ |  | 547 | 0.12 | –6 |
| PLK-II/2 | allochthonous | 571.5 |  | 0.3 | +2.5 |
| Caura silcrete (W-Australia) | allochthonous | 571 |  | 0.2 | +1 |
| Carneol | fossil silcrete | 520, 540 |  | 0.03 | n.d. |
| (Schramberg/ | (Rotliegend) |  |  | – |  |
| Black Forest) |  |  |  | 0.05 |  |

Samples FG-II-H, Fe-bearing silcrete and PLK-II/2 from Cape Province, South Africa; sample Caura silcrete from W-Australia.

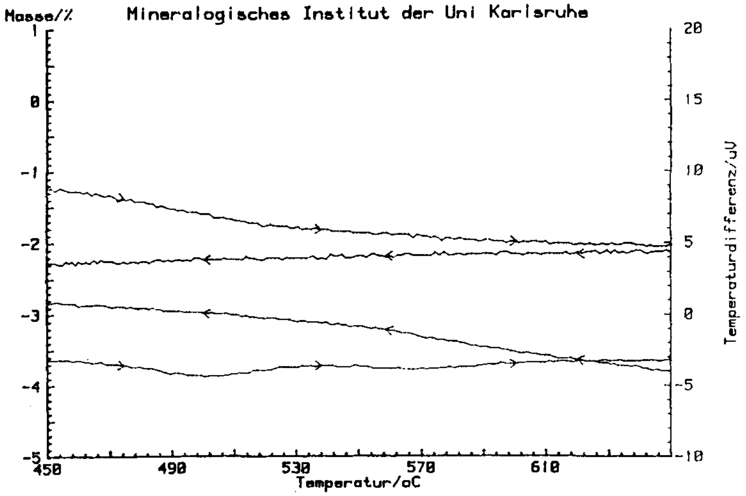

Fig. 12 DTA and TG curves of autochthonous Fort Grey silcrete (Cape Province)

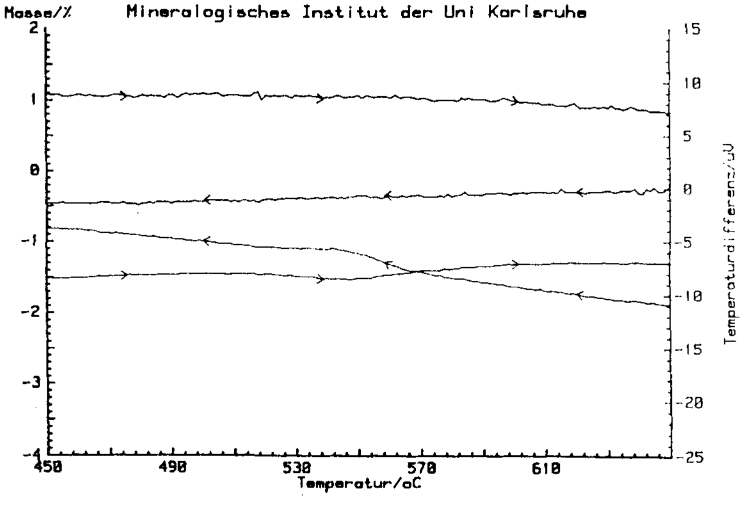

Fig. 13 DTA and TG curves of autochthonous Fe-bearing silcrete

higher inversion temperatures (e.g. 571–572°C, Figs 10 and 11, Table 2), higher intensities and a very small hysteresis effect mirroring low degree of disorder. The '*in situ*' silcretes exhibit broad and flat inversion effects with maxima around 500–550°C±5°C and large hysteresis (Figs 12 and 13, Table 2).

The microcrystalline carneol sample (No. 102, Fig. 14) represents a fossil (Permian, Rotliegend) silcrete which mineralogically consists of opal-CT and cryptocrystalline chalcedony (fibrous quartz). The inversion effects are very weak.

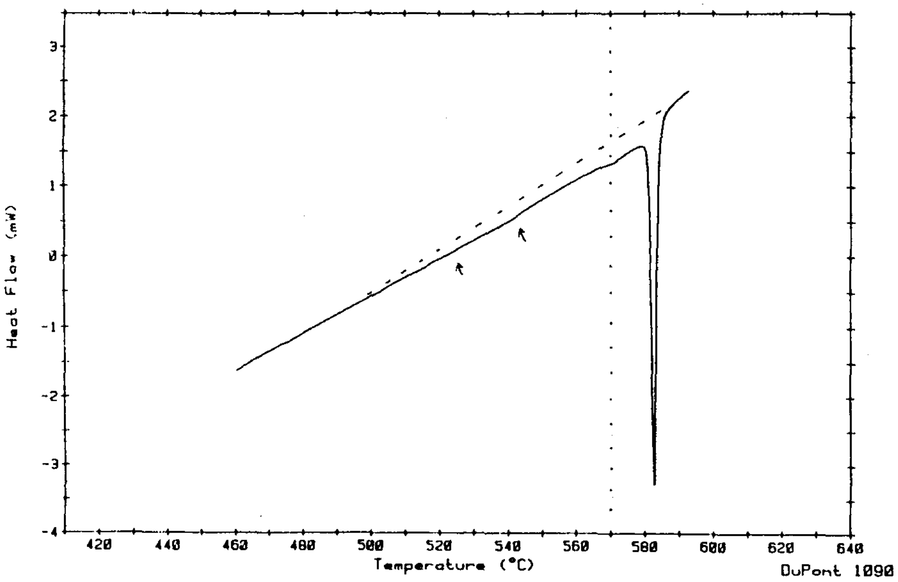

Fig. 14 DSC curve of sample No. 102 (microcrystalline quartz from the Carneol horizon in Rotliegend sandstone). All curves from first heating (from Smykatz-Kloss and Klinke [28])

It is striking that 'allochthonous' silcretes (playa sediments) consist of quite well-ordered microcrystalline quartz (chalcedony), exhibiting relatively high inversion temperatures, while the soil formations (in situ silcretes) show weak effects with low inversion temperatures (Table 2, Figs 12 and 13). The reasons for these differences are still under examination (Smykatz-Kloss *et al.* [48]).

## 6. Conclusions

The suggestions of Tuttle [4], who expected to use the high-low quartz inversion as a geologic thermometer, and of Kresten [22], who recommended the method for geologic thermometry and barometry, have been shown to have been too optimistic. However, in many cases the quartz inversion behaviour (the temperature of inversion and the shape of the inversion effect in thermal curves) has been reported to be a suitable tool for petrologic interpretations and for petrogenetic characterizations. To achieve this, the DTA (DSC) runs have to be highly standardized in order to avoid any influence of preparative or instrumental factors on the inversion characteristics. The use of standardized preparation and run conditions and of an internal temperature standard (cryolite; $K_2SO_4$) markedly improves the accuracy and reproducibility of the measurements. Especially the influences of the heating rate and of the mechanical treatment (crushing and grinding) have to be considered. A heating rate of 5–10°C $min^{-1}$ and the use of whole crystal pieces (no grinding at all!) 10–50 mg in mass have proved clearly beneficial. DTA is a suitable method for measurement of the quartz inversion temperatures, but DSC is better as concerns the resolution of overlapping effects and the use of small sample amounts.

The study of metamorphic quartz crystals is quite complicated. However, in special cases, e.g. in the study of rock series or metamorphic terrains and especially in the characterization of contact-metamorphic aureoles, the method has yielded interesting results. The same holds for some special applications on igneous rocks. Nevertheless, the main field of application is that of quartz formations in sediments and soils, where low energies of (trans)formations lead to a distinct degree of crystalline disorder, and hence to a broadening of the inversion effect and (mostly) to a lowering of the inversion temperature. This is illustrated by the study of quartz authigenesis in sediments and soils (including duricrust formations such as silcretes). The differentiation between quartz crystals newly formed in sediments and crystals inherited from igneous or metamorphic rocks (i.e. which have been transported into the sedimentary environment) is possible even in sandstones. From preliminary investigations on silcretes, it seems possible to use the method for a clear differentiation between allochthonous (sedimentary, playa lake formation) and autochthonous (soil formation) silcretes. Thus, the method really does provide a key for the understanding of the petrogenesis of (numerous) quartz-bearing rocks.

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