GEOLOGIJA *36*, 211–222 (1993), Ljubljana 1994

UDK 548.4:549.5=20

Pyroelectrically caused twisting of quartz crystals

Mirjan Žorž
LEK Ljubljana, Verovškova 57, 61107 Ljubljana, Slovenia

Abstract

The twisting of quartz crystals is conditioned by Dauphiné twinning. Each twisted crystal shows morphological characteristics confirming this type of quartz twinning.

A linear mathematical correlation based on morphological parameters measured on quartz crystals elongated and twisted along their polar [2$\bar{1}$.0] a-axis has been deduced. It was demonstrated that the twisting angle is the function of the twisting constant and some of the crystal dimensions. This constant has the same value ~4° as the declination of the [2$\bar{1}$.0] edge of the crystal twisted around the [2$\bar{1}$.0] a-axis which also corresponds to the surface distribution of the positive charge observed with Dauphiné-twinned quartz crystal on cooling. A similar quartz feature is the twisting of a quartz crystal around the c-axis. A proposed theory describing the reasons for crystal twisting, development of different crystal forms and types of twisted quartz crystals is thus based on the pyroelectrically accelerated growth from slowly cooling and slightly supersaturated quartz-bearing solutions.

Introduction

Quartz crystals elongated and twisted along the [2$\bar{1}$.0] a-axis (der Gwindel in German) are typical features of Alpine-type veins that are always associated with quartz crystals of the Friedlaender type. They are considerably rare crystal forms mostly found in the Swiss Alps and are not so frequent in the French, Italian and Austrian Alps. Another regions where they have also been found is the Polar Ural (Dodo and Puiva) in CIS and Corinto, Minas Geraes, Brazil.

Two new locations yielding twisted quartz crystals have been discovered in recent years in Bosnia and Hercegovina (Busovača) and in Macedonia (Berovo). Over 300 twisted crystals from all the aforementioned locations are discussed in this study. Their morphological parameters were measured (Figs. 1*a* and 1*d*) and some typical features, i. e. morphological hand, colour and form were noted as well. The predominant colour is smoky. Colourless crystals are considerably rare. Of all the crystals studied, 83.2 % were from Switzerland, 8.7 % from CIS, 3.6 % from Macedonia, 3.0 % from France, 1.2 % from Austria and 0.3 % from Bosnia and Hercegovina. Of all the mentioned crystals, 51.3 % were left-handed.

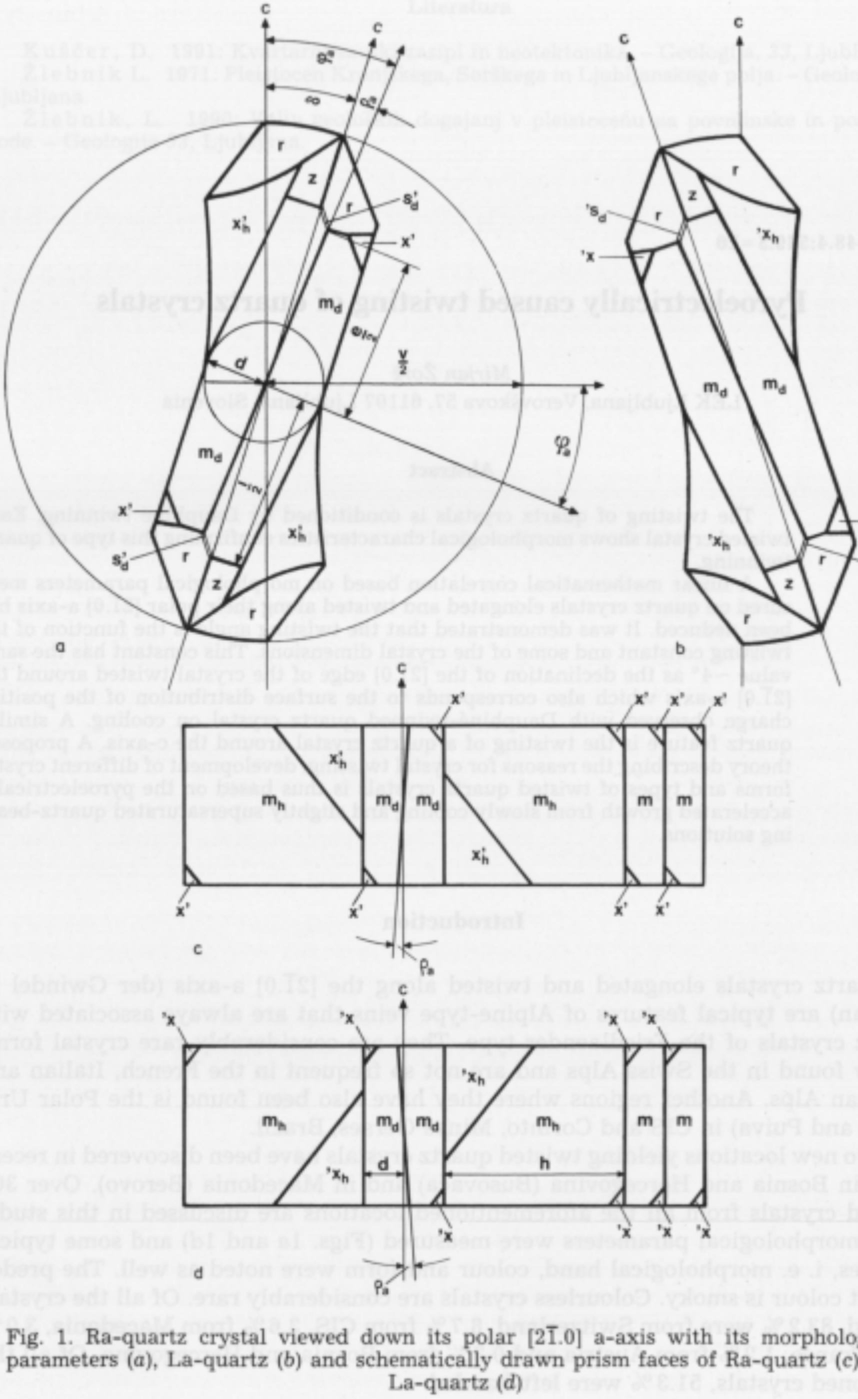


Fig. 1. Ra-quartz crystal viewed down its polar [21̄.0] a-axis with its morphological parameters (*a*), La-quartz (*b*) and schematically drawn prism faces of Ra-quartz (*c*) and La-quartz (*d*)

Quartz crystals twisted around c-axis are also typical features of Alpine-type veins and are again associated with quartz crystals of the Friedlaender type. This twisting is not as distinctive as it is in the case of gwindels.

Observations and measurements on twisted crystals

Since a particular crystal is attached to a matrix from which it grows and since its termination twists – if the crystal is viewed down its $[2\bar{1}.0]$ a-axis – to the left with left-handed, and to the right with right-handed crystals (Figs. 1*a* and 1*b*), the denotations La-quartz or Lc-quartz for left-handed and left-twisted crystals and Ra-quartz or Rc-quartz for right-handed and right-twisted quartz crystals will be used further in the text.

Measurements have shown that there is a correlation between twisting angle φ_a, prism $\mathbf{m}_h$ height h and prism $\mathbf{m}_d$ diameter d (Figs. 1*a* and 1*d*).

The equation is:

$$\varphi_a = k \frac{h}{d} \tag{1}$$

where k is the twisting constant.

The linear regression line was calculated from the measured morphological parameters. The final expression is:

$$\varphi_a = -0.101^\circ + 3.980^\circ \frac{h}{d} \tag{2}$$

with a correlation coefficient 0.980. The uncertainty of the k-value derived from the possible errors of the morphological measurements is about 23 %. It can be seen from equation (1) that the twisting angle φ_a is larger with thinner and higher La- and Ra-quartz. Fig. 2*a* shows the dependence of the twisting angle φ_a from h/d quotient.

The limit:

$$\lim_{h \to d} k \frac{h}{d} = k = \varrho_a \tag{3}$$

shows that twisted crystals whose prism $\mathbf{m}_h$ height h approaches $\mathbf{m}_d$ diameter d would show only a declination of the $[2\bar{1}.0]$ edge. The declination angle ϱ_a of this edge between $\mathbf{m}_d$ prisms away from the direction of the c-axis is ~4° and can be observed with La- and Ra-quartz crystals and especially with crystals where the trapezohedron $\mathbf{x}_h$ faces are not developed (Figs. 1*a* – 1*d*). This edge is declined to the left with La- and to the right with Ra-quartz. The $[2\bar{1}.0]$ edge however does not show this declination (Figs. 1*c* and 1*d*).

Discussion

F r o n d e l (1978) calculated the twisting period (180° turn) from angle δ (Fig. 1*a*) of a particular crystal and obtained values between 20 and 600 cm, and twisting degrees between 0.05 and 0.85 °mm⁻¹. R y k a r t (1989) measured angle δ, obtaining twisting degrees between 0.02 and 0.5 °mm⁻¹. It can be seen from equation (1) and

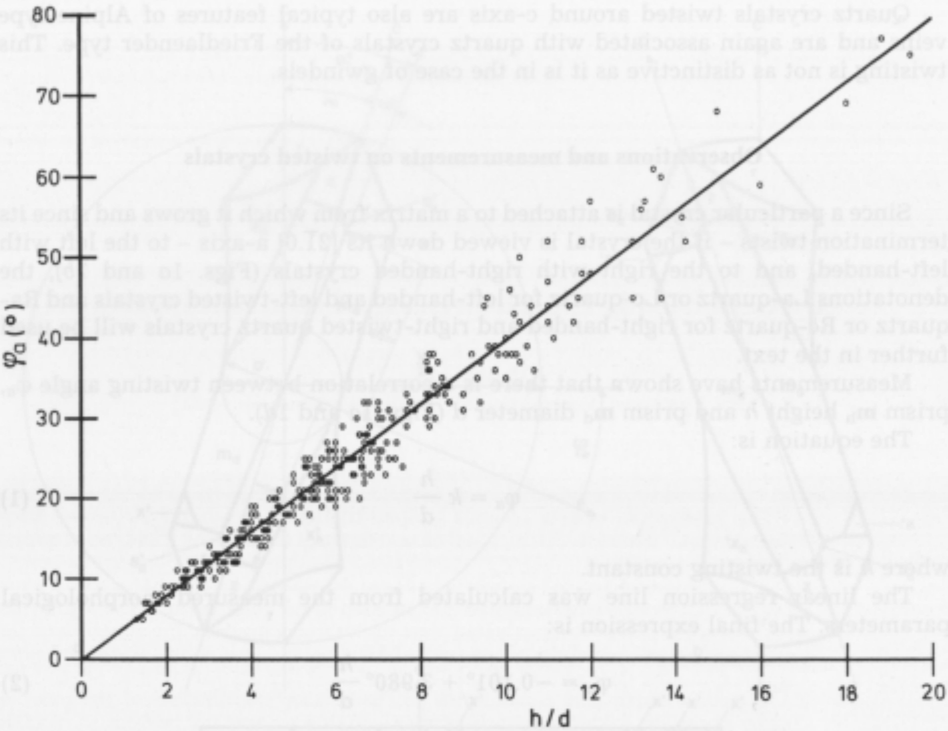


Fig. 2a. Data and evaluated linear regression line of measured La- and Ra-quartz crystals

from Fig. 2*b* that twisting degree φ_a/h is the function of the prism $\mathbf{m}_d$ diameter *d*. The twisting degree decreases with increasing *d*. Diameters under 3 and over 25 mm were not observed with the crystals measured in this study. The distribution of *d* is shown in Fig. 2*b*. A complete 180° turn would be achieved with a crystal whose height *h* would be approximately 45 times larger than its diameter *d* (2). This is not very likely to occur. As the crystal grows it becomes both higher and thicker, which causes a simultaneous decrease in twisting angle φ_a. That is why the twisting period is not a suitable parameter for the description of the crystal twisting rate. More illustrative is the twisting degree quotient φ_a/h.

La- and Ra-quartz from all the mentioned locations have given the same values for the twisting constant *k*. This means that twisting is controlled by a mechanism that cannot be ascribed to structural dislocations and temperature only. It is most probable that the pyroelectrical phaenomenon also contributes to the formation of twisted quartz crystals. Linck (1923) and Lang (1974) described quartz's pyroelectrical properties and showed some illustrations based on Kundt's dust method for determining the charge distribution on a crystal by use of red lead oxide and sulphur. In pictures shown it can be seen that the charge distribution on a Dauphiné-twinned quartz crystal is such that the lines of charge are declined by ~4° away from the prism edges and the c-axis direction. Frondel (1978) showed that the edge [2$\bar{1}$.0] of La- and Ra-quartz crystals acquires a positive charge on cooling. Observations on the

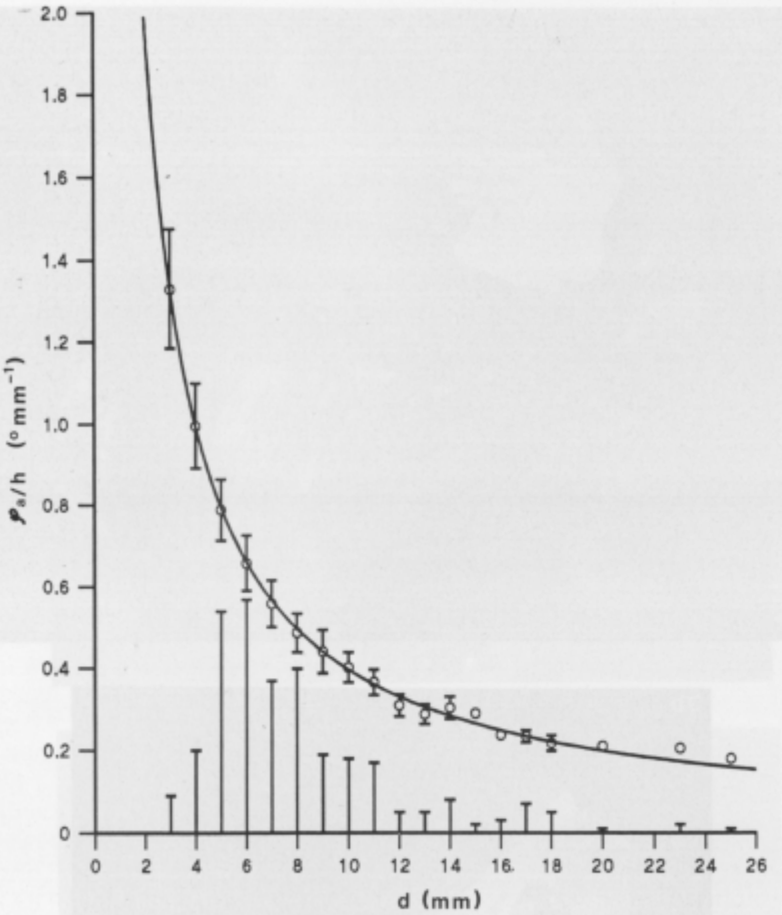
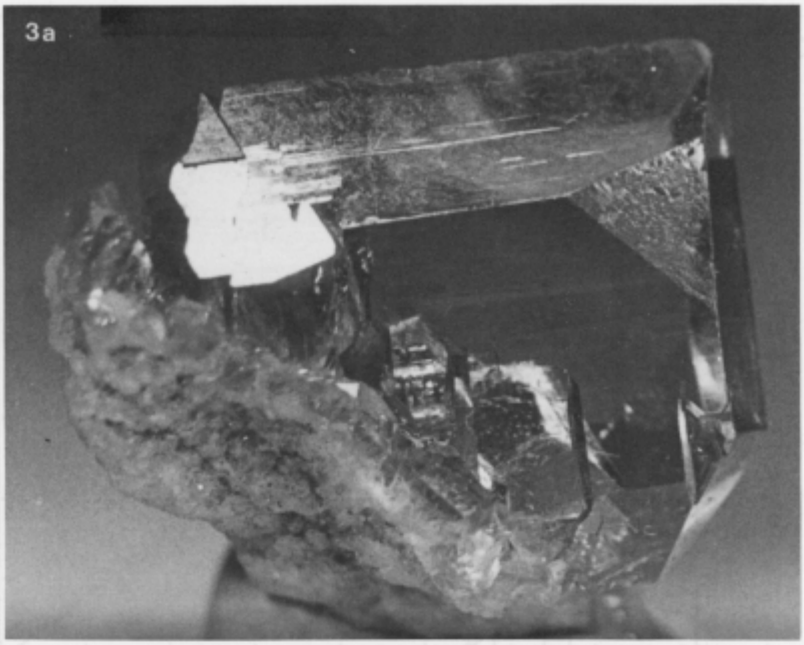


Fig. 2b. Twisting degree φ_a/h of the La- and Ra-quartz in the dependence of the $\mathbf{m}_d$ prism diameter *d*. Standard deviations are given for points of at least five measured crystals. Solid line represents theoretical twisting degree calculated with $k = 3.98°$. Distribution of measured $\mathbf{m}_d$ prism diameters is shown on the abscissa. In this case each 0.2 digit represents twenty crystals

La- and Ra-quartz crystals have shown that all of them show morphological characteristics typical of Dauphiné twinning, i.e. trapezohedrons or bipyramids in twinning positions and/or an etching pattern on crystal faces confirming this twinning. It can be concluded that the growth of a quartz crystal in the [2$\bar{1}$.0] a-axis direction in the Alpine-type vein milieu under the conditions of only slightly supersaturated, slowly cooling solutions is accelerated by this effect. The termination of growing La- or Ra-quartz serves as a positive anode attracting $[SiO_4]^{4-}$ ions from the vein solution. Since the leading, positively charged [2$\bar{1}$.0] edge is declined by ~4° at any time, a crystal grows most quickly in the direction of polar [2$\bar{1}$.0] a-axis, simultaneously turning around it with constant degree. The crystallization rate is thus higher in comparison


3a


3b

3c

3d

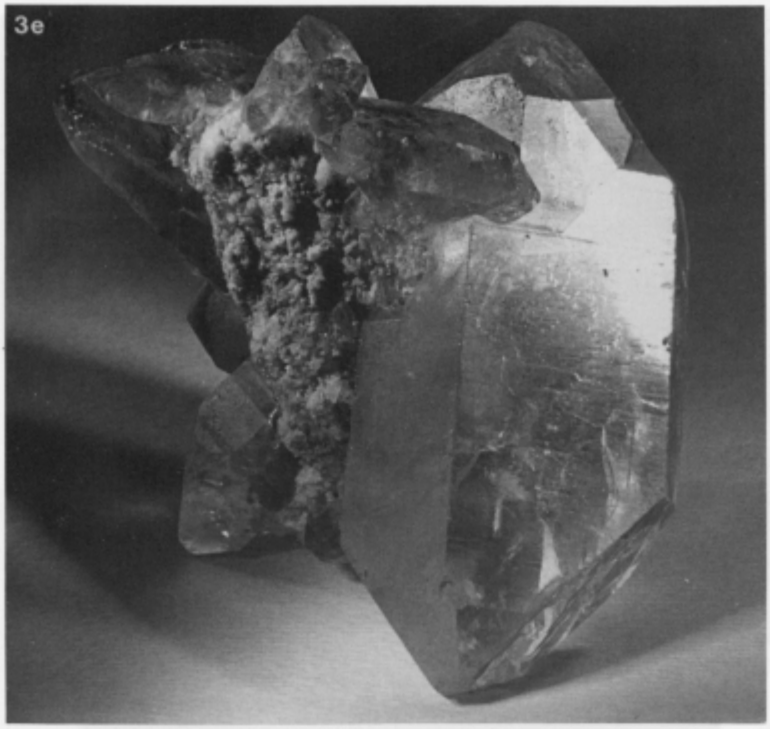


Fig. 3. Ra-quartz (18 × 20 mm) of young closed type with *e*/*v* ratio of 0.7 from Piz Gendusas in Switzerland (*a*), slightly opened La-quartz (30 × 32 mm) with *e*/*v* ratio of 0.6 from unknown Swiss locality (*b*), open La-quartz (47 × 47mm) with *e*/*v* ratio of 0.2 from Piz Gendusas (*c*), closing Ra-quartz (88 × 78 mm) with *e*/*v* ratio of 0.1 from Mont Blanc in France (*d*) and old closed Ra-quartz (59 × 34 mm) with *e*/*v* ratio of 0.4 from Berovo in Macedonia (*e*)

to one controlled only by diffusion of $[SiO_4]^{4-}$ ions from the solution towards the crystal surfaces under the same conditions. A tabular crystal elongated along the $[2\bar{1}.0]$ a-axis with an extremely developed $\mathbf{m}_h$ faces is formed (Figs. 1*c*, 1*d* and 3*a*–3*e*). A prerequisite is the orientation of the seeding Dauphiné-twinned quartz crystal whose $[2\bar{1}.0]$ edge must be attached in parallel and whose $[2\bar{1}.0]$ a-axis must be perpendicular to the matrix. The higher growth rate in the $[2\bar{1}.0]$ a-axis direction (V_a) explains the unusually well-developed trapezohedrons $\mathbf{x}_h$ and rarely well developed, Dauphiné twinning showing bipyramid $\mathbf{s}_d$ faces (Figs. 1*a* and 1*b*). The reason is the rate of trapezohedron $\mathbf{x}_h$ growth which, in this case, is lower in comparison with that of $\mathbf{m}_d$, $\mathbf{s}_d$ and $\mathbf{x}_d$. The $\mathbf{s}_d$ faces are frequently present and are, in fact, as narrow as an edge. The declination of the $[2\bar{1}.0]$ edge is visually pronounced in the presence of the $\mathbf{s}_d$ faces (Figs. 1*a* and 1*c*). Trapezohedron $\mathbf{x}_d$ faces with La- and Ra-quartz are only exceptionally developed.

The growth of a particular La- or Ra-quartz crystal can be divided into several phases. In the first phase the crystal grows from the matrix along its $[2\bar{1}.0]$ a-axis and is twisted in a particular direction. The crystal growth rate along [2$\bar{1}$.0] a-axis (V_a) is higher in comparison with growth rate along its c-axis (V_c), i.e. $V_a >> V_c$. Crystals in this phase are tabular with well-developed $\mathbf{x}_h$ faces. Neither reentrant angles nor typical sutures on twisted and smoothly developed faces occur. These crystals tend to be relatively small. This is a young closed type. The quotient of the [2$\bar{1}$.0] edge length e and crystal length v in the c-axis direction – e/v ratio – is up to 0.9 (Figs. 1*a* and 3*a*). In the next growth phase ($V_a > V_c$) reentrant angles and some sutures appear on the crystal, otherwise the crystal faces are smooth. The e/v ratio decreases to lower values (Fig. 3*b*). Further growth ($V_a \approx V_c$) causes deepening of the reentrant angles and sutures, making it look as if the crystal were resolved to many »subindividuals«. The e/v ratio decreases to 0.1. This is an open type (Fig. 3*c*). During the next phase ($V_a < V_c$) the reentrant angles tend to disappear again. A crystal thus formed has again only slightly resolved »subindividuals« with a still low e/v ratio (Fig. 3*d*). Further growth ($V_a << V_c$) results in the formation of an old closed type with smooth faces, less developed or undeveloped $\mathbf{x}_h$ trapezohedrons and again a higher e/v ratio (Fig. 3*e*).

The e/v ratio is characteristic of degree of the development of the particular La- or Ra-quartz. There are no sharp limits between the types mentioned, especially between those of the open type whereas the young and old closed type are easily distinguished from the others. The crystals of the old closed type are less twisted and have a tendency of k-value decrease. The reason is the growth which is not controlled by the pyroelectrical effect. This causes healing of the reentrant angles, increase in the $\mathbf{m}_d$ diameter and decrease in the twisting angle φ_a. This is especially the case with crystals that had been tectonically detached from the matrix and continued their growth in a different position. Such crystals with k-values between 1.6 and 3.0 (Fig. 3*e*) represent 7.5 % of all the studied La- and Ra-quartz crystals. It is worth mentioning and stressing that each La- or Ra-quartz represents only one crystal regardless of degree of its development. It can be concluded that the occurrence of »subindividuals« with typical reentrant angles and sutures results from the structural defects caused during crystal growth in the c-axis direction. At the last stage of growth all reentrant angles can be rehealed, which results in an almost normal quartz crystal with slightly curved faces. The smallest angle φ_a observed was 5° and the most twisted quartz had 77°. The La- and Ra-quartz found are of all aforementioned types with heights h rarely exceeding 10 cm.

Frondel (1978), Vollenweider (1986) and Vital (1972) described quartz crystals twisted around their c-axis. The twisting sense considered in this study with Lc- and Rc-quartz is the same as the one described for La- and Ra-quartz (Figs. 4*a*-4*d*). If the same mechanism is taken into account then $\varrho_c = \varrho a = k$ and the twisting angle φ_c can be expressed with the following mathematical equation:

$$\varphi_c = k\frac{l}{d} \tag{4}$$

Parameter l is the height of prism $\mathbf{m}$ and d its diameter (Figs. 4*a* and 4*d*). Measurements of the twisting angle with crystals twisted around their c-axis were made by Vollenweider (1986). He pointed out that twisting around the c-axis is a common feature of Alpine quartz crystals of the Friedlaender type. The twisting constant k calculated from his measurements is about 0.7°. Considerably twisted quartz crystals of this type are rare. One of the most twisted quartz crystal of this type (Richards, P. personal communication) has a twisting constant of about 2°. The

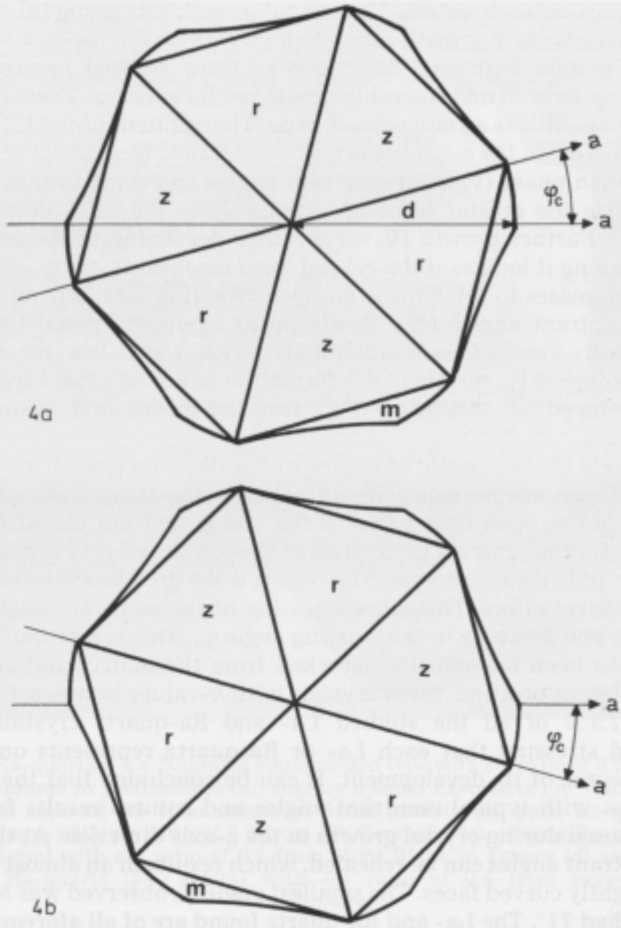
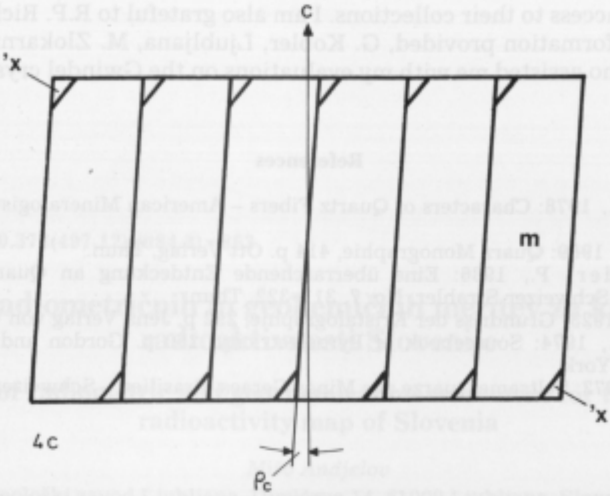
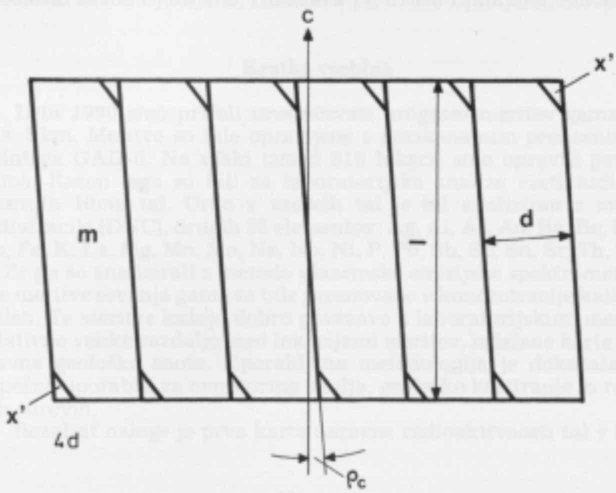


Fig. 4. Lc-quartz viewed down its c-axis with its morphological parameters (*a*), Rc-quartz (*b*) and schematically drawn prism faces of Lc- (*c*) and Rc-quartz (*d*)

reason for the lower *k*-values is a higher growth rate in the direction of the c-axis ($V_c >> V_a$) which caused the formation of an old closed type crystal. Lc- or Rc-quartz of the open type is resolved into a number of »subindividuals« around the c-axis. Crystals of this type are composed of many small crystals sprouting around the principal crystal. Their c-axes are parallel. Since $V_c >> V_a$ the sprouting »subindividuals« are relatively quickly rehealed into one crystal. The pyroelectrical growth effect is thus manifested in the slightly curved and sutured crystal faces. That is how the macromosaic structure manifested in the striae and structural misfit converging to the center of the crystal of Friedlaender type quartz crystals can be explained.





Acknowledgments

I wish to thank L. Golič for his thorough revision of the manuscript. I thank G. Niedermayr from Naturhistorisches Museum Wien, B. Moser and W. Postl from Steiermarkisches Landesmuseum (Joanneum) Graz, H. M. Hamm from Mineralogisch-Petrologisches Institut und Museum der Universität Bonn in Poppelsdorfer Schloss, R. Hollerbach from Mineralogisches Museum der Universität zu Köln, C. J. Stanley from the British Museum (Natural History) London, B. Hofmann and P. Vollenweider from Naturhistorisches Museum Bern, R. Rykart from Natur-Museum Luzern and J. Arnoth from Naturhistorisches Museum Basel for their support for this study and access to their collections. I am also grateful to R.P. Richards, Oberlin, Ohio for the information provided, G. Kobler, Ljubljana, M. Zlokarnik, Leverkusen and all those who assisted me with my evaluations on the Gwindel crystals from their collections.

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