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# The oxygen isotope fractionation behaviour of kyanite in experiment and nature

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**Abstract** The oxygen isotope fractionation between kyanite and calcium carbonate has been investigated experimentally at four temperatures in the range between 625 and 775 °C at 13 kbar. Because of low exchange rates, the isotopic reaction was enhanced by polymorphic transformation of andalusite to kyanite. With this experimental modification a close approach to equilibrium was reached in all runs. The temperature dependence of the equilibrium fractionation is described by the equation $1000 \ln \alpha_{\text{ky-cc}} = -2.62 \times 10^6/T^2$. Application of the experimental results to natural quartz-kyanite-garnet assemblages indicates the preservation of the oxygen isotope composition of kyanite acquired during its formation, reflecting its extremely low oxygen diffusivity. This refractory behaviour restricts the use of kyanite for thermometry but opens the possibility to use its O-isotope composition as an indicator for recognition of polymetamorphic rock histories and reconstruction of the prograde evolution of a metamorphic sequence.

## Introduction

The $Al_2SiO_5$ polymorphs kyanite, andalusite and sillimanite are of major importance in metamorphic petrology. However, they have not been commonly involved in oxygen isotope studies because of analytical difficulties and the lack of a reliable calibration of their isotopic fractionation behaviour. Owing to their refractory nature, $Al_2SiO_5$ polymorphs should not exhibit a marked retrograde isotopic exchange and thereby retain high-temperature information, even during slow cooling. So, these minerals are potentially ideal candidates for the reconstruction of peak metamorphic temperatures. Additionally, investigations in the fractionation behaviour of the $Al_2SiO_5$ polymorphs should be helpful in understanding the influence of crystal structure on isotope enrichment in minerals (avoiding crystal chemistry effects). In this paper, we present the first experimental calibration of the oxygen isotope fractionation between kyanite and calcite as a foundation for isotopic geothermometry involving the aluminosilicate polymorphs.

The problems of incorporation of the $Al_2SiO_5$ polymorphs in oxygen isotope investigations seem to be solved by two new analytical and experimental techniques. The laser induced fluorination of minerals enables routine oxygen isotope analysis of refractory phases that could only partially be decomposed by conventional fluorination techniques (Sharp 1995). The carbonate exchange technique developed by Clayton et al. (1989) in combination with the partial exchange method of Northrop and Clayton (1966) now allows the calibration of minerals with low oxygen exchange rates. In these experiments the minerals under investigation are mixed with a carbonate phase and are equilibrated in piston cylinder apparatus at high pressures. Previous studies (Clayton et al. 1989; Chiba et al. 1989; Fortier et al. 1994; Rosenbaum 1994; Chacko et al. 1996) give a set of oxygen isotope fractionation factors for silicates and oxides relative to calcite. These experimental data are in good agreement with various theoretical and semi-empirical models. The carbonate technique has several advantages over the classic approach of mineral-water exchange experiments which are discussed in detail by Clayton et al. (1989).

Several theoretical and semi-empirical methods for the calculation of fractionation coefficients of minerals (Kieffer 1982; Zheng 1993a, b; Hoffbauer et al. 1994; Smyth and Clayton 1988) yield results which are in general agreement with experimental and natural data. Nevertheless, an experimental determination of the $Al_2SiO_5$ fractionation behaviour is valuable because, especially in this case, the published empirical and calculated estimates of the fractionation involving the

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aluminosilicates are distinctly different (Table 1). The empirical calibration (Sharp 1995) found a common fractionation coefficient of $A_{\text{qtz-as}} = +2.25 \pm 0.2$ for all three aluminosilicates (as). The modified increment methods of Zheng (1993a) and Hoffbauer et al. (1994) postulate different values for $A_{\text{qtz-as}}$ depending on Al coordination in kyanite, andalusite and sillimanite. The fractionation coefficients in these two calibrations are similar in their relative order, but show distinct differences in absolute values. The electrostatic site potential approach (Smyth 1989) predicts fractionation coefficients that are comparable with those for kyanite and sillimanite (but not andalusite) of Hoffbauer et al. (1994) on the one hand, and with those for sillimanite and andalusite (but not kyanite) of Sharp (1995) on the other hand. As described below, our experimentally determined calibration of the oxygen isotope behaviour of kyanite most closely approximates the semi-empirical equation of Hoffbauer et al. (1994).

## Methods

### Experimental procedures

The experimental charges and methods of product analysis used in carbonate-silicate oxygen isotope exchange experiments were originally described by Clayton et al. (1989) and by Chiba et al. (1989). Our procedures followed theirs, except as noted here. The interested reader is referred to the original papers for further details.

The experiments were performed in a standard piston cylinder apparatus with the "piston-in" procedure of Johannes (1973) using NaCl-pyrophyllite assemblages and silver capsules filled with mineral mixtures containing equal amounts of oxygen for each component. The accuracy of the experimental run conditions is ±10 °C and ±0.1 kbar. Depending on the run temperature, aragonite (experiments at 625 and 675 °C) or calcite (725 and 775 °C) appears as the stable carbonate phase. Because no fractionation is observed between these two polymorphs (Clayton et al. 1975), there is no effect on the kyanite-calcium carbonate oxygen isotope fractionation.

Two different experimental methods were used in this study in order to determine equilibrium fractionations: (1) direct oxygen isotope exchange between kyanite and calcium carbonate at 13 kbar and 725 °C without any other reaction type occurring during the experiments; (2) oxygen isotope exchange between kyanite and calcium carbonate accompanied by the polymorphic andalusite–kyanite transformation at 13 kbar between 625 and 775 °C at temperature intervals of 50 °C, with andalusite as starting material.

The experimental *P*,*T* conditions were restricted by the stability relations in the system $Al_2SiO_5$-$CaCO_3$ (Fig. 1) and the necessity for significant isotope exchange in order to be able to determine reliable equilibrium fractionations. Direct oxygen isotope exchange runs between kyanite and calcite (method 1) at 725 °C and 13 kbar showed only low amounts of exchange (approximately 25%), so we combined the oxygen exchange reaction with the polymorphic andalusite–kyanite transformation to give much higher exchange yields. At temperatures higher than 575 °C complete phase transition occurs. The highest selected run temperature was 775 °C because at higher temperatures the paragenesis $Al_2SiO_5 + CaCO_3$ reacts to $CaAl_2Si_2O_8 + Al_2O_3 + CO_2$ (Berman et al. 1987).

### Starting materials

Five different calcium carbonates were employed in the exchange experiments, three of which were synthetic reagent grade powders. The fourth was a natural specimen from Ihalainen, Finland, a fifth calcium carbonate was from a carbonatite near Siilinjärvi, Finland, both with trace amounts of Mg and Fe. The isotopic compositions of the carbonates were selected in order to bracket the oxygen isotope compositions of the aluminosilicates (Table 2). The kyanite used in the direct exchange experiments was a gem quality crystal of unknown origin with 0.1 wt% each of FeO and $Cr_2O_3$. The andalusite was a specimen from Rio Jarama, Spain. The main non-stoichiometric components were FeO (0.3 wt%) and MgO (0.1

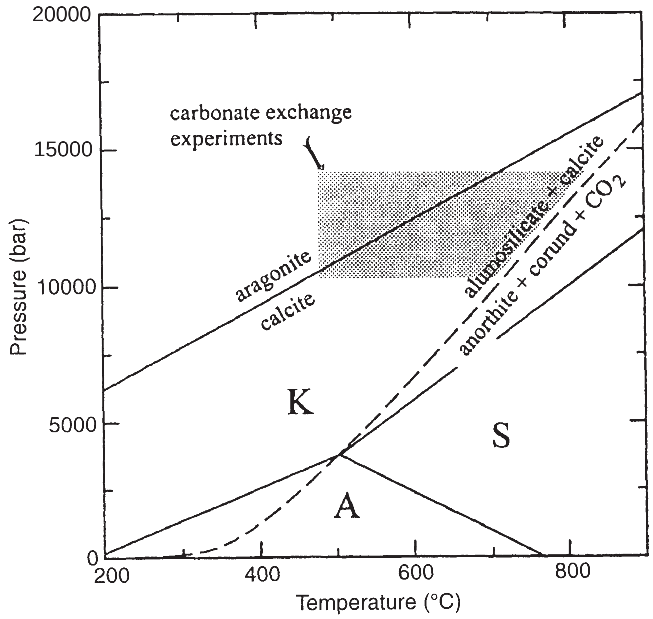


**Fig. 1** *P-T* phase diagram for the system $Al_2SiO_5$-$CaCO_3$. Run conditions in this study were restricted to those of the *shaded region.* The reaction as + cc ↔ an + co + $CO_2$ restricts the experiments to high temperature. Diminishing oxygen exchange defines the lower temperature and lower pressure limits. Experiments at pressures above 13 kbar were not possible due to technical limitations

**Table 1** Quartz-aluminosilicate fractionation coefficients ($A_{\text{qtz-min}}$) according to the equation $1000 \ln \alpha_{\text{qtz-min}} = A_{\text{qtz-min}} \times 10^6/T^2$

| | Kyanite | Andalusite | Sillimanite | Calibration method |
|---|---|---|---|---|
| Sharp (1995) | 2.25 | 2.25 | 2.25 | Empirical |
| Zheng (1993a)[a] | 1.82 | 1.63 | 1.37 | Increment method |
| Smyth (1989) | 2.79 | 2.23 | 2.29 | Electrostatic site potentials |
| Hoffbauer et al. (1994) | 2.87 | 2.63 | 2.22 | Increment method |
| This paper | 3.00 | – | – | Experimental method |

[a] $1000 \ln \alpha_{\text{qtz-min}}$ at 725 °C

**Table 2** Isotopic composition of the starting materials

| Mineral | $\delta^{18}O$[‰] | 1000 ln $\alpha_i$ (andalusite-calcite) | Andalusite-calcite mix |
|---|---|---|---|
| Kyanite | +12.71 | | |
| Andalusite | +11.18 | | |
| Calcite Merck I | +10.88 | +0.30 | A |
| Calcite Merck II | +18.30 | −7.02 | C |
| Calcite Merck III | +14.59 | −3.37 | D |
| Calcite Ihalainen | +20.42 | −9.10 | B |
| Calcite Siilinjärvi | +8.33 | +2.82 | E |

wt%). In each of the natural minerals employed, the sum of all other non-stoichiometric components was less than 0.1 wt%.

The natural specimens were ground in an agate mortar under acetone. The powders were suspended in acetone and decanted after two minutes. Only the mineral content in the suspension was used for the experiments. Calcite and aluminosilicate were weighed in proportions such that the atomic ratio of oxygen was unity, and ground again together under acetone to attain homogenization.

### Isotopic analysis and data evaluation

Oxygen isotope analyses of the minerals were done using standard techniques: reaction of calcium carbonate with phosphoric acid treatment at 25 °C (McCrea 1950) and aluminosilicate oxygen extraction in nickel autoclaves using purified fluorine (Asprey 1976) followed by $O_2$-$CO_2$ conversion via combustion of a heated graphite rod (Taylor and Epstein 1962). Since it is known that kyanite is refractory to fluorination, the reaction temperature was raised to 700 °C for 15 hours and increased for another 50 °C for 1 hour. With this procedure we achieved a decomposition rate of 75%. Nevertheless, 100% extraction of oxygen is evidently not necessary for a reliable isotopic characterisation of refractory phases (Kyser 1986). Laser fluorination analysis of the aluminosilicate run products were not possible in the earlier, experimental stage of this study, because the laser-fluorination system was not installed. In the later stage of the investigation a laser line was used for the analysis of natural samples. However, comparison of results by laser fluorination of aluminosilicate grains and conventional fluorination of powders in autoclaves showed no significant difference in $\delta^{18}O$ values, in spite of the previously mentioned low reaction yields by conventional fluorination (Table 4). The isotopic compositions of the $CO_2$-samples were measured with a VG-ISOGAS PRISM mass spectrometer.

The isotope analysis of the experimental reaction products was done stepwise. After decomposition of the carbonate the residual aluminosilicate was carefully rinsed with distilled water and then reacted by the fluorine technique. The advantage of analysing both reaction products over determination of only the carbonate and calculation of the silicate via mass balance is in avoiding mistakes due to mineral decomposition or leaky capsules.

The equilibrium oxygen isotope fractionations between kyanite and calcium carbonate were determined by the partial exchange method of Northrop and Clayton (1966). It was assumed that at identical experimental conditions, the same exchange yields are achieved in a set of experiments with isotopically different starting materials. On this assumption it is possible to estimate the equilibrium fractionation $1000 \ln \alpha_e$ by extrapolation. Plotting the initial fractionation $1000 \ln \alpha_i$ against the experimental shift 1000 ($\ln \alpha_f - \ln \alpha_i$), the data points should fit on a straight line. The intercept of this straight line with the y-axis represents the equilibrium fractionation. The inverse slope of the straight line gives the amount of exchange in percent. This evaluation method was developed for so-called "true exchange reactions", i.e. runs involving isotopic exchange only and no other kind of reaction (O'Neil 1986). Nevertheless, it was applied in this study to the kyanite-calcium carbonate calibration, because involving the intracrystalline andalusite–kyanite transformation was viewed as only a slight deviation from the Northrop/Clayton method.

## Results and discussion

### Direct exchange experiments

The first attempt to determine the oxygen isotope fractionation between kyanite and calcite by direct exchange (method 1) at 725 °C resulted in small exchange yields of about 15% (Table 3). The exchange yield seems to have been independent of the experimental run duration. This indicates surface reactions or partial recrystallisation as the exchange mechanism. In contrast, volume diffusion was apparently negligible. Although the initial fractionation changed in the direction of expected equilibrium such low reaction rates preclude reliable determination of the equilibrium fractionation and we abandoned this experimental approach.

### Experiments coupled with andalusite–kyanite phase transition

Since an increase of the isotope exchange rate during a polymorphic phase transition can be expected, we chose andalusite as starting material since it would transform to kyanite at the experimental conditions. The use of polymorphic phase transitions to accelerate isotopic exchange has been previously employed by others. The calcite-water fractionation was studied by Clayton (1959) using the aragonite–calcite transition and the quartz-water fractionation was investigated by Matsuhisa et al. (1979) via the cristobalite–quartz transition. In our case, the extent of reaction achieved between kyanite and calcite (Table 3, Fig. 2) was virtually complete. In the case of $SiO_2$-$CaCO_3$ exchange experiments, Clayton et al. (1989) found a small (0.1–0.2‰) shift to larger fractionations if metastable cristobalite was used instead of quartz. It is possible therefore, that our ky-cc fractionation factor is also a little too large in relation to the true equilibrium fractionation. If this kinetic shift is indeed in the same order as reported by Clayton et al. (1989), our experiments would strongly support the calculation of Hoffbauer et al. (1994).

The oxygen isotope composition of the kyanite run products was determined both by direct measurement and by mass balance calculation. The maximum discrepancy between the two values is 0.2‰, and provides

**Table 3** Results of the direct kyanite-calcium carbonate exchange experiments (PDC) and experiments with coupled andalusite-kyanite transformation. Results marked with * have not been used for the calculation of $1000 \ln \alpha_e$

| Experiment # | Mix # | $t$ [h] | $T$ [°C] | $1000 \ln \alpha_i$ | $\delta^{18}O_{f\text{-calcite}}$ [‰] | $\delta^{18}O_{f\text{-kyanite}}$ [‰] | $1000 \ln \alpha_f$ | $1000 \ln \alpha_e$ | Exchange [%] |
|---|---|---|---|---|---|---|---|---|---|
| PDC 01 | | 24 | 725 | +1.81 | +11.19 | +12.40 | +1.20 | | 15 |
| PDC 02 | | 72 | | | +10.86 | +12.73 | +1.85 | | |
| PDC 03 | | 144 | | | +11.28 | +12.31 | +1.02 | | |
| PDC 04 | | 336 | | | +11.24 | +12.35 | +1.10 | | |
| PAC-02 | A | 72 | 625 | +0.30 | +13.80 | +10.43 | −3.33 | −3.12 | 94 |
| PAC-22 | C | | | −7.02 | +16.20 | +13.28 | −2.88 | | |
| PAC-32 | D | | | −3.37 | +14.46 | +11.31 | −3.11 | | |
| PAC-12 | B | | | −9.10 | +18.02 | +13.58 | −4.37* | | |
| PAC-03 | A | 72 | 675 | +0.30 | +11.83 | +10.24 | −1.59* | −3.16 | 106 |
| PAC-23 | C | | | −7.02 | +16.45 | +13.03 | −3.37 | | |
| PAC-33 | D | | | −3.37 | +14.49 | +11.28 | −3.17 | | |
| PAC-13 | B | | | −9.10 | +17.74 | +13.86 | −3.82* | | |
| PAC-04 | A | 72 | 725 | +0.30 | +12.41 | +9.76 | −2.62 | −2.60 | 98 |
| PAC-24 | C | | | −7.02 | +15.99 | +13.49 | −2.46 | | |
| PAC-34 | D | | | −3.37 | +14.24 | +11.53 | −2.68 | | |
| PAC-14 | B | | | −9.10 | +17.15 | +14.52 | −2.59* | | |
| PAC-44 | E | | | +2.82 | +10.96 | +8.55 | −2.39* | | |
| PAC-05 | A | 72 | 775 | +0.30 | +12.57 | +10.01 | −2.53 | −2.30 | 100 |
| PAC-25 | C | | | −7.02 | +16.10 | +13.38 | −2.68 | | |
| PAC-35 | D | | | −3.37 | +13.73 | +12.04 | −1.67 | | |
| PAC-15 | B | | | −9.10 | +14.27 | +14.27 | −2.99* | | |

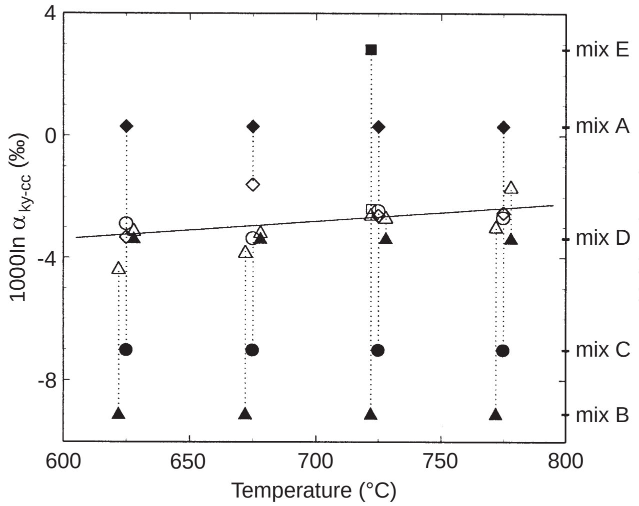


**Fig. 2** Results of the kyanite-calcium carbonate exchange experiments with coupled andalusite-kyanite transformation. *Dark symbols* represent initial fractionations, *open symbols* final fractionations. Data points are slightly distorted on temperature scale for clarity. The *solid line* is the calculated fit to the experimental data

proof that the isotopic exchange took place in a closed system in each run.

The $\delta^{13}C$ values of the carbonate phase changed by only a few tenths of permil. Larger alteration would indicate a significant decomposition of the carbonate which can complicate the interpretation of the data (Fortier et al. 1994). Admittedly a slight reduction of the carbonate in each run apparently did occur as indicated by a grey colouring of the reaction products, presumably by precipitated graphite. The shade of grey, and thereby the graphite content increased with temperature and was intensified at the capsule rims. Clayton et al. (1989) assumed small amounts of organic matter derived from acetone used in the milling process as possible source of carbon. This can be excluded as the only origin because in this case there would be no temperature dependence in the graphite amount. The higher amount of graphite at the capsule rims indicates that the carbon producing process was influenced from parameters outside the capsule. Goldsmith (1994) supposed that the infiltration of hydrogen through the walls of the silver capsule in the course of the experiments caused the reduction of $CO_2$ in the capsule. Hydrogen is generated at the graphite heating rod from absorbed water in the salt pressure medium.

The use of natural and synthetic starting materials can result in different exchange yields (R.N. Clayton, personal communication). This may be the explanation for apparent discrepancies in the results of exchange experiments at 625 and 675 °C with natural calcite (mix B, Fig. 2). This is comparable at all temperatures but the discrepancy gets smaller with increasing temperature. Although the influence to the resulting data is not very large, the equilibrium fractionation is determined from the experiments with synthetic calcites only (Fig. 3).

The experimental results given in Table 3 reveal that all runs closely approached equilibrium. The partial exchange method was used to calculate the equilibrium fractionations. The estimated extent of exchange deduced from the slope of the fitted line in the Northrop/Clayton – diagram varied from 94 to 106%. The overstep at 675 °C may be due to the fact that the slope of

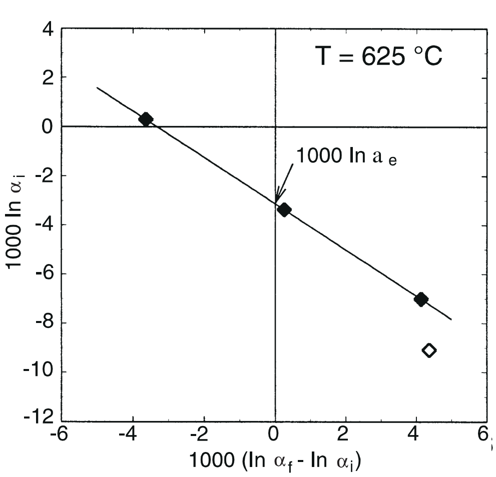


**Fig. 3** Northrop and Clayton plot for kyanite-calcium carbonate exchange experiments performed at 625 °C using synthetic carbonate (rhomb); the *open symbol* stands for natural carbonate

the regression line is defined by two points only in this experimental set. In Fig. 4 the 1000 ln $\alpha_e$ values are plotted versus $10^6/T^2$, the commonly accepted linear relationship between oxygen isotope fractionation and high temperature. The results are described by the equation:

$$1000 \ln \alpha_{\text{cc-ky}} = 2.62 \pm 0.2 \times 10^6/T^2 \qquad (1)$$

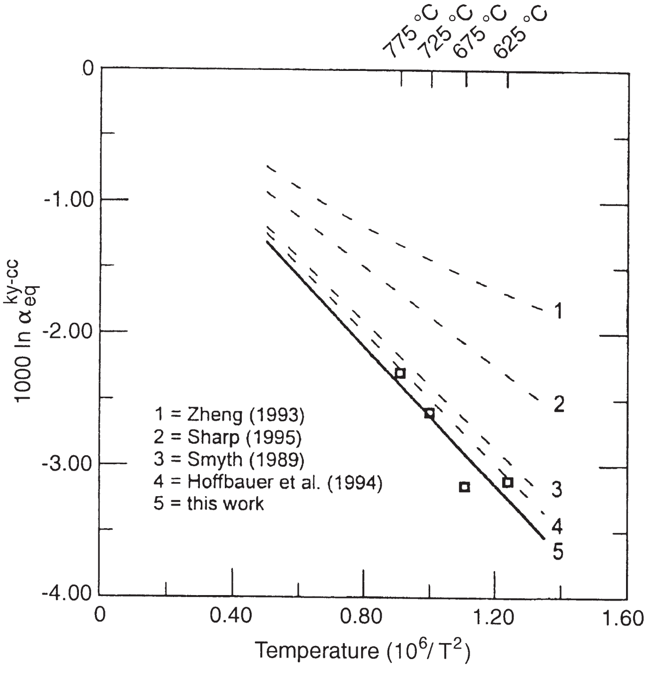


**Fig. 4** Plot of the temperature dependence of the oxygen isotope fractionation (1000 ln α) between kyanite and calcium carbonate. Data are given in Table 3, only results for runs with synthetic $CaCO_3$ are taken into account. *Curves labeled 1 to 4* represent the results of various published calibrations

Combined with the experimental quartz-calcite calibration (Clayton et al. 1989), we obtain from Eq. (1) the geologically more important quartz-kyanite fractionation:

$$1000 \ln \alpha_{\text{qtz-ky}} = 3.00 \pm 0.2 \times 10^6/T^2 \qquad (2)$$

This value of the quartz-kyanite fractionation coefficient ($A_{\text{qtz-ky}}$) is distinctly greater than the semi-empirical and empirical values published by Zheng (1993a) and Sharp (1995) (Table 1; Fig. 4), but is in agreement with the values calculated by Hoffbauer et al. (1994) and Smyth (1989) taking the statistical error into account. A rigorous treatment of the error is very problematic because of experimental and analytical uncertainties. Whereas the analytical error of the calcite isotope analysis will be in the order of ±0.05 to 0.1‰, the experimental error will depend on many factors and is difficult to estimate. An integral error could best be estimated from Fig. 2, where the deviation of the individual runs from the calculated equilibrium fractionation can be seen. We therefore estimate the uncertainty of the fractionation coefficients given above with ±0.2.

The fractionation coefficient for quartz-sillimanite (see Table 1) deduced by Sharp (1995) from natural paragenesis is in agreement with the coefficients of Hoffbauer et al. (1994) and Smyth (1989). A quartz-sillimanite fractionation coefficient of about +2.3, in contrast to the reported $A_{\text{qtz-ky}}$ value of 3.0, indicates that not only the chemical composition, but also the lattice configuration is indeed critical for the fractionation behaviour of oxygen isotopes in minerals.

## Fractionation behaviour of kyanite in nature

We have evaluated the degree of equilibrium attained in quartz-kyanite-garnet assemblages with known formation temperatures on the basis of new and previously published stable isotope data (see Table 4). In Fig. 5, the Δ qtz-ky fractionations are plotted against Δ qtz-gar for rocks grouped according to petrologically deduced temperatures. Even though there are some cases of obvious isotopic disequilibria (open symbols), the main impression regarding quartz-garnet fractionations is that of broad coincidence with petrological temperature estimations. The spread in natural quartz-kyanite fractionations shows a fan-shaped distribution which covers the field of existing calibrations, limited by small fractionations by Zheng‘s (1993b) increment method and the large fractionations by the experimental calibrations of Lichtenstein and Hoernes (1992) (quartz-garnet) and this work. Clearly, the empirical quartz-kyanite curve of Sharp (1995) must plot more or less in the centre, since it uses quartz-garnet fractionations as a basis, illustrating the problematics of using natural mineral-kyanite fractionations for temperature estimations, but also, the dependence of the equilibrium-disequilibrium consideration on calibration. The disequilibria may be caused by

**Table 4** Published stable isotope data of quartz-kyanite-garnet assemblages and quartz-aluminosilicate nodules. Numbers with * are laser-fluorination data. (references: [*1*] Sharp et al. 1992, [*2*] Sharp et al. 1993, [*3*] Zheng et al. 1996, [*4*] B. Hagen unpublished, [*5*] Hoernes and Hoffer 1979, [*6*] Hoernes and Friedrichsen 1980, [*7*] Sharp 1995, [*8*] Miller 1990, [*9*] Miller 1974, [*10*] Purtscheller 1969, [*11*] own analyses, [*12*] Todd and Engi 1997)

| | Reference | Petrological temperature [°C] | $\delta^{18}O$ quartz [‰] | $\delta^{18}O$ kyanite [‰] | $\delta^{18}O$ garnet [‰] | Isotopic temperature | |
|---|---|---|---|---|---|---|---|
| | | | | | | Qtz-ky [°C] | Qtz-gar [°C] |
| Grospydite | [1] | 1200 | 8.62 | 7.98 | 7.53 | 1890 | 1450 |
| Whiteschist PM1 | [2] | 725 | 8.54 | 6.08 | 5.57 | 830 | 770 |
| Whiteschist GM1 | [2] | 725 | 8.20 | 6.12 | 5.51 | 930 | 820 |
| Eclogite Dabie Shan | [3] | 770 | −6.8 | −8.5 | −9.8 | 1060 | 760 |
| Felsic granulite 359/68b | [4; 11] | 900 | 11.29<br>11.22* | 9.99<br>9.86* | 8.77<br>8.59* | 1250 | 860 |
| Felsic granulite 359/68c | [4; 11] | 900 | 10.71 | 8.15 | 8.50<br>8.42* | 810 | 930 |
| Felsic granulite 359/161 | [4; 11] | 900 | 12.01 | 9.85<br>9.89* | 9.17<br>9.28* | 910 | 790 |
| Pelitic schist B184 | [5] | 600 | 14.0 | 10.9 | 9.5 | 710 | 570 |
| Metapelite TS76/70C | [6; 12] | 650 | 19.9 | 17.8 | 17.0 | 920 | 780 |
| Metapelite TS76/71 | [6; 12] | 650 | 10.6 | 8.0 | 6.1 | 800 | 570 |
| Metapelite TS76/71Y | [6; 12] | 650 | 10.35 | 4.7 | 6.0 | 460 | 590 |
| Metapelite TS76/71A | [6; 12] | 650 | 10.45 | 7.15 | 5.55 | 680 | 540 |
| Metapelite TS76/3 | [6; 12] | 600 | 14.0 | 10.15 | 10.15 | 610 | 640 |
| Bünderschiefer TS76/14 | [6; 12] | 625 | 23.05 | 18.5 | 18.6 | 540 | 580 |
| Bündnerschiefer TSF12 | [6; 12] | 575 | 18.55 | 15.5 | 14.6 | 720 | 630 |
| Antigorio | [7] | 550 | 13.19 | 9.78 | 8.51 | 670 | 560 |
| Dabie Mountains | [7] | 700–840 | 5.17 | 3.99 | 3.30 | 1320 | 1030 |
| SQ92-3 | [7] | 700 | −7.29 | −9.06 | −10.25 | 1030 | 770 |
| 1871 | [7] | < 700 | 12.33 | 9.87 | 8.40 | 830 | 630 |
| Camperio | [7] | > 550 | 19.86 | 16.73 | 15.95 | 710 | 630 |
| Mas30a | [7] | ≈500 | 11.87 | 10.38 | 10.05 | 1150 | 1060 |
| Eclogite SK | [11; 8] | 600 | 7.52* | 5.23* | 4.71* | 870 | 800 |
| Eclogite SKP | [11; 8] | 600 | 9.69* | 6.04* | 6.04* | 630 | 670 |
| Nodule T253 | [11; 9] | < 550 | 13.92 | 12.36 | | 1110 | |
| Nodule T518 | [11; 9] | < 550 | 11.95 | 9.42 | | 820 | |
| Nodule T528 | [11; 9] | < 550 | 12.70 | 13.14 | | – | |
| Nodule T606 | [11; 9] | < 550 | 15.30 | 12.41 | | 750 | |
| Nodule Ö6 | [11; 10] | ≈650 | 13.81 | 13.13 | | 1830 | |
| Nodule Ö95 | [11; 10] | ≈650 | 12.87 | 10.22 | | 790 | |
| Nodule Ö7 | [11; 10] | ≈650 | 12.82 | ky 9.53<br>and 9.81 | | 680<br>660 | |

the restricted volume diffusion of oxygen in kyanite, as already recognised in the exchange experiments.

Calculation of oxygen diffusion in kyanite according to the method of Fortier and Giletti (1989) confirms the extremely refractory behaviour of kyanite with regard to O-isotope exchange (Fig. 6). In comparison, garnet, known to represent a refractory phase as well, has a calculated diffusion rate two orders of magnitude higher. The low oxygen diffusion rate leads us to conclude that kyanite has a very high closure temperature with respect to oxygen exchange (Dodson 1973). So kyanite preserves its isotopic composition acquired during crystallization as long as the lattice is not forced to exchange (e.g. by strain-induced recrystallization).

From petrological work it is known that kyanite forms over a wide range of physical conditions and through many different mineral reactions. Therefore, information of the kyanite-formation event and the metamorphic evolution of the rock is essential for the interpretation of isotopic data. It is also well known that $Al_2SiO_5$ phases may persist metastably within the stability fields of the other polymorphs during prograde or retrograde metamorphism. One example, given for comparison in Table 4 (sample Mas 30a), is cited by Sharp (1995). From the polymetamorphic Ötztal-Stubai Alps (Austria) Purtscheller (1969) described the distribution of $Al_2SiO_5$ polymorphs in metapelitic gneisses and intercalated quartz-aluminosilicate nodules. Within the nodules, kyanite pseudomorphs after andalusite can be observed, sometimes the polymorphic transition is incomplete within one crystal. This clearly demonstrates disequilibrium among these phases.

Recently, Ghent and Valley (1998) published O-isotope data from coexisting quartz-kyanite samples from British Columbia. Applying different calibrations including Zheng (1993b) and Hoffbauer et al. (1994) they concluded that the empirical calibration of Sharp (1995) closest coincided with petrological estimates of the parageneses investigated. However, excluding the quartz-aluminosilicate nodules which will be addressed later, we note that the metamorphic temperatures as deduced by cation thermometry of three of their ten rock samples

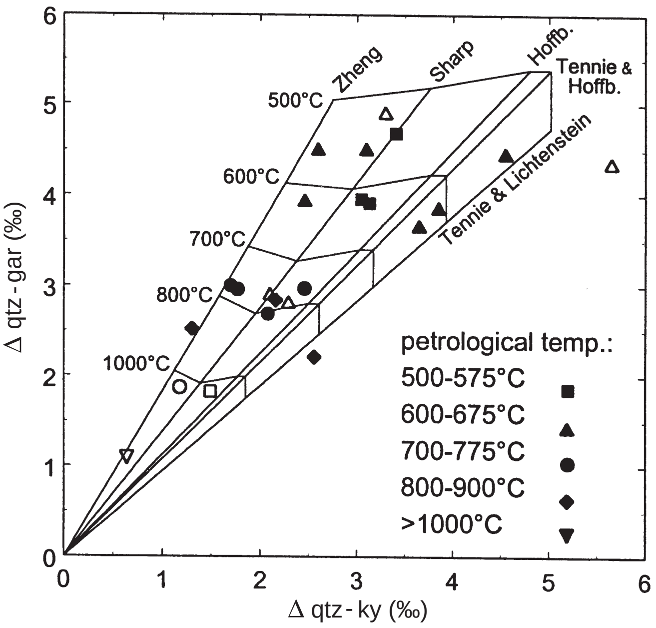


**Fig. 5** Plot of the qtz-gar fractionation versus. Δ qtz-ky with the different calibrations: Zheng (1993b); Sharp (1995); Hoffbauer et al. (1994); this study combined with Hoffbauer et al. (1994) and this study combined with Lichtenstein and Hoernes (1992). *Open symbols* represent samples far outside isotopic equilibrium. *Closed symbols*: statement on the degree of equilibrium depends on which calibration is used. As discussed in the text, in most natural examples kyanite is not in equilibrium with the other phases due to it's extremely refractory nature

(DR-194, DR 219, SM-76-1) are better mirrored by the fractionation data of Hoffbauer et al. (1994) than by their preferred calibration. In two other sillimanite-bearing samples (3–8, 3–10), both calibrations (Hoffbauer et al. 1994; Sharp 1995) give within the limits of error identical temperatures.

Even though bimineralic associations as frequently given in quartz segregations within Al-rich metasediments might represent ideal candidates for oxygen isotope thermometry as stated by Ghent and Valley (1998) because one of the phases closes to isotopic exchange at high temperatures (Eiler et al. 1993), quartz-kyanite nodules may not be well suited for O-isotope thermometry. As noted earlier by structural geologists, quartz segregations in rocks of pelitic composition normally form early, parallel to the first cleavage. During prograde deformation, they become folded, sometimes refolded, where fold hinges may become disrupted from their limbs and finally form more or less spherical or elongated nodules (Voll 1960; Nabholz and Voll 1963; Slater et al. 1994). During prograde metamorphism they might become mineralized where the growing phases are controlled by the type of mineral reactions occurring in the country rock. Quartz segregations have also been interpreted as representing the preferred sites of fluid expulsion from the rocks, forming thus more or less open systems. Compatible with this observation, Hoernes and Hoffer (1985) noted that nodule quartzes in metapelites of the Damara Orogen are usually depleted in $^{18}$O in comparison to quartz of their country rocks. For these reasons it may be questionable that quartz-kyanite parageneses of nodules represent isotopic equilibria. To test this assumption, we analysed several quartz-kyanite and also one quartz-kyanite-andalusite-bearing nodules from different locations within the Eastern Alps (Austria). The isotopic and petrographic data are summarized in Table 4. With one exception, the temperatures calculated from quartz-kyanite fractionations are much too high compared with petrological temperature estimations, confirming thus the presumed state of isotopic disequilibrium. Interestingly, the only exception where quartz-kyanite and quartz-andalusite fractionations yield petrologically reasonable temperatures results from a typical non-equilibrium paragenesis (kyanite replacing andalusite) and might be accidental. From the five nodules reported by Ghent and Valley (1998), our calibration and that of Hoffbauer et al. (1994) indicate much too high temperatures. However, also applying Sharp's (1995) calibration, three of these samples yield temperatures far outside the accepted range. This is clearly an indication for the state of isotopic disequilibrium, given in nodules of this type.

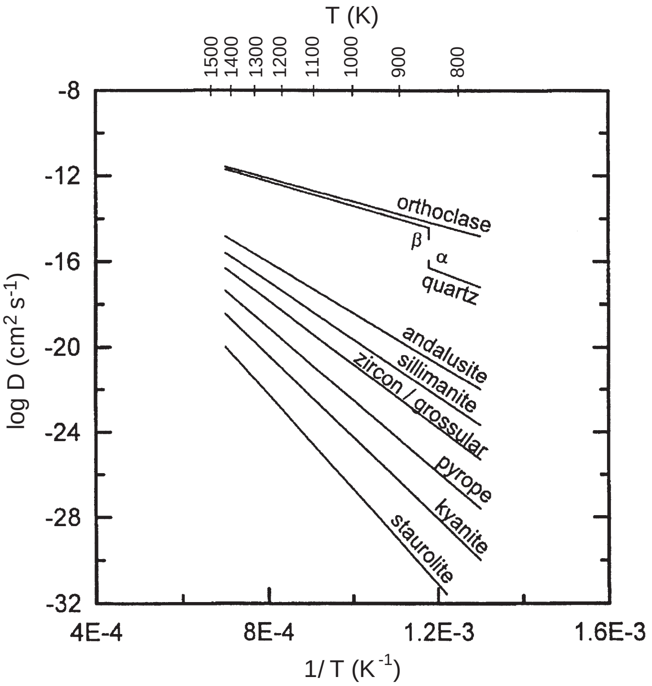


**Fig. 6** Plot of the diffusion coefficients of several minerals as a function of temperature (Fortier and Giletti 1989)

Hoernes and Friedrichsen (1980) analysed a set of kyanite-bearing samples from the Swiss Central Alps. The rock units there are dominated by polymetamorphic (Variscan) ortho- and paragneisses and Mesozoic rocks overprinted during Alpine metamorphism. Among other characteristics, the different metamorphic histories of the Variscan and Mesozoic rocks are reflected in the measured mineral $^{18}$O-fractionations (Fig. 7). In the

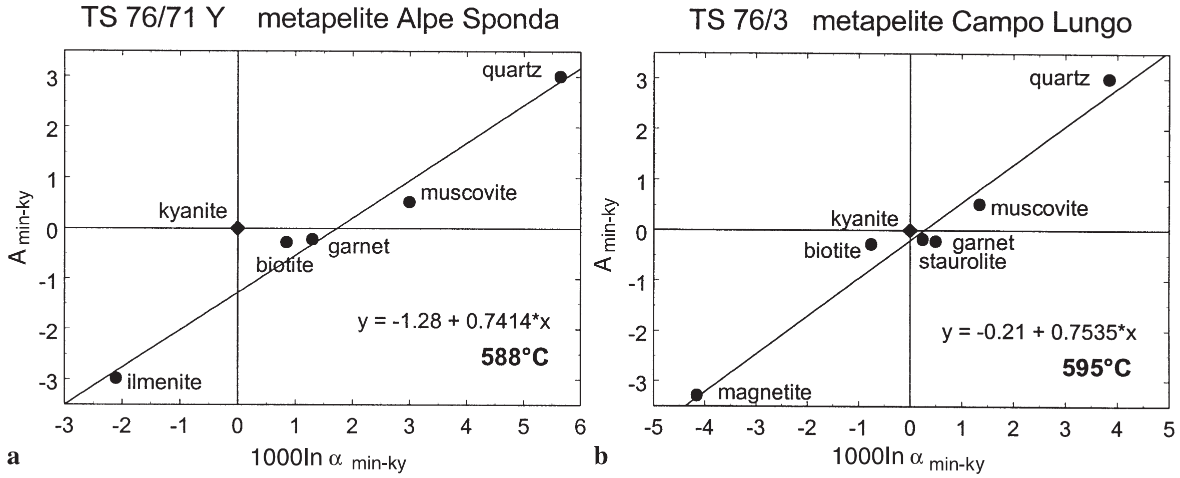
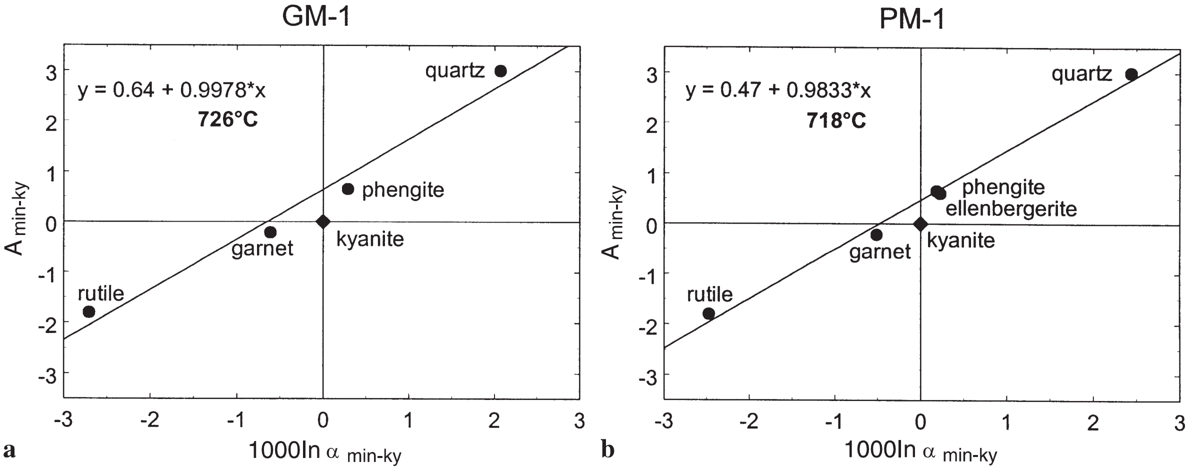


**Fig. 7a,b** Comparison of the observed mineral-kyanite fractionations in polymetamorphic (TS 76/71 Y) (**a**) and monometamorphic (TS 76/3) (**b**) rocks from the Lepontin Alps, Switzerland. In the rock with the polymetamorphic history (**a**) kyanite is out of isotopic equilibrium, but it is part of the equilibrium assemblage in the mono-metamorphosed rock (**b**), where the regression line passes through the origin (in contrast to the polymetamorphic example)

polymetamorphic paragneisses kyanite is in disequilibrium with the other minerals in the rock. In these rocks incomplete re-equilibration occurred during Alpine metamorphism. As an example, a metapelite sample from Alpe Sponda (Ticino, Switzerland), famous for its kyanite-staurolite occurrence, is discussed in some detail: The kyanite, formed most likely during an earlier (Variscan?) event, retained its isotopic composition of formation due to its extremely refractory behaviour. In a diagram in which the fractionations are normalised to kyanite, minerals not in isotopic equilibrium with kyanite may be arranged along a linear array which will not pass through the origin (Fig. 7a). The slope of the best fit (excluding kyanite) permits the calculation of an average isotopic temperature of 588 °C which is not in agreement with petrological calculations of Todd and Engi (1997) for late Alpine metamorphic conditions for this locality (around 650 °C). In contrast, kyanite is close to isotopic equilibrium with the other mineral phases in a sample from Campo Lungo, representing a rock which suffered only Alpine metamorphism (Fig. 7b), and the best fit straight line, again excluding kyanite, approaches closely the origin, demonstrating that kyanite belongs isotopically to the paragenesis and might be included in the calculation of the slope. In this case, the average isotopic temperature of 595 °C is in perfect agreement with Todd and Engi (1997).

The preservation of the isotopic composition of kyanite can also be demonstrated from data on the "whiteshists" of the Dora Maira Massif in the Italian Western Alps analysed by Sharp et al. (1993). These rocks have been intensively investigated during the last decade (e.g. Chopin 1984; Schertl et al. 1991), so the metamorphic evolution is well known. Using the experimentally determined fractionation coefficient of kyanite, a clear isotopic disequilibrium exists for all

**Fig. 8a, b** Mineral-kyanite fractionations (Sharp et al. 1993) of whiteshists of the Dora Maira Massif in the Italian Western Alps plotted against mineral-kyanite fractionation coefficients (this study combined with Hoffbauer et al. 1994, and for rutile with Agrinier and Javoy, 1987). Results show kyanite in disequilibrium with the other minerals in the rock. For explanation see text



phases relative to kyanite. This is graphically demonstrated plotting again the kyanite-normalized fractionations against the mineral-kyanite fractionation coefficient (Fig. 8a, b). Again, the isotopic disequilibrium pattern can best be explained assuming a constant isotopic value of kyanite after its formation at about 560 °C during the following prograde metamorphism up to temperatures of 725 °C. The prograde *PT*-path can be described schematically by the three reactions (Schertl et al. 1991):

At 560 °C/16 kbar chlorite + quartz = talc + kyanite (3)

At 700 °C/28 kbar chlorite + kyanite + talc = pyrope + $H_2O$ (4)

At 725 °C/28 kbar talc + kyanite = pyrope + coesite + $H_2O$ (5)

From this it is obvious that kyanite formed at 560 °C and served in the following stages only as a reactant. However, the temperature calculated from the slope of the best fit to the fractionations (again excluding kyanite) is in agreement with the 720 °C estimated by Sharp et al. (1993). Postulating isotopic equilibrium among all phases, sample PM-1 has been included in the data set to calibrate empirically the kyanite fractionation factor (Sharp 1995). Taking into account the metamorphic evolution of these rocks, our conclusion concerning the isotopic disequilibrium of kyanite seems justified.

## Concluding remarks

Kyanite-calcite direct exchange experiments showed that the calibration of the fractionation behaviour of oxygen isotopes is hampered by the low diffusivity of oxygen in kyanite. By combining oxygen isotopic exchange with the andalusite–kyanite transformation, we were able to determine equilibrium fractionations. From these experimental results, a fractionation coefficient of $A_{\text{ky-cc}} = -2.62 \pm 0.2$ follows. When combined with the experimentally determined quartz-calcite fractionation coefficient of Clayton et al. (1989), we find the geologically relevant quartz-kyanite value, $A_{\text{qtz-ky}} = +3.00 \pm 0.2$.

A critical assessment of the oxygen isotope compositions of minerals in kyanite-bearing rocks demonstrates that kyanite is not very suitable for thermometric investigations. However, kyanite can be used to distinguish mono- from polymetamorphic rock histories. Even during subsequent metamorphic events at very high temperatures kyanite is extremely resistant towards isotopic changes.

The refractory nature of kyanite offers thus the possibility to characterise the polymetamorphic history of a rock. Kyanite may also represent a tool to prove, whether or not the system was isotopically reset with respect to oxygen during metamorphic evolution. A similar conclusion has been drawn by Valley et al. (1994) based on isotopic and diffusion data for zircon which appears to be even less refractory than kyanite.

Finally we have presented evidence for the problematic use of natural parageneses to empirically calibrate the O-isotope fractionation of kyanite.

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