

# Metamorphic differentiation; a mechanism indicated by zoned kyanite crystals in some rocks from the Lukmanier region, Switzerland

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**ABSTRACT.** Two samples of garnet-kyanite-staurolite schist from Lukmanier, Switzerland, each contain two chemical varieties of kyanite which occur in texturally distinct areas of the rock. Type 1 form large idiomorphic crystals within an open crenulation cleavage  $S_3$ . They exhibit a systematic zonation of  $Fe_2O_3$ , with core values of 0.8% decreasing to 0.3% at the crystal margin. Type 2 form small, much less abundant crystals in areas between  $S_3$  cleavage zones, and have a homogeneous distribution of 0.3%  $Fe_2O_3$  throughout the crystal.

It is suggested that the first-nucleated crystals contain the highest core concentration of  $Fe_2O_3$  and are the largest. A positive correlation between core  $Fe_2O_3$  values and crystal size is interpreted as a nucleation and growth sequence. This indicates that the first crystals formed preferentially in  $S_3$  (Type 1), with Type 2 crystals growing later outside the  $S_3$  zones.

Concentration of kyanite in  $S_3$  zones produces a distinct mineral banding in the rock. A mechanism for the development of metamorphic differentiation by preferred nucleation of kyanite in  $S_3$  is proposed.

**KEYWORDS:** metamorphic differentiation, kyanite, schist, Lukmanier region, Switzerland.

THE term 'metamorphic differentiation' was first used by Stillwell (1918), but the first detailed description was given by Turner (1941) when he described compositionally layered schists formed from originally massive, unbedded greywackes from Otago.

Explanations for metamorphic differentiation presented in the literature are mainly based on models involving the passive concentration of more dense, less soluble mineral phases by the solution and selective removal of more soluble phases. This occurs in response to metamorphic processes, closely associated with shearing stress during deformation (Sander, 1930; Eskola, 1932; Ramberg, 1952; Bennington, 1965; Talbot and Hobbs, 1968; Spry, 1969; Gray, 1977).

Layering found in mylonites was considered by Schmidt (1932) to be the result of different mechanical behaviour of various minerals. Amphibole and

mica, being more ductile, adjust by gliding and recrystallization and are smeared out into intensely sheared layers. More brittle minerals, such as feldspar and quartz, are rotated and segregate into layers between the shears.

Ghaly (1969) described some Lewisian rocks from NW Scotland which showed a gradation from hornblende-feldspar schist to striped and banded schist and gneisses, through to hornblende and felsic lenses and pods. He proposed that they had been formed by a process of metamorphic differentiation involving solution, recrystallization, and mechanical differentiation acting simultaneously or separately. Deformation was an essential prerequisite for its operation.

Talbot and Hobbs (1968) and Gray (1977) described differentiation associated with discrete crenulation cleavages. Gray produced analytical data which showed that all the cleavage zones studied had a consistent decrease in  $SiO_2$ , and increases in  $Al_2O_3$  and  $K_2O$  with respect to the host rock. He concluded that the differentiated nature, microfabrics, and microtextural relations of discrete crenulation cleavages suggested that they were 'solution planes'. Characteristically there was a passive concentration of relatively insoluble materials such as mica, chlorite, etc. due to the solution and removal of quartz along the cleavages.

The aim of the present study is to show that kyanite may have nucleated and grown preferentially in  $S_3$  cleavage zones, and that neither selective solution or mechanical processes as described above can account for this. This interpretation is based on petrographic evidence and analytical data for kyanite.

*Sample location.* The location of the Lukmanier Pass is shown in fig. 1. The samples were taken from the Stgir Formation near Camperio in zone 4 (Fox, 1975), corresponding to the metapelitic assemblage biotite-staurolite-garnet-chlorite-kyanite.

*Petrography.* The petrography of the Lukmanier

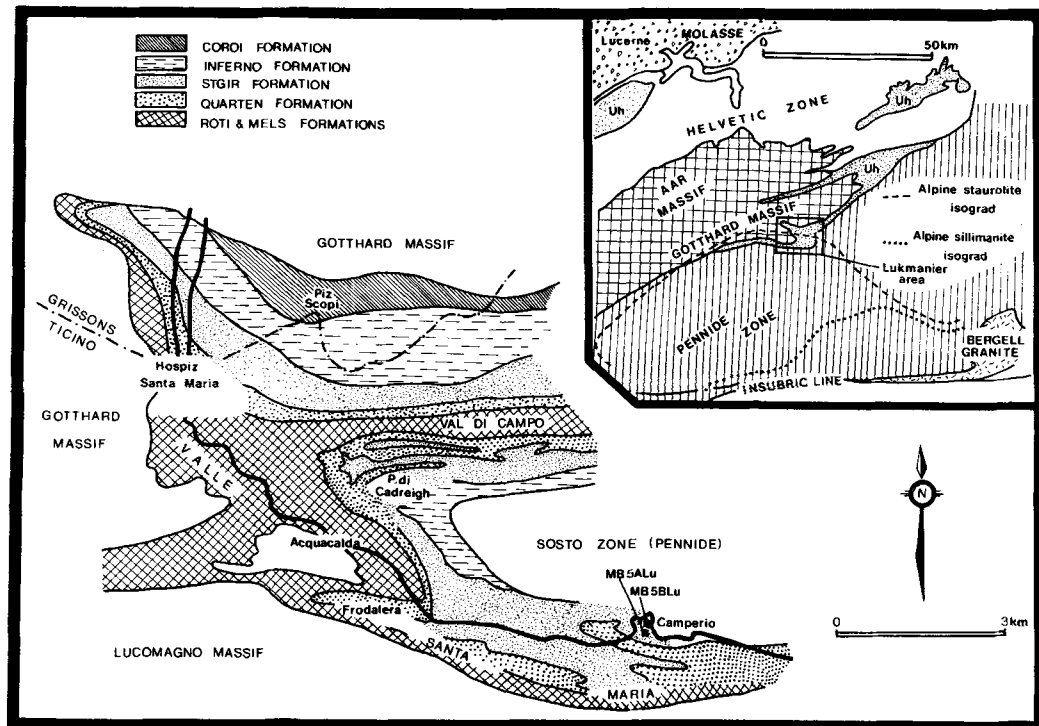


FIG. 1. The geology and location of the present samples in the Lukmanier Pass Area, Switzerland (after Chadwick, 1968). The relationships between the geology and alpine tectonic zones is shown, and Niggli's (1970) isograd boundaries are marked.

area has been documented by a number of workers (Niggli, 1929; Chadwick, 1968; Frey, 1969; Fox, 1975). The Mesozoic Ultrahelvetic marls, semipelites, and pelites underlying the pass have been subjected only to Cenozoic Alpine Orogeny (Fox, 1975). They have undergone four phases of deformation and the dominant rock type in the sample locality is garnet-kyanite-staurolite schist.

In hand specimen the sampled rock is dark grey with  $S_2$  forming the main, penetrative fabric of the rock.  $S_3$  is well developed and made conspicuous by the formation of white/blue kyanite along the limbs of open  $S_3$  crenulations, which have a wavelength interval of 0.3 to 2.5 cm. This produces bands up to 2 mm wide at approximately  $70^\circ$  to  $S_2$ .

The rock is composed of (%) muscovite 45, quartz 25, biotite 15, kyanite 5, garnet 3, staurolite 2, and opaques, clinozoisite, epidote, chlorite, tourmaline, and plagioclase 5. Any original sedimentary fabric in the present specimens has been obliterated by the development of  $S_2$ , which is formed by preferred orientation (001) planes of sheet silicates and dimensional orientation of elongate quartz, opaques, and clinozoisite.  $S_3$  is an open crenulation

of the  $S_2$  foliation with no significant segregation of micas into the crenulation limbs. Examples of non-kyanite bearing rocks from the present area with a more intensely developed  $S_3$  cleavage, also show no evidence of segregation of layer silicates from quartz and feldspar. In all the thin sections examined, time relationships of mineral growth to cleavage formation are clear.

Staurolite occurs as porphyroblasts up to 4 mm in length. The habit varies from prismatic to xenomorphic with some crystals possessing corroded margins. Cruciform shapes also occur and sector-twinning is common in all forms. Staurolite is nearly always packed with inclusions of quartz, opaques and occasionally biotite, chloritoid, and epidote. The  $S_1$  fabric is largely planar with some curving towards the rims of crystals. The  $S_6$  fabric is much more intensely deformed by  $D_3$ , although  $S_1$  and  $S_6$  are continuous. This indicates that staurolite growth was largely post- $S_2$  to early syn- $S_3$ , and the more intense crenulation of  $S_6$  indicates that growth stopped before the end of  $D_3$  deformation.

Plagioclase forms colourless anhedral (amoeboid) porphyroblasts up to 6 mm. in diameter, with

twinning usually absent. Inclusions of opaques, quartz, and occasionally biotite form an  $S_1$  fabric which is often planar, but in many cases is curved towards the margin of the porphyroblast.  $S_1$  is usually continuous with  $S_e$ . Plagioclase therefore grew post- $S_2$  to syn- $S_3$ , but growth ceased before the end of  $D_3$  deformation as  $S_1$  is never as tightly crenulated as  $S_e$ .

Garnet forms porphyroblasts up to 7 mm. in diameter, varying in shape from sub- to euhedral. They contain numerous inclusions of opaques, quartz, clinozoisite, epidote, tourmaline, and tiny staurolites (up to 100  $\mu\text{m}$  diameter). Larger staurolite and kyanite crystals are sometimes partially included.  $S_1$  varies from being straight at the crystal core becoming curved at the margins, to an S-shaped  $S_1$  fabric. Generally  $S_1$  is continuous with  $S_e$ , but the  $S_1/S_e$  relationships at crystal margins indicate that, in some cases, rotation of garnet after growth has occurred.  $S_1$  is never as strongly crenulated as  $S_e$ . Garnet also has a tendency to be elongate, with the long axis parallel to  $S_3$  cleavage planes. Some crystals possess rounded margins characteristic of resorption, while alteration to biotite or chlorite is also visible at the rims of individual porphyroblasts. The garnet growth

varies in age from post- $S_2$  to syn- $S_3$ , but all growth ceased before the end of the  $D_3$  deformation phase.

Two types of kyanite occur in the present specimens (fig. 2). Type 1 characteristically forms idiomorphic crystals from 0.5 to 3.0 mm. in length, concentrated in the limb zones of the  $S_3$  crenulation cleavage. Inclusions of quartz, opaques, epidote, and mica occur, but a clear  $S_1$  fabric is not usually well developed and in such cases the crystals cross-cut the  $S_e$  fabric which is crenulated by  $S_3$ . However, some kyanites do overprint  $S_3$  and have continuous  $S_1/S_e$  relationships exhibiting a post- $S_3$  age. All the Type 1 crystals tend to be oriented with the prism faces parallel to  $S_3$ .

Type 2 crystals are much less abundant than Type 1. They are typically 0.1 to 0.5 mm in length, usually idiomorphic and found in areas between  $S_3$  cleavage zones with the prism faces lying parallel to the  $S_2$  cleavage orientation. Tiny inclusions of quartz and opaques form an  $S_1$  fabric which is approximately planar and concordant with  $S_e$ , indicating that no relative rotation has occurred.

*Analytical results.* Kyanite crystals of both textural types were analysed using a Cambridge Geoscan Mark II electron microprobe, fitted with a Link Energy Dispersion system running at 20 kV

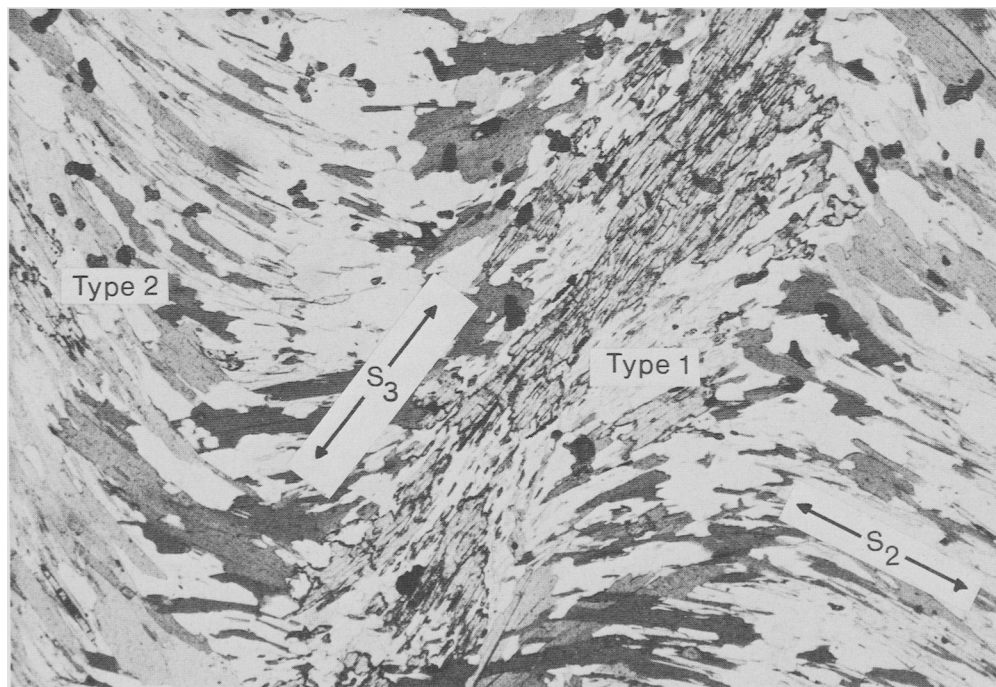


FIG. 2. Type 1 kyanites formed on the limbs of an  $S_3$  crenulation cleavage, and smaller Type 2 kyanites formed outside this  $S_3$  cleavage zone (Photomicrograph  $\times 20$ ).

and a beam current of 4 nA. A count time of 200 seconds was used to increase the detection sensitivity. The centres of over thirty individual kyanite crystals of each textural type were analysed.

The results (fig. 3) show that centre  $\text{Fe}_2\text{O}_3$  compositions of Type 1 kyanites vary from 0.35 to 1.18 wt. %, and those of Type 2 kyanites vary from 0.13 to 0.45 wt. %. In both cases a positive correlation between crystal size and centre  $\text{Fe}_2\text{O}_3$  composition occurs.

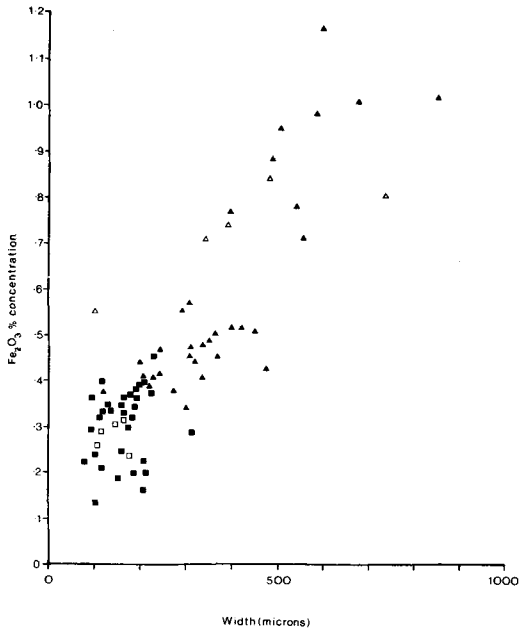


Fig. 3. Graph showing the positive relationship between centre  $\text{Fe}_2\text{O}_3$  % concentration and crystal width (i.e. perpendicular to (100) planes). Type 1 kyanites (triangular symbols), and Type 2 kyanites (square symbols). Unshaded symbols show five of each type selected for measurement of compositional profile.

Five Type 1 and Type 2 crystals were analysed for  $\text{Fe}_2\text{O}_3$  using Wavelength Dispersion techniques in order to increase the detection sensitivity. Since the compositional profiles of individual types do not vary significantly, two typical sets of results are presented for each.

Figs. 4(a) and 4(b) show profiles for Type 1 kyanites. In both cases traverses were made parallel and perpendicular to the (100) cleavage planes. Traverses perpendicular to the cleavage (A-B and E-F) show a relatively smooth, symmetrical profile with a marked increase in  $\text{Fe}_2\text{O}_3$  concentration from approximately 0.3% at the edges to 0.8% at

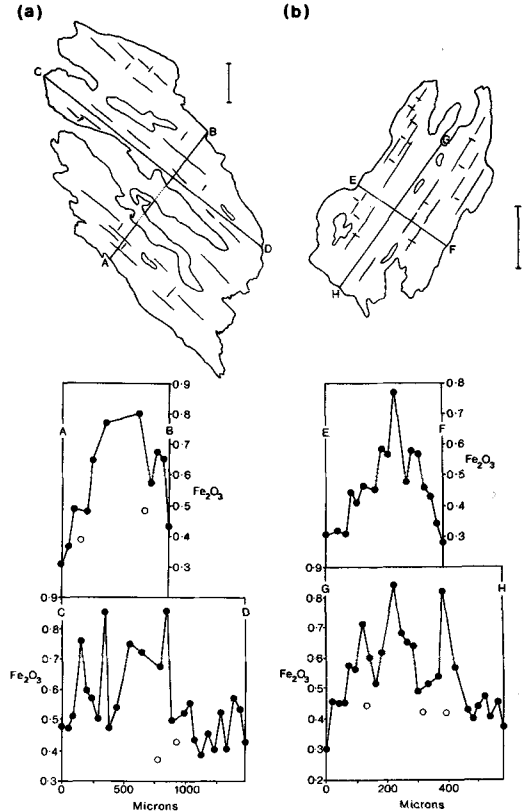


Fig. 4. Typical microprobe profiles of  $\text{Fe}_2\text{O}_3$  across Type 1 kyanite crystals. The unshaded symbols represent points close to cleavage cracks. Scale bars in both (a) and (b) are 200 microns.

the cores. The profiles produced from traverses parallel to the crystal cleavage (C-D and G-H) exhibited a general trend of low  $\text{Fe}_2\text{O}_3$  concentration at the edges, to a high at the core. However it is not as well defined as in the profiles measured perpendicular to crystal cleavage. Points analysed very close to, but not in, cleavage cracks possess low  $\text{Fe}_2\text{O}_3$  concentrations of approximately 0.3%.

Figs. 5(a) and 5(b) show typical profiles for Type 2 kyanites with, in each case, traverses parallel and perpendicular to the (100) cleavage planes. No significant variation in  $\text{Fe}_2\text{O}_3$  concentration in either direction occurs, the average value being approximately 0.3% throughout the crystals.

*Discussion.* The petrographic evidence indicates that there are two distinct types of kyanite present, but their relative ages could not be determined. It is clear that Type 1 kyanites are syn- to post- $S_3$  in age, and form predominantly larger crystals. Type 2 kyanites are at least post- $S_2$  in age.

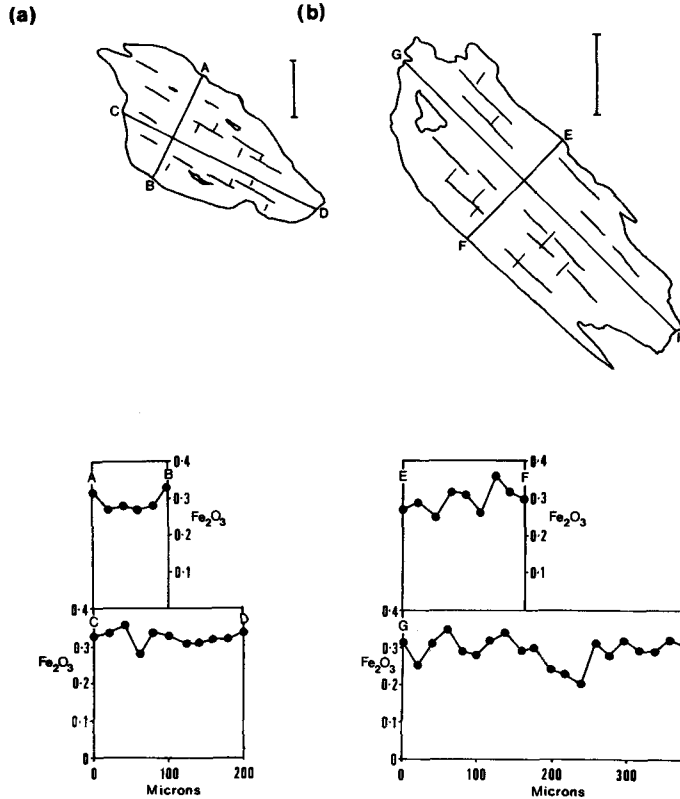


FIG. 5. Typical compositional profiles of  $\text{Fe}_2\text{O}_3$  across Type 2 kyanite crystals. The scale bar in (a) is 50 microns, and in (b) is 100 microns.

Relatively few analyses for kyanite are presented in the literature, the most recent being given by Deer *et al.* (1982). These show that small concentrations of  $\text{Fe}_2\text{O}_3$  (max. 1.12%),  $\text{TiO}_2$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{K}_2\text{O}$ , and  $\text{Na}_2\text{O}$  can occur. Type 1 kyanites are zoned, with the highest concentration of  $\text{Fe}_2\text{O}_3$  (up to 1.18%) detected at the crystal core and decreasing to 0.3% at the margin. Type 2 kyanites are not zoned, having a homogeneous distribution of approximately 0.3%  $\text{Fe}_2\text{O}_3$  throughout the crystal. The writer could find no record in the literature of the occurrence of compositional zoning in kyanite.

Any explanations for the present data must not only account for the fact that kyanite has grown preferentially in  $S_3$  cleavage zones, but also for the  $\text{Fe}_2\text{O}_3$  zoning and correlation between crystal size and centre  $\text{Fe}_2\text{O}_3$  composition.

Two possible explanations exist.

(i) Segregation of precursor minerals for kyanite-forming reaction occurred parallel to the  $S_3$  crenulation limbs, due to shearing or differential solution

or both as suggested in the literature (*op. cit.*). This is considered unlikely to account for the differentiation in the present rocks because in non kyanite-bearing rocks from the same locality no such segregation is observed. Moreover the  $S_3$  cleavage developed is a rather open crenulation, and it seems probable that the amount of strain produced would not have been sufficient to have caused differential solution or any sort of mechanical segregation of minerals. Published examples of segregation of precursor minerals (Carpenter, 1968; Spry, 1969) appear to occur in rocks with a much more intensely developed cleavage. Further, this mechanism does not explain the zoning present in kyanite.

(ii) Kyanite preferentially nucleated in  $S_3$  crenulation cleavage zones due to the fact that high strain, and therefore dislocation density, produced more reactive sites in these zones. When the kyanite-forming reaction was initiated the reactant minerals would have been more unstable in these regions. Nucleation events would also be favoured

due to enhanced diffusion in such zones. Further, new nuclei could be more easily accommodated in zones of high lattice strain thus increasing their chance of survival to the growth stage.

Such preferential nucleation and growth of kyanite in  $S_3$  must mean that concentration gradients are set up, and this would further reduce the chance of nucleation between the  $S_3$  cleavage zones.

If it is assumed that all kyanite crystals grow at the same rate at any given time, then first-formed nuclei will grow to produce the largest crystals and subsequently formed nuclei will develop into progressively smaller crystals. It also seems reasonable to assume that all kyanite growing at any given time should have the same composition, as is generally accepted for garnet (Kretz, 1974; Finlay and Kerr, 1979).

As Type 1 kyanites form the largest crystals and have the highest concentrations of  $Fe_2O_3$ , it must be concluded that they were the first-nucleated crystals. It follows that Type 2 kyanites are the latest-formed crystals, and the positive correlation shown in fig. 3 can be interpreted as a nucleation sequence.

An alternative explanation for the zoning pattern is a diffusion mechanism as suggested by Anderson and Buckley (1973) for garnet. All kyanite crystals might have grown with the same composition at the same time, but later re-equilibration caused the composition to change. Limited diffusion would allow the centres of the largest crystals to retain their original composition. This is considered unlikely for the following reason.

The anomalous low values of  $Fe_2O_3$  (approx. 0.3%) recorded near to cleavage cracks in Type 1 kyanites are probably because the cracks have acted as channels for diffusion between the crystal and the matrix. The values of 0.3% correspond to edge compositions found in all the kyanites in the present rocks. Assuming that this value represents the equilibrium concentration between the final growth of kyanite and the matrix, it seems likely that re-equilibration has occurred between the crystal and matrix along, and therefore in close proximity to, these cracks. As the cleavage spacing in the large kyanites seems to be exactly the same as that in the small kyanites, the opportunity for re-equilibration should be the same irrespective of crystal size. Thus all crystals should possess a uniform composition of approximately 0.3%. As this is not the case in the present examples, some other explanation is required.

In summary, it is concluded that two distinct textural and chemical varieties of kyanite were formed at Lukmanier. Compositional profiles and

the correlation between core  $Fe_2O_3$  composition and size indicates that kyanite nucleated first and preferentially in the  $S_3$  crenulation cleavage zones. It may therefore be interpreted as an example of metamorphic differentiation by a mechanism of preferred nucleation and growth in zones of high shear.

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