

## SHORT COMMUNICATIONS

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### A note on the controls of the retrograde transformation of andalusite to kyanite

PURTSCHELLER (1969) reported some intriguing examples of disequilibrium among aluminium silicate polymorphs in metamorphic rocks from the Ötztal, Austria. In particular, in certain rock compositions, a primary metamorphism produced andalusite both as small crystals in pelitic rocks and as large crystals (several cm) in quartz pods in the rocks. During retrograde metamorphism, some large crystals in quartz pods were converted to kyanite pseudomorphs, others were not changed and the ground-mass fine andalusite of the host rock was little changed. One may well ask what factors controlled the response to the retrograde process. If they were understood they might suggest which parts of a rock might contain the best clues on both prograde and retrograde metamorphic history.

*Geologic setting.* In an area about 2600 km<sup>2</sup> of the central part of the Eastern Alps (Ötztal-Stubai Alps, Tyrol) large and mainly postkinematic quartz segregations occur within aluminous pelitic schists. Besides quartz, the segregations contain large crystals of andalusite, kyanite, and cordierite and occasionally sillimanite in varying amounts. The regional distribution of the aluminosilicates is clearly dependent on the metamorphic grade of the host schists.

In the pelitic rocks, postkinematic metamorphism can be attributed to a heat dome in Caledonian times (Purtscheller, 1969) and three zones have been mapped, a kyanite zone, a sillimanite zone, and an andalusite plus sillimanite zone. Within quartz segregations kyanite is found as a primary mineral only in the first zone and andalusite in the second and third zones. Cordierite in segregations is restricted to the third zone.

In several places large andalusite crystals in quartz segregations have been transformed into a fine-grained aggregate of kyanite crystals. The product kyanite is orientated with its *c*-axis parallel to the *c*-axis of the primary andalusite. Purtscheller (1969) considered that this transformation represented response to decreasing temperature at more or less constant pressures during the cooling period of the heat dome. The transformation has not occurred uniformly over the whole region and the degree of transformation may be highly variable in a single outcrop or segregation (for example see Fyfe, 1969; Purtscheller, 1971). The same type of transformation has been reported from many other places, perhaps one of the most spectacular being from Rhodesia (Workman and Cowperthwaite, 1963).

#### *Controlling factors*

A number of factors can be thought of that might be important in controlling whether or not transformation occurs.

*Stress.* It is well known from experimental studies that stress may have a spectacular catalytic influence on the rate of solid state transitions. Examination of a few specimens suggested that this could be a possible control but when a large number of examples was studied it became clear that this was not the case: altered and fresh andalusite crystals in the same sample were not at significantly different orientations.

*Chemical composition.* Much has been written (see Amer. Journ. Sci. 1969, 267, 257-456) suggesting that the phase transitions of  $\text{Al}_2\text{SiO}_5$  polymorphs need not be univariant but all transitions could be smeared due to significant concentrations of species such as  $\text{MnO-Fe}_2\text{O}_3$ . This could imply that certain crystals might transform while others would remain stable.

Samples from the specimen figured in Fyfe (1969) were analysed and included a large andalusite totally transformed to kyanite and an andalusite in the same sample almost untouched. Wet chemical analysis showed only trace amounts of  $\text{MnO}$ ,  $\text{MgO}$ , and  $\text{TiO}_2$  but for andalusite,  $\text{Fe}_2\text{O}_3$  1.64 % and for kyanite, 1.82 %. As Purtscheller (1971) pointed out, the high  $\text{Fe}_2\text{O}_3$  content in the primary andalusite is restricted to a relatively small area; in most of the Ötztal mass the  $\text{Fe}_2\text{O}_3$  content varies between 0.26 and 0.60 %. There is no relationship between the transitions of the  $\text{Al}_2\text{SiO}_5$  polymorphs and the iron content of the primary andalusite either in a regional scale or in different single crystals of one single segregation as is shown in 59 X-ray fluorescence analyses of andalusite.

Electron-probe scans of unchanged, totally transformed, and partially transformed crystals showed considerable zoning with respect to  $\text{Fe}_2\text{O}_3$ , with the range of concentrations in kyanite and andalusite overlapping. In partially transformed areas, impurities appear to be concentrated at the transition boundary. In general, there appears to be no obvious correlation between the degree of transformation and the chemical composition.

*Wet or dry?* An obvious question is whether or not the reaction proceeded in the solid state or through an aqueous film. This is a rather difficult question to answer. Experience on the reactivity of the  $\text{Al}_2\text{SiO}_5$  polymorphs in experimental studies would suggest that unless high shearing stresses were operative, the solid state reaction would be unlikely even in geologic times. There is no evidence for significant deformation. The phases are associated with small amounts of hydrates like pyrophyllite and muscovite and Purtscheller has found large cordierite crystals in the same environment replaced by hydrous phases such as muscovite, pyrophyllite, and chlorite. It would thus be difficult to preclude a small amount of an active fluid phase: a phase that eventually must be absorbed in formation of hydrates such as pyrophyllite.

*A model for the process.* One, and in fact the only, observation providing a significant clue to the control of the reactivity is that transformed crystals are generally enclosed in quartz. Thus in the sample shown in Fyfe (1969) the largest transformed crystals are inside the quartz, andalusites on the edge are unchanged. In other samples (see Purtscheller, 1971) where crystals are elongated normal to the schist-segregation border, the tips inside quartz may be changed while the ends adjacent to schist are

still fresh andalusite. It is also of note that much smaller crystals of andalusite in the host rocks are not transformed. It seems clear that transformation occurs most easily in 'clean' parts of the rock.

There may be two factors involved in these observations. Prograde regional metamorphism is rarely reversed simply because water is not available in sufficient quantities. In the host schist with its complex mineralogy and chemistry, traces of water left after peak metamorphism will be absorbed by hydrate formation during cooling; the general situation will be  $P_{\text{total}} \gg P_{\text{fluid}}$  during unloading. But if one considers a fluid inclusion in a pure quartz or andalusite crystal, this fluid may exist and be preserved (with  $P_{\text{fluid}} \approx P_{\text{total}}$ ) until temperatures appropriate to pyrophyllite formation are encountered, about 400 °C (Kerrick, 1968). Thus fluid films in quartz might exist and be preserved to catalyse the reaction, a process possibly assisted by the large negative volume change of the andalusite  $\rightarrow$  kyanite reaction.

A second important factor may also enter into the rate processes. Studies on simple systems (e.g. carbonates, see Bischoff and Fyfe, 1968) indicate that impurities able to form stable compounds with polymorphs tend to nucleate on reactive sites (dislocations) and block activity on that site. Thus phases such as micas and chlorites, which could form from common impurities, could lead to very low activity of the phases both during solution and growth steps of the transformation process. The chemical purity of the quartz segregation could thus also lead to a higher degree of chemical reactivity, small amounts of impurities being first eliminated in very early stages of the retrograde process. These two factors may be adequate to explain the selective nature of the process involved.

*Concluding remark.* It seems possible that simple or isochemical retrograde metamorphic reactions may occur most rapidly in chemically simple environments, particularly in veins and segregations. If this is the case, these may be the important sites in a rock in which to search for reactions recording retrograde metamorphic history.

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