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توزیع اندازهٔ بلوری در سنگهای دگرگونی: مثالی از تأثیر دمای ماورای تعادل در نرخ هسته‌بندی و رشد

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چکیده: توزیع اندازهٔ بلوری در سنگهای دگرگونی اطلاعات اساسی را در ارتباط با سرعت هسته‌بندی، سرعت رشد، زمان رشد و میزان حرارت ماوراء در تعادل ارائه می‌کند. بررسی توزیع اندازهٔ بلوری برای بلورهای استرولیت، کیانیت و آندالوزیت در هالهٔ دگرگونی آردارا بیانگر این است که کانیهای نخست تشکیل یافته (گارنت) دارای بالاترین چگالی جمعیت و کوتاهترین زمان رشد، و کانیهای تشکیل یافته در فاز نهائی دگرگونی (آندالوزیت) دارای پایین‌ترین چگالی جمعیت و طولانی‌ترین زمان رشد هستند. چگالی جمعیت و زمان رشد استرولیت و کیانیت یکسان بوده و از این حیث حد واسط گارنت و آندالوزیت قرار میگیرند. این اطلاعات مؤید تأثیر درجه ماوراء تعادل بر روی سرعت هسته‌بندی و رشد کانیها در دگرگونی است.

واژه‌های کلیدی: *توزیع اندازهٔ بلوری، حرارت ماورای تعادل، هسته‌بندی.*

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Crystal size distribution in metamorphic rocks: an example for the relationship between nucleation and growth rates with overstepping

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Abstract: Crystal size distribution (CSD) in metamorphic rocks provide fundamental information about crystal nucleation and growth rate, growth time and the degree of overstepping. CSD data for garnet, staurolite, kyanite and andalusite crystals from the aureole demonstrate that the earliest formed of these minerals, garnet, has the highest population density and the shortest growth time. The last formed mineral, andalusite, has the lowest population density and longest growth time. Kyanite and staurolite have the similar population density and growth times intermediate between those of garnet and andalusite. These data demonstrate the effect of the degree of overstepping on the nucleation and growth rates of minerals during metamorphism.

Keywords: *Crystal size distribution, Overstepping, Nucleation.*

1. Introduction

It is essential when explaining any rock texture to note the number, overall grain size and variations in relative size between the constituent mineral phases [1]. The formation of a new metamorphic mineral requires heterogeneous nucleation, growth and transport of reactants to the mineral-growth site [2]. The rates of these processes are dependent on the pressure, temperature [3], bulk rock composition, stress and strain [1].

Numerous studies have presented theoretical formulations of nucleation and growth rates for metamorphic minerals [3-5]. On the basis of these theoretical formulae the rates of nucleation and growth of a phase are a function of the affinity of reaction (Ar):

$$-Ar = \Sigma\ v_i\ \mu_i \tag{1}$$

where μ_i is the chemical potential of phase *i* at the temperature, pressure and composition of interest, and v_i is the stoichiometric coefficient of phase *i* in the reaction. Accordingly, the affinity of reaction is a function of the departure of a system from equilibrium (temperature overstep). An important point is that nucleation and growth rates have different functional dependences on Ar [3].

According to Ridley and Thompson [3] the rate of interface-controlled mineral growth is an exponential function of Ar, whilst the diffusion-controlled growth rate varies linearly with Ar. In contrast, they noted that the nucleation rate of a phase is an exponential function of $(Ar)^2$. The result is that the relative importance of nucleation vs. growth changes as a function of the degree of overstepping. The dependence of nucleation and growth rates on the affinity of reaction can be seen in the idealised plot in Fig. 1, where for low degrees of overstepping, growth rate is much larger in comparison with nucleation rate resulting in a few large crystals. In contrast, at large amounts of overstepping, nucleation rates are high relative to growth rate resulting in numerous small crystals.

The earliest kinetic studies of crystallisation in metamorphic rocks were concerned with crystal size distribution (CSD) [6-11]. An important approach to describing crystal size distribution is the application of population density models. The crystal size distribution (CSD) theory introduces a distribution function (population density) which is defined by the solution of a differential equation. The physical parameters (e.g., nucleation and growth rates) which affect the crystal size distribution are nested in the differential equation [12]. This method was developed by Randolph and Larson [12] to study batch crystallisation in chemical engineering systems and has been applied by Marsh [13], Cashman and Marsh [14] and Cashman and Ferry [15] to igneous and metamorphic crystallisation. They provided a population balance equation which described the change in numbers and sizes of crystals as a function of their residence times in the system and also as a function of the addition or loss of crystals to the system.

In the present study crystal size distribution data are presented for garnet, kyanite, staurolite and andalusite crystals in three rocks from the Ardara aureole. For comparison garnet crystals in a regionally metamorphosed pelitic rock from Perthshire, Scotland have also been analysed. The aim is to consider the quantitative information about crystal nucleation and growth rates, and the influence of the degree of overstepping on crystal size distribution of these minerals in the thermal aureole of the Ardara pluton.

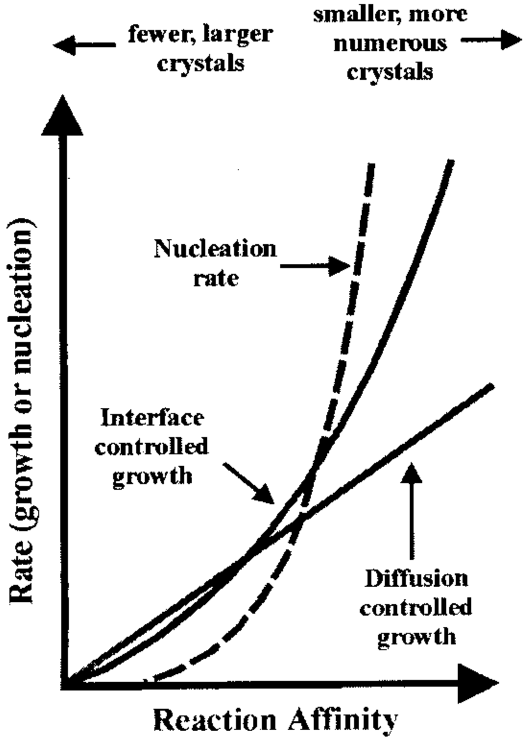

Fig. 1 Shematic plot showing relationship between nucleation and growth rates as function of reaction affinity (Ar). Ar is function of amount of overstepping in temperature from equilibrium. For low degree of overstepping, growth rate is much larger than nucleation rate, whilst at higher amount of overstepping nucleation rates are high [3].

2. Geological setting

The Donegal region is located in the north west of the Republic of Ireland (Fig 2). The country rocks of Donegal granites consist of Dalradian metasedimentary and meta-igneous rocks that range in age from Late Precambrian to Middle Cambrian. This group of rocks subsequently underwent major deformation (the Caledonian orogeny) during Late Cambrian to Late Ordovician. The granites of Donegal have been divided into six units having different ages, composition and modes of emplacement (Fig. 2).

The Ardara pluton, which is the southernmost of the Donegal granites, has a tear-drop shape and is about 8 kilometres in diameter. It consists of two units, an outer ring of quartz-monzodiorite and an inner core, with the composition varying from quartz-monzodiorite to granodiorite. The Ardara aureole represents a forcibly emplaced, diapiric intrusion [16,17].

The Ardara aureole consists of a pelitic horizon (locally referred to as the Clooney Pelitic Group) and an adjacent limestone unit (the Portnoo Limestone). The pelitic horizon of the Ardara aureole consists of interlayered aluminous pelites and semipelites. Lenses and pods of metadolerite are also common in a zone extending about 200 metres from the contact with the Ardara pluton [16].

The metamorphic effects of the Ardara pluton extend nearly 1.5 km from the intrusion contact. The Ardara aureole has been divided into following units [17]:

- An outer unit which is made up of the non-porphyroblastic rocks showing minor contact effects and characterised by new thermal biotite flakes crosscutting the regional schistosity,
- An inner unit which comprises three zones [18] (Fig. 3) on the basis of prismatic Al_2SiO_5 polymorphs found,
    - ✓ An outer kyanite-bearing andalusite zone,
    - ✓ A middle kyanite-free andalusite zone,
    - ✓ An inner prismatic sillimanite zone.

Naggar and Atherton [18] demonstrated that kyanite in the Ardara aureole is restricted to rocks with MgO/(MgO+FeO) values higher than 0.50 and lower bulk-rock MgO/(MgO+FeO) ratios precluded kyanite as a phase in the assemblage.

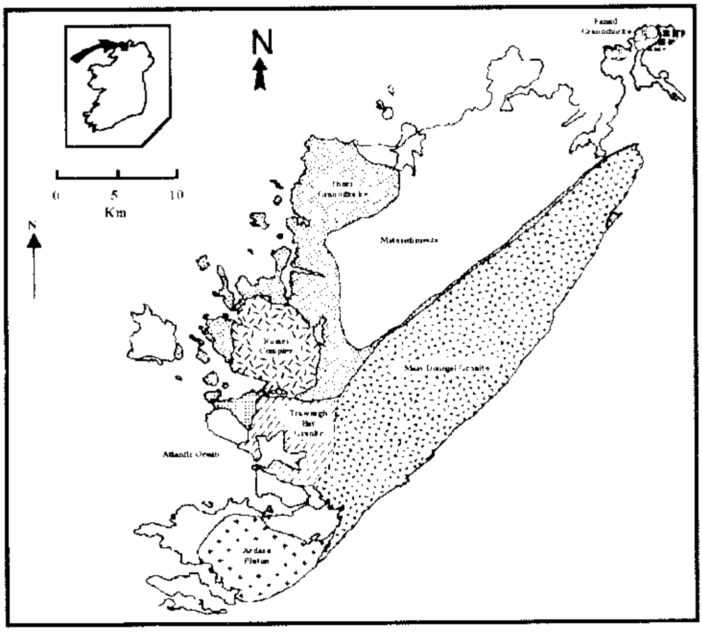

Fig. 2 Donegal granitic complex, northwestern Irland.

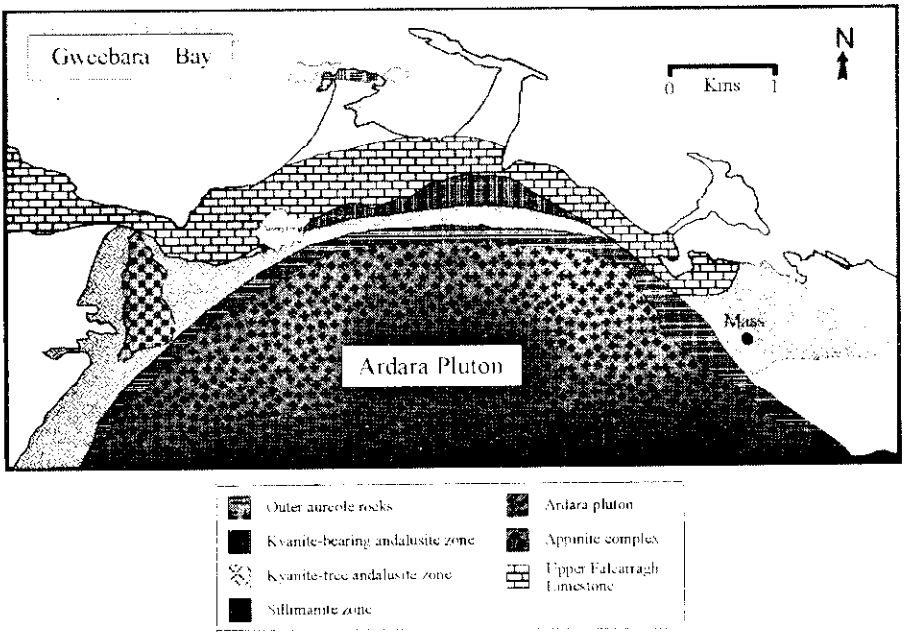

Fig. 3 Geology of the northern portion of the Ardara pluton and surrounding country (modified from ref. [17,18]).

The details of textural and mineralogical characteristics of aluminium silicate-bearing rocks from the contact aureole of the Ardara pluton are given elsewhere [19]. In brief, dark porphyroblastic schists with conspicuous andalusite on most surfaces characterise the outer kyanite-bearing andalusite zone. In thin section, typical rocks consist of quartz + plagioclase + biotite + muscovite ± chlorite ± staurolite ± garnet ± kyanite ± andalusite ± fibrolite. Graphite and ilmenite are also present. Kyanite takes place as small idioblastic to subidioblastic prisms (0.15-0.35 mm in length) (Fig. 4). Crosscuted by kyanite, biotite is usually not disturbed along the kyanite boundaries. Idioblastic kyanite occurs as inclusions within andalusite porphyroblasts. Kyanite is also found included in plagioclase poikiloblasts. Staurolite commonly takes place as small (0.12 - 0.35 mm in diameter) subidioblastic generally inclusion free grains (Fig. 5). In some slides made from these rocks staurolite can be seen as irregular grains, or clusters of grains, disseminated throughout the rock (Fig. 6). Staurolite is also found as relatively large porphyroblasts (0.4 to 0.9 mm in diameter) containing continuous curved trails of quartz inclusions (Fig. 7). Staurolite, with good crystal faces, is commonly included in andalusite and plagioclase porphyroblasts. In many examples staurolite and kyanite occur as intergrowths (Fig. 8), suggesting simultaneous growth of these two minerals. Garnet occurs only in kyanite-free rocks i.e., kyanite and garnet never occur together in the same rock. It develops as tiny (0.09 to 0.13 mm in diameter) idioblastic crystals in the groundmass (Fig. 9). It also occurs as inclusions in andalusite, plagioclase and staurolite suggesting garnet was formed earlier than these minerals. Andalusite comes as large porphyroblasts (1 to 5 mm in diameter) and includes quartz, staurolite, kyanite, garnet and ore minerals. Plagioclase always takes place as porphyroblasts (0.5 to 4 mm in diameter). It generally shows "S"-shaped inclusion trails of quartz. The textures exhibited by plagioclase could easily be mistaken as textures evolving from rotated porphyroblasts. However, these textures are clearly formed by overprinting regional microfolds (S_2-S_3) in the groundmass.

Within the kyanite-free andalusite schists, andalusite can be seen to consist of an inclusion-free pink pleochroic core with the mantle of colourless poikilitic andalusite. A common feature in idioblastic andalusites is the development of textural sector-zoning and matrix displacement [19] (Fig. 10). Other common minerals are garnet, staurolite and fibrolite. Staurolite and garnet display similar textural features to those in the kyanite-bearing andalusite zone.

Fig. 4 Kyanite (Ky) crystal lying at small angle with the biotite (Bt) folia. Width of photo corresponds to 0.8 mm. Sample 9, kyanite-bearing analusite zone.

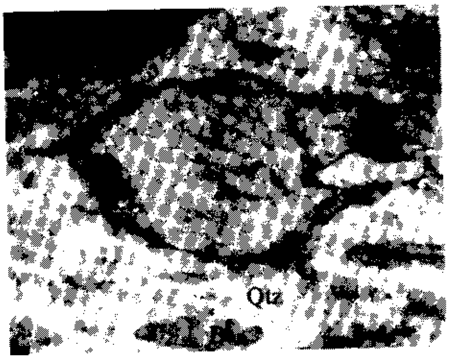

Fig. 5 Small euheral, inclusion-free staurolite crystal in the matrix, of biotit (Bt) an quartz (Qtz). Width of photo corresponds to 0.4 mm. Small 19, kyanite-bearing andalusite zone.

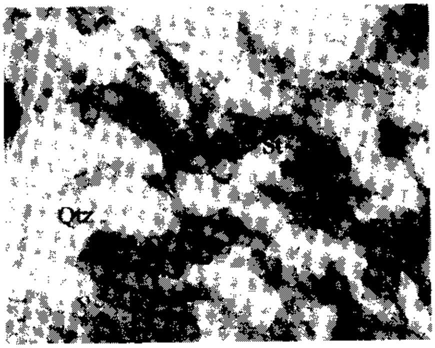

Fig. 6 Small grains of staurolite (St) issminated throughout the rock. Other minerals are biotite (Bi) an Quartz (Qtz). Width of photo corresponds to 0.6 mm. Sample 12, kyanite-bearing andalusite zone.

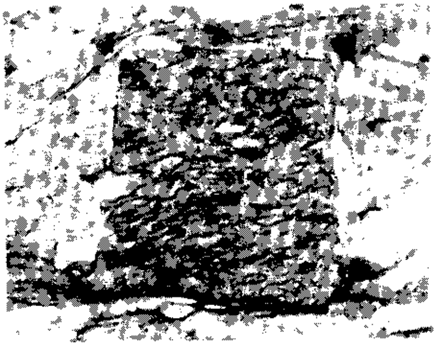

Fig. 7 Staurolite (St) porphyro-blast containing continous curve traile of quartz (Qtz) inclusions. Width of photo correspons to 0.8 mm. Sample 9, kyanite-bearing analu-site zone.

Fig. 8 Kyanite (Ky)-staurolite (St) intergrowth. Width of photo correspons to 0.4 mm. Sample 9, kyanite-bearing andalusite zone.

Fig. 9 Tiny garnet (Grt) crystals within the grounmass. Width of photo corresponds to 1.6 mm. Sample 20, kyanite-bearing andalusite zone.

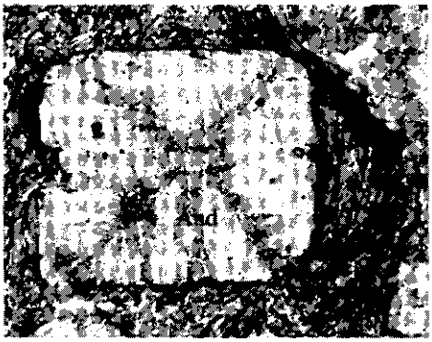

Fig. 10 Texturally sector-zone anda-lusite (And). Note well developed cleavege dome in right hand side of andalusite. Width of photo corres-ponds to 2.2 mm. Sample 55, kyanite-free andalusite zone.

The inner sillimanite zone is characterised by dark brown hornfelses with biotite, garnet and occasionally sillimanite visible in hand specimens. Under the microscope the overall textures of the rock suggest that the transformation from the kyanite-free andalusite zone to the sillimanite zone was accompanied by a wholesale textural reconstitution [20]. Sillimanite appears as long prisms, growing from the groundmass as well as large grains to show symplectic intergrowth with quartz in the groundmass. In some of the specimens, sillimanite is formed by the coarsening of fibrolite groundmass (Fig. 11). Staurolite occurs as tiny subhedral grains throughout the groundmass. Garnet in most of the samples from the sillimanite zone displays two different habits. Away from the contact it occurs as small idioblastic to subhedral crystals in biotite clusters after regional garnet (Fig. 12). At the immediate contact with the pluton garnet is present as large porphyroblasts (1 to 1.5 mm in diameter) which contain inclusions of biotite, quartz and fibrolite (Fig. 13). Cordierite can be seen as xenoblastic grains throughout the groundmass. It also occurs as large porphyroblasts (4 to 8 mm in diameter) which contain inclusions of fibrolite and biotite.

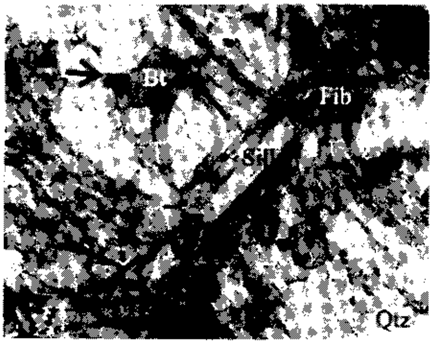

Fig. 11 Euhedral prismatic sillimanite (Sill) replacing fibrolite (Fib). Width of photo corresponds to 1.2 mm. Sample 77, Sillimanite zone.

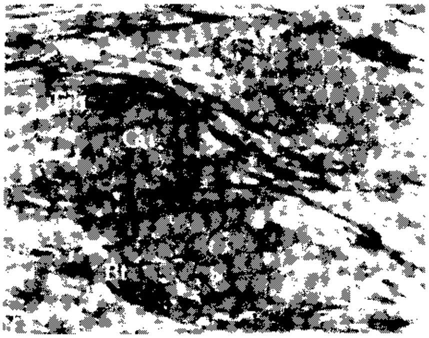

Fig. 12 Pseudomorphs after regional garnet altered mainly to fibrolite (after biotite). New crystals of thermal garnet are found growing in clusters. Width of photo corresponds to 2.2 mm. Sample 73, sillimanite zone.

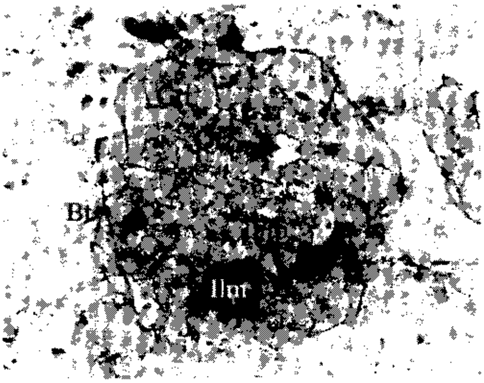

Fig. 13 Garnet (Grt) porphyro-blast containing inclusions of quarts (Qtz) and inmenite (Ilm). Width of photo corresponds to 2.2 mm. Sample 76, silimanite zone.

3. Methods

Acquiring accurate crystal size distribution data from thin sections can be a difficult process. Direct automated image analysis from thin section is only possible when the crystal population of interest can be efficiently distinguished from other minerals [21]. Unfortunately, direct discrimination by image analysis for minerals of interest (garnet, staurolite, kyanite and andalusite) was not possible. Therefore, for accurate measurement, the author preferred to trace the outline of crystals (except for garnet crystals from the Ardara aureole) from photomicrographs where the identity of each crystal has been confirmed. As the size of garnet crystals from the Ardara aureole are very small, it was difficult to trace the outline of garnet crystals from photomicrographs. Therefore, crystal size distribution of garnet crystals was done from scanning electron microscope (SEM) backscattered electron (BSE) images, by laying a tracing paper over the BSE image and drawing around garnet grains. The tracing then was subjected to image analysis. Crystal size distributions were measured using a computer package called Scion image. The crystal dimension measured is the longest diameter.

The ln(n) (n = number of crystals per unit volume, per unit length) against L (the crystal length) graph for each crystal was produced using the Microsoft Excel crystal size distribution program of Peterson [21]. This shows the population density (ln (no)) and GT (G is the average growth rate and T is the growth time) of the sample and allowed the data to be seen in relation to the predicted linear trend. Population density is the total number of grains per unit volume, per unit length. This means that many grains in a small volume provide a high population density whilst a few grains in a large volume give a small population density. GT is the actual time the crystal has spent growing. Therefore, a crystal with a high GT will be large and a crystal with a small GT will be small.

4. Results

1) Garnet crystals in sample 6 from the kyanite-bearing andalusite zone of the Ardara aureole (Fig. 14).

In this sample 724 garnet grains in an area of 0.37 mm^2 were measured. The garnet in this sample has a relatively high population density of 20.85 mm^{-4}. The GT is 0.002 mm, which is fairly small. The data broadly fit the CSD linear plot apart from some fluctuations above and below the line.

2) Staurolite crystals in sample 4 from the kyanite-bearing andalusite zone of the Ardara aureole (Fig. 15).

In this sample 105 staurolite crystals in an area of 460 mm^2 were measured. The population density of staurolite crystals is 3.623 mm^{-4}, which is lower than garnet crystals from sample 6. The GT is 0.104 mm and obviously is higher than garnet crystals of sample 6. The CSD plot is linear apart from at the largest grain sizes.

3) Kyanite crystals in sample 4 from the kyanite-bearing andalusite zone of the Ardara aureole (Fig. 16).

In this sample 79 kyanite crystals in an area of 460 mm^2 were measured. The kyanite in this sample has a population density of 3.271 mm^{-4} and GT of 0.117 mm, which is fairly close to those from staurolite. The data only really fit the CSD linear plot in the mid range of grain sizes.

4) Andalusite crystals in sample 55 from the kyanite-free andalusite zone of the Ardara aureole (Fig. 17).

In this sample 54 andalusite crystals in an area of 544 mm^2 were measured. The andalusite in this sample has a population density of .2.362 mm^{-4} and GT of 0.887 mm. The population density of andalusite is lower and the GT is higher compared to garnet, staurolite and kyanite crystals from the Ardara aureole. The CSD plot is linear apart from at the largest grain sizes.

5) Garnet crystals in sample S1 from regionally metamorphosed pelitic rocks from Perthshire, Scotland (Fig. 18).

In this sample 47 garnet crystals in an area of 645 mm^2 were measured. The population density of garnet crystals is -1.483 mm^{-4}, which is lower compared to garnet crystals of thermal metamorphosed rock from the Ardara aureole. The GT is 0.89 mm and is much higher than garnet crystals of sample 6 from the Ardara aureole. The CSD plot is linear apart from at the largest grain sizes.

CSD data for thermal garnet, staurolite, kyanite and andalusite crystals from the Ardara aureole and regional garnet crystals from Perthshire, Scotland are shown in Fig. 19 for comparison.

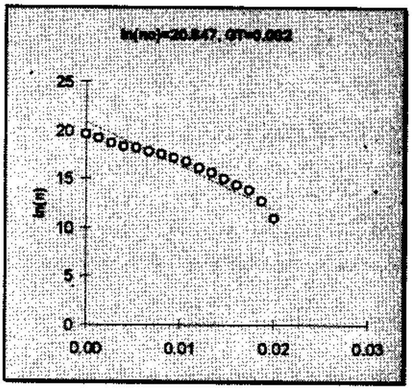

Fig. 14 CS data for thermal garnet crystals from the Ardara aureole.

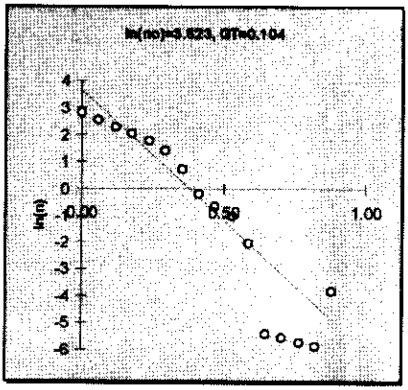

Fig. 15 CSD data for staurolite crystals from the Arara aureole.

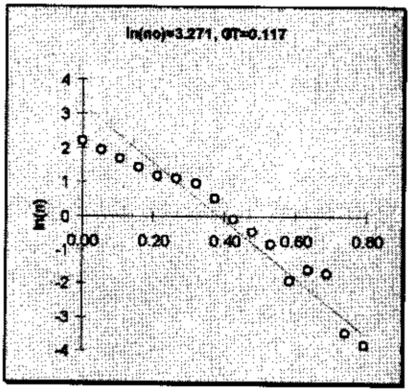

Fig. 16 CSD data for kyanite crystals from the Ardara aureole.

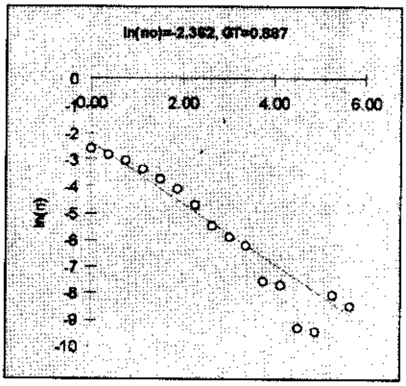

Fig. 17 CSD data for analusite crystals from the Ardara aureole.

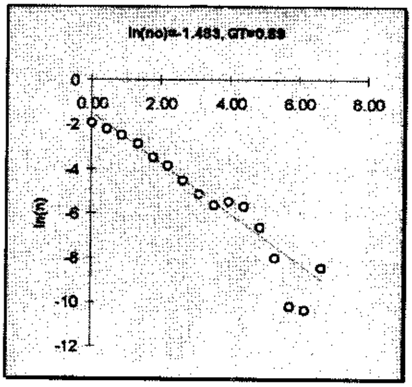

Fig. 18 CSD data for garnet crystals from the regionally metamorphosed pelitic rocks from Perthshire, Scotland.

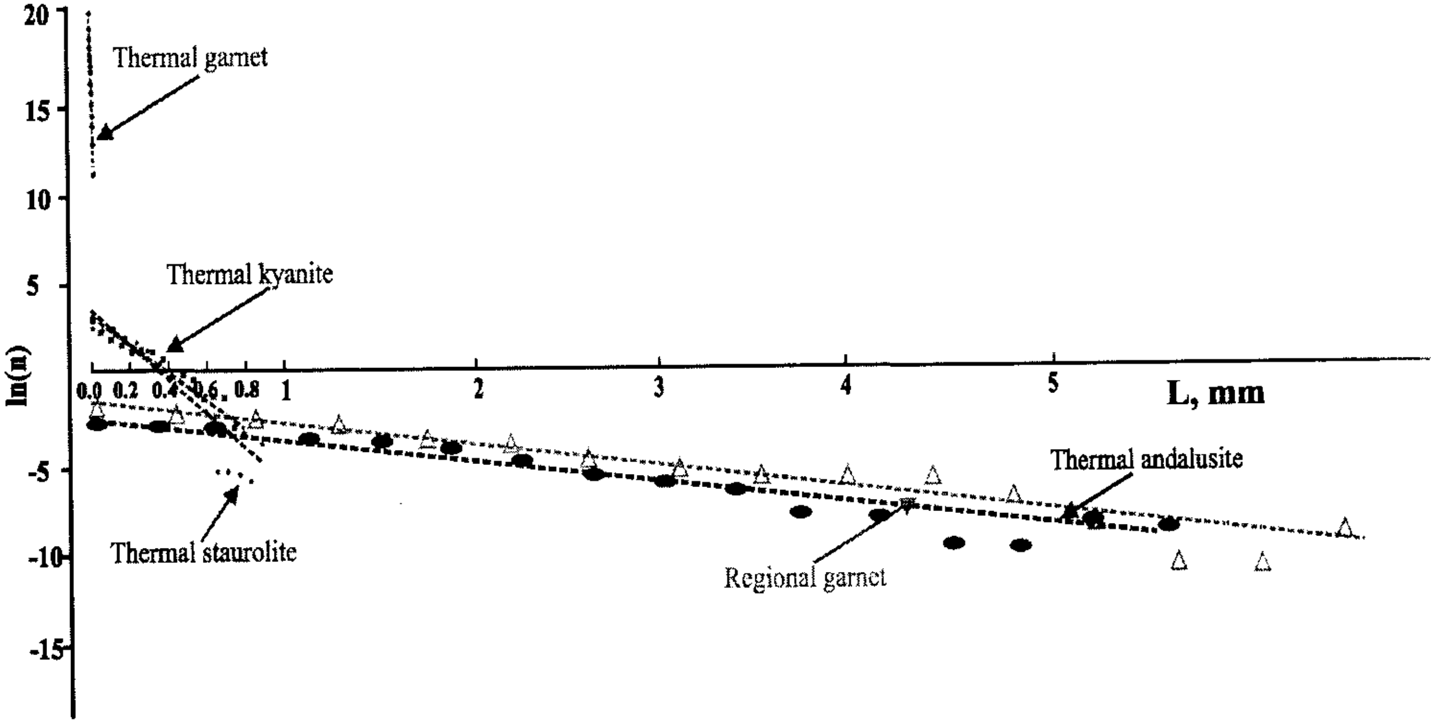

Fig. 19 CSD data for thermal garnet, staurolite, kyanite and andalusite crystals from the Ardara aureole and regional garnet crystals from the pelitic rocks of Perthshire, Scatland.

5. Discussion

From textural evidence a sequence of crystallisation for garnet, staurolite, kyanite and andalusite within the Ardara aureole is evident. Garnet crystals occur as tiny inclusions in andalusite and staurolite, suggesting garnet was formed earlier than these minerals. Kyanite and staurolite occur as small equidimensional crystals occasionally in parallel growth. They are enclosed by the large andalusite, never the reverse, suggesting a definite difference in time of nucleation. The most interesting finding about CSD data of garnet, staurolite, kyanite and andalusite crystals from the Ardara aureole is that the first formed minerals in the metamorphic history of the aureole have a higher population density and shorter growth time. It has long been recognised that the nucleation and growth rates of a mineral during metamorphism are a function of the degree of overstepping. At large amounts of overstepping, nucleation rates are high relative to growth rate resulting in numerous small crystals. In contrast, for low degrees of overstepping, growth rate is much larger in comparison with nucleation rate resulting in fewer larger crystals.

This interplay in the relative rates of nucleation and growth can be used to explain the observed CSD results for garnet, staurolite, kyanite and andalusite crystals in the pelitic rocks from the Ardara aureole. As can be seen in Fig. 14 garnet from the Ardara aureole has quite high population density (20.85 mm^{-4}) but very small GT (0.002 mm). On the basis of the theoretical rate laws presented in section 1 rapid heating in the early stages of Ardara pluton emplacement caused a large overstepping of the garnet-producing reaction resulting in high nucleation rates relative to growth rates. From Figs. 15 and 16 it is clear that staurolite and kyanite have lower values of the population density and higher values of the GT in relation to thermal garnet. However, their population density and GT are similar. These data may reveal that kyanite and staurolite were produced together from a common reaction when the heating rate was slower than that for the garnet-producing reaction. The small size of staurolite and kyanite however, reveals that the heating rate in the Ardara aureole was still high enough for significant overstepping. Andalusite porphyroblasts from the Ardara aureole (Fig. 17) have a low population density but fairly small GT, similar to those for garnet from regional metamorphosed rocks (Figs. 17 and 18). This most probably reveals that andalusite in the Ardara aureole was formed at nearly equilibrium conditions (limited or no overstepping) allowing the growth kinetics to dominate.

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