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Ordering of the intermediate plagioclase structure during heating

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Abstract

Hydrothermal annealing of volcanic intermediate plagioclase An 66 with diffuse *e* reflections at 870°C, 2 kbar for 50 days orders the intermediate superstructure and sharpens satellites. This increase in long-range order at subsolidus conditions is interpreted to be produced by a similar mechanism as in spinodally decomposing metals. The wavelength of the superstructure increases and the orientation changes with annealing time.

Introduction

Superstructures in calcic plagioclase vary with thermal history, but most phase transformations are sluggish and therefore difficult to observe in the laboratory. This has the advantage that high-temperature structures can easily be quenched and are preserved, which makes the structural state of plagioclase a valuable petrogenetic indicator. Since Laves and Goldsmith (1954) conducted heating experiments on anorthite and produced diffuse superreflections, on the basis of which they postulated presence of antiphase domains, numerous experiments have been done. Most of them were concerned with *disordering* of low-temperature structures. In this note we report an *ordering* reaction observed in intermediate plagioclase during subsolidus annealing.

Intermediate plagioclase is characterized by satellite reflections which express a long-range superstructure (Cole *et al.*, 1951). This structure has been described in plutonic and metamorphic andesines and labradorites. Diffuse satellites have also been observed in rapidly cooled volcanic labradorite (Wenk, 1966). Thus the intermediate plagioclase superstructure exists both in rocks which recrystallized below 650°C and cooled slowly and in others which were quenched from temperatures close to the melting point of plagioclase. This raises the question whether the superstructure forms during growth or is the result of subsolidus ordering. With that in mind we decided to do long-period heating experiments of crystals which had a poorly established superstructure.

Material and experimental procedure

Among various crystals of different labradorite specimens which were used in the heating experiments, large clear phenocrysts from Surtsey, Iceland (Steinthorsson, 1965; H. R. Wenk, 1966), which were quenched during the ash eruption of the volcano in 1963, showed the most interesting results. An content is 66 percent (H. R. Wenk *et al.*, in preparation), optical properties are those of high plagioclase (E. Wenk *et al.*, 1964). Crystals show highly diffuse *e* satellites in positions typical of strong satellites in plutonic and metamorphic crystals and weak and diffuse *c* reflections streaked parallel to b^* (Fig. 1b). The refinement of the average structure in space group $C\bar{1}$ from X-ray and neutron diffraction data shows that Al and Si are mostly disordered (Joswig *et al.*, 1976). The $\langle T_1(O)–O \rangle$ distance is slightly longer (1.681 A) than the other $\langle T–O \rangle$ distances (1.662 A).

Crystal fragments (0.1–1.0 mm) were dry-heated at 1200°C in air in a standard furnace for two months. Other fragments of the same material were hydrothermally annealed for 50 days at 870°C and 2 kbar in a cold-seal pressure vessel with externally controlled pressure. The sample was sealed in a gold capsule with a small amount of water.

Crystals were then analyzed with the X-ray precession method. We are aware that this technique has its drawbacks because satellites are not exactly in the plane of the photograph, but we found it most convenient to document changes during heating. Application of a graphite monochromator improved the peak-to-background ratio dramatically and allowed

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us to image diffuse and weak reflections clearly (compare Fig. 1a with Fig. 1b). The exposure time had to be increased by about one-third over beta-filtered radiation. The same crystal—a sphere of 0.7 mm in diameter—was analyzed before heat treatment and after hydrothermal annealing at 870°C, thus permitting an unambiguous comparison of the X-ray patterns. This was necessary to document the subtle changes.

The results are quickly summarized. No changes were observed after heating at 1200°C for 2 months in air. Both *e* and *c* reflections were still present and equally diffuse. This is in agreement with Gay and Bown (1956), who showed that *e* reflections in calcic plagioclase disappeared only after heating for very long periods close to the melting point. But after hydrothermal annealing at 870°C for 50 days, diffuse satellites (*e* reflections) became sharper and changed their position. Additionally, in reciprocal lattice positions typical of strong *b* reflections in anorthite (Rainey and Wenk, 1978) sharp *b* reflections appeared (compare Fig. 1b with Fig. 1c). Diffuse *c* reflections did not change and were very persistent in all types of heat treatments.

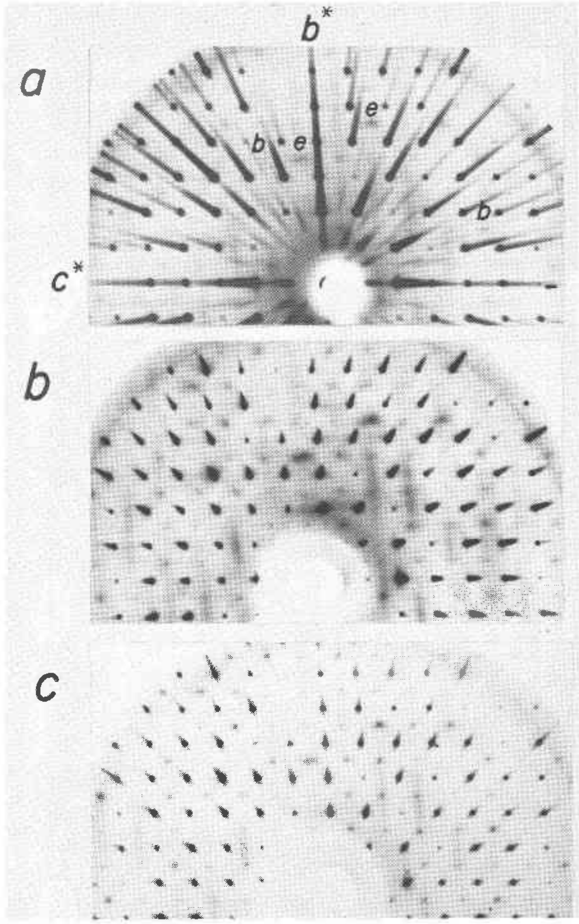

Fig. 1 Precession 0*kl* photographs of a sphere of Surtsey labradorite (Mo-radiation). Some strong *e* and *b* reflections are indicated in (a).

(a) Before heat treatment; Zr-filter, 5-day exposure.

(b) Before heat treatment; graphite monochromator, 5-day exposure. Notice the elimination of continuous radiation and improvement in peak-to-background ratio compared to (a).

(c) Same sphere after heating at 870°C and 8 kbar for 50 days; monochromator, 4-day exposure. Notice that on this photograph with weaker *a* reflections subsidiary *e* and *b* reflections are stronger and sharper.

Discussion

The most significant aspect of the experiments is the possibility of *ordering* a high-temperature structure in calcic plagioclase at subsolidus conditions. Diffuse satellites indicative of small irregular domains became sharper, *i.e.* domains attained a better periodicity. The integrated intensity of satellite reflections before and after annealing is more difficult to assess, but it appears that it became stronger, which suggests that the atomic distribution giving rise to the superstructure is more highly ordered. The satellite vector $\vec{t}$, which is difficult to measure accurately because of considerable diffuseness, changed orientation from $01\bar{3}$ to $01\bar{2}$ (measured in 0*kl* sections) and got shorter (Fig. 2a and b, from $1/30\ A^{-1}$ to $1/42\ A^{-1}$), thus the superstructure wavelength was enhanced. The change in orientation observed in this An 66 volcanic labradorite during heating corresponds to a change in composition from An 50 to An 65 in plutonic plagioclase, according to Bown and Gay's (1958) measurements. [The satellite vector $\vec{t}$ connects two satellites in a pair. $|\vec{t}|$ is the distance between two satellites and measured in reciprocal Angstroms. $T = 1/|\vec{t}|$ is the spacing of fringes in TEM micrographs imaged with a pair of *e* reflections and measured in Angstroms, *cf.* Smith 1974, p. 152. The wavelength of the superstructure is $2 \cdot T$, *e.g.* Korekawa, 1967]. It is not uncommon in spinodally decomposing metals to find an increase in wavelength during annealing (*e.g.* Wu and Thomas, 1977), and we anticipate that the intermediate structure forms by a similar mechanism. Because of the complicated structure of plagioclase, governed by both Ca/Na and Al/Si distribution, decompositional ordering does not result in a simple phase separation as in metals but rather in a complex superstructure with antiphase relationships. Also changes in wavelength may not be continuous and proceed to completion but become "locked" in a

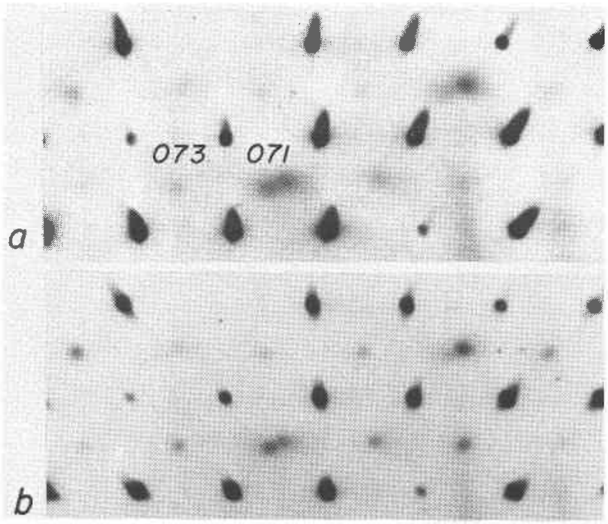

Fig. 2 Enlarged portions of Figs. 1b and c. 073 is a typical *b* reflection which increased in intensity after heat treatment. 071 is a pair of strong *e* satellites which became sharper (the separation can clearly be seen) and spacing and orientation have changed.

crystallographically favorable periodic superstructure (compare the discussion of Jagodzinski and Korekawa, 1976). Periodic APB's give rise to translational symmetries which are expressed as systematic extinctions in the satellites (Korekawa, 1967). Kitamura and Morimoto's (1977) model with albite and anorthite layers stacked in an antiphase relationship conforms with such a decomposition mechanism. Diffuse *c* reflections streaking parallel to b^*, observed in Surtsey labradorite both before and after heat treatment, are suggestive of narrow "anorthite-like" lamellae approximately parallel to (010).

We have shown that the intermediate structure can be produced by ordering of a high-temperature phase and are inclined to accept that it may always be the result of structural decomposition and not of growth, both in the volcanic crystal from Surtsey which was quenched from around 1200°C and also in metamorphic plagioclase which crystallized below 650°C (E. Wenk and H. R. Wenk, 1977, H. R. Wenk, 1977).

During annealing at 870°C we also observe appearance of sharp *b* reflections (Fig. 2b), which agrees with electron diffraction evidence of McConnell (1974). The cause of this may be development of domains with $I\bar{1}$ structure though at this point TEM evidence is lacking. After annealing, Surtsey labradorite resembles labradorite phenocrysts from lava flows at Plush (Lake County, Oregon) of equal chemical composition but with sharp *b* reflections (Stewart *et al.*, 1966) and closely spaced and diffuse *e* satellites (Rainey and Wenk, 1978).

The successful ordering of volcanic intermediate plagioclase has opened a wide field to experimentally study the kinetics of the ordering mechanism and the influence of time, temperature, and composition on the geometry of this complicated superstructure. We are pursuing this but thought it worthwhile to report briefly these preliminary results, which may be important in ongoing discussions of the actual atomic arrangement in intermediate plagioclase (Kitamura and Morimoto, 1977, Korekawa and Horst, 1974, Toman and Frueh, 1976).

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