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Changes in the domain structure of anorthites induced by heating

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With 3 figures and 2 tables in the text

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Abstract: The effects of heat-treatment on domains in natural anorthites was studied by means of high voltage (650 kV) transmission electron microscopy. No significant change in texture and diffraction contrast of the *c*-domains was observed in anorthite (An 94.5) heated at 500 and 600° C for 7 days and then quenched or slowly cooled down, but *c*-domains could not be observed in samples heated at 1200° C for 7 days or at 1430° C for 1/2 hour and subsequently quenched.

Heating of anorthite specimens (An 97 and An 100) inside of the electron microscope with a hot stage up to about 575° C showed that the diffraction contrast of the *c*-antiphase domain boundaries disappears at temperatures above 200—250° C. It reappears, however, after cooling and there is no change in position, shape and size of the antiphase domain boundaries. These observations strongly suggest that the antiphase domain structure as observed at room temperature is not affected by the processes at 200—250° C but controlled by the pattern of structural disorder formed at much higher temperatures.

Electron irradiation of heated anorthite caused structural disorder.

Key words: Electron microscopy, high temperature, antiphase domains, anorthite.

Introduction

Recent transmission electron microscopic studies of the feldspars bytownite and anorthite have revealed antiphase domains up to several μ in size which were separated by antiphase domain boundaries (CHRISTIE et al., 1971; CZANK et al., 1972; HEUER et al., 1972; LALLY et al., 1972; MÜLLER et al., 1972, 1973; WENK et al., 1972). While such domains were the first time directly seen in the transmission electron microscope, X-ray crystallographers had postulated their presence years ago (LAVES & GOLDSMITH, 1954; GOLDSMITH & LAVES, 1955; MEGAW, 1962). We abstain from giving complete satisfaction to the literature and refer the reader to references listed in the above-mentioned papers and to the review on structural studies of plagioclase feldspars by SMITH & RIBBE (1969). Our study is part of a research program to investigate the domain structure of anorthite and to evaluate its use as an indicator for the geological history of rocks. In our previous work, we discussed structural variations in natural anorthites and related them to their geological history (MÜLLER et al., 1972; WENK et al., 1972). Presently, we report on electron microscopic results from heating experiments of well-defined natural anorthites.

Two different types of antiphase domains and their corresponding antiphase domain boundaries may occur in anorthite: Type *b* ones which can be imaged by *b*-reflections ($h + k$ odd, ℓ odd) and type *c* ones which can be imaged by type *c*-reflections ($h + k$ even, ℓ odd). As will be discussed in detail in a separate publication (MÜLLER et al., 1973), the antiphase vector of the *b*-antiphase domain boundaries is $1/2\ [a + b]$ and that of the *c*-antiphase domain boundaries is $1/2[a + b + c]$. The latter vector was predicted from X-ray work (cf. LAVES & GOLDSMITH, 1955; RIBBE & COLVILLE, 1968) and a preliminary electron microscopic determination has already been published (MÜLLER et al., 1972).

In the present paper, we are concerned with the *c*-domains. The structural variations in anorthite are best revealed in reciprocal space by the intensity and diffuseness of the *c*-reflections and in direct space in the presence, size and shape of the *c*-domains. The structural interpretation of the observations on the basis of atomic coordinates will be attempted later along with a quantitative analysis of X-ray data.

Material and experiments

The heating experiments have been done with three natural anorthites which showed little zoning according to microprobe analyses. Tab. 1 gives some parameters of these specimens.

Grass Valley anorthite occurs as intenseley twinned crystals in an anorthosite on the western border of the Sierra Nevada batholite in California. The crystals are partly decomposed to sericite but there are sufficiently large areas of unaltered material. The *c*-domains range in size from a few hundred to about 2000 Å (Fig. 1 a). The usually elongated domains can be imaged in the electron microscope in dark field using *c*-reflections but were also observed under corresponding bright field conditions. Electron diffraction patterns (Fig. 1 b) show very slightly diffuse *c*-reflections as can be seen in the original plates.

The structure of the Pasmeda anorthite has recently been refined by WAINWRIGHT & STARKEY (1971). The large size of the *c*-antiphase domains (up to several μ) point to the high anorthite content and to slow cooling (Fig. 2 a and 3 a). The *c*-reflections are sharp.

Tab. 1. Starting material used in the heating experiments.

Locality	Geological occurrence (rock type)	Chemical composition	*c*-reflections	*c*-domains (size)
Grass Valley[1] (Calif. Sierra Nevada)	plutonic (anorthosite)	An 94.5	slightly diffuse	500—2000 Å
Schiesone[2] (Bergell Alps, N-Italy)	regional metamorphic (calcsilicate rock)	An 97	sharp	up to several μ
Pasmeda[3] (Predazzo, N-Italy)	contact metamorphic (marble)	An 100	sharp	up to several μ

[1] LAVES & GOLDSMITH (1954), GAY (1953)
[2] MÜLLER et al. (1972)
[3] WAINWRIGHT & STARKEY (1971)

Schiesone anorthite has similar characteristics as the anorthite from Pasmeda. Electron micrographs of the large *c*-domains have been shown previously (MÜLLER et al., 1972).

The contrast responsible for the visibility of *c*-domains in Grass Valley anorthite is thought to be partly due to differences in crystal structure. The *c*-domains which shine up bright in dark field possess a (relatively) ordered structure which gives rise to *c*-reflections ("primitive anorthite"). Those areas which remain dark do less or do not contribute to the *c*-reflections and have a structure mainly of the "body-centered" type. Fig. 1 which shows *c*-domains in the anorthite from Grass Valley may be compared with the antiphase domains in the anorthite from Pasmeda (Fig. 2 a and 3 a). In this case, all domains have long range order, i.e. the "primitive anorthite" structure, and are separated by antiphase domain boundaries.

Heating experiments have been done at high (1200° C) and intermediate temperatures (500—600° C) for the duration of one week or longer. After the experiment, the specimens (2—5 mm in size) were quenched in water. The high temperature heating was done in an atmospheric furnace, the intermediate and lower temperature annealing was done in bombs at 1 kb pressure dry and with water. One heating experiment was done at 1430° C in an Argon atmosphere for half an hour; the specimen has been subsequently airquenched. Other heating experiments up to 575° C were done directly in the electron microscope in order to observe immediate changes during heating. Some experimental details will be given along with the description of the results.

Suitably thin specimens for the transmission electron microscope were prepared by the ion-thinning technique (cf. BARBER, 1970). The preparation conditions were: Ar-beam, accelerated by 5—6 keV, 1—1.3 μAmp/mm^2 beam current; 15—20° angle tilt of the specimen against the ion beams. The specimens were coated with carbon and then studied with a high voltage (650 kV) electron microscope of the type Hitachi HU 650.

Results

Changes produced by heating outside of the electron microscope

The starting material for these experiments was the anorthite from Grass Valley. The results of the electron microscopic study are summarized in Tab. 2.

Tab. 2. Electron microscopic observations of heat-treated Grass Valley anorthite.

Heat treatment	Result
1430° C 1/2 hour	No *c*-domains observed; *c*-reflections very diffuse and weak
1200° C 7 days	No *c*-domain observed *c*-reflections very diffuse
1200° C; 7 days 500° C; 7 days	lamellar domains, 150 Å in width, visible in dark field with *c*-reflections operating; *c*-reflections diffuse
500° C; 7 days	No significant change compared to the untreated sample
500° C; 7 days 1 kb, hydrothermal conditions	No significant change
600° C, 7 days; cooled down in steps of 100° C/day; 1 kb, hydrothermal conditions	No significant change

1430° C: The anorthite heat-treated at this temperature for 1/2 hour and subsequently air-quenched to room temperature showed very weak and diffuse *c*-reflections (Fig. 1 d). No *c*- nor *b*-domains were observed in the electron microscope.

1200° C: After heating the anorthite for one week at 1200° C under atmospheric conditions and then quenching it to room temperature the *c*-reflections became very diffuse. No *c*- nor *b*-domains were observed.

500 and 600° C: Heating of the samples at these temperatures under dry and hydrothermal conditions and quenching them to room temperature or cooling down in steps did not produce any significant change in the domain structure (Fig. 1 c).

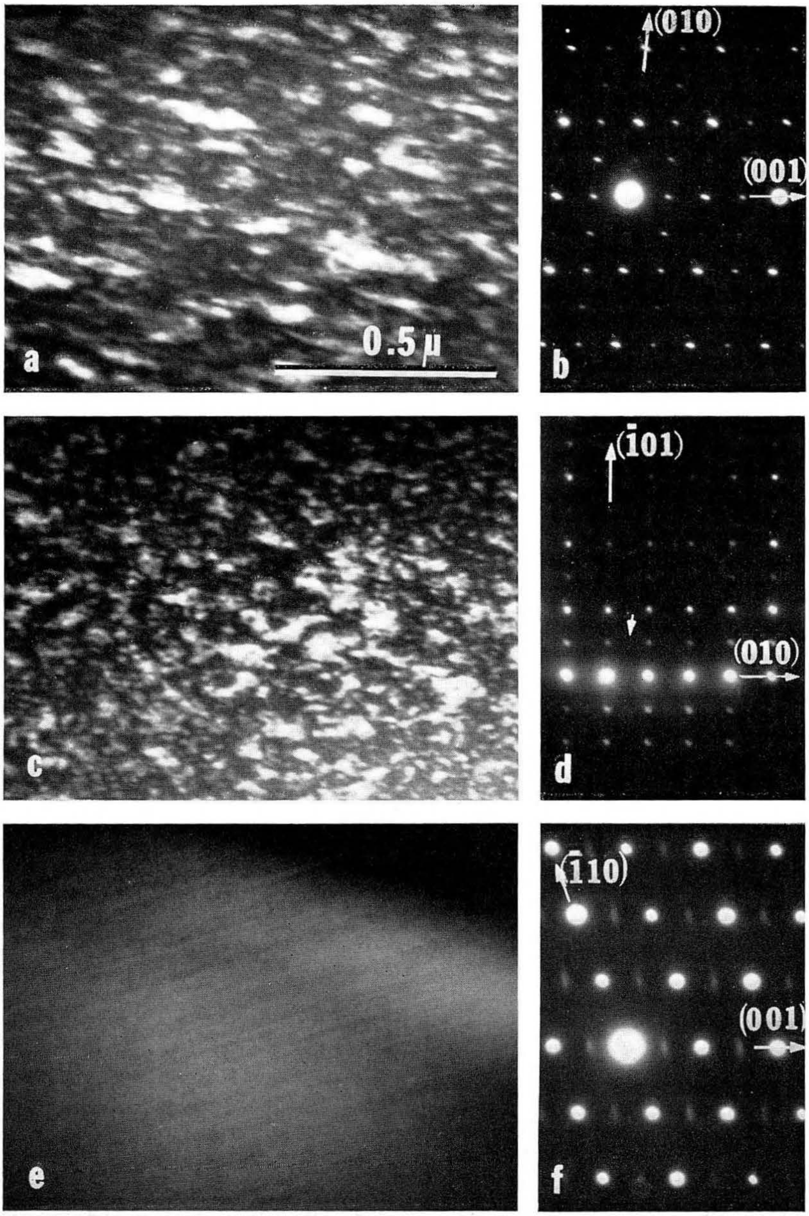

Fig. 1. Grass Valley anorthite. Dark field electron micrographs and electron diffraction patterns. (a) *c*-domains in anorthite not heat-treated. (b) Selected area electron diffraction pattern of the area shown in (a). (c) *c*-domains in anorthite

1200, 500° C: Disordering of the anorthite at high temperatures and subsequent annealing at intermediate temperatures produced diffuse and elongated *c*-ueflections and a fine barely resolvable lamellar domain structure which could only be imaged with *c*-reflections (Fig. 1 e and f). It appears to be the beginning stage of formation of *c*-domains but its exact nature is not yet clear. The diffraction pattern (degree of diffuseness of the *c*-reflections) seems to be intermediate between the anorthite from lunar basalt 14310 and the Miyake anorthite (Fig. 3 a and b in MÜLLER et al., 1972).

Changes produced by heating inside of the electron microscope

Heat-treatments of anorthite foils inside of the electron microscope up to 575° C were performed using a hot stage which could be tilted up to 10° and rotated. The samples studied were the anorthite from Schiesone and from Pasmeda (see Tab. 1). Both anorthites exhibit long range ordered domains up to several μ in size and sharp *c*-reflections. Heating of the anorthite foils causes an increasing diffuseness and elongation in the electron diffraction pattern until they nearly disappear at about 200—300° C. This observation agrees with X-ray results of BROWN et al. (1963), FOIT & PEACOR (1967), and LAVES et al. (1970). No *c*-antiphase domain boundaries could be imaged at temperatures higher than about 200—250° C. After cooling the *c*-reflections reappear and the antiphase domain boundaries are again observable. Preliminary experiments indicated that electron irradiation of heated anorthite causes radiation damage (see also LALLY et al., 1972). In order to be able to separate possible heating effects from radiation damage, we did not irradiate some areas at all during heating and studied them only at room temperature before and after heating. The detailed study of heating effects in a foil of Pasmeda anorthite is particularly interesting and we describe the results in the following paragraphs.

a) Anorthite not irradiated during heating

A set of heating experiments to 275, 330, 400, 500, 575, 375, and 375° C was carried out. At every given temperature the sample was heated for 10 minutes and cooled to room temperature before the next heating step was taken. The heat-treatments did not produce any change in position, shape and size of the antiphase domains as can be seen in Fig. 2 where the

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heated at 500° C for 7 days. (d) Anorthite heated at 1430° C for 1/2 hour. The arrow points to the *c*-reflection ($\bar{1}11$). (e) *c*-domains (?) in anorthite heated at 1200° C for 7 days and annealed at 500° C for 7 days. (f) Selected area electron diffraction pattern of the area shown in (e). All dark field electron micrographs were imaged with *c*-reflections operating. (a, b, e, f): 300 kV acceleration voltage; (c, d): 650 kV.

same area before and after heating up to 575° C is shown. No radiation damage was observed. LALLY et al. (1972) found that the domain structure in anorthite (An 94—96) from lunar sample 15415 after cooling from 400° C was similar in scale to the initial one but there was no evidence for the preservation of the shape. CZANK et al. (1972) heated anorthite (An 97.6) from Monte Somma, Vesuvius, to different temperatures with the electron beam current and found that the size of the *c*-domains decreases with rising temperatures and becomes larger with falling temperatures. These results are difficult to compare with those obtained by us, because in the experiments of CZANK et al. (1972) the heating temperatures are not well known; they may have been much higher than in our experiments.

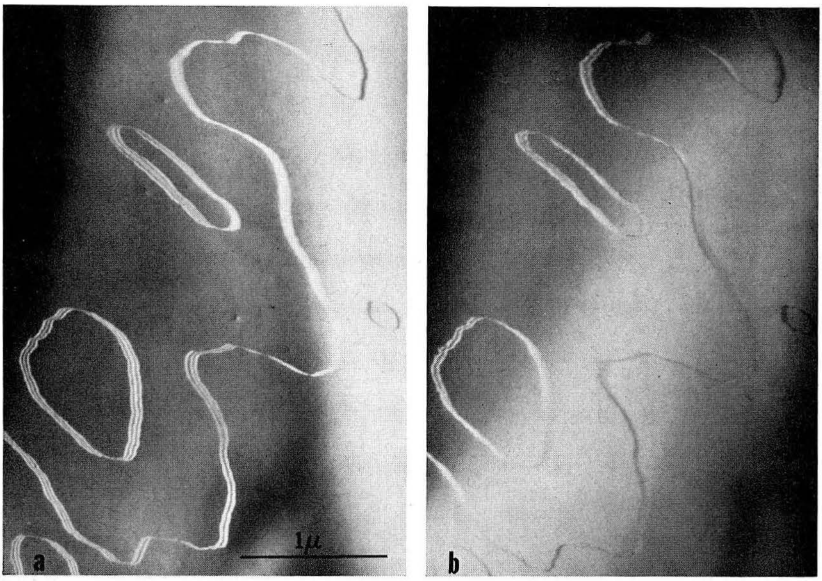

Fig. 2. Pasmeda anorthite. Dark field electron micrographs of *c*-antiphase domain boundaries imaged with *c*-reflections operating. (a) Before heating. (b) Same area as in (a); after heating up to 575° C for 10 minutes. See text. 650 kV acceleration voltage.

b) Anorthite irradiated during heating

Irradiation of the specimen by the electron beam during heating to temperatures higher than about 250 to 300° C caused radiation damage. After cooling diffuse and little dark patches (about 100 to 400 Å in diameter) appeared in dark field micrographs taken with *c*-reflections (Fig. 3). They were out of contrast using *a*-reflections (h + k even, l even). Therefore, these areas are disordered regions in a fairly long-range ordered structure

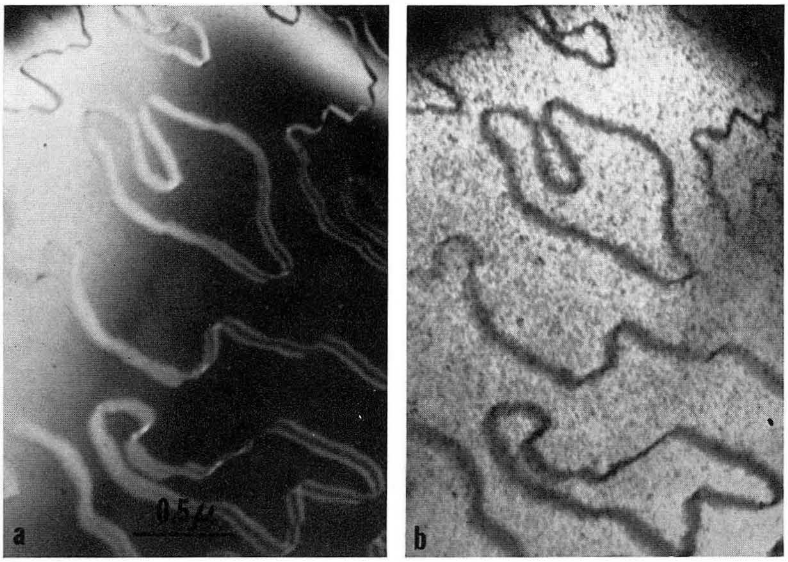

Fig. 3. Electron radiation damage in anorthite. Same foil as in Fig. 2. (a) Not irradiated during heating. (b) Irradiated with the electron beam during heating up to 375° C. The micrograph was taken at room temperature. Note the little dark patches of disordered anorthite. — Dark field micrographs imaged with *c*-reflections operating. 650 kV.

with the initial antiphase domain boundaries still present. No dark field images with *b*-reflections have been obtained, because with the limited tilting capability of the hot stage no suitable crystallographic zone was reached. The electron radiation damage as described occurred after about 5 minutes of observation of the heated anorthite; the condenser aperture was inserted. In another area of the same anorthite foil the antiphase domain boundaries were completely destroyed after about 10 minutes of irradiation. Similar results were obtained in experiments with a foil from anorthite from Schiesone.

Conclusions

The electron microscopic observations on anorthite samples heat-treated outside of the electron microscope are consistent with the X-ray results of Laves & Goldsmith (1954). Heating of Grass Valley anorthite (An 94.5) to high temperatures (1200° C for 7 days and 1430° C for ½ hour) produced a structural state which gives rise to very diffuse and weak *c*-reflections; no *c*-domains have been observed. These heat-treatments obviously cause a degree of structural disorder which is incompatible with the formation of sufficiently large and ordered *c*-domains which can be revealed by means of electron microscopy. May be the Al/Si distribution which is probably partially disordered under these conditions is an important factor for the formation of *c*-domains.

A series of heating experiments in situ up to about 575° C on anorthite from Schiesone and Pasmeda (An 97 and An 100, resp.) showed that at temperatures above about 200—250° C the *c*-reflections become very weak and diffuse and accordingly the antiphase domain boundaries become invisible and apparently disappear. Yet, upon cooling the *c*-antiphase domain boundaries are seen again exactly at the same position in the same shape and size as before. It is clear, therefore, that the antiphase domain structure at room temperature is not affected by the processes taking place around 200—250° C but controlled by structural changes which occur at much higher temperatures and which are not influenced by heating to a few hundred ° C.

Note added in proof: Prof. Dr. F. LAVES kindly informed us that M. CZANK, J. VAN LANDUYT, H. SCHULZ, F. LAVES & S. AMELINCKX have submitted a paper entitled "Electron microscopic study of the structural changes as a function of temperature in anorthite" to. Z. Kristallogr. We refer the reader also to the paper "Temperature dependence of domains in anorthite" by the same authors which appeared very recently in Naturwiss. **52**, 646 (1972).

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