

## Superstructure variation in metamorphic intermediate plagioclase

HANS-RUDOLF WENK

Department of Geology and Geophysics, University of California  
Berkeley, California 94720

### Abstract

It has long been known that the wavelength of the intermediate plagioclase superstructure changes as a function of chemical composition. This paper documents a similar change with metamorphic grade in plagioclase An 25 to An 70 in regionally-metamorphosed rocks from the Central Alps. The wavelength of the superstructure in An 65 labradorite decreases from 70A in high-grade amphibolite ( $\sim 850^\circ\text{C}$ ) to 25A in medium amphibolite facies ( $\sim 600^\circ\text{C}$ ), and the orientation changes from  $(01\bar{1})$  to  $(10\bar{3})$ . This is interpreted as further evidence of an origin of this conspicuous structure by a continuous ordering mechanism.

### Introduction

Intermediate plagioclase (An 30 to An 70) has a long-range ordered periodic superstructure which accommodates the two different Al/Si ordering arrangements of albite and anorthite. This superstructure is expressed by satellites symmetrical about positions of  $a$  reflections ( $f$  satellites) and  $b$  reflections ( $e$  satellites) in the diffraction pattern. While  $e$  satellites are observed over the whole range of intermediate plagioclase,  $f$  satellites are confined to the calcic part of the series. Gay (1956) and Bown and Gay (1958) have established a relationship between the orientation and spacing of  $e$  satellites and chemical composition. They found that the orientation of the satellite vector  $\mathbf{t}$  changes from normal to  $(10\bar{3})$  to  $(01\bar{1})$  and  $T$  increases from 30 to 70A as the composition changes from andesine to calcic laboradorite. (The reciprocal vector  $\mathbf{t}$  connects two  $e$  satellites in a pair.  $1/|\mathbf{t}| = T$  is the spacing of a periodic structure corresponding to the distance between two satellites.) Recently Grove (1977) and Slimming (1976) have made similar observations on samples from anorthosites and other igneous rocks.

The first suggestions for a more complicated relationship emerged when E. Wenk *et al.* (1975) described an andesine-labradorite intergrowth from amphibolite-facies metamorphic rocks in which An 66 had  $e$  satellites with spacing and orientation typical of plutonic andesine. They first thought that this different orientation was due to the intergrowth, and that the andesine enforced its superstructure on the labradorite. Since then many more crystals of meta-

morphic intermediate plagioclase have been analyzed, and a regular influence of metamorphic grade on the geometry of the intermediate plagioclase superstructure has been documented.

### Material and experimental techniques

All samples (Table 1) are from regionally-metamorphosed rocks in the Central Alps. In this region metamorphic grade ranges from greenschist to high amphibolite facies with anatexis and granitization in the high grade Bergell Alps (*e.g.* H. R. Wenk *et al.*, 1977) and is well established by the study of mineral assemblages (*e.g.* E. Wenk, 1970). Metamorphic grade increased with temperature, accompanied by a moderate increase in pressure. Labradorite crystallized over the temperature range 500–900°C. Figure 1 shows the geographic distribution of the specimens and indicates the region (C) in which plagioclase more calcic than albite ( $>\text{An } 10$ ) crystallized during the Tertiary Alpine metamorphism. Figure 1 also shows the field (B) in which mobilization of migmatites and pegmatites occurred, and the region (A) where temperatures were sufficiently high to produce extensive granitization. Textural and geochemical evidence precludes substantial retrograde recrystallization or superposition of several metamorphic episodes. Therefore sample series collected at the same locality which contains plagioclases of different chemical compositions are interpreted to have crystallized nearly simultaneously (compare, for example, the study of the banded gneisses from Val Carecchio by E. Wenk and H. R. Wenk, 1977). Plagioclases in

Table 1. Analyzed samples of metamorphic plagioclase, ordered with increasing An

Collection number	Locality	Rock	Composition mole% An	Metamorphic grade (Fig.1)	Characterization of satellites $\bar{I}$ in Å
1. Vz 743a	P. Barone	leucocratic gneiss	15-20	C	no satellites
2. Vz 419c	V. Osola	biotite schist	17-23	B	no satellites
3. Vz 593l	V. Carecchio	leucocratic gneiss	23	B	very diffuse
4. Sci 849	Plan Canin	granite	23	A	no satellites
5. Vz 593f	V. Carecchio	garnet-kyanite-biotite schist	29	B	very diffuse
6. Sci 579a	Sciora	granite	28	A	no satellites
7. Sci 949	Sciora	granite	30	A	diffuse (21)
8. Sci 954	P. Badile	granite	30	A	20.7
9. Blen 37	Sosto	marble	30-35	C	very diffuse
10. Vz 316	S. Bartolomeo	biotite-hornblende gneiss	30-32	B	diffuse (25)
11. Vz 530	V. Porta	biotite-hornblende gneiss	30-39	B	28-30
12. Vz 746b	V. Carecchio	calcsilicate	33	B	no satellites
13. Trem 12	Airolo	calcareous schist	35	C	diffuse
14. PK 834	A. Rovina	amphibolite	40 (38-45)	B	30, strong
15. Sci 1399	Filorera	tonalite	41	A	25-30
16. Sci 1014	A. Sivigia	hypersthene-amphibolite	45-50	A	30-35
17. Sci 714	Bagni Masino	tonalite	46	A	36-40
18. Sci 1379	Lizol	amphibolite	47	B	28.0
19. HP 472	Frasco	marble	65	C	25-30
20. Vz 433	Gordemo	calcsilicate	66	C	26.7
21. Vz 746b	V. Carecchio	calcsilicate	66	B	34.0
22. Vz 491b	V. Osola	garnet-hornblende gneiss	66-70	B	b + diffuse c
23. Vz 660	Bre-Monteggia	diopside-marble	66	B	35-40, strong
24. Spl 43f	A. Dorca	calcite mylonite	66	C	35-40
25. Sci 974	V. Sissone	amphibolite	65	A	51.4
26. Vz 699	V. Carecchio	calcsilicate	85	B	diffuse b
27. Vz 746g	V. Carecchio	calcsilicate	90	B	b + c

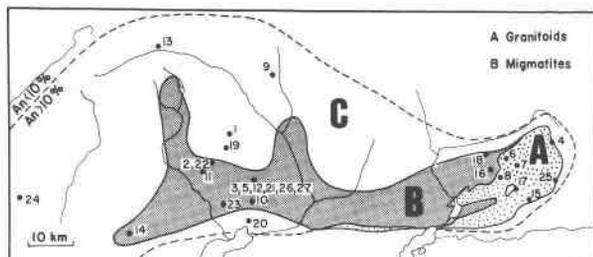


Fig. 1. Map of the Tertiary metamorphic region in the Central Alps. Indicated are sample locations (numbers refer to Table 1), distribution of migmatites (after E. Wenk, 1970) and Alpine granitic rocks, and an isograd beyond which no plagioclase with An > 10 percent crystallized during metamorphism. Region A is higher than 800°C with extensive granitization; B ranges between 600 and 800°C with mobilization of migmatites; and C is estimated between 400 and 600°C.

other suites have the same chemical composition, mainly An 30-35 and An 65-70, but occur at different metamorphic grades.

The chemical composition of each plagioclase was determined before and in some cases after the X-ray analysis, either by universal-stage analysis (applying the zone method) or by electron microprobe. Suitable crystals were then removed from thin sections for subsequent X-ray analysis.

In this survey we relied mainly on precession X-ray *0kl* photographs. Clearly this is not an ideal method for describing the geometry of irrational satellite reflections, but practical reasons for using it were the availability of instruments and the ease of orienting small fragments picked from petrographic thin sections. The satellite vector *t* is never more than 30° off

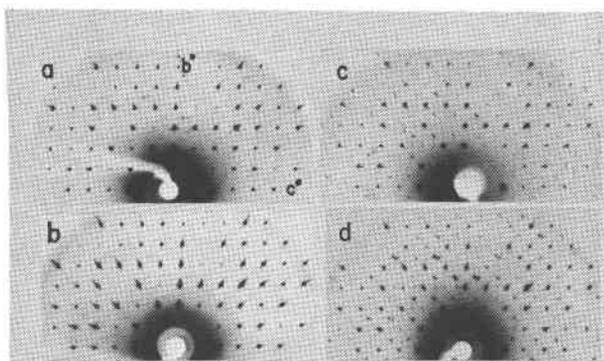


Fig. 2. Precession  $0kl$  photographs of selected intermediate plagioclases. Graphite monochromator,  $\mu = 25^\circ$  MoK $\alpha$  radiation. (a) An 30. Sample 8 from Central Bergell granite. (b) An 35. Sample 9 from medium amphibolite facies. (c) An 70. Sample 25 from high-grade contact with granite. (d) An 66. Sample 20 from medium amphibolite facies.

the  $0kl$  section, and the distance between  $e$  reflections on these photographs corresponds closely to their true spacing. Some crystals were photographed with graphite-monochromatized MoK $\alpha$  radiation, which provides excellent resolution of the weak and often diffuse reflections (H. R. Wenk, 1978a). Examples of such  $0kl$  photographs are shown in Figure 2. In many specimens small amounts of submicroscopic albite and pericline twins produced additional reflections which are easily recognized and do not interfere with satellites.

On a few selected specimens the orientation of satellites was determined accurately on a computer-controlled CAD 3 diffractometer. The procedure involves automatic centering of about 30 strong  $a$  reflections of medium  $2\theta$ -range ( $20^\circ$ – $40^\circ$ ), in order to obtain an accurate orientation matrix and angular settings which were used to obtain refined lattice

constants (Table 2). The weakness of  $e$  reflections requires the use of rather large crystals, and therefore estimated standard deviations are higher than usual. Positions of strong satellites are then determined with an automatic centering program. All diffractometer angles  $\phi$ ,  $\chi$ , and  $\theta$  are refined in two cycles using different apertures. Out of 30 attempts the program usually finds about 15  $e$  reflections, and those are used to calculate the satellite vector with an accuracy which is probably higher than that of conventional photographic techniques (Table 2).  $\theta$ - $2\theta$  scans of  $e$  satellites show fairly sharp peaks, although they are generally slightly broader than those of  $a$  reflections of comparable intensity.

## Results

Figures 2c and 2d show precession  $0kl$  photographs of two metamorphic labradorites of composition An 65–70. They both display an intermediate plagioclase superstructure with  $e$  satellites;  $f$  satellites are either absent or too weak to be visible. There is a large variation in the geometry of the superstructure in these crystals of similar chemical composition. In a sample of high metamorphic grade, Sci 974, the wavelength of the superstructure,  $T$ , is 51A, while for a medium amphibolite facies crystal, Vz 433, it is 27A. The orientation of  $t$  changes from normal to  $(01\bar{1})$  at high grade to  $(10\bar{3})$  at low grade. Similarly, in andesine An 30–35 (Figs. 2a,b) from the Tertiary Bergell granite, the spacing between satellites is 20A; in andesine associated with labradorites of 30A spacings, satellites are extremely diffuse (Fig. 2d) or missing. In a microscopically-intergrown labradorite-andesine pair, andesine shows no satellites and labradorite has  $e$  satellites with a 34A spacing; these

Table 2. Lattice constants and parameters defining the satellite vector of selected plagioclase crystals used in this study. Determinations were done with single-crystal diffractometry. Standard deviations in parentheses

	An 30 Sci 954	An 33 Vz746b <sub>2</sub>	An 47 Sci 1379	An 66 Vz 433	An 66 Vz 746b <sub>2</sub>	An 65 Sci 974
a (Å)	8.155 (3)	8.154 (2)	8.126 (3)	8.151 (3)	8.154 (4)	8.152 (4)
b (Å)	12.858 (5)	12.838 (4)	12.805 (5)	12.829 (5)	12.825 (6)	12.834 (6)
c (Å)	14.222 (5)	14.220 (4)	14.151 (5)	14.206 (7)	14.63 (9)	14.157 (8)
$\alpha$ (°)	93.66 (2)	93.64 (1)	93.60 (1)	93.62 (3)	93.47 (2)	93.49 (2)
$\beta$ (°)	116.38 (1)	116.33 (1)	116.22 (1)	116.21 (3)	116.13 (2)	116.13 (2)
$\gamma$ (°)	89.30 (2)	89.71 (1)	89.89 (1)	89.70 (2)	90.22 (2)	90.40 (2)
$\Delta h$	.103 (13)	no	.077 (7)	.080 (9)	.038 (18)	.015 (5)
$\Delta k$	.006 (32)	satellites	.040 (7)	.031 (8)	.073 (22)	.080 (7)
$\Delta l$	-.339 (17)		-.250 (9)	-.261 (10)	-.193 (23)	-.109 (11)
T (Å)	20.7 (3)		28.0 (4)	26.7 (.3)	34.0 (.7)	51.4 (1.1)

labradorites also occur as isolated crystals with the same superstructure geometry.

These observations indicate that thermal history and metamorphic grade, in addition to the chemical variation suggested by Gay (1956), have decisive influence on the geometry of the intermediate plagioclase superstructure. The relationship is illustrated in a composition-temperature diagram (Fig. 3) which shows samples and is contoured for various  $T$  values. The ordinate representing temperature is qualitatively labeled "metamorphic grade." The regions that have been suggested for homogenous and possibly stable plagioclase compositions (from E. Wenk and H. R. Wenk, 1977) are also shown. For each composition, except pure albite, there is a minimum temperature below which no metamorphic plagioclase has been found (compare experimental results in the system plagioclase-zoisite by Goldsmith, 1978). I find, in agreement with Gay (1956), that at constant temperature,  $T$  increases with increasing An content. However I also notice that for constant composition,  $T$  increases with increasing temperature.

The change in  $T$  is accompanied by a change in the orientation of  $t$ . From the few accurate determinations I have made (Table 2), it appears that with changing metamorphic grade the satellite vector  $t$  follows the same path in space as with changing chemical composition (Fig. 4). The change in  $T$  is nearly parallel to that of the lattice angle  $\gamma$  (Table 2).

At first it seemed surprising that Gay (1956) and

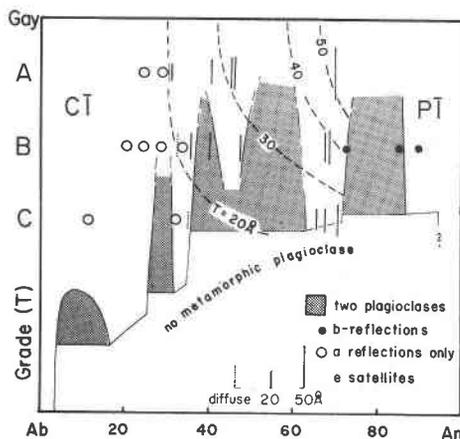


Fig. 3. Hypothetical temperature-composition diagram in which the analyzed samples are plotted. Metamorphic grade corresponds to regions in Fig. 1. Isolines show the variation of wave length of the intermediate plagioclase superstructure. At high grade the composition dependence coincides with that described by Gay (1956). Tentative miscibility gaps in metamorphic plagioclase are indicated for reference (after E. Wenk and H. R. Wenk, 1977).

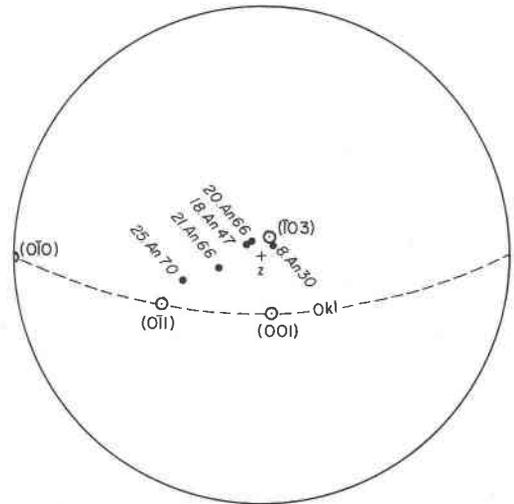


Fig. 4. Stereographic projection illustrating the direction of the satellite vector for five specimens measured on the single-crystal diffractometer. They follow the same path as that described by Gay (1956) but there is no regular variation of composition. Indices indicate poles to corresponding planes.

the numerous investigators who repeated his experiments never observed any exceptions to the established rule. On a closer look I find that most of their data points come from crystals from only a few localities, the famous schiller labradorites from Labrador, Norway, and Finland anorthosites. All of these samples and some high-grade metamorphic bytownites crystallized at high temperature (800–900°C) and display the maximum spacing  $T$  for a given composition.

### Interpretation

If two atomic species initially randomly arranged redistribute themselves over two or more atomic sites, then such ordering may start at a nucleus and proceed by growth of an ordered domain. Microstructures resulting from such an ordering mechanism are often characterized by curved antiphase boundaries (APB's), which are commonly observed in calcic plagioclase. Alternatively ordering may take place homogeneously throughout the crystals, especially at larger undercooling below the equilibrium transformation temperature. In *spinodal ordering* a site distribution is attained gradually, with slight ordering in the initial stages which becomes more enhanced as the transformation proceeds. This has been documented, for example, in the system FeCo (Grosbras *et al.*, 1976). The final product is an ordered superstructure generally with a larger unit cell. The new unit cell determines the spinodal wave-

length. In contrast to spinodal exsolution there is no variation of this wavelength with temperature and no subsequent coarsening. However, if such spinodal ordering is convoluted with a long-range modulation, which may originate from deviations from stoichiometry or the necessity to compromise between the Al/Si ordering principles in albite and anorthite, then a longer wave period will be superimposed on the short spinodal wavelength, thereby creating non-conservative periodic APB's. These are first diffuse but become more defined as the transformation proceeds. In such *continuous ordering* (de Fontaine, 1974) the spacing of APB's is, in analogy to spinodal exsolution, a function of temperature (Cahn, 1968) and, during annealing, periodic APB's will tend to annihilate by recombination rather than attain a larger wavelength by a mechanism analogous to coarsening in an exsolution system. Microstructures and diffraction patterns in  $\text{Cu}_3\text{Au}$  (Chen *et al.*, 1977) and  $\text{Ni}_3\text{Mo}$  (Van Tendeloo *et al.*, 1974) have been interpreted as the result of continuous ordering, and I think that the intermediate plagioclase superstructure formed by a similar mechanism. To my knowledge this study of metamorphic plagioclase contains the first documentation of wavelength variation of a periodic APB structure with temperature in continuous ordering.

Further evidence for continuous ordering is the presence of a high-temperature form of An 66 in volcanic rocks (e.g. Lake County, Oregon) with *b* reflections and *b* APB's. This phase is viewed as the stable superstructure forming by homogeneous or heterogeneous nucleation and growth (Rainey and Wenk, 1978; Wenk *et al.*, in preparation). Heating experiments are also in accord with such a model. During annealing of largely disordered plagioclase at 850°C, the periodic structure can be enhanced (Wenk, 1978a). Prolonged annealing of plagioclase with *e* reflections at 900°C produces a *b* structure (McConnell, 1974; and unpublished data of H. R. Wenk). This is viewed as the result of recombination of APB's. In fact I have observed in some metamorphic labradorites (by TEM) changes in superlattice fringe patterns which resemble strikingly those documented in heat-treated  $\text{Ni}_3\text{Mo}$  (Van Tendeloo *et al.*, 1974), with periodic APB's combining and migrating out of the structure, ultimately only leaving a few stretched-out loops which correspond to *b* APB's (Fig. 8 in Wenk, 1978b). This may be the reason for the presence of *b* reflections instead of *e*'s in some metamorphic laboradorites (e.g. Vz 419b).

The superstructure of intermediate plagioclase, one

of the most common rockforming minerals, may be a useful indicator for metamorphic grade. The easily-measured wavelength *T* changes from 20 to 70Å over the important temperature range 500°–800°C. Effects of other environmental conditions such as pressure, partial pressure of water, strain, and time are more difficult to evaluate. Among the 27 samples examined there were only two exceptions to the temperature–wavelength correlation. Both samples showed a larger wavelength than expected, suggesting that special conditions prevailed which facilitated decomposition. Clearly additional complications have to be considered in every case. However, in the Alpine samples examined, temperature emerged as the most critical factor affecting the spacing of satellite reflections.

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