A PARABOLIC HOURGLASS STRUCTURE IN TITANAUGITE

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Abstract

The titanaugite phenocrysts of a 5.5 m-thick fourchite sill near Ste. Dorothée, Quebec, display a well developed hourglass structure in which the surface separating the (010) from the (100) sector is a parabolic cylinder. The combination of the diffusion controlled growth of (010) and the phase-boundary reaction controlled growth of (100) could produce an hourglass feature of this type.

Introduction

The origin of hourglass features in various minerals has been the subject of considerable discussion recently. The sector zoning of staurolites, for example, has been carefully described by Hollister and Bence (1967) and Hollister (1970), and the hourglass feature of certain augites by Preston (1966) and Strong (1969). These studies have been mainly concerned with the nature and cause of the compositional differences between sectors. The present paper, however, ignores this aspect of hourglass structures and concentrates instead on their shape. In particular, an attempt is made to interpret a parabolic hourglass structure that has been found in certain titanaugites in terms of the growth-controlling mechanisms of different crystal faces.

The Hourglass Structure of Titanaugites from the Ste. Dorothée Sill

An unusual variety of hourglass structure is well developed in the titanaugite phenocrysts of a 5.5 meter thick fourchite sill near Ste. Dorothée, Quebec (the sill has been described by Howard 1922 and, more recently, by Philpotts and Hodgson 1968). In (001) sections through these crystals the boundaries between the (100) sectors and the adjacent (010) sectors are approximately parabolic. The noses of these parabolas are in most sections truncated by the (001) sector volumes (Fig. 1). The sectors are readily distinguished from one another by slight differences in their extinction properties. The position of the sector boundaries were carefully measured with an eyepiece net micrometer in a section of a crystal that was approximately parallel to (001) (see Fig. 2a). In this crystal the (010)–(100) sector boundary can be shown to be precisely parabolic (Fig. 2b). The symmetry axes of the parabola (Fig. 2a) are however slightly skewed with respect to the trace of the (010) face. These features would suggest that the three-dimensional form of the surface
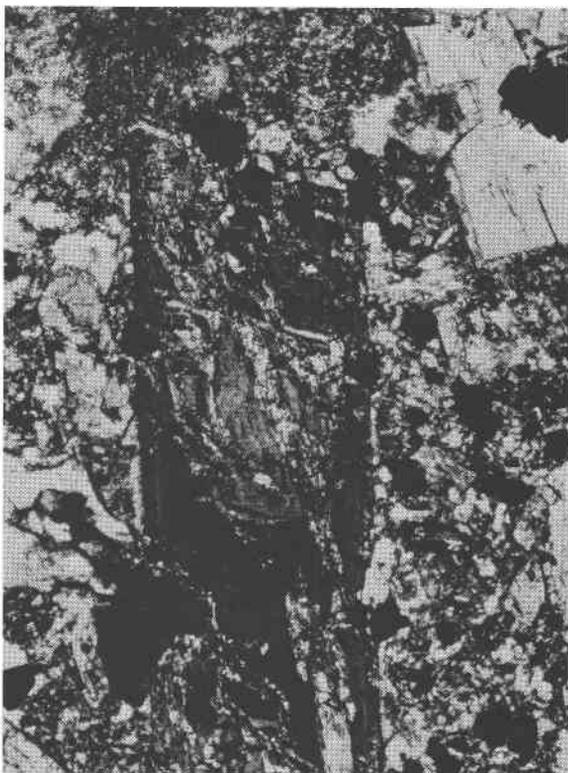
Fig. 1. Photomicrograph of a (001) section through a titanaugite crystal from the Ste. Dorothée sill showing an approximately parabolic hourglass structure.

separating the (010) and (100) sectors is a parabolic cylinder rather than a paraboloid of revolution.

The sector boundaries in the Ste. Dorothée titanaugite phenocrysts also coincide with the loci of intersections of the oscillatory zoning in adjacent sectors (Fig. 1). Since the individual oscillatory zones are continuous around each crystal, the surfaces separating the (010) and the (100) sectors must represent the locus of the (010)–(100) edge positions during growth. The fact that this surface is parabolic would suggest that the relative growth rates of the (010) and (100) faces varied systematically as the crystal grew. The way in which this might possibly have occurred is examined in the following sections.

KINETICS OF CRYSTAL GROWTH

In order that a crystal grow, material must be transported from the surroundings, rearranged to conform to the crystal structure, and even-
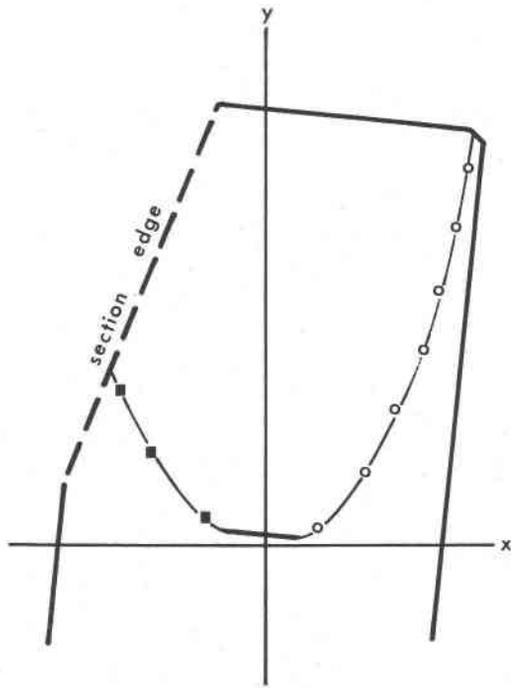
(a)
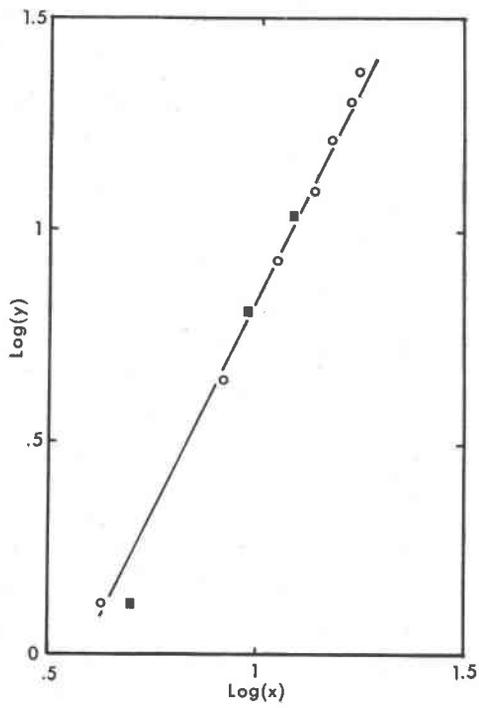
(b)

tually precipitated onto a surface. The growth rate of the crystal will thus be limited by the rate of the slowest step in this complex sequence of events. The limiting process may, of course, be different on each face. Processes that can be rate-controlling have been thoroughly discussed by Nielsen (1964), Kahlweit (1965), and Brice (1967) and are thus only briefly reviewed here. In the following discussion the directions perpendicular to (100), (010) and (001) are defined as x, y and z respectively.

i) *Diffusion Control. At high values of supersaturation, $\bar{c}$, diffusion is* probably the dominant growth-controlling process providing it is the only operating transport mechanism. The growth rate, dx/dt, of a (100) face when diffusion controlled is (Nielsen 1964)

$$\frac{dx}{dt} \propto \bar{c}t^{-1/2} \tag{1}$$

where t is time. The distortion of the diffusion field at the edges and corners of the face is ignored by this equation but if surface diffusion is capable of rapidly redistributing material over the surface it may still be valid.

ii) *Surface Nucleation Control.* If the growth of a (100) face is limited by the rate of surface nucleation, or any other process which is dependent upon the surface area of the face, Nielsen (1964) has shown that

$$\frac{dx}{dt} \propto \bar{c}^p yz \tag{2}$$

where p is a constant related to the concentration dependence of the process and yz is, of course, proportional to the surface area of the face. iii) *Dislocation Growth Control.* At very low levels of supersaturation the growth of the (010) face may be limited by the rate at which spiral dislocations can grow. For this mechanism Nielsen (1964) obtained

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FIG. 2. The parabolic form of the hourglass structure in a Ste. Dorothée titanaugite crystal. In (a) the best parabola is drawn through the points that were measured on the (010)-(100) sector junction of a titanaugite crystal in thin section (this crystal is not the one illustrated in Fig. 1). These same data are plotted in (b) on a log(x) versus log(y) graph (x and y being the axes of the parabola in (a)). The slope of the line drawn through these points is 2.0 indicating the accuracy of the parabolic fit.

$$\frac{dx}{dt} \propto \bar{c}^2 \tag{3}$$

iv) *Phase Boundary Reaction Control*. In addition to the processes considered by Nielsen (1964), Kahlweit (1965) examined the possibility that an interface reaction involving the rearrangement of material prior to precipitation may control the growth rate of a crystal. For a first order phase-boundary reaction he deduced that

$$\frac{dx}{dt} \propto \bar{c} \tag{4}$$

Other growth controlling mechanisms are also possible but their kinetic expressions are much more complex.

Model Hourglass Structures

The hourglass features that could develop in a simple model of a crystal can be deduced by examining the growth kinetics of the whole crystal when various growth-controlling processes are operating on its faces. For example, if the growth of its (100) face is limited by the rate of a phase-boundary reaction, (010) by surface nucleation, and (001) by diffusion, the growth of the crystal must simultaneously satisfy

$$\frac{dx}{dt} = k_x\bar{c} \qquad \text{(reaction controlled growth)}$$

$$\frac{dy}{dt} = k_y\bar{c}^p xz \qquad \text{(surface nucleation controlled growth)} \tag{5}$$

$$\frac{dz}{dt} = k_z\bar{c}t^{-1/2} \qquad \text{(diffusion controlled growth)}$$

where k_x, k_y and k_z are constants.

The surfaces separating the sectors must therefore be

$$x = \frac{k_x}{4k_z^2\bar{c}}\, z^2 \qquad \text{between the (100) and (001) sectors}$$

$$y = \frac{4k_yk_z\bar{c}^{(p-1/2)}}{5k_x^{3/2}}\, x^{5/2} \qquad \text{between the (010) and (100) sectors}$$

$$y = \frac{k_yk_x\bar{c}^{(p-3)}}{40k_z^4}\, z^5 \qquad \text{between the (010) and (001) sectors}$$

provided the supersaturation $\bar{c}$ is constant throughout growth. The form

of the hourglass structure for other combinations of the growth-controlling mechanisms of the faces can be similarly derived.

In most observed hourglass features the surfaces separating the various sectors are planes. These planar sector boundaries could be the result of the growth on each face being limited by the same mechanism—either diffusion, dislocation growth, or a phase boundary reaction. The parabolic form of the hourglass structure in the Ste. Dorothée titanaugite can however be explained by this simple model only if the growth of its (100) faces was either dislocation growth or phase-boundary reaction controlled and the growth of its (010) faces diffusion controlled (cf. eq. (5)).

Kastner and Waldbaum (1968) have described an hourglass feature of some authigenic albites in which the surfaces separating the (010) and (001) sectors are hyperbolic cylinders. This type of hourglass structure would be expected if the growth of both its (001) and (010) faces were limited by the rate of surface nucleation. If

$$\frac{dy}{dt} = k_y xz \qquad \text{(surface nucleation control on (010))}$$

$$\frac{dz}{dt} = k_z xy \qquad \text{(surface nucleation control on (001))}$$

(6)

we have

$$\frac{dy}{dz} = \frac{k_y}{k_z} \frac{z}{y}$$

which is the equation of a hyperbolic cylinder if surface nucleation is not growth controlling on both faces until the size of the crystal is y_o, z_o.

$$i.e. \quad k_z y^2 - k_y z^2 = k_z y_0{}^2 - k_y z_0{}^2 \tag{7}$$

In certain cases the variation of the supersaturation during the growth of a crystal may play an important role in determining the shape of its hourglass structure. For example, if the growth of one face is controlled by a phase boundary reaction and an adjacent face is dislocation growth controlled the surface separating their respective sectors must satisfy

$$\frac{dx}{dy} = \frac{k_x}{k_y} \bar{c} \tag{8}$$

If however, the growth of both faces are dislocation growth controlled the sector boundary should remain planar during growth since $\bar{c}$ is not involved in the expression for dx/dy.

A growth-inhibiting impurity that is preferentially absorbed by one face could also change the shape of the hourglass structure. However, except in extremely fortuitous circumstances this mechanism does not seem to be capable of producing accurately parabolic or hyperbolic sector boundary surfaces.

Conclusions

The model of hourglass features developed here is admittedly extremely oversimplified and certainly the validity of the kinetics assumed for the various growth mechanisms can be questioned. Nonetheless, it does offer an explanation for the unusual hourglass features found in the Ste. Dorothée titanaugites and in the authigenic albites described by Kastner and Waldbaum (1968) as well as the more common planar type hourglass structure. There are perhaps other explanations for the shape of hourglass features and one purpose of this note is to stimulate the search for them.

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