

## OSCILLATORY ZONING IN MINERALS: A COMMON PHENOMENON

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### ABSTRACT

Crystals characterized by oscillatory zoning show evidence for a quasi-cyclic alternation in the chemical composition of discrete growth-shells from tens of nanometers to tens of micrometers in thickness. Oscillatory zoning is most commonly observed and studied in crystals of magmatic plagioclase, but sensitive imaging techniques (*e.g.*, Nomarski interference contrast microscopy, cathodoluminescence, back-scattered electron imaging, X-ray topographs) reveal its presence in many other minerals. Through the application of these techniques and an exhaustive review of the literature, oscillatory zoning is shown to occur in at least 75 rock-forming and accessory minerals comprising most major mineral classes: silicates (hydrous and anhydrous), sulfides, oxides, halides, carbonates, phosphates, and sulfates. Such mineral zoning is a common but often well-concealed phenomenon in magmatic rocks (particularly alkaline ones), hydrothermally altered rocks, mineralized rocks, and carbonate sequences. Mechanisms of oscillatory zoning are discussed, including the less-studied effects of adsorption and elastic stress in near-surface growth-layers. Its "non-equilibrium chemistry" makes oscillatory zoning a rich subject for further research.

*Keywords:* oscillatory zoning, growth banding, crystal growth, nonlinear dynamics, Nomarski interference microscopy.

### SOMMAIRE

Les cristaux zonés de façon oscillatoire résultent d'une alternation quasi-cyclique en composition chimique d'enveloppes de croissance distinctes, dont l'épaisseur varie de dizaines de nanomètres à des dizaines de micromètres. Le phénomène est le plus couramment observé et étudié dans les cristaux de plagioclase magmatique, mais il est aussi développé dans plusieurs autres espèces, comme en témoignent les techniques sensibles de microscopie par contraste d'interférence Nomarski, cathodoluminescence, répartition des électrons rétrodiffusés, et images topographiques des rayons X. L'application de ces techniques et un bilan complet de la littérature montrent que la zonation oscillatoire a été documentée pour au moins 75 minéraux principaux et accessoires des roches, y inclus des silicates (hydratés ou non), sulfures, oxydes, halogénures, carbonates, phosphates et sulfates. Une zonation oscillatoire est courante dans les roches magmatiques, mais elle peut être cryptique, surtout dans les roches alcalines, les roches affectées par une altération hydrothermale, les roches des gîtes minéraux et les séquences de carbonates. Nous revoyons les mécanismes de zonation oscillatoire, et faisons allusion aux rôles de l'adsorption et de la déformation élastique dans les couches de croissances près de la surface, facteurs qui sont moins bien étudiés. Les écarts de la composition à l'équilibre font de la zonation oscillatoire un riche sujet de recherche.

(Traduit par la Rédaction)

*Mots-clés:* zonation oscillatoire, couche de croissance, croissance cristalline, dynamique non linéaire, microscopie à interférence Nomarski.

### INTRODUCTION

Minerals characterized by oscillatory zoning contain multiple compositionally varying growth-shells (layers, if viewed in cross-section) that are generally

parallel to crystallographic planes of low Miller indices and have thicknesses ranging from tens of nanometers to several tens of micrometers. Although the term "oscillatory" is used, the fluctuations in zone thickness and composition need not be regular or harmonic. The concentration of inclusions, dislocations, and possibly point defects also may vary across and between growth-layers. The zoning in magmatic plagioclase is a common phenomenon, so much so that publications on the subject date back over a century (Rutley 1875,

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Herz 1892, Harloff 1927, Phemister 1934). Its occurrence in other minerals (*e.g.*, nepheline, augite, zircon) has been known for nearly as long. However, few textbooks in mineralogy treat the topic in any detail.

We have used back-scattered electron (BSE) imaging, X-ray element maps, cathodoluminescence (CL), and Nomarski interference-contrast (NIC) microscopy to study various minerals, and we review the large number of published observations of oscillatory zoning. As will be shown, oscillatory zoning visible using the above techniques is typically not visible using standard petrographic or routine microbeam analytical techniques. Oscillatory zoning is considerably more common than may generally be realized (Table 1). In our opinion, its occurrence in many different minerals implies that a generalized

small-scale growth mechanism(s) is responsible, and that theoretical work has focused too narrowly upon plagioclase–melt systems.

## OBSERVATIONS IN MINERALS SHOWING OSCILLATORY ZONING

### Methods of observation

Table 1 documents the presence of oscillatory zoning in numerous minerals. The data consist of published observations of investigators who have used various techniques (optical microscopy, CL, NIC, BSE, transmission electron microscopy, X-ray topography, and ion, electron, or X-ray microprobes), plus our own optical, NIC, BSE, and microprobe

TABLE 1. MINERALS SHOWING OSCILLATORY ZONING

Elements	Phosphates	Inosilicates
Diamond C(3)	Apatite N(1) O(2) C(3) B(27) X(49)	Aegirine O(26)
Arsenic N(4)	Monazite O(41) B(41)	Aemigmatite O(6)
	Plumbogummite B(31)	Arfvedsonite O(41) B(41)
<b>Sulfides, sulfosalts</b>	Xenotime B(22)	Augite O(2) N(7) B(14)
		Clinoenstatite O(40)
Arsenopyrite N(4)	<b>Halides</b>	Combelte O(1)
Galena N(4)	Fluorite O(2) C(3)	Diopside–hedenbergite O(2) N(7)
Pyrite (incl. bravoite var.) N(4)	Halite O(2)	Jadeite B(30)
Safflorite N(4)		Kaersuite N(1) O(1)
Skutterudite N(4)	<b>Tungstates</b>	Magnesianomilitende–actinolite B(33)
Sphalerite N(4) O(2) C(3)	Ferberite–huebnerite O(5)	Pargasite N(1) O(1)
Tetrahedrite–tennantite N(4)	Scheelite–powellite O(5)	Richterite O(41) B(41)
		Spodumene X(39)
<b>Oxides, hydroxides</b>		Tremolite C(3)
Baddeleyite C(3)	<b>Nesosilicates</b>	<b>Phyllosilicates</b>
Böhmite O(47)	Andradite–grossular O(2) C(3) B(18)	Biotite O(23)
Cassiterite N(4) O(2) C(3)	Olivine N(7) C(42)	Lepidolite C(3)
Chromite (course zoning) B(8)	Titanite C(3) B(19)	Muscovite O(17)
Columbite–tantallite B(34)	Topaz C(3)	Phlogopite O(2) B(24)
Corundum O(2) C(3)	Zircon N(10) O(2) C(3) B(9) M(11)	Prehnite B(12)
Magnetite N(4)		
Perovskite O(28)	<b>Sorosilicates</b>	<b>Tectosilicates</b>
Pyrochlore–microlite O(2) B(15)	Åkermanite N(1) O(2)	"Adularia" C(46)
Rutile O(2)	Allanite O(2) B(25)	Anorthoclase M(32)
<b>Carbonates</b>	Epidote O(6) B(14)	Brewsterite–(Ba) B(29)
Ankerite B(20)	Eudialyte O(6)	Nepheline N(1) O(2) C(3)
Calcite N(1) C(3)	Vesuvianite B(43) O(1)	Orthoclase N(44)
Dolomite C(3)	Wöhlerite C(48)	Plagioclase N(16) O(2)
Gregoryite O(35)	Zoisite O(2)	Quartz C(3) M(45)
Magnesite B(21) C(50)	<b>Cyclosilicates</b>	Sandine O(13)
Siderite O(1) B(1)	Beryl O(12) C(3) X(38)	Sodalite O(2)
<b>Sulfates</b>	Tourmaline O(2) C(3)	
Anhydrite C(3)		
Barite O(2) C(3)		
Celestine C(36) M(36)		

*Methods of observation:* O: optical microscopy, C: cathodoluminescence, B: back-scattered electron imaging, M: electron or ion microprobe, N: Nomarski interference contrast, reflected-light microscopy, or chemical staining of etched minerals, X: X-ray topography.

*References:* 1 This study, 2 Phillips & Griffen (1981), 3 Marshall (1988), 4 Ramdohr (1980), 5 Falache *et al.* (1944), 6 Deer *et al.* (1986), 7 Clark *et al.* (1986), 8 Allan *et al.* (1988), 9 Paterson *et al.* (1992), 10 Pidgeon (1992), 11 Chakoumakos *et al.* (1987), 12 Sinkankas & Read (1986), 13 Smith & Brown (1988), 14 Yardley *et al.* (1991), 15 Černý *et al.* (1992), 16 Anderson (1984), 17 Roycroft (1992), 18 Jamveit (1991), 19 Paterson & Stephens (1992), 20 Searle (1990), 21 Purvis (1989), 22 Miller *et al.* (1992), 23 Kwak (1981), 24 O'Brien *et al.* (1988), 25 Sorenson (1991), 26 Eriksson (1985), 27 Ramsbo (1989), 28 Treiman & Essene (1985), 29 Robinson & Grice (1993), 30 Ernst (1993), 31 Nickel (1981), 32 Havette & Nativel (1977), 33 Kawakatsu & Yamaguchi (1987), 34 Lathi (1987), 35 Peterson (1990), 37 Roedder (1969), 38 Graziani *et al.* (1990), 39 Authier & Zarka (1977), 40 Philpotts & Gray (1974), 41 D.D. Hogarth, pers. comm., 42 Steele (1995), 43 Groat *et al.* (1993), 44 Dickson (1994), 45 Perry *et al.* (1992), 46 Mertz *et al.* (1990), 47 Shelley *et al.* (1977), 48 Mariano & Roeder (1989), 49 Phakey & Leonard (1970), 50 Spötli (1991).

observations. We list several minerals in which oscillatory zoning either has not been previously documented (e.g., kaersutite, pargasite, siderite, and combeite), or in which NIC microscopy has not been previously used to study the fine details of such zoning (e.g., apatite, calcite, melilite, and nepheline). In total, at least 75 rock-forming or accessory minerals

comprising most major mineral classes (silicates, sulfides, oxides, halides, carbonates, phosphates, and sulfates) exhibit such zoning. It occurs in minerals from magmatic rocks, hydrothermally altered rocks, rocks in ore deposits, and carbonate sequences.

Oscillatory zoning is readily observed in plagioclase and in the clinopyroxene of alkaline rocks because these minerals commonly occur as large euhedral crystals that combine significant short-range compositional variation (i.e., growth-layers  $\sim 1\text{--}10\ \mu\text{m}$  in thickness), with compositionally sensitive optical properties. These characteristics make zoning clearly visible in the optical microscope. Oscillatory zoning in other minerals may be visible in thin section, although in many instances its detection requires optically oriented crystals in doubly polished sections and the use of a stopped-down condenser lens. Commonly, variations in the color or birefringence of minerals showing oscillatory zoning are less visible than are the schlieren-like bands that arise from small contrasts in the indices of refraction of the growth zones.

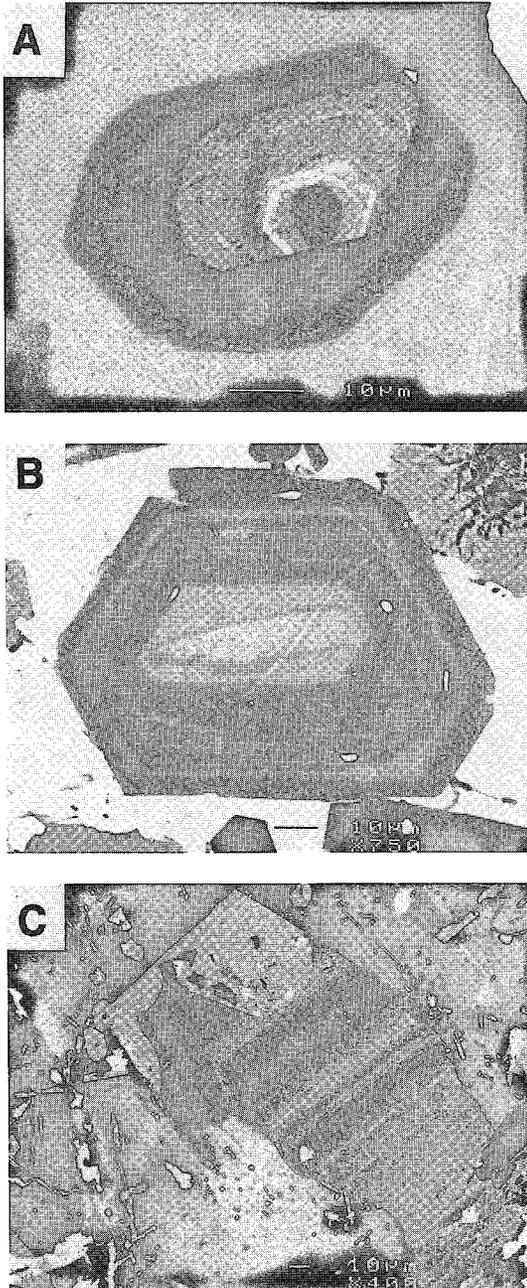


FIG. 1. Back-scattered electron photomicrographs; contrast-optimized 300-second scans on JEOL 6400 SEM equipped with JEOL solid-state detector (Carleton University). A) Oscillatory zoning in apatite crystal in syenite (pulaskite) from Mount Johnson, Quebec. The bulk rock contains 0.48 wt.%  $\text{P}_2\text{O}_5$ ,  $93 \pm 10\ \mu\text{g/g}$  La and  $199 \pm 20\ \mu\text{g/g}$  Ce. Growth zones in the apatite crystal vary from  $\leq 0.6$  wt.% (dark) to  $\sim 3.6$  wt.% combined  $\text{La}_2\text{O}_3 + \text{Ce}_2\text{O}_3$  (bright). Note the very small size of the unzoned core ( $\sim 10\ \mu\text{m}$ ), and the asymmetry between growth layers on equivalent crystal-faces. The image contrast has been optimized to enhance the zoning within the apatite. As a consequence, the grain of kaersutite enclosing the apatite crystal, which itself shows oscillatory zoning, appears black on the image (see Fig. 2E, a photomicrograph of similarly zoned crystal of kaersutite from the same specimen). A magnetite grain in the upper right corner of the frame appears white. B) Nepheline phenocryst in nephelinite, Oldoinyo Lengai, Tanzania. The contrast in mean atomic number is primarily due to variations in Fe concentration (presumably  $\text{Fe}^{3+}$  substituting for Al). Compare BSE resolution to that of NIC photomicrograph of similar crystals (Fig. 2C). C) Siderite-magnesite crystal in amygdule in a gabbroic dike, Montreal. The  $\text{Mg}/(\text{Mg} + \text{Fe})$  of the growth layers ranges from 0.55 (darkest) to 0.29 (lightest). Despite the large variation of mean atomic number in the crystal (requiring less extreme contrast than used in Fig. 1A), the contrast between the adjacent quartz, kaersutite, plagioclase and ilmenite is barely sufficient for petrographic purposes.

In other cases, CL (Marshall 1988), NIC microscopy of etched crystals (*e.g.*, Pearce & Kolisnik 1990), BSE imaging (*e.g.*, Halden & Hawthorne 1993), or X-ray topography (*e.g.*, Lang *et al.* 1991) may be required to detect zoning. Fundamentals of CL and BSE imaging are given in Marshall (1988) and Goldstein *et al.* (1992), respectively. The basic principles of X-ray topography are discussed in Lang *et al.* (1991); although extremely sensitive to dislocations and changes in unit-cell parameters, this technique is not widely used in the Earth sciences, being best suited for large, highly perfect single crystals. Nomarski interference-contrast microscopy uses optical interferometry to enhance small variations in the surface relief of a specimen. Polishing relief emphasizes grain boundaries; zoning within crystals is best brought out by etching highly polished surfaces with appropriate acid mixtures. Under ideal conditions (*i.e.*, an unscratched highly reflective near-planar surface), variations in surface relief as small as 2–10 nm may be resolved by NIC microscopy (Nomarski & Weill 1954). However, the lateral resolution is much poorer (300–500 nm).

Table 1 does not list every method that has been used to detect oscillatory zoning in a given mineral. Certain well-studied minerals (*e.g.*, zircon, apatite) have been examined with optical microscopy, Nomarski interference-contrast microscopy, back-scattered electron imaging, cathodoluminescence, electron microprobe, proton microprobe, secondary ion microprobe, X-ray topography, autoradiography, fission-track analysis, and so on. No single method is ideally suited for detecting zoning in all minerals. With back-scattered electron imaging, detector conditions must be optimized if very small differences in the mean atomic number of the mineral growth-zones are to be revealed. Such a procedure may not be compatible with routine petrographic and textural examination of specimens because the 8-bit dynamic range typical of digital images currently obtained with scanning electron microscopy (SEM) (*i.e.*, 256 shades of grey) is rarely sufficient to show zoning within a mineral and simultaneously maintain adequate contrast among the various minerals (Fig. 1). Furthermore, our experience with certain specimens of kaersutite, augite, and apatite has shown that weak zoning that is detectable by optical or NIC methods cannot be resolved even using carefully optimized operating conditions for the SEM and the detector. Clearly, potential ionic substitutions such as  ${}^{VI}\text{Fe}^{3+} + {}^{IV}\text{Al} \rightleftharpoons {}^{VI}\text{Fe}^{2+} + {}^{IV}\text{Si}$  would cause little change in the mean atomic number of a mineral.

In addition to low image-contrast in some minerals characterized by oscillatory zoning, the spatial resolution of the BSE technique may be inadequate. In electron-microprobe analysis, the minimum volume sampled is on the order of 5–10  $\mu\text{m}^3$ , a fundamental limit of resolution imposed by electron scattering and

secondary X-ray fluorescence within the sample (Goldstein *et al.* 1992). This limit applies to a point analysis, line profile, or two-dimensional X-ray map. Interferometric methods such as NIC microscopy have greater spatial resolution than the electron microprobe, but are qualitative in nature.

#### *Textures and microstructures of crystals showing oscillatory zoning*

The growth layers of crystals showing oscillatory zoning are typically parallel to crystallographic planes of low Miller indices, and commonly concentric with external margins of the crystal. This finding indicates that such crystals maintained a euhedral shape throughout much of their growth. Such zoned crystals are generally rather equant; it is considerably less common for crystals with dendritic, acicular, or highly plate-like habits to exhibit such zoning. One of the few exceptions that we have observed is plate-like Fe-rich augite microphenocrysts in certain East African nephelinites. [Tightly packed monomineralic arrays of microcrystalline fibers (*e.g.*, agate: Merino *et al.* 1995, Heaney & Davis 1995) or dendrites (*e.g.*, sphalerite: Fowler & L'Heureux 1995) can exhibit banding similar to oscillatory zoning, although their mode of growth differs from that of single crystals.] Oscillatory zoning is observed in crystals as small as a few tens of micrometers [our own observations of apatite in pulaskite from Mt. Johnson, Quebec, nepheline and clinopyroxene in nephelinite from East Africa, and plagioclase in andesite from Montserrat; see also Vance (1962) and Cashman (1992) for additional examples of plagioclase], to several centimeters in size or larger. It may be present from the center to the margin of a crystal, but oscillatory zoning in crystals with an unzoned core or a monotonically zoned outer margin is fairly common. This is best documented for plagioclase (Smith & Brown 1988), but other minerals, such as diopside phenocrysts in alkaline magmatic rocks, possess similar features (Thompson 1973, O'Brien *et al.* 1988, Simonetti *et al.* 1996). Crystals of many minerals showing oscillatory zoning (*e.g.*, plagioclase, nepheline, diopside, melilite, kaersutite) contain a rich assortment of minor structures such as sieve-textured cores, embayed faces or rounded-off corners, individual growth-layers that vary in thickness on both crystallographically equivalent and non-equivalent faces, angular "unconformities" and "cross-bedding" between layers, and multicored crystals apparently formed through syneusis (*e.g.*, Figs. 1, 2; Allègre *et al.* 1981, Anderson 1984, Pearce & Kolisnik 1990). Planar growth-layers commonly cross twin planes or incorporate vesicles or foreign crystals with little or no disruption of subsequent layering.

Many of the rocks examined show oscillatory zoning in more than one mineral. Our observations, and those of other researchers, indicate that such zoned

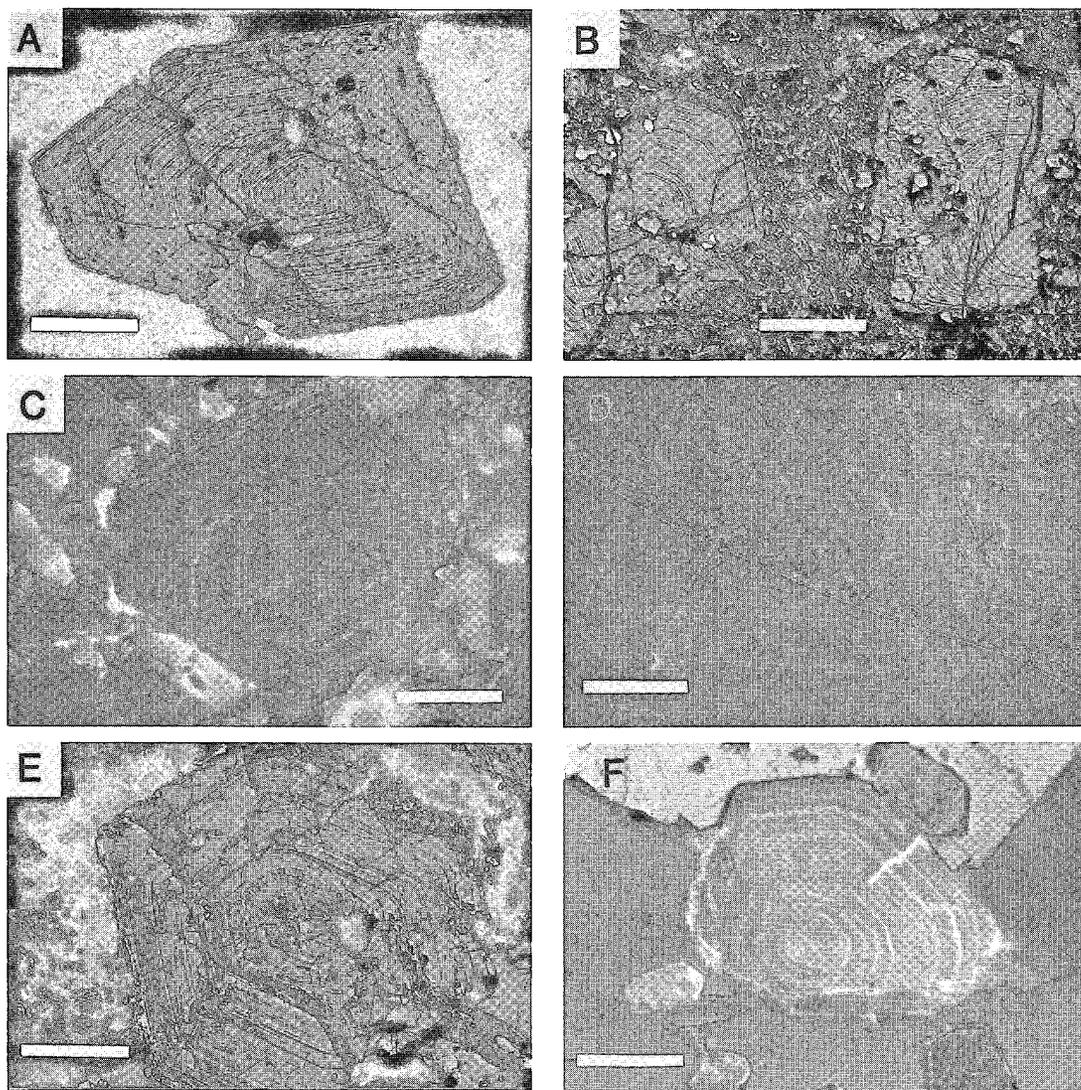


FIG. 2. Nomarski interference contrast micrographs of acid-etched crystals, showing characteristic minor features of oscillatory zoning. A) Strongly zoned crystal of diopside in leucite-bearing lava, Mt. Vesuvius. Section was etched for about 8 minutes at 20°C in a concentrated HF–HCl–citric acid mixture. On a fine scale, zoning is irregular, and many episodes of dissolution appear indicated by rounded corners, embayments, and angular unconformities. This crystal is very similar to those studied by Thompson (1973). Scale bar: 400  $\mu\text{m}$ . B) Melilite (åkermanite) crystals in nephelinite, Mt. Elgon, Uganda. Section was etched for 5 minutes at 20°C in 10% HCl. In addition to melilite, phenocrysts of nepheline and diopside in this lava also show oscillatory zoning. Scale bar: 100  $\mu\text{m}$ . C) Nepheline crystals in nephelinite, Oldoinyo Lengai (from same sample as Fig. 1B). Section was etched for 2–3 minutes at 20°C in 10% HCl. Fine details of zoning are similar to those commonly found in plagioclase. Areas of irregular or apparently unzoned growth are present. Oscillatory zoning is also developed in phenocrysts and microphenocrysts of clinopyroxene, sodalite, and combeite in this lava. Scale bar: 100  $\mu\text{m}$ . D) Detail of a different phenocryst of nepheline from same thin section as Fig. 2C. Regular zoning is sharply truncated by a dissolution surface, and subsequent growth is extremely irregular. This feature is only present in one corner of the crystal, which is  $\sim 2$  mm across. Scale bar: 40  $\mu\text{m}$ . E) Kaersutite crystal in pulaskite, Mt. Johnson. Section was etched for 8–10 minutes at 20°C in a concentrated HF–HCl–citric acid mixture. Transmitted-light microscopy reveals only broad, weak color-banding; enhanced BSE imaging did not show the growth zoning. Scale bar: 400  $\mu\text{m}$ . F) Apatite crystal from same sample of pulaskite as in Fig. 2E. Section was etched for 30 seconds at 20°C in 10% HCl. The crystal is partially enclosed in magnetite (medium grey) and subsequently overgrown by pyrite (very light grey). Asymmetrical growth of equivalent crystal faces is evident, and is likely due to growth that continued after the apatite crystal became attached to magnetite. Compare to Fig. 1A. Scale bar: 40  $\mu\text{m}$ .

minerals are particularly common in alkaline rocks. For this reason, and because pristine crystals, particularly those of easily altered minerals (*e.g.*, nepheline, melilite), are best found in fresh volcanic rocks, we examined the University of Ottawa's collection of alkaline volcanic rocks (varying from olivine nephelinite to trachyte) from the East African Rift, in addition to several samples provided by Dr. Keith Bell of Carleton University. We found that the majority (at least 31 out of 47 phenocryst-bearing lavas from eight volcanic centers) contain phenocrysts with oscillatory zoning, most commonly of diopside and nepheline. Certain of these rocks also contain other minerals with oscillatory zoning, such as apatite, titanite, melilite, sodalite, and combeite. Peterson (1989) described oscillatory zoning in phenocrysts of aegirine-augite, nepheline, and titanian andradite in highly differentiated peralkaline nephelinites from Shombole Volcano, Kenya. Intrusive rocks containing several different minerals displaying oscillatory zoning also are found. Using CL, Wenzel & Ramseyer (1992) studied oscillatory zoning in apatite, plagioclase, and K-feldspar from a diorite-to-monzonite sequence of rocks. Using optical and NIC microscopy, we observed finely zoned plagioclase, clinopyroxene, kaersutite, and apatite in syenite and alkaline gabbro from Mt. Royal and Mt. Johnson, both Monteregian complexes in Quebec. In these rocks, apatite with oscillatory zoning can be found as inclusions within magnetite, titanite, and oscillatorily zoned crystals of kaersutite. Asymmetrical growth-layers within apatite crystals indicate that oscillatory zoning continued during growth even as the apatite crystals were being enveloped by other minerals (Fig. 1A).

#### *Chemical variations in minerals displaying oscillatory zoning*

Oscillatory zoning generally does not involve unusual compositions, but rather "normal" compositions that vary over short distances. In many rock-forming silicates, oscillatory zoning involves substitution of <sup>IV</sup>Al for <sup>IV</sup>Si, plus a coupled substitution to maintain electroneutrality (*e.g.*, NaSi  $\rightleftharpoons$  CaAl in plagioclase). In pyroxenes and amphiboles, more complicated substitutions involving major and minor elements may apply (*e.g.*, Thompson 1973, Kawakatsu & Yamaguchi 1987), and in accessory minerals, substitution involving minor or trace elements may predominate. The variation in the concentration of major elements within an oscillatorily zoned mineral is strongly constrained by crystal chemistry and crystal-liquid equilibria; trace elements may show much greater variability in concentration [*e.g.*, diopside: Shimizu (1990); zircon: Chakoumakos *et al.* (1987), Halden *et al.* (1993); titanite: Paterson & Stephens (1992)]. An extreme example is provided by a crystal of diopside, in which Shimizu (1990)

measured up to 44-fold variations in the concentration of Cr.

Many observations of oscillatory zoning show that it is binary, *i.e.*, the short-range zoning varies between two stable or gradually varying compositional end-members. [The end-members may themselves be complex solid-solutions.] Ternary or higher-order zoning has rarely been reported in the literature. In the aforementioned ion-microprobe study of an aluminian diopside ("augite") phenocryst in an alkaline basalt, Shimizu (1990) detected  $\mu\text{m}$ -scale, large-amplitude antithetic variation between compatible (Cr, Sc) and moderately incompatible (Ti, V, Sr, Zr) elements. This result is consistent with electron-microprobe studies of other cases of oscillatory zoning in igneous clinopyroxenes (*e.g.*, Thompson 1973). An interesting exception is a dolomite crystal studied by Fraser *et al.* (1989), in which the concentrations of Fe, Mn, and Zn vary independently of each other. Possible reasons for this case are discussed below.

In certain minerals showing oscillatory zoning, the growth mechanism(s) was sufficiently sensitive to fractionate such geochemically similar elements as Nb and Ta, Mo and W, and Zr and Hf [*e.g.*, columbite-tantalite: Lahti (1987); powellite-scheelite: Palache *et al.* (1944); zircon: Speer (1982)]. In contrast, in other occurrences, levels of the rare-earth elements vary sympathetically with those of such geochemically distinct elements as U and Th, and nonradiogenic Pb [*e.g.*, zircon: Chakoumakos *et al.* (1987), Pidgeon (1992), Halden *et al.* (1993); titanite: Paterson & Stephens (1992)]. Because of the potential for complex multi-element substitutions, the detailed interpretation of zoning detected by BSE requires additional, element-specific micro-analytical techniques such as X-ray mapping.

#### *Form and preservation of chemical zoning*

Oscillatory zoning is commonly superposed upon longer-scale zoning, either normal (*i.e.*, the concentration of less compatible elements increases toward crystal margins) or reverse. In minerals for which detailed measurements have been made, the short-wavelength compositional zoning typically has an asymmetrical sawtooth form, with the less compatible or lower-temperature component increasing smoothly outward, followed by an abrupt return to the higher-temperature component at the start of the next layer [plagioclase: Bottinga *et al.* (1966), Pearce & Kolisnik (1990); diopside: Shimizu (1990); columbite: Lahti (1987)]. Estimates of maximum short-range variations in proportion of major elements of ~5–10 mol% in plagioclase and clinopyroxene have primarily been determined from electron-microprobe analysis in combination with an optical study (Smith & Brown 1988; Thompson 1973). Because of limitations of resolution for the micro-analytical techniques used to

date, the exact pattern of compositional variation within and between individual growth-layers in crystals showing oscillatory zoning is unclear. In a study of oscillatory and sector zoning in authigenic dolomite crystals, Reeder & Prosky (1986) used transmission electron microscopy to observe compositional layering on a scale of tens of nm. Further high-resolution studies of oscillatory zoning in minerals by TEM, analytical electron microscopy, electron energy-loss spectroscopy, or secondary-ion mass spectrometry would be useful. The precise pattern or waveform of the compositional zoning is of interest because different models predict different patterns (e.g., Allègre *et al.* 1981, Haase *et al.* 1980, Ortoleva 1990, Jamtveit 1991, L'Heureux & Fowler 1994). However, simple numerical modeling that we have carried out demonstrates that solid-state diffusion in magmatic crystals will cause zoning to relax toward a lower-amplitude, sinusoidal form, regardless of the pattern of the original zoning. Even if one assumes that zoning on such fine scales as observed by Reeder & Prosky (1986) could form in magmatic minerals, its preservation would seem unlikely. Thus the long-term thermal evolution of the system is an important factor to bear in mind for the study of oscillatory zoning, particularly in minerals of magmatic rocks.

Minerals with zoning involving homovalent substitution of low-field-strength elements such as alkalis or alkaline earths will be more susceptible to diffusive homogenization than minerals with zoning involving charge-compensated  ${}^{\text{IV}}\text{Al} \rightleftharpoons {}^{\text{IV}}\text{Si}$  or high-field-strength elements. In plagioclase, calculated rates of homogenization are slow enough that fine-scale zoning is only likely to be overprinted in large mafic intrusions (Grove *et al.* 1984). It is likely that preservation potential of oscillatory zoning varies markedly among different minerals. Zoning in certain minerals (e.g., plagioclase, clinopyroxene, zircon) is preserved even in large igneous bodies, whereas zoning in others (e.g., spinels, sulfides, olivine, alkali feldspar) appears confined to low-temperature or rapidly grown and cooled parageneses.

Exsolution, hydrothermal alteration, and strain-induced recrystallization may also overprint or eliminate fine-scale zoning. Studies of the effects of metamorphism or deformation on oscillatory zoning (e.g., Wayne & Sinha 1988, Pidgeon 1992) are few. In certain minerals, such zoning is known to survive metamorphism to the middle to upper amphibolite facies [e.g., plagioclase: Cannon (1966); zircon: Paterson *et al.* (1992); allanite: Sorensen (1991); xenotime: Miller *et al.* (1992); columbite: Černý *et al.* (1992)]. The reverse situation, *i.e.*, the development of oscillatory zoning during metamorphism, seems uncommon beyond the special cases of mineralization in skarns and hydrothermal veins. Examples of the few porphyroblastic minerals found with oscillatory zoning include jadeite in blueschist (Ernst 1993), garnet in

eclogite (Dudley 1969) and in phyllite (Anderson & Olimpio 1977), and plagioclase in medium-grade schist (Menard & Spear 1996). A common assumption of theoretical models of oscillatory zoning is that diffusion in the solid phase is negligible throughout the period of growth. This assumption is not generally true in cases of regionally metamorphosed rocks. Because of the paucity of data, such rocks will not be discussed further.

## ORIGINS OF OSCILLATORY ZONING

### *Background information*

In common with most investigators, we interpret oscillatory zoning as a primary growth-texture. The euhedral, distinctly planar nature of the compositional layers indicates that such crystals maintained a faceted morphology throughout much of their growth history, with the implication that a two-dimensional layer-spreading mechanism of growth was operative. Many observations of crystals growing at low supersaturation have shown that growth parallel to partially formed surface-layers occurs much more rapidly than growth perpendicular to such layers (e.g., Baronne 1984, Tiller 1991a, b). Thus, although Pearce (1994) cautioned that laterally continuous discrete growth-layers do not necessarily represent time-equivalent horizons, we consider it reasonable to assume that they are at least close to being time-equivalent.

A model of the origin(s) of oscillatory zoning must explain the abrupt shifts in chemical composition within and between growth-layers. The oscillations in chemical composition are seemingly incompatible with slow, near-equilibrium growth. Such compositional shifts appear to violate the second law of thermodynamics because systems cannot spontaneously reverse their growth composition to lower-entropy states, given stable conditions of growth. This situation has given rise to various physical models that rely upon cyclic wholesale changes in pressure, temperature, or bulk composition to vary the composition of the growing crystal. The interpretation of oscillatory zoning then becomes straightforward: the composition of each layer was controlled by the local (P,T,X) environment at the time of growth. Satisfactory explanations for such large-scale repetitive changes have, however, proved elusive. Many recent investigators explain the growth as being due to nonlinearities caused by coupling of growth parameters such that chemical variations spontaneously arise. Indeed, these types of systems, which are termed "chemical oscillators", are now well recognized in chemistry (Gray & Scott 1990). Theoretical models of oscillatory zoning (Sibley *et al.* 1976, Haase *et al.* 1980, Allègre *et al.* 1981, Ortoleva 1990, L'Heureux 1993, L'Heureux & Fowler 1994) have mainly focused on plagioclase, with some authors even considering it

to be a phenomenon restricted to that mineral (*e.g.*, Allègre *et al.* 1981).

The presence of inclusions, cross-bedded growth layers, resorbed surfaces, *etc.*, in crystals that have oscillatory zoning signifies that the causative mechanism is robust, because such perturbations in crystal substrates or local conditions of growth commonly have little effect on subsequent growth-layers. [This is additional evidence for a layer-spreading mechanism of growth.] From our observations of oscillatory zoning in several different minerals within the same rock, we infer that such zoning does not require exceptional physical or chemical conditions to form.

#### *Mechanisms of oscillatory zoning in magmatic minerals*

Explanations of oscillatory zoning fall into two broad genetic categories. Extrinsic mechanisms involve physical or chemical changes within the bulk system that are partially or wholly independent of local crystallization, such as crystal settling, large-scale convection, fluid mixing, reservoir replenishment, *etc.* In comparison, proposed intrinsic mechanisms link crystal growth to purely local phenomena. Primarily, these involve coupling between the rate of crystal growth and solute diffusion through the crystal–melt boundary layer. Intermittent small-scale boundary-layer convection, buildup and relaxation of elastic strain due to cell-parameter mismatch in zoned growth-layers, and cyclic “poisoning” by adsorbed growth-inhibiting ions are also mechanisms that have been mentioned in the literature.

#### *Extrinsic mechanisms (magmatic)*

Bowen (1928) suggested that crystals of plagioclase characterized by oscillatory zoning were advected throughout a convecting magma in a chamber, and differences in temperature, pressure, or chemical composition within the chamber were reflected in the composition of the plagioclase growth-layers, assumed to be in equilibrium with the local melt. This model remains widely quoted (*e.g.*, Singer *et al.* 1995). Wiebe (1968) suggested that poor correlation of zoning among crystals was due to late convective mixing of different batches of phenocrysts. Plagioclase crystals have densities relatively close to those of common silicate melts, such that their suspension and retention are feasible in convecting calc-alkaline or tholeiitic magmas. However, one would expect denser minerals (*e.g.*, zircon, titanite, pyrochlore, andradite, aegirine) to settle out rapidly, particularly in low-viscosity alkaline or carbonatitic magmas. In addition, textures suggestive of large-scale convection (*e.g.*, modal layering or preferred orientation of minerals) are commonly absent in intrusive rocks, including many in

which minerals show oscillatory zoning. Unequivocal evidence of magmatic convection (*e.g.*, direct measurements of fluctuations in flow or temperature) has not yet been obtained, such that it remains an untested (albeit physically plausible) phenomenon.

Phemister (1934) proposed that cyclic changes of dissolved volatile species (largely H<sub>2</sub>O) led to changes in the composition of the liquidus plagioclase. Although volatiles can be rapidly exsolved from magmas at low pressures, and geothermal phenomena such as geysers are commonly periodic on a short time-scale, changes in the concentration of dissolved H<sub>2</sub>O at higher pressure will be buffered by its solubility and rate of diffusive transport. The dehydration (*i.e.*, exsolution, vesiculation, and volatile loss) of a batch of magma would appear in most cases to be an irreversible process. It is also unclear how P(H<sub>2</sub>O) would significantly affect the composition of zircon, pyrochlore and titanite. As well, this explanation fails to account for occurrences of oscillatory zoning in clinopyroxene in anhydrous lunar basalt (Thompson 1973), plagioclase in (typically H<sub>2</sub>O-undersaturated) mid-ocean ridge basalt (Allègre *et al.* 1981), and minerals in pegmatites crystallized from closed-system, volatile-rich derivative liquid (Lahti 1987, Černý *et al.* 1992).

Importantly, such extrinsic models fail to explain critical observations, such as tenfold (or greater) variations in the concentration of trace elements in certain minerals, or the decoupling of geochemically similar elements in accessory minerals. The presence of oscillatory zoning in a broad range of minerals in magmatic rocks ranging from mid-ocean-ridge basalt to carbonatite implies that some form of general growth-mechanism is responsible. It has long been noted (Greenwood & McTaggart 1957, Wiebe 1968) that fine oscillatory layers in plagioclase cannot be correlated among crystals. On a slightly smaller scale, we have observed sharply different patterns of zoning in apatite crystals from Monteregean syenites, even among crystals of similar size enclosed in a single amphibole or magnetite host-crystal. This is a strong argument against a simple extrinsic mechanism of oscillatory zoning.

#### *Intrinsic mechanisms (magmatic)*

Many proposed intrinsic mechanisms invoke feedback between crystal growth and solute diffusion or surface effects as a source of nonlinearity in the crystal-growth kinetics. In essence, a growing crystal is surrounded by a (narrow) boundary layer that is depleted in growth constituents with respect to bulk liquid; the interplay of chemical diffusion, thermal diffusion, and rates of crystal growth may lead to oscillatory (or cyclic) growth-rates and patterns of chemical zoning within crystals. Although qualitative suggestions along these lines were long ago proposed

for plagioclase (Harloff 1927), zircon (Brammell & Harwood 1923), and apatite (Groves & Mourand 1929), the prevailing opinion then was that a stable steady state would rapidly establish itself, with crystal growth constrained by chemical or thermal diffusion. At any rate, the physical parameters required for such modeling (species diffusivities,  $\mu\text{m}$ -scale mineral compositions, partition coefficients, *etc.*) were poorly known, and the application of nonlinear differential equations remained unexplored until the mid-1970s. Pearce (1994) has summarized a number of recent models (Sibley *et al.* 1976, Haase *et al.* 1980, Allègre *et al.* 1981, Loomis 1982, Simakin 1983, Ghiorso 1987, Pearce 1993, Wang & Merino 1993). We refer readers to this review, but add specific comments regarding the model of Loomis (1982).

A possible consequence of a rejected-solute boundary layer around crystals [largely ignored except by Loomis (1982), who emphasized the role of rejected  $\text{H}_2\text{O}$ ], is the formation of small-scale convection currents. Generally, the rejected solute and undepleted bulk solution will have contrasting densities. The potential effects of cyclic gravity-driven separation of crystal and liquid, or depleted and bulk solution, cannot be summarily discounted: for example, convective instabilities caused by as little as 5 ppm Ag or Sn can disrupt the growth of extremely pure Pb crystals (Tiller 1991b). However, oscillatory zoning is observed in various minerals with crystal sizes as small as 10–30  $\mu\text{m}$ . The small size of such crystals, coupled with the typically slow rates of crystallization in geological systems (see below), should have allowed chemical diffusion to reduce density variations between depleted and bulk liquid to a very low level, particularly in the case of growth of accessory minerals. Therefore, we do not consider boundary-layer convection to be a particularly promising mechanism for the formation of oscillatory zoning.

Nonlinear models of oscillatory zoning not reviewed by Pearce (1994) include those of Jamtveit (1991), Wang & Merino (1992), L'Heureux (1993), and L'Heureux & Fowler (1994). L'Heureux (1993) and L'Heureux & Fowler (1994) proposed constitutional undercooling as a mechanism using experimentally determined growth-rates of plagioclase and a major component partition-coefficient modified after Lasaga (1982). Oscillatory behavior was found for geologically reasonable conditions without the need for an arbitrary term to account for dissipation in the growth equation. The mechanism is generally applicable, but requires well-characterized growth rates of minerals. [The models of Jamtveit (1991) and Wang & Merino (1992) are summarized in the next section.]

#### *Zoning in minerals grown from aqueous solution*

Many of the minerals listed in Table 1 grew from

aqueous solutions. Explanations proposed for oscillatory zoning in these crystals can also be divided into extrinsic (*e.g.*, change in solution composition, pressure, or temperature) and intrinsic mechanisms (*e.g.*, adsorption of growth inhibitors). It is difficult to isolate the causes of oscillatory zoning in minerals formed in chemically open aqueous systems. Such minerals grow from relatively dilute solutions, requiring that pore- or vein-filling fluids be exchanged or recharged many times during mineralizing episodes. Nevertheless, evidence is mounting that intrinsic mechanisms may play a significant role, particularly at the microscopic scale in carbonate and sphalerite.

#### *Extrinsic mechanisms (aqueous)*

Meyers (1974, 1978) postulated an extrinsic mechanism that relates fine-scale zoning in carbonate rocks to paleohydrogeology. Alternating cathodoluminescent and nonluminescent zones in diagenetic carbonate cements were interpreted to be due to fluctuations in the concentration of Fe and Mn. Accordingly, the bands were modeled to have formed in response to fluctuating redox conditions during meteoric diagenesis. Correlation of similar sequences of bands has led to the concept of "carbonate cement stratigraphy", wherein widely distributed bands are correlated, and interpreted to have formed as a result of bulk changes in fluid over the scale of  $10^2$ – $10^5$   $\text{km}^2$  (Meyers 1991). Correlations are made by matching "unique" aspects of samples from the same sequence or, if correlations are not unique at the fine scale, by "lumping packages of zoned sequences" (Goldstein 1991). Temporal relationships are deduced through stratigraphy, cross-cutting relationships, and oxygen isotope variations in cements.

At a detailed level, Machel & Burton (1991) proposed that concentric zoning in carbonate minerals could be divided into two types: cyclic and oscillatory. They defined cyclic zoning as a set of two or more intensities in cathodoluminescence color that occur repetitively, and characterized oscillatory zoning as a subset of cyclic zoning in which zones of two distinct intensities in color, rarely more than a few  $\mu\text{m}$  wide, oscillate. Cyclic zoning consisting of only two zones can be difficult to distinguish from oscillatory zoning, except that color intensities of the former "correspond to zones that are less regular and have dissimilar thicknesses in comparison to those of oscillatory zonation". [Machel & Burton (1991) also stated that oscillatory zoning should be avoided for correlation purposes because individual zones cannot be correlated among adjacent crystals.]

Evidence consistent with an external control of oscillatory zoning is present in other minerals of diagenetic or hydrothermal origin. For example, we noted earlier that Fraser *et al.* (1989) measured independent variations in the concentrations of Mn, Fe,

and Zn in oscillatory zoned dolomite [*cf.* the diopside crystal studied by Shimizu (1990)]. Because these divalent cations are all slightly larger (and presumably less compatible in dolomite) than Mg, correlated variations in their concentrations might be expected if an intrinsic-type mechanism of zoning had operated.

Episodic flow of fluid during hydrothermal mineralization has been postulated (Cathles & Smith 1983, Sibson 1987, Fowler & Anderson 1991, Yardley *et al.* 1991, Jamtveit *et al.* 1993), and long hiatuses may separate periods of rapid crystallization. These episodes may be responsible for coarse, cm-scale banding within Mississippi-Valley-type ore deposits, as opposed to fine-scale banding that is interpreted to be due to crystal-growth dynamics (Fowler & L'Heureux 1996). In hydrothermal vugs and veins, medium to coarse growth-bands (tens of micrometers to millimeters thick) have been correlated among separate crystals of tourmaline (Dietrich 1985), apatite (Knutson *et al.* 1985), beryl (Graziani *et al.* 1990), and prehnite and epidote (Yardley *et al.* 1991). Such minerals may well have grown in large (tens to hundreds of meters in dimension) but hydraulically continuous systems.

Geographically extensive correlations appear reasonable where applied in a very general fashion, such as where correlations involve a small number of broad growth-bands within similar-sized authigenic crystals in little-deformed sedimentary formations. The correlation of individual  $\mu\text{m}$ -scale growth-bands over distances of tens of kilometers (*e.g.*, McLimans *et al.* 1980) is much more problematic, and may be based more upon the natural tendency to seek patterns in "noisy" data than upon the presence of truly correlated growth-bands, such as would be shown by a series convolution or signal analysis (*e.g.*, Fowler & L'Heureux 1996). Moreover, it is possible that in some cases, correlations are due to phase locking of chemical oscillators (wherein chemical reactions occur synchronously over localized regions owing to feedback effects: Gray & Scott 1990) and not to external controls. Oscillatory chemical reactions do not intrinsically require large variations in fluid temperature, pressure, or composition (Gray & Scott 1990). Extremely fine, laterally continuous oscillatory zoning is present in sphalerite in many veins that show textural evidence of open-space growth, with only a limited number of discrete events (*e.g.*, brecciation or change of mineral assemblage). We have investigated sub- $\mu\text{m}$  zoning of Ag, Sn, and Sb in decimeter-thick sphalerite veins from British Columbia (studied by Beaudoin 1991). Attributing each of these tens or hundreds of thousands of layers to an event of episodic flow, such as a crack-seal cycle, may not be necessary, if one considers that similar zoning can be produced in minerals grown in isothermal gels or unstirred solutions (Reeder *et al.* 1990, Putnis *et al.* 1992).

### *Intrinsic mechanisms (aqueous)*

Reeder & Paquette (1989) showed that sector zoning in natural calcite commonly involves the elements Mg, Mn, Fe, and Sr. They replicated sector zoning in synthetic calcite, and demonstrated that incorporation of  $\text{Mn}^{2+}$  in the solution influences the relative growth-rate of different crystallographic forms. Reeder *et al.* (1990) induced oscillatory zoning in calcite from Mn-doped aqueous solutions. The zoning arose spontaneously, and from isothermal solutions wherein the chemical composition was not changed. Wang & Merino (1992) mathematically modeled the adsorption and desorption of  $\text{Mn}^{2+}$  ions in calcite growing from solution. By considering the interaction of the electrical charge of the calcite surface (controlled by pH and equilibrium involving carbonate species) with  $\text{Ca}^{2+}$  and  $\text{Mn}^{2+}$  adsorption, they obtained oscillatory behavior for certain combinations of growth parameters. The application of this mechanism to the case of magmatic minerals would be difficult.

Jamtveit (1991) proposed non-ideal solid solution between mineral end-members to explain oscillatory zoning in grossular-andradite garnet in skarns. An important point, allowing a damping term in the growth-rate equation used by the author, is that strain within growth-layers should occur owing to the different unit-cell dimensions of andradite and grossular (~5.5 % difference in volume). In a study of oscillatory zoning in synthetic barite-celestite crystals, Putnis *et al.* (1992) also noted that substantial elastic strain energy would occur owing to the significantly different unit-cell dimensions of the two solid-solution end-members (~12.7 % difference in volume). This is a general phenomenon that is readily applicable to minerals of any origin. Briefly, if the equilibrium composition (based on the P, T, X of the growth solution) of a crystallizing phase differs from that of the crystal substrate already present, then interplay between chemical potential energy and elastic strain energy could arise even in ideal solid-solutions. A necessary condition for this mechanism is that a minimal amount of crystal-liquid re-equilibration occur; in other words, the ratio of the crystal growth-rate to the rate of chemical diffusion within the near-surface layers must be large.

### IMPLICATIONS AND CONCLUSIONS

#### *Favored mechanisms of growth*

In our opinion, the great concentration of research on the albite-anorthite system has delayed investigation into a number of potentially significant mechanisms of oscillatory zoning. Plagioclase-melt systems have been intensively studied, and the effects of changing temperature,  $P(\text{H}_2\text{O})$ , and bulk or boundary-layer melt composition are well known. The

same cannot be said of chemically more complex minerals such as clinopyroxenes, amphiboles, and tourmaline. The unusually small variation (<1%) of the molar volume of plagioclase from albite to anorthite means that little elastic strain energy is associated with zoning in plagioclase, but this is not generally true of other solid-solutions. In addition, plagioclase growth can be modeled with some success by considering only the concentration of major species such as Na, Ca, Al, and Si. Thus the role of adsorbed ions of improper charge or radius, alone or in charge-coupled substitutions, has been largely neglected in numerical models of oscillatory zoning, with the exception of the work of Wang & Merino (1992). The presence of oscillatory zoning in minerals that are nearly compositionally invariant, such as quartz (Perny *et al.* 1992) or diamond (Lang *et al.* 1991), cannot be explained by fluctuating ratios of major constituent species in a boundary layer. Impurities are likely incorporated into such crystals in an organized manner more consistent with adsorption-controlled growth.

Adsorption of minor or trace constituents has been proposed as a mechanism for sector zoning in crystals grown from magmas (Dowty 1977) and aqueous solution (Reeder & Grams 1987), and may be applicable to oscillatory zoning as well. [These two types of zoning occur together in a number of minerals.] The large short-range variations in trace-element concentration in some cases of oscillatory zoning in crystals seem to require some form of disequilibrium partitioning (*e.g.*, Shimizu 1990). Adsorption is likely to be a less effective inhibitor of growth in magmas than it is in low-temperature dilute solutions or very pure melts (Baronnet 1984, Tiller 1991a), owing to both the exponential dependence on temperature of attachment and detachment kinetics (Tiller 1991a) and increased solid-solution in minerals at high temperatures. This is not to say that such effects are negligible in igneous systems. For example, Beattie (1994) used a combination of elastic theory with a simple ionic model of a crystal to successfully model equilibrium olivine-melt partition coefficients by estimating the lattice-strain energy associated with substitutional cations. The possible connection to the previously mentioned work of Jamtveit (1991) is clear. In many minerals showing oscillatory zoning, substantial short-range tensional and compressional forces must exist within growth layers. Carefully controlled experiments on semiconductor crystals of simple composition have demonstrated that short- and medium-range elastic stresses associated with differences in ionic size considerably affect the selection of incorporated species (*e.g.*, Tiller 1991a, b). A similar argument can be made for the electrostatic forces associated with adsorbed ions of incorrect charge.

In light of the variety of minerals that show oscillatory zoning and the wide range of their

conditions of formation, we suggest that such zoning, rather than being pathological (*cf.* Allègre *et al.* 1981), may be a normal result of crystal growth under certain circumstances. What those circumstances may be is presently unknown, but nature and experimental igneous petrology hold some clues. Allègre *et al.* (1981) suggested that synthetic plagioclase rarely shows oscillatory zoning because of the short duration and larger undercooling of experimental runs (compared to natural crystallization). The typical absence of such zoning in experimental charges may thus place an upper limit on growth rates of plagioclase and clinopyroxene of  $\sim 10^{-10}$  m/s. Order-of-magnitude lower limits ( $\sim 10^{-13}$  m/s) can be estimated from timescales of diffusive re-equilibration (Grove *et al.* 1984), crystal-size distributions (Cashman 1990, 1992, Resmini & Marsh 1995), heat fluxes from magma bodies (Brandeis & Jaupart 1987), and other calculations of mean residence-times of batches of magma, such as uranium decay-series disequilibria (Volpe & Hammond 1991). In qualitative terms, oscillatory zoning is favored by moderately rapid growth, on the order of  $10^{-11}$  to  $10^{-13}$  m/s for common rock-forming magmatic silicates, and proportionately less for accessory minerals of smaller size. Clearly, fewer constraints exist on the growth rates of crystals in aqueous systems.

#### *Areas of future research*

One reason for the profusion of proposed mechanisms for oscillatory zoning is that research has largely been theoretical, or concentrated on observations on plagioclase. To our knowledge, no comprehensive study of oscillatory zoning has been attempted. Such a study would ideally include the examination of natural occurrences, experimental synthesis, and theoretical modeling.

Very few of the many published observations of oscillatory zoning have been made at the important 10–100 nm scale. Properly oriented thin foils of crystals showing oscillatory zoning could give key information if studied with the transmission electron microscope combined with energy-dispersion microanalysis. Minerals of igneous origin would have to be carefully selected in order to minimize the “smearing” effect of prolonged solid-state diffusion at high temperatures; for this reason, minerals of hydrothermal origin might be more suitable for such a study.

Experimental synthesis has been perhaps the least explored approach to the study of oscillatory zoning (and is thus possibly the most promising). Very few controlled experiments have produced oscillatory zoning in minerals, exceptions being Mn-doped calcite (Reeder *et al.* 1990) and celestite–barite solid-solutions (Putnis *et al.* 1992). However, a number of other experiments have produced such zoning in non-systematic fashion [*e.g.*, spinel: Wang & McFarlane

(1968), plagioclase: Lofgren (1980), majorite garnet: Kato *et al.* (1988), phlogopite: Sun & Baronnet (1989), ruby: Hughes (1990), diamond: Lang *et al.* (1991)]. Carrying out a silicate crystallization experiment with a duration of several months or years poses numerous technical difficulties. A more practical alternative is to grow carbonate, sulfate, molybdate, tungstate, or sulfide crystals in isothermal gels or aqueous solutions doped with minor or trace levels of impurities (*e.g.*, Putnis *et al.* 1992). A battery of such experiments with different concentrations of reagent and dopants, and different growth-rates, could readily be carried out in order to investigate key factors underlying the formation of oscillatory zoning in crystals, including, one would hope, some factors also relevant to magmatic crystals.

Oscillatory zoning occurs in at least 75 different minerals, ranging in origin from phenocrysts in magmatic rocks to cements in sandstone. Further investigations are needed both to fully characterize the details of the zoning found in minerals and to understand the underlying mechanism(s) of growth. Such an understanding will be required in order to determine the significance that oscillatory zoning may have in determining the history of the host rocks.

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