Oscillatory zoning in metamorphic minerals: an indicator of infiltration metasomatism

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Abstract

Examples of oscillatory zoning in metamorphic minerals, imaged using a Back-Scattered Electron Detector on the SEM, are described from a series of contrasting environments. These are a prehnite vein sampled by drilling in the Mirvalles geothermal field, Costa Rica, a pyroxene vein developed in a regional metamorphic shear zone in the Yilgarn block, Western Australia, and a bedded metasomatic diopside rock from regionally metamorphosed metasediments in Connemara, Ireland. In each case the formation of oscillatory zoning can be ascribed to mineral growth under supersaturated conditions due to fluid infiltration. Oscillations can be related in the first example to periodic episodes of pressure release and boiling in the geothermal field, but in the regional metamorphic examples actualistic models are harder to define. The development of oscillatory zoning is likely to be a characteristic feature of infiltration metasomatism and can be used as a criterion in the recognition of metasomatic mineral growth in metamorphic rocks outside the vein environment.

KEYWORDS: zoning, metamorphic minerals, infiltration metasomatism.

Introduction

THAT extensive chemical changes, i.e. metasomatism, can accompany regional and contact metamorphism has been recognised for many years, but despite the existence of the necessary physicochemical basis for the understanding of metasomatic rocks (Korzhinsky, 1959) there is still sometimes controversy as to whether a particular group of rocks has been metasomatised. We attempt to show here that a particular class of nonequilibrium texture, oscillatory zoning, is well developed in solid solution minerals that have grown in a range of open-system environments, and suggest that it may be a diagnostic characteristic of open-system behaviour during metamorphism, acting both as an indicator for metasomatism when it is found and an argument against a metasomatic origin in rocks from which it is absent. As we shall see, a critical factor promoting the development of such zoning is that growth takes place under conditions that are removed from equilibrium, and thus the meaning of the term 'open system' in the context of this paper is a system into which a fluid is introduced which is not in chemical equilibrium with the pre-existing assemblage of phases. Recirculation of a single fluid type through material with which it is close to equilibrium is not included in this definition.

Three examples of oscillatory zoning from metamorphic settings are illustrated here. The first, in prehnite from a vein formed recently in a geothermal field that is still active, is not only from a setting where the case for open-system behaviour is unambiguous (a fracture-fill), but its setting is sufficiently well understood to permit an actualistic model for the origin of the oscillations. The second case is similarly of a vein mineral, pyroxene, but from a deep setting where the metasomatic processes are less well understood. Finally, we demonstrate similar textures from a rock that occurs as a distinct bed within a metasedimentary sequence, and show that metasomatism of the bulk rock produces similar textures to those found in veins.

Origin of oscillatory zoning in minerals

Oscillatory zoning is a widespread phenomenon which is developed in minerals from a wide range of environments, ranging from carbonate cements to igneous plagioclase or pyroxene phenocrysts. In metamorphic environments it is best known from skarn garnets and pyroxenes

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(e.g. Morgan, 1975; Kwak, 1987), but despite considerable work on the origin and significance of the phenomenon in both sediments (e.g. Meyers, 1974; Reeder *et al.*, 1990) and igneous (e.g. Bottinga *et al.*, 1966; Kirkpatrick *et al.*, 1979; Haase *et al.*, 1980; Smith and Lofgren, 1983) environments, relatively little attention has been paid to its significance in metamorphic rocks. The increasing application of sophisticated imaging techniques capable of resolving subtle chemical variations, such as cathodoluminescence microscopy (Marshall, 1988; Yardley and Lloyd, 1989; Ramseyer and Mullis, 1990) and back-scattered electron imaging on the SEM (Lloyd, 1987), to metamorphic textures will doubtless lead to many more examples being discovered.

Oscillatory zoning can be produced as a result of regular alternations in the externally controlled intensive parameters prevailing in the environment of crystal growth, but it can also be a product of geochemical self-organisation (Ortoleva *et al.*, 1987) as crystals form in a supersaturated environment. Thus if crystals grow from a melt rapidly relative to the rate at which material diffuses through the melt to the surface of the growing crystal, then, provided the melt is supersaturated, the crystal may continue to grow zones of a composition which does not represent equilibrium with the bulk of the melt (Harloff, 1927). According to Ortoleva *et al.* (1987), the essential requirements for the formation of features such as oscillatory zoning are: chemical disequilibrium, a feedback mechanism to change the reaction rate in response to the reaction that has already taken place, and some sort of noise in the system to help instigate the development of the patterning. We shall discuss actualistic mechanisms for each of the examples of zoning we describe in turn.

Zoned prehnite from the Mirvalles geothermal field, Costa Rica

Active geothermal fields are the only examples of contemporary metamorphism within the reach of drilling, and they therefore provide an invaluable source of information about metamorphic processes, despite their very different physical environments compared to most metamorphic settings. The Mirvalles field is developed on the southwest flank of the Mirvalles volcano in northwest Costa Rica. It occupies part of a caldera and the geothermal reservoir is developed within a layered sequence of andesitic lavas and tuffs with rare lacustrine sediments (Miladowski *et al.*, in prep.). Much of the deep permeability is due to fractures and several types of vein have been found in drillcore. Veins containing prehnite and epidote occur in the hotter part of the field (Rochelle *et al.*, 1989) and have been sampled in well PGM11. They occur at depths from around 970–1300 metres, but the sample studied here is from a depth of about 970 m, where the present temperature is near 250 °C.

Both prehnite and epidote display oscillatory zoning due to $Fe^{3+} = Al^{3+}$ exchange in this sample, but the zoning in prehnite is the more marked. Similar patterns of zoning of prehnite and epidote were reported by Bird *et al.* (1984) at the Cerro Prieto field in Mexico. Fig. 1 illustrates the zoning of prehnite crystals filling a vein lined with K-feldspar and quartz (see also Rochelle *et al.*, 1989). Microprobe analyses along the traverse A–B are plotted in Fig. 2. The prominent dark band, corresponding to an Fe-poor composition, can be traced as a marker through all the prehnite crystals in the vein, and matches an Fe-poor zone in coexisting epidote. Thinner dark bands also act as 'stratigraphic markers' but are less amenable to quantitative chemical analysis. Rochelle *et al.* (1989) showed that calculations utilising matched zones in epidote and prehnite from this sample yield temperatures of around 250 °C from the prehnite–epidote geothermometer of Rose and Bird (1987), irrespective of Fe-content.

Oscillatory zoning can reflect externally imposed fluctuations in intensive thermodynamic variables (P, T, f_{O_2}, etc.) in the system, or may arise purely through local disequilibrium between an individual crystal and the adjacent fluid medium. In this instance, it seems clear that the cause of the oscillations is external to the immediate vein, because all grains of both prehnite and epidote show the same zoning. The zoning therefore reflects either changes in the activity ratio:

$$a_{Fe^{3+}}/a_{Al^{3+}}$$

in the fluid phase, or changes in the distribution of Al and Fe between fluid and mineral. Since the zoning has developed approximately isothermally, the latter possibility can probably be excluded.

In the view of the setting in which these crystals grew, we propose that the oscillations reflect fluctuations in $a_{Fe^{3+}}$ in the fluid phase as a consequence of rapid changes in the redox state of the fluid. Temperature increases with depth below the water table along a curve close to the boiling curve of water in the upper part of high-T geothermal fields, such as that penetrated in well PGM11 (Rochelle, 1990). Thus periodic increases

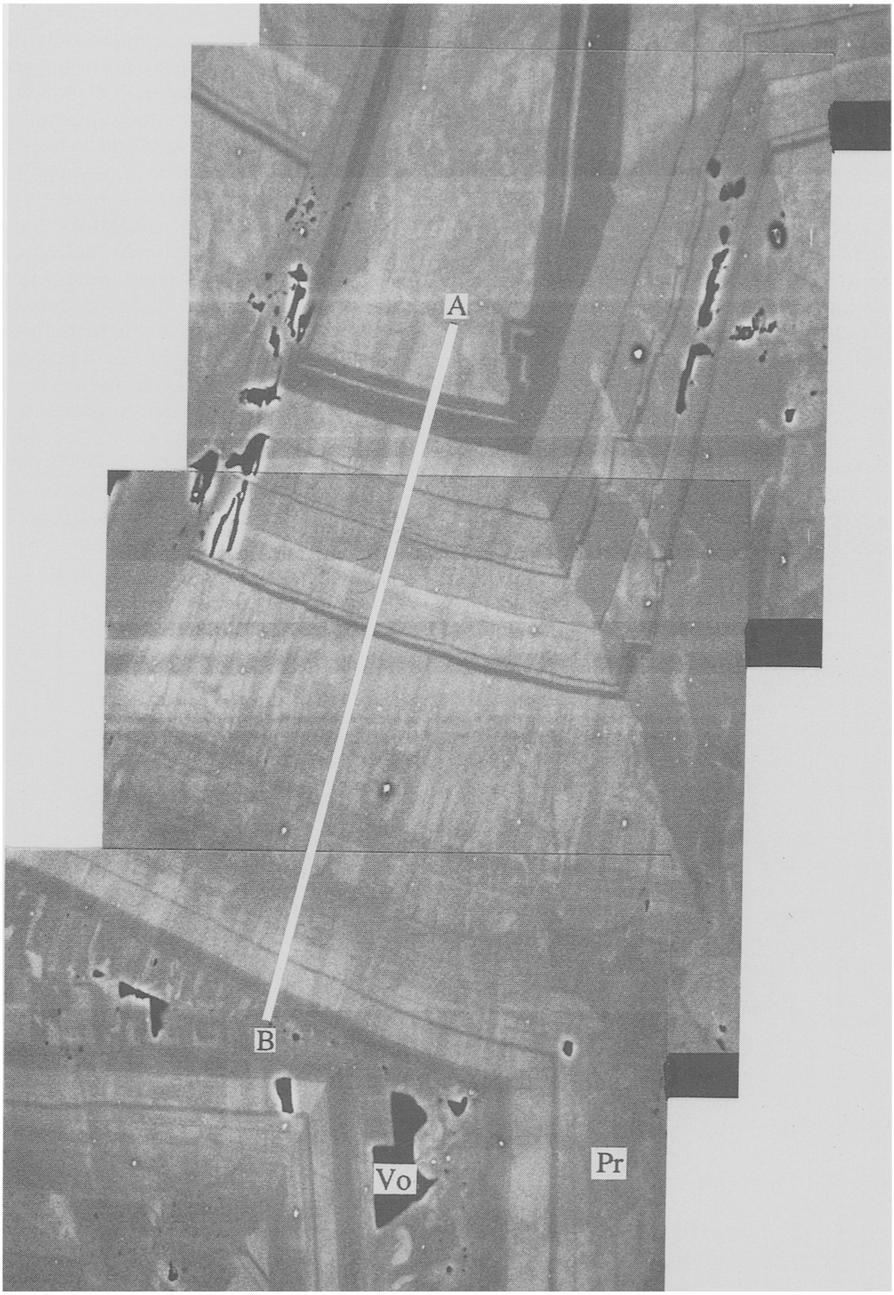

FIG. 1. Back Scattered Electron Microscope (BSEM) image of zoned prehnite (Pr), occurring in a vein at *c*. 970 m depth in well PGM11, Mirvalles geothermal field, Costa Rica. Vo denotes a void. Light bands are of higher mean atomic number (i.e. contain more Fe). A microprobe traverse along the line A–B is shown in Fig. 2.

in the amount of flashing of fluid are a common feature of geothermal areas, occurring as a response to pressure fluctuations which may be a result of hydrofracturing or linked to seismicity.

Hydrogen is very strongly partitioned into the steam phase when water boils (Giggenbach, 1980), and this must cause oxidation of the residual liquid due to dissociation of H_2O, since $f_{H_2} \gg f_{O_2}$. Once boiling has ceased, however, interaction between fluid and wall rock will tend to reduce the fluid back to an f_{O_2} value that is locally buffered by rock. Hence we interpret the Fe-rich prehnite and epidote zones as having formed from fluid that has been oxidised by boiling, while the Al-rich zones grew from a more reduced fluid that was locally buffered by Fe^{2+}-bearing silicates.

Zones pyroxenes from mineralised shear zones, Western Australia

The Yilgarn craton of Western Australia comprises a granite–greenstone terrane with high-grade gneisses in the west (see review by Barley and Groves, 1990). Greenstone belts developed in two phases at *c.* 3.0 and 2.7 Ga, and the bulk of the granitoid plutons were emplaced in the period 2.7–2.6 Ga. Metamorphism followed very soon after the extensive plutonism. The whole Yilgarn craton is dissected by numerous shear zones, with which extensive gold mineralisation is associated. While many of these shear zones and the associated vein systems are retrogressive, the mineral assemblages within them parallel the local metamorphic grade fairly closely. At higher metamorphic grades there are high-grade mineralised shear zones for which deduced metamorphic conditions are indistinguishable from those of the wall rocks. At Fraser Mine in Southern Cross (31°14′S, 119°41′E), mineralisation is confined to a suite of oblique-slip shear zones hosted in amphibolite facies ultramafic rocks. The shear zones contain numerous small (<20 mm) veins each with a narrow (<30 mm) set of alteration zones around them. The veins are of quartz,

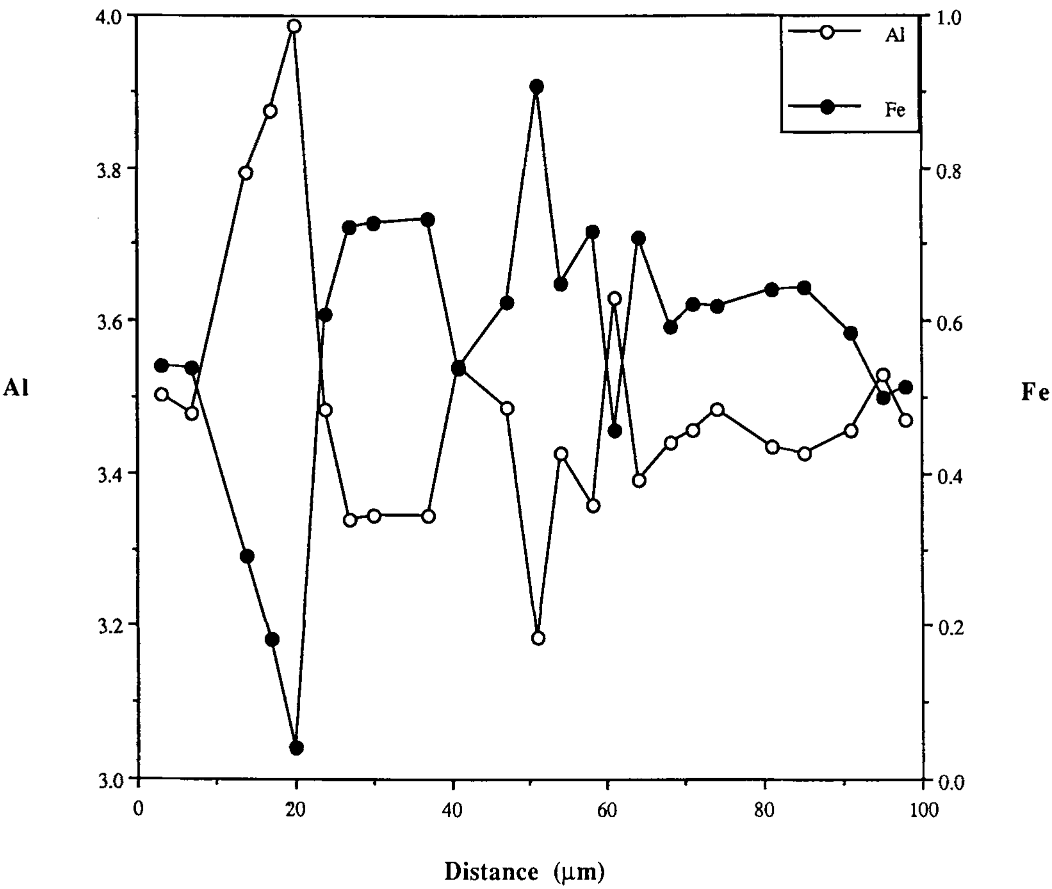

FIG. 2. Microprobe traverse along the line A (left) to B (right) shown on Fig. 1. Analyses are expressed as nos. of atoms per formula unit.

quartz + clinopyroxene or clinopyroxene and may also contain some of pyrrhotite, tremolite, calcite and gold. Alteration zones of tremolite and tremolite + biotite surround the veins. Calcic plagioclase may also be present. The remainder of the shear zone consists of biotite-rich assemblages not spatially associated with any single vein. Veins and alteration haloes occur in varying states of deformation, with little-deformed veins cutting strongly boundinaged or foliated ones, indicating continuing mineralisation during progressive shearing. The mineralisation is estimated to have developed at *c.* 550 °C and 2–3 kbar (Barnicoat, 1990).

Fig. 3 illustrates clinopyroxene from one of these quartz-free segregations, which displays marked oscillatory zoning; accompanying tremolite is also zoned but in a less regular fashion. Zoning in both minerals is predominantly due to $Fe^{2+} = Mg^{2+}$ exchange; Mg-rich ($X_{Mg} = 0{\cdot}75$) zones in the clinopyroxene illustrated in Fig. 3 are darker than Fe-rich ones ($X_{Mg} = 0.63$). The clinopyroxenes display a complex pattern of alternating Mg- and Fe-rich zones throughout, with at least some zones correlating between different crystals. Detailed examination of the apparent cut-offs resulting from the changing euhedral outlines reveals that the apparently discontinuous layers actually continue as extremely thin zones around each grain core.

The mineral assemblages developed at Fraser Mine resulted from the interaction of an externally derived, quartz-saturated fluid with the ultrabasic wall rocks. The oscillatory zoning seen within the minerals of these veins could be due to externally imposed changes in the composition of the infiltrating fluid, due perhaps to changes in the flow path. Alternatively, the oscillatory zoning may be the result of variations in the rate of fluid flow. In this case, periods in which the fluid composition was externally buffered (Fe-rich pyroxene layers grew) would have alternated with periods when it was internally buffered (rock-dominated, Mg-rich growth). Despite the appreciable integrated fluid flow through the veins, it is unlikely that there were significant local temperature fluctuations due to this factor (Brady, 1988).

Oscillatory zoning in pyroxene from a bedded rock unit, Connemara, Ireland

The previous examples were both of mineral growth in veins, where the evidence for growth in an open system is very clear. The vein assemblages have few minerals, and the veins represent

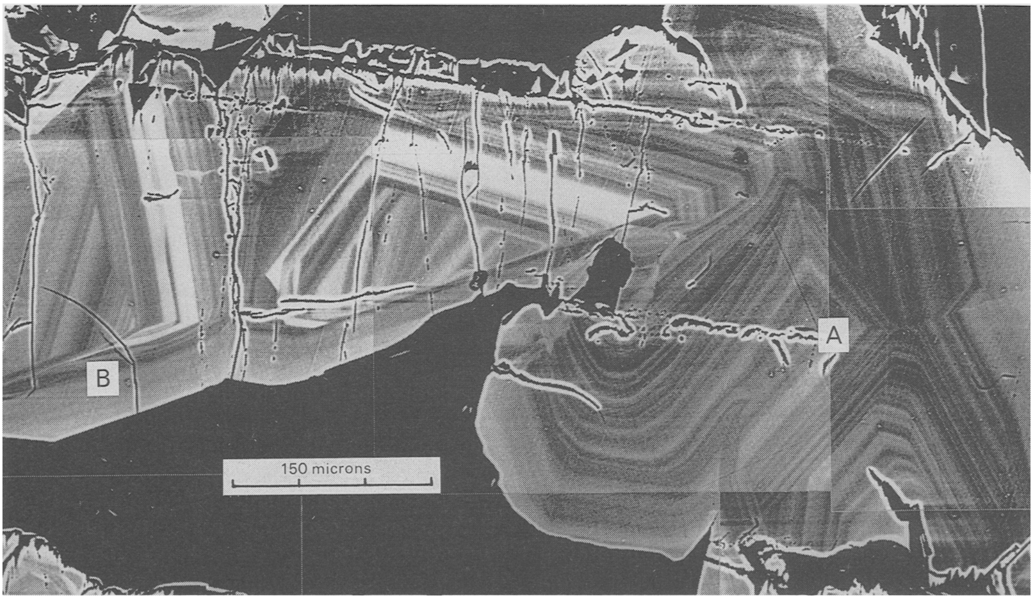

FIG. 3. BSEM photomicrograph illustrating oscillatory zoned pyroxenes from Fraser Mine, W. Australia. The sample is of a thin pyroxene vein with calcite (black) and pyrrhotite (not shown). All the crystals seen are in the same crystallographic orientation. Note the re-entrants in the zoning pattern at A, possibly the result of progressive overgrowth of the branches of an originally dendritic crystal. Variation in the growth rate on different faces is demonstrated by the variation in the thickness of individual zones around the crystal, seen at B.

zones of markedly different chemistry from their hosts, with some degree of gradation present in the immediate wall rocks. There are, however, many instances where metasomatism has affected, or has been supposed to affect, the bulk of a rock unit, and our final example is one such case.

The Connemara region of western Ireland comprises a folded series of Dalradian metasediments which underwent relatively low-P, high-T metamorphism. The metamorphic heat was derived from syn-orogenic calc-alkaline intrusions (Yardley *et al.*, 1987), the earliest of which were emplaced at around 490 Ma (Jagger *et al.*, 1988).

Low in the Dalradian succession and occurring almost exclusively in the metamorphic sillimanite zone is the Connemara Marble Formation, which includes both calcite and dolomite marbles, with ophicarbonate rocks and calc-silicate lithologies (Leake *et al.*, 1975). Recent mapping has demonstrated that, where it is not faulted, the upper member of this marble formation in contact with overlying schists is in many places a bed of diopside rock (Yardley *et al.*, 1991). This rock is composed almost exclusively of coarse random diopside crystals, commonly several cms in length, and cut by thin quartz veins approximately perpendicular to bedding. Thin ribs of quartzite are commonly preserved within the diopside rock. Apart from diopside and the quartz (with minor K-feldspar) in the cross-cutting veins, the diopside rock generally contains only retrograde calcite and tremolite (in fractures and along grain boundaries) and accessory titanite.

The diopside rock has been interpreted as a metasomatic rock by Yardley *et al.* (1991) on the basis of its unusual bulk composition, monomineralic assemblage and isotopic composition. It is regarded as resulting from the infiltration of aqueous fluid derived from adjacent schists into an original dolomite–quartz marble at amphibolite-facies temperatures. Fig. 4 is a BSEM mosaic showing chemical variation within optically uniform coarse diopside. It is apparent that the diopside crystals have extremely complex internal textures. Core regions are of homogeneous, Mg-rich diopside (X_{Mg} *c.* 0.98) which appear dark in the back-scattered electron image and often have rounded, corroded outlines. These are overgrown by more Fe-rich (lighter) diopside which develops euhedral outlines and displays marked oscillatory zoning. The compositional variation is in the range X_{Mg} = 0.88 to 0.95. The dark diopside cores are also cut by thin cracks filled with more Fe-rich diopside, which can often be traced out and found to merge with a specific zone in the outer part of the crystal.

The complex diopside textures can be interpreted as the result of an initial phase of essentially isochemical diopside growth from pre-existing dolomite and quartz, followed by metasomatic diopside growth due to the interaction of infiltrating quartz-saturated water with dolomite. The oscillatory zoning formed during the latter event, and the higher Fe-content of this diopside reflects the relatively high Fe/Mg ratio of fluid equilibrated with schist compared to the primary dolomite.

How does this scenario measure up against the theoretical requirements for the development of geochemical self organisation? Firstly, there can be no doubt that the infiltration of a water-rich fluid into a dolomitic rock under amphibolite-facies conditions leads to large departures from equilibrium, especially if the fluid is quartz-saturated (Slaughter *et al.*, 1975). The initial release of CO_2 into the fluid by reaction serves to enhance the overstepping further by lowering the solubility of silica (Walther and Orville, 1983). The effect of mineral precipitation on porosity will provide a feedback mechanism to link reaction and fluid infiltration, although the way in which it works is likely to be complex, changing from positive to negative feedback. The reaction:

$$\text{quartz} + \text{dolomite} = \text{diopside} + CO_2$$

has a large negative solid volume change, whereas the reaction:

$$SiO_2(aq) + \text{dolomite} = \text{diopside} + CO_2$$

does not. Thus while the initial reaction created extensive porosity and promoted infiltration (providing the noise to initiate the event), the oscillatory zoning could have developed in a regime in which precipitation tended to reduce porosity.

Rheological factors may also have provided a feedback mechanism for infiltration during the later stages of the development of the diopside rock. The abundant, centimetre scale, parallel quartz veins cutting the diopside rock provide mute testimony of its brittle character relative to the adjacent lithologies. This brittle behaviour is confirmed in the BSEM image (Fig. 4) by the presence of irregular crack fillings of ferroan dioside cutting through the crystal cores. Thus Fe-rich zones formed during episodes of fluid infiltration in response to brittle failure of diopside cores as the bed deformed during peak-metamorphic D3 folding (Yardley *et al.*, 1987), while the Mg-rich zones reflect Fe–Mg exchange re-equilibration of fluid with host rock. We conclude that this metasomatic rock actually has a rather more complex history than its monomineralic character would initially suggest, involving both an early isochemical stage and a later metasomatic stage.

Discussion and conclusions

These examples clearly demonstrate that oscillatory zoning can develop in minerals growing in an open system, and that in at least some common metamorphic minerals diffusion is sufficiently sluggish that the zoning can be preserved through the remainder of an amphibolite-facies regional metamorphic event. Two important questions remain if this observation is to be of real predictive value: can we exclude the possibility of oscillatory zoning forming during isochemical metamorphism, and is oscillatory zoning an inevitable consequence of infiltration?

Consider first the question of oscillations during 'normal' isochemical metamorphism. Once we have excluded fluid infiltration as a process, oscillations in the chemical potentials of solid solution end-members can only occur in response to variations in P and T. However, in a regional setting, or even during large-scale deep contact metamorphism, it is highly improbable that these parameters can oscillate in the rapid manner necessary to produce classic oscillatory zoning. This does not *prima facie* preclude the development of local oscillations due to growth from a supersaturated medium independent of changes in P and T, in a manner analogous to that proposed for growth of igneous oscillatory zoned crystals by Haase *et al.* (1980).

There are however two serious objections to extending the igneous model to metamorphism. Firstly, the very slow rate at which temperature and pressure can change in a large rock mass undergoing regional-scale metamorphism makes it unlikely that large degrees of overstepping are attained. It is true that reactions may be substantially overstepped in the immediate vicinity of intrusive igneous contacts (Yoder, 1990), and Carpenter and Putnis (1985) cite various instances of evidence for metastable growth of disordered mineral structures in metamorphism, which undergo subsequent ordering. However the detailed electron microscope studies that revealed such ordering have not revealed oscillatory zoning, and it is probable that the degree of overstepping was not sufficient (c.f. Smith and Lofgren, 1983). Secondly, however, the faster

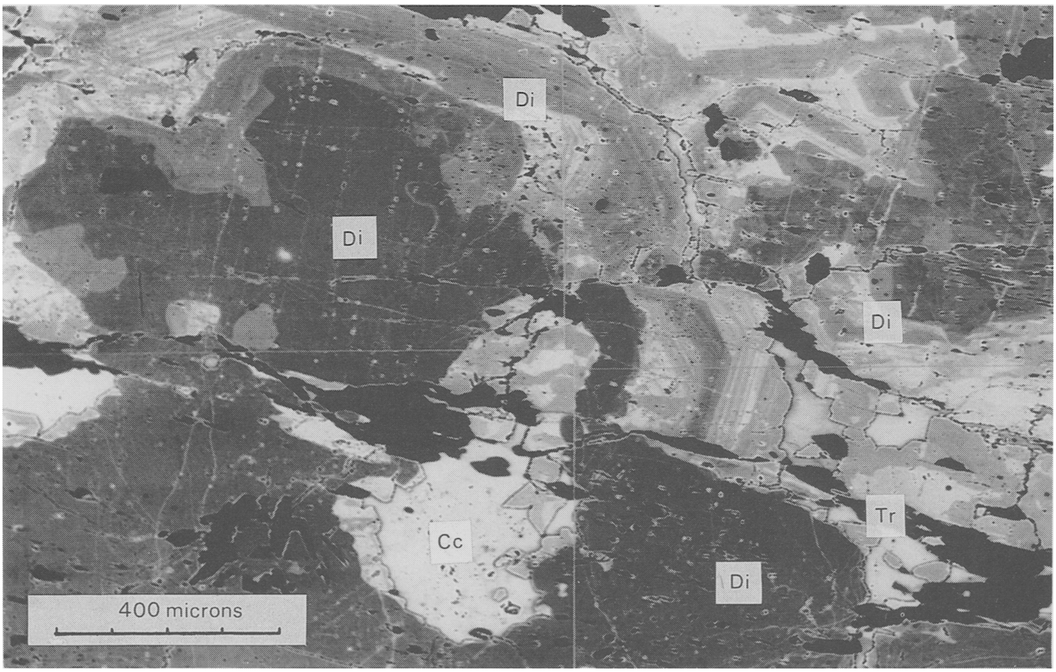

FIG. 4. Mosaic of BSEM photomicrographs of diopside rock from Connemara, Ireland. Diopside grains (Di) have homogeneous cores of dark (Mg-rich) diopside, cut by veinlets of lighter, more Fe-rich diopside. The cores have corroded outlines but are overgrown by oscillatory zoned diopside which develops a euhedral shape. Black grains, often lozenge shaped, are tremolite (Tr), white grains and crack fills are of calcite (Cc).

diffusion rates for species in an aqueous fluid compared to a silicate melt mean that the length scale over which chemical variations in the fluid phase can be sustained will be much larger than in igneous crystallisation, and is likely to be very large relative to the spacing between grains. This objection may be over-ruled in some cases of fluid-absent metamorphism, but is certainly valid for the sort of prograde amphibolite-facies metamorphism to which the schists adjacent to our third example were being subjected at the same time. Thus while we cannot absolutely preclude the possibility that oscillatory zoning could develop during normal, isochemical metamorphism, it would require very unusual circumstances, and must be very rare.

Finally, can we consider oscillatory zoning as an essential characteristic of solid-solution minerals grown in an open system? Provided the infiltrating fluid is not close to equilibrium with the rock with which it interacts, then the answer may prove to be yes, since the phenomenon is very widespread in skarns and other undoubtedly infiltrated rocks. The more extensive the chemical change that accompanied metasomatism, the more likely it is that this condition should be fulfilled. Oscillatory zoning is therefore a possible criterion to use in evaluating claims for extensive metasomatism.

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