New insights into the processes controlling compositional zoning in plagioclase

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A R T I C L E   I N F O

Article history:
Received 13 September 2013
Accepted 15 March 2014
Available online 28 March 2014

Keywords:
Phase equilibria
Numerical modeling
Convection
Zoning
MELTS algorithm

A B S T R A C T

Although plagioclase is the most abundant mineral in crustal rocks, the factors that control the magnitude of compositional zoning in plagioclase remain poorly constrained. The composition of magmatic plagioclase depends upon physical parameters such as temperature (T) and total pressure (P), as well as the full range of compositional controls, including the water content of the melt (wt.% H2O). The changes in these physical parameters can be quantified using available numerical phase equilibria models for various differentiation scenarios and the magnitude of these effects on plagioclase zoning can be calculated. The role of temperature, total pressure, and water content on plagioclase zoning has been experimentally investigated previously in a pure albite–anorthite (Ab–An) system. In this study, we use the MELTS algorithm to quantify the effects of P, T and water content of the melt on compositional zoning in plagioclase in a basaltic system.

Our first two simulations are designed to evaluate the magnitude of compositional changes that may be attributable to specific system changes exclusive of assimilation and recharge. The first scenario involves a two-step crystallization process. In the first step, magma rises from a deeper to a shallower chamber while crystallizing plagioclase at successively lower pressures. In the second step, the magma pools in the shallower magma chamber and continues to crystallize isobarically. If these two steps are repeated, the result is the development of reverse, normal, and oscillatory zoning in plagioclase. The second scenario involves plagioclase zoning in a large, convecting magma chamber where plagioclase crystallizes as the magma convects, resulting in oscillatory zoning. The third scenario involves a two-step process where crystallization is interrupted by multiple recharge events. In this case, magma crystallizes isobarically as a new batch of primitive magma is injected periodically to the magma chamber and crystallization continues after mixing. During the repetition of these two steps, plagioclase develops normal and reverse zoning.

Based on our results, we interpret zoning in plagioclase in terms of the partitioning of Na2O and CaO between the melt and plagioclase and the changes in the total volume during dissolution reactions of albite (ΔVAbdissolution) and anorthite (ΔVAndissolution) components. For the first two scenarios, our calculations show that as pressure decreases ΔVAbdissolution and ΔVAndissolution decrease while as pressure increases both of them increase. ΔVAbdissolution always being larger than ΔVAndissolution controls the zoning in plagioclase by compensating the larger volume change in the melt either by albite component dissolving into its oxides or by oxides reacting to produce albite component. Therefore, at a given temperature with decreasing pressure, Na2O partitions increasingly into the melt compared to CaO, making the coexisting plagioclase more An-rich. Thus, ascent of magma from a deeper to a shallower chamber isentropically, or convection of a magma in a large chamber polybarically, results in the development of reverse zoning in plagioclase. The magnitude of the effects is on the order of 3 mol% An per kbar for both decompression driven crystallization and isothermal/polybaric convection.

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1. Introduction

It has long been recognized that the zoning pattern characteristic of plagioclase in igneous rocks preserves a record of the processes that have acted on the magmatic system (Anderson, 1984; Blundy and Cashman, 2008; Blundy and Schimizu, 1991; Costa et al., 2008; Couch et al., 2001; Davidson and Teply, 1997; Ginibre et al., 2002; Ginibre

http://dx.doi.org/10.1016/j.lithos.2014.03.021
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et al., 2007; Kent, 2008; Nixon and Pearce, 1987; Ramos and Tepley, 2008; Ruprecht et al., 2012; Streck, 2008). Most of the previous work has focused on the development of techniques to interpret the compositional signal in terms of specific processes. What is known is that the composition and stability of plagioclase depend upon pressure, temperature, and melt composition, including water content. What is poorly understood are 1) the magnitude of the effect of pressure changes that result from circulation of magma on plagioclase zoning and 2) how to quantify changes due to magma mixing and temperature or pressure changes — together or alone.

Considerable analytical effort has been aimed toward understanding the role of specific physical parameters on plagioclase zoning (e.g., optical analysis, Nomarski interference imaging, back-scattered electron images and microanalysis). Until the advent of the general application of the electron microscope in the early 70s, interpretation of plagioclase zoning was based primarily on petrographic observations (Bottinga et al., 1966; Vance, 1965). Subsequently, numerical modeling (e.g., Allegre et al., 1981) has provided additional insights into the parameters that control plagioclase growth and resorption. Experimental studies in the Ab–An system have described the influence of P, T and melt composition (including H2O content, e.g., Sisson and Grove, 1993; Panjasawatwong et al., 1995). With the development of the electron microscope and other imaging and analytical techniques, the spatial relationship of major elements in single mineral crystals at a resolution of a few microns has been made possible (Pearce and Kolsnik, 1990). The zoning patterns (e.g. normal, reverse, oscillatory, etc.) record the relationships between melt composition and other intensive parameters and crystal growth.

One of the mechanisms that has long been cited as a cause of oscillatory zoning in plagioclase in andesitic lavas has been compositional changes resulting from thermally driven cycles of magmatic convection (Honnma, 1932). Over the past 80 years, many researchers have tried to correlate zoning in plagioclase with various dynamic stages and processes within the magma chamber. Most existing studies and models have concentrated on linking zoning profiles to magma mixing or magma recharge (e.g. recharge with complete chemical mixing — Singer et al., 1995; recharge involving variable recharge rates — Ginibre et al., 2002; and recharge characterized only by thermal effects — Couch et al., 2001; Ruprecht and Worner, 2007). Alternative models that are not dependent on mixing include decomposition driven crystallization (e.g. Blundy et al., 2006; Humphreys et al., 2006).

These studies, however, do not attempt to combine properties of magma movement within the crust with quantitative calculations of the effects of convection related pressure changes on phase equilibria with respect to magma mixing and recharge. In this investigation, we used the phase equilibria calculations of MELTS (Ghiorso and Sack, 1995) to quantitatively evaluate the role of P, T, and water content of the melt on plagioclase zoning along with the broader effects of the phase equilibria on melt composition. Further, we have developed a set of models for the generation of specific patterns and magnitude of plagioclase zoning (1) in a crystallizing magma rising adiabatically from a deeper chamber into a shallower chamber where it continues to crystallize isobarically, (2) in a convecting magma chamber within the crust, and (3) in a crystallizing magma chamber interrupted by injection of a mafic magma. Our approach was to test the consequences of three differentiation scenarios to the development of normal, reverse, and oscillatory zoning in a basaltic magma by using the MELTS algorithm and try to constrain the magnitude of the changes in P, T, and water content of melt for each process along with the rapid chemical changes in the melt composition due to co-precipitation or resorption of other Ca-bearing phases (clinopyroxene) besides plagioclase. In the first scenario, we modeled a crystallizing magma rising adiabatically within a system of magma chambers, where the magma continues to crystallize isobarically, and then rises, again adiabatically, to a shallower magma chamber (Fig. 1a). In many explosively erupting volcanoes, magma pooling followed by fractional crystallization is a commonly inferred sequence of events (Elsworth et al., 2008). Although the consequences of decompression and isobaric crystallization on plagioclase zoning have been discussed as separate cases in previous studies (Blundy et al., 2006; Humphreys et al., 2006; Kuritani, 1999), there is no quantitative evaluation of magnitude of changing parameters (P, T, and water content of melt) during these processes where both are involved as magma moves toward the surface.

Our second scenario seeks to relate plagioclase zoning to the effects of convection in a magma chamber at a specific range of depth (Fig. 1b). In this model we monitor plagioclase zoning as a parcel of magma crystallizing at the bottom of the magma chamber as it rises to the top of the chamber and then sinks back to the bottom. To individually understand the role of changes in total pressure and the presumable effects of other Ca-bearing phases on the phase equilibria, the first two models evaluated both crystallization of plagioclase alone and the co-crystallization of plagioclase with other Ca-bearing phases such as clinopyroxene and apatite.

Finally, in the third scenario, we simulate the effects of magma chamber recharge, using the model parent magma as the recharged component (Fig. 1c) where strong changes in the Mg number of the melt observed along with the changes in An-content of plagioclase as the crystallization progresses. In all models, pressure dependent partitioning of Na2O and CaO between the melt and plagioclase, itself a function of their partial mol volumes, and volume changes for dissolution reactions of albite and anorthite components controls the zoning of plagioclase.

2. MELTS calculations and boundary conditions for simulations

The magma composition (Table 1) used as a parent material for our calculations is a moderately primitive basalt composition from Foley Ridge, Central Oregon Cascades (Schmidt et al., 2008). This composition is specifically selected for the simulations since such systems are commonly characterized by complex zoning patterns. In addition, this composition was specifically selected because it is saturated with fewer Ca- or Na-bearing phases (only plagioclase, clinopyroxene, and apatite but not amphibole) near the liquidus. This is typical of many low-K-tholeitic arc basalts, and simplifies the interpretation of the effects of both mixing and changes in intensive variables. For the dynamic models (Models 1 and 2) where the pressure is the main driving factors in compositional zoning, simulations were also repeated with plagioclase-doped Foley Ridge basalt (50% An50) to favor the plagioclase crystallization over other Ca-bearing phases. This essentially helps to correctly discuss the individual effects of intensive variables (especially P) with eliminating the phase equilibria controls (existence of multiple Ca-bearing phases).

MELTS algorithm of Ghiorso and Sack (1995) which uses regular solution modeling to represent the thermodynamic properties of magmas is widely used to characterize and predict the behavior of magmatic systems (Asimow et al., 2001; Dogan et al., 2007; Kress and Ghiorso, 2004; Stewart and Fowler, 2001). Simulations involving closed–system isobaric and isothermal processes are based on the minimization of Gibbs free energy for all possible reactions under the constraints imposed on the system. In computations involving perfectly mobile components such as oxygen (open system), MELTS minimizes the Korzhinsk potential (Ghiorso and Kelemen, 1987). In adiabatic calculations, MELTS minimizes the enthalpy subject to fixed pressure and heat content. Once the starting composition, initial system parameters (P, T, wt.% H2O, and fO2), and different constraints for magma differentiation (isobaric, isothermal, polybaric crystallization or magma mixing/recharge) are specified, MELTS calculates for each temperature and pressure (1) the composition of crystallizing minerals, (2) the end-member compositions of solid solution minerals in terms of its mol percent, and (3) the composition of the residual liquids. Calculation of the mol percent of end-members for solid solution minerals such as
anorthite (XAn), albite (XAb) and sanidine (XOr) allows the plagioclase composition to be estimated as P, T, and wt.% H2O changing during various differentiation scenarios.

The effects of decreasing total pressure and increasing water pressure in the Ab–An system on plagioclase zoning have been studied by a number of investigators beginning with Yoder and Tilley (1962). The central goal of the current work is to be able to quantify the relative roles of changes in total pressure, temperature, and water content of the melt on complex zoning patterns in plagioclase from arc magmas and to set up the groundwork to differentiate compositional zoning produced by different magma processes. To achieve this, our first step is to extend the relationships that have been observed in pure Ab–An system regarding the effects of total pressure and water pressure on plagioclase zoning to a multi-component arc basalt. The simulations have been calculated using a starting composition typical of primitive arc basalts (Foley Ridge basalt — Schmidt et al., 2008) at 10 kbars and 1 bar under dry conditions and at 1000 bars with 0 wt.% and 1.5 wt.% water. Compositions of calculated plagioclase in the Foley Ridge basalt are then compared to that of pure plagioclase system in T (°C)-X (wt.%) diagrams. Having verified the expected relationship between total and water pressure on plagioclase zoning, as a second step, we have calculated the plagioclase compositions from the calculated melts that would be generated from this Foley Ridge basalt under three dynamic models. For all three simulations, starting fO2 and H2O content were set to QFM and 2 wt.% respectively which will be suitable for the type of basalt used in simulations. In the first model, consecutive decompression (isentropic) and isobaric crystallization cycles have been repeated for simulating the movement and crystallization of magma between multiple magma chambers from 4 to 2 kbars. In the second model, polybaric and isothermal convection has been simulated within a large magma chamber where bottom of the chamber corresponds to 4 kbars and top of the chamber corresponds to 3 kbars from the surface. In the third model, isobaric crystallization of the magmatic system (at 4 kbars) is periodically recharged by less differentiated parental magma.

Table 1
Chemical composition of Foley Ridge Basalt (Schmidt et al., 2008) used in computations.

<table>
<thead>
<tr>
<th>Oxide (wt.%)</th>
<th>Compositiona</th>
<th>Plag-dopedb</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>49.08</td>
<td>49.78</td>
</tr>
<tr>
<td>TiO2</td>
<td>1.51</td>
<td>0.78</td>
</tr>
<tr>
<td>Al2O3</td>
<td>16.94</td>
<td>24.10</td>
</tr>
<tr>
<td>FeO</td>
<td>9.57</td>
<td>5.12</td>
</tr>
<tr>
<td>MnO</td>
<td>0.18</td>
<td>0.09</td>
</tr>
<tr>
<td>MgO</td>
<td>9.03</td>
<td>4.55</td>
</tr>
<tr>
<td>CaO</td>
<td>9.83</td>
<td>11.82</td>
</tr>
<tr>
<td>Na2O</td>
<td>3.07</td>
<td>3.14</td>
</tr>
<tr>
<td>K2O</td>
<td>0.67</td>
<td>0.38</td>
</tr>
<tr>
<td>P2O5</td>
<td>0.33</td>
<td>0.17</td>
</tr>
<tr>
<td>Total</td>
<td>100.21</td>
<td>99.90</td>
</tr>
</tbody>
</table>

a Schmidt et al. (2008), Foley Ridge Basalt.
b Foley Ridge doped with 50% Ab70.
3. Discussion of results

3.1. Extending from synthetic plagioclase to multi-component basaltic system

3.1.1. Effects of total pressure (P) and water content of the melt (wt.% H2O) on plagioclase zoning

Reprising the work of Yoder and Tilley (1962) using a numerical simulation, we see that for a given temperature, decreasing total pressure (from 10 kb to 1 bar) or increasing water pressure (from 0 to 150 bars) results in an increase in the An-content of plagioclase (Fig. 2). However, the consequences of decreasing pressure and increasing water content on the An-content of plagioclase (mol% An) in a multi-component basaltic melt at fO2 ~ QFM (Fig. 3) have never been quantitatively determined.

It should be noted that the relationships illustrated in Fig. 2a and b pertain to pure plagioclase melts. In general, the presence of other components in the system will lower the plagioclase liquidus surface. Before, we start discussing the composite effects of total pressure, temperature, and water content of the melt within various dynamic models; first we must confirm how the basic trends observed in a pure plagioclase system extend to a multi-component basaltic melt (Fig. 3). To do this, isobaric crystallization is computed at every 5 °C starting from the liquidus temperature for the Foley Ridge basalt of 1160 °C at 1 bar and 1320 °C at 10 kbars (Fig. 3a) while the plagioclase composition is recorded at each step. In both cases, the anorthite content of plagioclase decreases in response to isobaric cooling (Fig. 3a). These basic trends confirm what we have assumed about the effect of isobaric crystallization, the An content of plagioclase...
decreases with decreasing temperature resulting in normal zoning. What remains an open question is the magnitude of the changes in those zoning profiles as one changes system parameters. For example, if crystallization of plagioclase takes place when the magma is rising resulting in decreasing total pressure, one would predict either a reduction of the magnitude of normal zoning, or the creation of reverse zoning. For example, if we consider the results at 1400 °C for the pure plagioclase system and at 1100 °C for the natural arc basalt system (Foley Ridge basalt), the An content of plagioclase increases from 58 to 72 mol% and from 34 to 54 mol% for Foley Ridge basalt with a decrease in total pressure from 10 kbars to 1 bar for these two systems respectively. In the absence of solid–liquid equilibration, a decrease in the total pressure at constant temperature causes reverse zoning in plagioclase. According to these calculations, the An content of plagioclase increases 14–20 mol% per 10 kbar decrease in total pressure or 1.4–2.0 mol%/kbar.

Another parameter that controls the An-content of plagioclase is water pressure ($P_{H2O}$). If we compare the calculated results for a pure plagioclase system (Fig. 2b) with the results for a multi-component basaltic melt (Fig. 3b) we see that, consistent with

![Graphs showing total pressure vs anorthite content relationship and water content vs anorthite content relationship.](image)

**Fig. 3.** Extending the effect of a. decrease in total pressure (bars) (from 10 kbar to 1 bar) and b. increase in water content in the melt (wt.%) (at 1 kbar from 0 wt.% to 1.5 wt.% $H_2O$) on the calculated liquidus of feldspar from pure Ab–An system to a multi-component system using Foley Ridge basalt, Central Oregon (Schmidt et al., 2008).

<table>
<thead>
<tr>
<th>Model 1</th>
<th>Crystallization (%)</th>
<th>Pressure (bars)</th>
<th>Temperature (°C)</th>
<th>Melt water content (wt.%)</th>
<th>Anorthite content (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decompressional 54</td>
<td>4000</td>
<td>1020.00</td>
<td>4.45</td>
<td>70.49</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>3000</td>
<td>1015.03</td>
<td>4.46</td>
<td>73.33</td>
<td></td>
</tr>
<tr>
<td>Isobaric 58</td>
<td>3000</td>
<td>1004.93</td>
<td>4.76</td>
<td>72.46</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>3000</td>
<td>994.93</td>
<td>5.06</td>
<td>71.59</td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>3000</td>
<td>984.93</td>
<td>5.36</td>
<td>70.71</td>
<td></td>
</tr>
<tr>
<td>Decompressional 62</td>
<td>2000</td>
<td>978.87</td>
<td>5.12</td>
<td>72.76</td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>2000</td>
<td>968.87</td>
<td>5.43</td>
<td>69.96</td>
<td></td>
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<tr>
<td>Isobaric 66</td>
<td>2000</td>
<td>958.87</td>
<td>5.76</td>
<td>69.16</td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>2000</td>
<td>948.87</td>
<td>6.10</td>
<td>68.35</td>
<td></td>
</tr>
</tbody>
</table>

Table 2

Changes in crystallization (%), pressure (bars), temperature (°C), melt water content (wt.%), and anorthite content of plagioclase (mol%) during decompressional and isobaric crystallization intervals of Model 1.
Yoder and Tilley (1962), the addition of water has the effect of suppressing the liquidus and solidus for plagioclase. In the case of the simple plagioclase system, increasing the total $P_{H2O}$ to 150 bars suppresses the liquidus temperature by approximately 100 °C (Fig. 2b). The effect on the equilibrium plagioclase content is approximately 15 mol% under isothermal conditions (e.g. An72 to An88). The calculated results for the Cascade basalt are comparable. The addition of 1.5% water at 1 kbar reduces the liquidus temperature of the basalt by ~150 °C. This translates to an isothermal offset of approximately 30 mol% (e.g. An$_{38-68}$ at 1050 °C). In either case, isobaric crystallization results in normal zoning, and that at a given $P$ and $T$, a more calcic plagioclase will crystallize in a water-bearing magma compared to a dry magma. These calculated results are very similar to the experimental results of Sisson and Grove (1993), Panjasawatwong et al. (1995) and others. The significance of these calculations is not that we can reproduce experimental results, rather it demonstrates that we can use them to simulate dynamic systems that are difficult or impossible to examine experimentally.

Fig. 4. The change in a. total pressure (bars), b. temperature (°C), and c. dissolved water content of melt (wt.%) with respect to percent crystallization (%) under decompression driven crystallization followed by isobaric cooling. The dashed lines in 4c indicate melt water contents calculated by plagioclase hygrometer of Lange et al. (2009).

Fig. 5. The change in anorthite content of plagioclase (mol%) with respect to percent crystallization (%) under decompression driven crystallization followed by isobaric cooling.
3.2. Discussion of dynamic system models

3.2.1. Normal and reverse zoning related to decompression driven crystallization

The first dynamic system we simulated involves several cycles of decompression driven crystallization followed by isobaric crystallization. The input parameters for this scenario include the starting composition, pressure (4 kbars to 2 kbars), oxygen fugacity (QFM), starting water content of the melt (2 wt.% H₂O), and the path of decompression and crystallization. Changes in the solid mass may be considered as a measure of the degree of crystallization (Table 2), which is related to the temperature by phase equilibria constraints, and the water content is constrained by mass balance. Melt water contents are also computed by plagioclase hygrometer of Lange et al. (2009) for each melt and plagioclase end-member composition at P–T ranges of dynamic models.

Fig. 6. The change in a. total pressure (bars), b. temperature (°C), and c. dissolved water content of melt (wt.%) with respect to percent crystallization (%) under polybaric–isothermal convection conditions. The dashed lines in 6c indicate melt water contents calculated by plagioclase hygrometer of Lange et al. (2009).

Fig. 7. The change in anorthite content of plagioclase (mol%) with respect to percent crystallization (%) under polybaric–isothermal convection conditions.
We start with a melt that stabilized plagioclase at 1025 °C at 4 kbars and decompress this magma adiabatically (under isentropic condition) to 3 kbars. During this process, the dissolved water content stays constant at 4.45 wt.% while the temperature decreases little, as expected, from 1020 °C to 1015 °C. Once this magma enters a magma chamber at 3 kbars, it continues to crystallize under isobaric conditions while the temperature decreases from 1004 °C to 984 °C and the water content in the melt increases significantly from 4.76 wt.% to 5.36 wt.%.

After isobaric crystallization at 3 kbars, magma again ascends adiabatically to a depth equivalent to 2 kbars with a very slight decrease in temperature (984 °C to 979 °C) and a decrease in water content (5.36 wt.% to 5.12 wt.%). During the final stage, the system is allowed to cool isobarically at 2 kbars with a decrease in temperature (979 °C to 948 °C) along with an increase in water content of the melt (5.43 wt.% to 6.10 wt.%).

If we interpret the calculated changes in An content as a function of changes in total pressure (P, bars), temperature (T, °C), and wt.% H₂O in the melt (Fig. 4a,b,c), we can see (Figs. 4, 5) that intervals of decompression result in increase in An content (reverse zoning — Intervals I and III), and intervals of isobaric crystallization result in decrease in An content (normal zoning — Intervals II and IV). For this specific scenario, the magnitude of the An increases is on the order of 2–3% An per kbar, interspersed with intervals of 4–5% An decreases. The total % crystallization represented by this sequence is on the order of 10%. These oscillations are on the same order as oscillatory or "saw tooth" zoning profile characteristic of many

![Fig. 8.](image)

Table 3: Changes in crystallization (%), pressure (bars), temperature (°C), melt water content (wt.%), and anorthite content of plagioclase (mol%) during ascend and descend intervals of polybaric-isothermal convection of Model 2.

<table>
<thead>
<tr>
<th>Model 2</th>
<th>Crystallization (%)</th>
<th>Pressure (bars)</th>
<th>Temperature (°C)</th>
<th>Melt water content (wt.%)</th>
<th>Anorthite content (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybaric-isothermal</td>
<td>56</td>
<td>4000</td>
<td>1020.00</td>
<td>4.45</td>
<td>70.49</td>
</tr>
<tr>
<td>Ascend</td>
<td>56</td>
<td>3500</td>
<td>1020.00</td>
<td>4.38</td>
<td>71.93</td>
</tr>
<tr>
<td>Polybaric-isothermal</td>
<td>57</td>
<td>3000</td>
<td>1020.00</td>
<td>4.32</td>
<td>73.76</td>
</tr>
<tr>
<td>Descend</td>
<td>57</td>
<td>3500</td>
<td>1020.00</td>
<td>4.38</td>
<td>71.93</td>
</tr>
<tr>
<td>Polybaric-isothermal</td>
<td>57</td>
<td>4000</td>
<td>1020.00</td>
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<tr>
<td>Ascend</td>
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<td>1020.00</td>
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<td>71.93</td>
</tr>
<tr>
<td>Descend</td>
<td>58</td>
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<td>1020.00</td>
<td>4.38</td>
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<td>4000</td>
<td>1020.00</td>
<td>4.45</td>
<td>70.49</td>
</tr>
</tbody>
</table>

Fig. 8. The change in instantaneous mass of phases crystallized and anorthite content of plagioclase (mol%) with crystallization (%) under decompression followed with isobaric crystallization conditions for systems a, b. saturated with more than one Ca-bearing phase and c, d. saturated only with plagioclase. Plag: plagioclase, cpx: clinopyroxene, opx: orthopyroxene. The dashed lines in 8a are Ca-free, solid lines are Ca-bearing phases formed during crystallization.
plagioclase phenocrysts in arcs (e.g. Ginibre et al., 2002; Ginibre et al., 2007).

3.2.2. Oscillatory zoning related to polybaric and isothermal convection

The second model involves polybaric and isothermal convection of magma, simulating the patterns that may be produced by density-driven convection within a single magma chamber. If we consider a parcel of melt in a convecting magma chamber (Fig. 1b), the site of most crystallization takes place in response to decreasing pressure on the ascending limb. Further crystallization on the down going limb depends on the extent of heat loss from the margin of the chamber and the increase in pressure. If the temperature gradient in the magma chamber is small, the process can be simulated as an isothermal, polybaric process.

In this scenario, the magma chamber is assumed to be at a depth of approximately 10 and 14 km, and has a total pressure of 3 kbars at the top and 4 kbars at the bottom. As a packet of magma cycles within the chamber, the pressure variation drives systematic increases in anorthite and water content (Figs. 6, 7; Table 3). The magnitude of the compositional oscillations is driven by the pressure difference from the top to the bottom of the chamber (assuming isothermal conditions). Given these specific assumptions, the products of such a magma chamber would exhibit a range of composition of approximately 3–4% An. During the ascending limb of convection, as the parcel of the magma moves from the bottom of magma chamber at 4 kbars to the top at 3 kbars, although the dissolved water content of the melt decreases from 4.45 wt.% to 4.38 wt.% (Fig. 6c), the decrease in total pressure from 4 to 3 kbars (Fig. 6a) produces an increase in the anorthite content of plagioclase during the polybaric crystallization intervals (Figs. 6, 7 Episodes I, III). During the descending portion of the convection, as the magma body moves from the top to the bottom of the chamber, while the dissolved water content of the melt increases from 4.38 wt.% to 4.45 wt.% (Fig. 6c), the increase in total pressure from 3 to 4 kbars (Fig. 6a) decreases the anorthite content of plagioclase during the convection (Figs. 6, 7 Episodes II, IV). Based on the trends shown in Fig. 7, for each full cycle of convection, a reverse and a normal zone can develop. If convection continues over several cycles, the net result should be the development of oscillatory zoning in plagioclase which was driven by changes in total pressure rather than dissolved water content in the melt.

It has been shown earlier experimentally that the composition of plagioclase changes with pressure most dramatically when coprecipitating with other Ca-bearing phases especially diopside (Nelson and Montana, 1992). Rapid chemical changes in the melt were observed as the amount of clinopyroxene decreases or even becomes unstable with decreasing pressure under isothermal or nearly isothermal conditions. Due to the increased solubility of clinopyroxene over plagioclase in the liquid at pressures less than 8–10 kbars, under decompressional

![Fig. 9. The change in instantaneous mass of phases crystallized and anorthite content of plagioclase (mol%) with crystallization (%) under polybaric–isothermal convection conditions for systems a, b. saturated with more than one Ca-bearing phase and c, d. saturated only with plagioclase. Plag: plagioclase, cpx: clinopyroxene, opx: orthopyroxene. The dashed lines in 8a are Ca-free, solid lines are Ca-bearing phases formed during crystallization.](image-url)
crystallization of model 1 or polybaric–isothermal convection of model 2 at pressures reaching the stability limit of clinopyroxene, the melt becomes enriched in Ca as the clinopyroxene to plagioclase ratio decreases (Episodes I and III, Fig. 8a,b and Fig. 9a,b).

In order to facilitate the early crystallization of plagioclase (at 1100 °C instead of 1020 °C) without coexisting with other Ca-bearing phases and therefore to eliminate the effects of phase equilibria on zoning when dealing with pressure control, Models 1 and 2 were repeated with 50% An70 doped Foley Ridge basalt composition. In the systems only saturated with plagioclase, the magnitude of changes in An-content of plagioclase with pressure found to be decreased considerably (Fig. 8c,d and Fig. 9c,d).

3.2.3. Oscillatory zoning related to isobaric crystallization followed by isobaric–isenthalpic recharge and mixing

The final dynamic model involves a two-step process where a crystallizing magma chamber is periodically recharged with the parent magma. In the first step, parental basalt fills the chamber and undergoes some extent of fractional crystallization at isobaric conditions. After a period of fractionation, a small amount (about 5%) of primary basaltic magma is injected into the magma chamber. This less evolved magma and the somewhat more evolved resident magma mix, and the mixed magma resumes differentiating under isobaric fractional crystallization conditions.

Magma mixing can be treated as an isothermal or isenthalpic process. Geologically an isothermal process is improbable because it requires that both the resident magma and mixing magma be at the same temperature. Since magma mixing by and large involves mixing of a more primitive magma (presumably at a higher temperature) with a more differentiated magma (typically at a lower temperature), isobaric–isothermal conditions are unrealistic for magma mixing. Calc-alkaline volcanoes are open systems, which mean that periodically a less differentiated magma can enter the resident magma chamber, causing mingling, mixing, or eruption (Sparks et al., 2000). A more realistic model keeps the enthalpy of the system constant and equivalent to the sum of enthalpies of the two magmas all at constant pressure (isobaric–isenthalpic conditions).

If we relate the calculated changes in An content as a function of changes in total pressure (P, bars), temperature (T, °C), and wt.% H2O in the melt (Fig. 10a,b,c), we see (Figs. 10, 11; Table 4) that intervals of isobaric crystallization result in decrease in An content (normal zoning — Intervals I and III). The magnitude of the zoning is ~4% An for this scenario, with decreasing temperature and intervals of isobaric–isenthalpic recharge/mixing result in increase in An content (reverse zoning — Intervals II and IV) with the increase in temperature and decrease in water content of the melt. For this specific scenario, the magnitude of the An increases is on the order of 1.3–5 mol% for 15–40 °C increase in temperature.

To discriminate among three scenarios under which significant compositional zoning in plagioclase observed with changing melt composition and intensive variables (P, T, and water content), Mg# of melt has been plotted against crystallization (Fig. 12). As texturally recorded by Ginibre et al. (2007) and quantified with the current study, changes in pressure, temperature, and water content (Models

Fig. 10. The change in a. total pressure (bars), b. temperature (°C), and c. dissolved water content of melt (wt.% with respect to percent crystallization (%) under isobaric crystallization followed by isobaric–isenthalpic recharge conditions. The dashed lines in 8c indicate melt water contents calculated by plagioclase hygrometer of Lange et al. (2009).
1 and 2) affect the An-content of plagioclase while causing much smaller changes in MgO and FeO content of the melt (Fig. 12a and b). In contrast, if An-rich spike in plagioclase is caused by a major change in melt composition — in this case crystallization followed by magma recharge (Model 3), the new growth zone also shows significantly different Mg and Fe contents compared to the adjacent older zone (Fig. 12c). In order to do further process identification between Models 1 and 2, besides phase equilibria modeling, physical aspects of zonation (textural studies) need to be investigated.

3.3. Partial molar volume effect on plagioclase zoning and calculation of volume changes for albite and anorthite dissolution reactions

During the intervals of adiabatic rise in decompression crystallization and polybaric/isothermal convection models, the An-content of the plagioclase increases as the total pressure on the magma decreases. Because changes in the Ab/An ratio in plagioclase are related to the amount of Na₂O and CaO in the melt, zoning must be strongly controlled with the partial molal volumes of Na₂O and CaO in the melt. In other words, as the pressure decreases, the component with the larger partial molal volume, Na₂O, partitions in favor of the melt, making the coexisting plagioclase more An-rich.

To interpret zoning in plagioclase in terms of the partitioning of Na₂O and CaO components between the melt and plagioclase phases, we calculated the volume changes for anorthite and albite dissolution reactions for various pressures and temperatures in the dynamic models discussed above.

The effect of pressure on feldspar stability can be expressed by the volume changes of the two dissolution reactions below:

\[ \text{CaAl}_2\text{Si}_2\text{O}_8 \text{solid} = \text{CaO} \text{liquid} + \text{Al}_2\text{O}_3 \text{liquid} + 2\text{SiO}_2 \text{liquid} \quad (1) \]

\[ \text{NaAlSi}_3\text{O}_8 \text{solid} = 0.5\text{Na}_2\text{O} \text{liquid} + 0.5\text{Al}_2\text{O}_3 \text{liquid} + 3\text{SiO}_2 \text{liquid} \quad (2) \]

The volume change in each reaction (\(\Delta V\)) depends on the partial molar volume of all oxide quantities in the liquid as well as the partial molar volumes of end-member components (anorthite and albite). \(\Delta V\) can be calculated by using the published partial molar volumes of reactants (plagioclase end-member components) (Berman, 1988) as well as the products (CaO, Na₂O, Al₂O₃, and SiO₂) (Lange, 1997) for various temperatures and pressures. Table 5 shows the calculated \(\Delta V\), for the dissolution reactions happening as the Foley Ridge basalt is going under decompressional crystallization followed by isobaric crystallization (Model 1) and polybaric and isothermal convection (Model 2). Calculation of \(\Delta V\) as a function of pressure and temperature shows that \(\Delta V_{\text{An dissolution}}\) is higher than \(\Delta V_{\text{Ab dissolution}}\) (Table 5). Therefore, during adiabatic decompression (Model 1) and polybaric–isothermal ascend during convection (Model 2), the mol percent of anorthite in plagioclase increases, as the pressure in the magma drops (Figs. 5, 7).

![Diagram](image-url)

**Fig. 11.** The change in a. anorthite content of plagioclase (mol%) and b. instantaneous mass of phases crystallized with respect to percent crystallization (%) under isobaric crystallization followed by isobaric–isenthalpic recharge conditions.
decreasing pressure, NaAlSi₃O₈ component in the melt dissolves into its oxide components to decrease the volume of the reaction which renders the plagioclase to be more An-rich and therefore produces reverse zoning. Conversely with increasing pressure CaAl₂Si₂O₈ dissolves into its oxide components, causing plagioclase to become more albitic and reaction favors normal zoning. This can be also explained in terms of partial molar volume changes for Na₂O and CaO with the pressure. The large partial molar volume of Na₂O in the melt (29.65 cm³/mol Lange, 1997) at higher pressures forces Na₂O into the coexisting plagioclase in preference to CaO, and causes plagioclase to be more albitic while with decreasing pressures, smaller partial molar volume oxide (CaO, 16.90 cm³/mol, Lange, 1997), goes into plagioclase, resulting in a more anorctic composition and reverse zoning. This interpretation supports the conclusion reached by Ghiorso and Carmichael (1987) earlier. (See Table 5).

4. Conclusions

The roles of changing total pressure and water content of the melt on the development of compositional zoning in plagioclase have been extended from the synthetic Ab-An system to a multi-component arc basalt from Foley Ridge, Central Oregon Cascades (Schmidt et al., 2008). We calculated a number of simulations using this relatively primitive arc basalt together with MELTS algorithm of Ghiorso and Sack (1995) in an attempt to quantify the magnitude of the relationships between the changes in total pressure and melt water content on plagioclase zoning in multi-component melts. On the first order, our results support the conclusions reached in Yoder and Tilley’s (1962) study of the Ab-An system. More significantly, our results extend the inferences from that simple system into a complex multi-component system. Specifically, the anorthite content of a plagioclase phenocryst will increase or

<table>
<thead>
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<th>Model 3</th>
<th>Crystallization (%)</th>
<th>Pressure (bars)</th>
<th>Temperature (°C)</th>
<th>Melt water content (wt.%)</th>
<th>Anorthite content (mol%)</th>
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<td>1027.34</td>
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</table>
decrease as a function of increasing or decreasing pressure at a rate of approximately 3 mol%/kbar. The zoning pattern for any phenocryst then depends on the physical scenario being proposed. Regardless, the observed range of normal, reversed and oscillatory zoned feldspars characteristic of natural arc systems can be generated by a combination of magma chamber convection, isobaric crystallization and vertical transport (decompression crystallization). The fact that such changes in anhorthite content may be generated by different processes suggests that we need to examine natural systems for additional discriminatory criteria such as physical characteristics as suggested by G nibre et al., 2007 combined with phase equilibria models as done here.

In addition, in order to model a wider range of natural systems, we must consider the effects of the changes in phase equilibria for systems saturated with multiple Ca-, Na- and Al-bearing phases (e.g. amphibole). For example, basic phase equilibria tells us that as we increase the number of phases with which the system is saturated, changes in temperature will have greater impact on the system's crystallinity. In that case, we might speculate that all of the phenomena described in this paper may be magnified.

Acknowledgments
Authors benefitted greatly from the detailed and constructive comments by Mark Ghiorso, and an anonymous reviewer in the earlier versions of the manuscript.

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