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Constraints on mingling of crystal populations from off-center zoning profiles: A statistical approach

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ABSTRACT

Major- and trace-element and isotopic analyses of single crystals can reveal temporal changes in the thermodynamic and mechanical behavior of magmatic systems. Additionally, zoning can be used to define crystal populations that have shared a common environment based on the correlation of zoning profiles among groups of crystals. However, as is evident in petrographic thin sections, comparison of zoning patterns is complicated by the geometric distortions resulting from crystal sections that are off-center. Because of these distortions, identification of crystal populations becomes increasingly difficult with increasing degrees of geometric non-ideality. In addition, because of the inherent complexity of zoning profiles, often there is ambiguity in determining what level of correlation is significant, even for ideal cases. Consequently, significance levels must be determined for each correlation technique and set of natural profiles. We evaluate the effectiveness of standard correlation, wavelet-based correlation (WBC), and profile-normalization techniques designed to counter the effects of non-ideality using Monte Carlo experiments correlating synthetic profiles. Results from the experiments show that adaptive profile normalization provides more significant correlations from fewer profiles than other techniques indicating that it is at least partially effective in counteracting the effects of non-ideality.

INTRODUCTION

The use of crystals as recorders of changing magmatic environments has proven a powerful way to recognize open-system and in situ crystal growth and transport (Davidson et al. 2001; Druitt and Bacon 1989; Singer et al. 1995). This approach has been used to demonstrate that individual crystals can record transit through diverse isotopic or compositional environments. Integrating of individual crystal data with whole-rock analyses is difficult because whole-rock analyses can represent an integration of multiple events, crystal populations, and variable degrees of assimilation (Tepley III et al. 1999, 2000; Vazquez and Reid 2002; Waight et al. 2001; Wolff and Ramos 2002). Assigning significance to the various scales at which magmatic processes are represented requires bridging the gap between single-crystal data, whole-rock analyses, and conceptual models of system behavior.

One way in which populations of crystals have been used to interpret magmatic systems is with crystal size distributions (CSD), which can provide constraints on nucleation and growth rates. However, interpretation can become complicated when CSDs deviate from log-linear relationships (Marsh 1998). Curved CSDs result from either complicated growth and nucleation relationships, or mingling of populations where crystals may have grown under different conditions, similar to the issues between whole-rock and single-crystal data with deviations from pure fractionation. If crystal populations determined by comparison of zoning patterns can be determined independently from the CSD, the extent of mingling can be constrained and separate growth histories determined by CSD modeling (Higgins 1996). Another way in which crystal populations can be studied is the correlation of high-resolution compositional zoning profiles. Based on the assumption that crystals with equivalent zoning profiles record the same environment, it has been proposed that grouping crystals into populations on the basis of profile similarity can reveal a progression of shared environments (Wallace and Bergantz 2002). In this method, one-dimensional zoning patterns in profiles from crystal sections are compared using a statistical measure of correlation. Groups of mutually correlating crystals are then labeled as a population in that they have shared some common magmatic environment.

Pearce (1984) recognized that zoning profiles measured from off-center sections are distorted and developed a quantitative method of estimating the probability of obtaining ideal sections. An ideal section is a cut, or plane, though a crystal that passes through the core of the crystal and is perpendicular to a crystallographic axis (Fig. 1). Zoning profiles measured from sections with different orientations and positions in the same crystal can appear qualitatively different even though they record an overlapping interval of the zoning pattern. Consequently, the correlation of profiles without considering the effects of section orientation can lead to both false correlations and missing true correlations. Thus, the combination of non-ideality and the inherent complexity of zoning profiles preclude a priori assessment of statistical significance of a correlation. Therefore, normalization techniques to account for the effects of non-ideal profiles and a statistical framework in which the significance of correlation coefficients can be evaluated are needed to reliably interpret correlation data.

We developed a statistical framework by performing Monte

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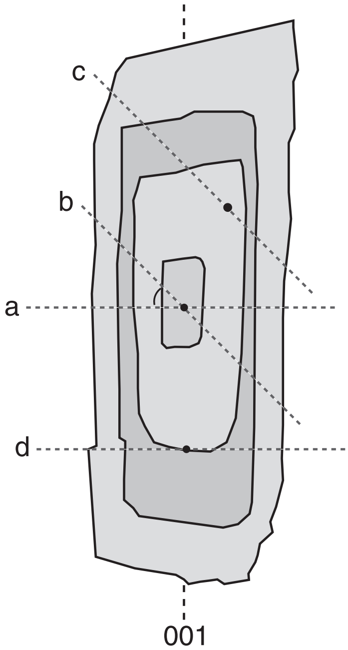

FIGURE 1. Two-dimensional schematic of a plagioclase crystal with ideal and non-ideal sections indicated by dashed lines. This grain has an aspect ratio of 2.8:1. Dots on sections represent the core or apparent core of the section. All sections can be generalized to three dimensions with the addition of an extra degree of freedom. **(a)** Ideal section that passes through the core of the grain, and the grain is perpendicular to the section. **(b)** Poorly oriented section that passes though core, but is misoriented. **(c)** Poorly oriented, off-center section: section misses the earliest 30% of growth (by distance). Stretching for the right side of profile is the same as for **b**. **(d)** Ideally aligned, off-center section. Section misses the earliest 60% of growth (by distance). No stretching. The effects of non-ideality can be parameterized as a combination of stretching and truncation. Truncation of the near-core part of the zoning profile occurs in profiles measured from sections that are off-center. Truncation is an irreversible loss of information that can affect the variance of the profiles and thus either increase or decrease correlation levels. Stretching of profiles causes zone peaks to misalign reducing overall correlation. These effects must be considered prior to correlation.

Carlo experiments based on the correlation of synthetic zoning profiles. Comparison of Monte Carlo results using different correlation and normalization techniques is used to refine guidelines for crystal selection, analysis, and the minimum number of profiles needed to resolve zoning populations. Although we focus on plagioclase, the approach presented here is applicable to any compositionally zoned mineral phase in igneous, sedimentary, or metamorphic rocks.

CORRELATION

The correlation coefficient is a measure of the similarity of zoning profiles. Correlation of zoning profiles compares co-located points in each profile to the mean and variance. Two methods used in correlation are standard correlation and wavelet-based correlation (WBC) (Wallace and Bergantz 2002). WBC uses a digital filter to select specific zoning scales, and is suited to assess the similarity of specific zoning types– such as oscillatory zoning or baseline compositional trends. Standard correlation calculates a correlation coefficient from the entire zoning pattern and is suited to general assessment of profile similarity. Standard correlation, r, is calculated as:

$$r = \frac{\operatorname{cov}(x,y)}{\sqrt{\operatorname{var}(x)}\sqrt{\operatorname{var}(y)}} \tag{1}$$

and covariance is:

$$\operatorname{cov}(x,y) = \frac{N\Sigma_{i=1}^{N} x_i y_i - \Sigma_{i=1}^{N} x_i \Sigma_{i=1}^{N} y_i}{N(N = 1)} \tag{2}$$

variance is:

$$\operatorname{var}(x) = \frac{1}{N = 1}\sum_{i=1}^{N}\left[x_i - \bar{x}\right]^2 \tag{3}$$

where N is the number of points in profiles x and y, and x-bar is the mean of profile x. In Equation 1, covariance values are normalized against variance to unit values. Covariance evaluates similarity among points by comparing their relative deviations from the mean, or expected value, of each profile. If zoning profiles have multiple types of features with different amounts of variance, each type of feature will have a weighting in the correlation coefficient proportional to its variance. For example, normal zoning trends have more variance than oscillatory zoning in plagioclase and will consequently have a stronger influence on the correlation coefficient.

Wavelet-based correlation (WBC) restricts correlation of zoning profiles to features of selected wavelengths (Fig. 2). Features are selected by filtering out larger and smaller scales of zoning than the features of interest using the wavelet transform (Kumar and Foufoula-Georgiou 1997; Torrence and Compo 1998). The wavelet transform converts a one-dimensional zoning profile into a two-dimensional matrix of locations and scales of features, and has the functional form (Fig. 2):

$$W(s,\tau) = \frac{1}{s}\int f(x)\phi\left(\frac{x-\tau}{s}\right)dx \tag{4}$$

where $f(x)$ is the profile, ϕ is the wavelet function, s is the scale of the wavelet function, and τ is the translation of the wavelet function relative to the profile. The wavelet function is chosen to be similar in shape to features in the zoning profile, and can be stretched to different scales to tune sensitivity to different widths of features in the zoning profile. The wavelet function is similar to the sine function in Fourier analysis. Likewise, scale is analogous to wavelength. The derivative of Gaussian (DOG) wavelet is used for analysis of plagioclase zoning profiles (Wallace and Bergantz 2002):

$$\phi(x) = \left(\frac{2}{\sqrt{3}}\pi^{-1/4}\right)\left(1 - x^2\right)e^{-x^2/2} \tag{5}$$

WBC uses the wavelet coefficient matrix to filter out unwanted components of the zoning profile. By excluding coefficients corresponding to features of greater or smaller scale than those of interest, the wavelet coefficient matrix acts as a band-pass filter leaving only features with the desired wavelength for correlation. Equation 1 is then applied to the remaining coefficients to calculate a correlation coefficient weighted by only features within the scale range of interest.

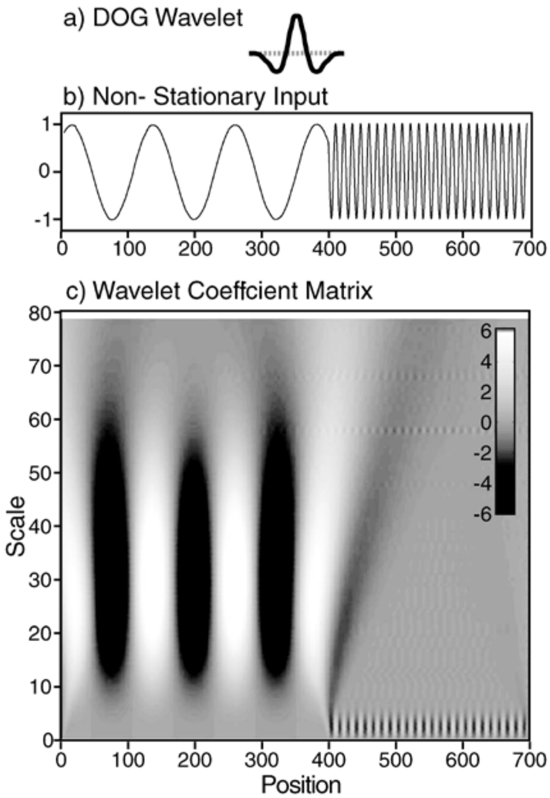

FIGURE 2. Wavelet analysis of a sample signal. Convolution of the wavelet function **(a)** with the data series **(b)** produces a wavelet coefficient matrix **(c)**. The wavelet coefficient matrix can be used as a band-pass filter by extracting a scale range corresponding to the wavelength of the feature of interest. There is a 3:1 proportionality between wavelength and scale for the derivative of Gaussian (DOG) wavelet. For example, to extract the portion of the signal with wavelengths between 90 and 120 points, the wavelet coefficient matrix is windowed to include scales between 30 and 40. (Modified from Wallace and Bergantz 2002).

With standard correlation or WBC, correlation coefficients only can be calculated from profile segments with the same number of points. Profiles may have different numbers of points if they are from crystals of different sizes, measured at different resolutions, or measured at different orientations within a crystal. In addition to changing the amount of each profile that can be compared, stretching that results from misoriented profiles can change the correlation coefficient by altering the positions of zoning features.

PROBABILITY AND GEOMETRIC EFFECTS OF NON-IDEAL SECTIONS

Two-dimensional examples provide a basis for understanding distortion effects and help to develop guidelines for measurement of zoning profiles from sections (Fig. 1). There are two types of distortion that can result from the measurement of zoning profiles from non-ideal sections: truncation of the near-core part of the zoning profile and stretching. The amount of truncation is proportional to the distance of the section from the core of the crystal. The amount of stretching is related to the angle between the zoning profile and growth faces. For example, in Figure 1, section *a* is ideal, whereas section *d* is aligned but off-center. Because section *d* is subparallel to the zoning pattern near the core, there will be a region of homogeneous composition in the inner third of profiles measured from the section. As oriented sections are cut further from the core of the crystal, the subparallel region widens and profiles develop a widening area of homogeneous composition. Section *c* is both off-center and aligned improperly, but not parallel to the zoning pattern, so there is no homogeneous region near the core. However, there is asymmetry in zone widths on either side of the apparent core because the section cuts across different crystal faces. As off-center sections rotate to increasing degrees of misorientation, the subparallel part of the profile develops asymmetry, and the apparent core shifts to the edge. If zone orientation changes in the middle of a profile, there is an accompanying change in the amount of stretching that is difficult to account for. It is better to keep the amount of stretching constant over the entire profile length.

Distortion can be minimized by using criteria that require profiles to have constant crystallographic orientation from the core to rim. Profiles measured from sections with asymmetry or obviously subparallel regions marked by homogeneous composition at the core, should be measured along the shortest core-to-rim distance. Sections with symmetry should be measured so that the number of points in the profile is similar to other measured profiles. Alternately, only profiles from on-center sections can be measured. However, the criteria for identifying ideal sections may introduce selective bias and exclude some crystal populations.

If crystals are distributed randomly within a rock volume, non-ideal sections will outnumber ideal sections in most petrographic thin sections. Pearce (1984) showed that the probability of obtaining a section within a distance d from the core of a crystal of core to rim width D is (Fig. 3):

$$P(d) = d/D \tag{6}$$

Considering that the probability of obtaining a section within λ-degrees of the ideal orientation is $\sin(\lambda)$, as few as one crystal per thin section will be ideal (Pearce 1984, 2000, personal communication). However, because volume increases as D^3, precisely on-center grains are not critical to reveal the majority of the growth history by volume (Pearce 1984). For spherical, orthorhombic, and tetragonal crystals, the probability of sampling a given volume fraction f is (Fig. 3):

$$P(f) = \sqrt[3]{1-f} \tag{7}$$

This result means that half of the crystals in a thin section will expose 87.5% of their growth history by volume. Equation 7 is only approximate for crystals that have not grown with constant aspect ratio. If the volume crystallized is considered a more appropriate index of growth history than the linear core-to-rim distance, then sampling criteria can be relaxed, allowing more sections to be used from a given thin section.

Regardless of the amount of the growth history recorded in a zoning profile, some degree of distortion is likely to be present even in sections that are nearly ideal. If non-ideal profiles are to be correlated successfully, some form of stretching and aligning should be considered to compensate for the distortion.

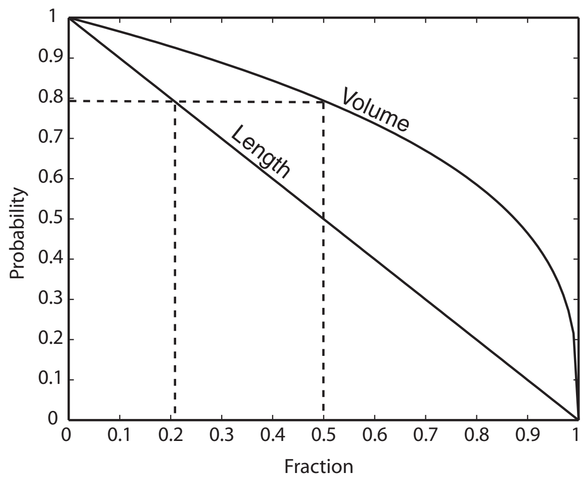

Figure 3. Probability of cutting a section through a grain with a given fraction of the length or volume of the crystallization history represented in the zoning pattern. The dashed line shows the difference in probability between representing 50% of the history by volume or by core-to-rim distance. The relationship between length fraction, l, and volume fraction, f, for spherical and tetragonal crystals is $l = -(1 - f)^{1/3} + 1$.

Profile normalization

Profile normalization alters the length and alignment of profiles to compensate for the effects of non-ideal sections. There are three options for normalization: no-normalization, common length normalization, and adaptive normalization (Table 1). Although it is not possible to correct for truncation without knowing the zoning pattern of the core of the grain, differences in orientation resulting in stretching can be compensated for by changing the length of profiles. The simplest assumption is that profiles have not been stretched and that profiles can be left at their measured lengths for correlation. If it is assumed that there has been stretching but no truncation, then profiles can be normalized to a common length. However, if both truncation and stretching have affected profiles, then an adaptive approach that uses variations in profile characteristics to guide stretching and alignment of profiles is needed.

Two adaptive approaches appropriate to normalization of zoning profiles are Fourier-based normalization and correlation optimization. Fourier-based adaptive normalization is based on the assumption that features in zoning profiles have characteristic wavelengths or frequencies. If this assumption is true and profiles are at the same degree of stretching, Fourier analysis will reveal the same frequency spectra for each profile. For example, if two sine waves with different wavelengths are analyzed, the difference in their dominant frequencies will be proportional to their difference in wavelength. The sine waves can be normalized by stretching one of the profiles until their spectra match (Atlas 2002, personal communication). Because frequency analysis only compensates for stretching and has no spatial reference, a known point, such as the crystal rim, must be used to align the profiles.

If profiles do not have characteristic frequencies, the utility of Fourier-based normalization techniques is difficult to assess. Natural zoning profiles have complex spectral characteristics, such as poorly defined peaks and low signal-to-noise ratios, and, when zoning patterns are self-similar, have variable zone widths or few large compositional spikes. When profiles have complex spectral characteristics, many of the issues encountered in the alignment of zoning profiles are encountered when aligning frequency spectra. Some studies of oscillatory zoning in plagioclase have documented dominant frequencies (Ginibre et al. 2002), but analysis of entire zoning patterns usually result in complex spectra due to the superposition of zoning types and gradational changes in shape and amplitude between zoning features.

Another approach to adaptive normalization is to align profiles on a pair-by-pair basis to optimize their correlations. First, one profile is designated as the reference and the other as the variable profile. The variable profile is replicated and interpolated to a range of lengths resulting in an array of stretching. Then, each copy of the variable profile is translated past the reference profile and a correlation coefficient calculated at each position. The combined stretching and translation with the highest correlation coefficient is selected as the optimal normalization for that pair of profiles. The addition of translation in the normalization routine provides partial compensation for inconsistent rim selection in plutonic or glomerocrystic crystals where it is difficult to consistently determine rim positions. No translation is needed if rim positions are the same for all profiles. Because baseline trends dominate variance, this adaptive normalization technique aligns primarily on the similarity of baseline trends and secondarily on the distribution of smaller scale zoning features. Adaptive normalization by correlation optimization is more reliable for the alignment of plagioclase zoning profiles than Fourier-based techniques and is the technique used in the Monte Carlo experiments below.

Once profiles have been normalized using one of the techniques above, they can be correlated by either standard correlation or WBC. Correlation of the same set of profiles will produce different coefficients for each of the normalization and correlation approaches. If different techniques produce different results, then each technique is also likely to have different significance levels. The question now is: "What is a significant correlation?"

Table 1. Normalization techniques for profiles measured from non-ideal sections

Technique	Approach	Assumptions
No-normalization	Leave profiles at their measured length	Profiles are on-center, measured along the same crystallographic axes, at the same resolution
Common-length normalization	Interpolate profiles to a common length	All sections are on-center, crystals have a common nucleation time and differences in length are due to section misorientation and/or measurement resolution
Adaptive normalization	Parametric alignment and stretching	All profiles have a common feature, such as wavelength of zoning or baseline trend, that can be used to match profiles

Reference distributions and statistical significance

There is no generic formula for the determination of significance levels for profile correlation due to stretching, truncation, and the variability of crystal sizes, zoning types, and patterns – all of which affect correlation. Statistical significance is determined by comparing measurements to a reference distribution, which provides a measure of the probability that a measurement is distinguishable from random association (Box et al. 1978). For example, if a value is greater than 95% of a distribution, it is considered significant at the 95% level (Fig. 4). Changes in the reference distribution will change significance levels and affect the identification and interpretation of populations from correlation coefficients. Therefore, a reference distribution must be determined independently for each set of profiles to correctly evaluate correlation coefficients. For the correlation of zoning profiles, the reference distribution must represent the probability of a pair of random zoning profiles correlating at a given value.

Reference distributions must be determined for each type of normalization and correlation technique. Each approach to profile correlation will have a different amount of inherited correlation from the assumptions used to align profiles and the differences in profile variance due to digital filtering. Because of the complexity of zoning profiles, it is difficult to determine significance levels from a theoretical basis. However, a Monte Carlo approach in which many profiles with defined characteristics are correlated provides a way to determine significance levels. If profiles with random characteristics are correlated, the distribution of the correlation coefficients provides a proxy for the reference distribution of false matches from which significance levels can be determined. The correlation value that 5% of false correlations are above is the 95th percentile significance level for profiles with the defined characteristics.

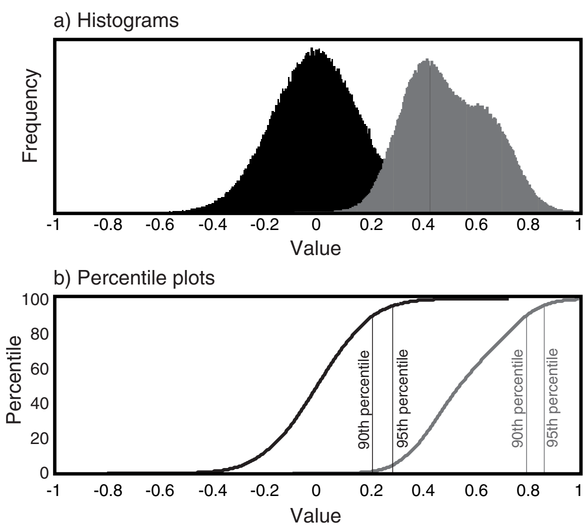

Figure 4. Graphical representations of two random data sets in the range ward1 to 1. **(a)** Histogram of all data points. Black histogram is normally distributed. Gray histogram is not normally distributed. **(b)** Percentile distributions with 90th and 95th significance levels marked by index lines. Colors as above. For the normal distribution, values greater than 0.3 are significant above the 95% level. However, for the gray population, values greater than 0.86 are significant above the 95% level.

Monte Carlo statistical model

Monte Carlo experiments provide an adaptable method for determining reference distributions. This approach parameterizes the effects of non-ideal sections and the diagnostic features of zoning in sets of synthetic zoning profiles (Fig. 5). Histograms of the correlation of synthetic profiles with random characteristics are used as reference distributions. Two sets of profiles were generated for this study: the first set of profiles consists of random profiles that are used to develop reference distributions, and the second set of profiles contains initially identical profiles. Correlation of a population of initially identical profiles provides a method of evaluating the effectiveness of different analytical approaches as the ideal correlations are known a priori. As the number of synthetic zoning profiles in each set increases, the histogram of their correlations will converge on an appropriate reference distribution. Each Monte Carlo experiment consists of 40 sets of 30 profiles, excluding correlations of a crystal against itself, giving 34 800 correlations (Figs. 6 and 7).

Synthetic zoning profiles

Because reference distributions are generated by the correlation of synthetic zoning profiles, the synthetic profiles must mimic the diagnostic zoning features found in natural zoning profiles. If inappropriate synthetic profiles are used, reference distributions will provide incorrect significance levels. The diagnostic features of plagioclase zoning profiles are distinctive shapes and amplitudes of changes in the anorthite content. Plagioclase zoning is divided into three categories: type I zoning, type II zoning, and a baseline trend (Pearce and Kolisnik 1990). Type I, or oscillatory, zoning is characterized by zones from <1 to 10 μm in width and 1 to 10% An, with most zones less than 5% An. Type II zoning is characterized by variations greater than 5% An, and widths of 3 to 100 μm. Type II zones are commonly preceded by a resorption event followed by crystallization at higher An content resulting in a sawtooth shape (Pearce 1994). Baseline chemical trends span the full length of the zoning profile and range from flat to tens of percent change in An.

Synthetic profiles are constructed by simulating each zoning types and then superposing them on a baseline trend (Fig. 7). Each type of zoning feature is tailored to match natural zoning profiles, but the position and amplitude of zoning features is assigned randomly to prevent biasing correlation coefficients. Type I zoning is simulated by white noise with variable amplitude to match specific data sets. For the analyses presented here, amplitude is set to the range –1 to 1. Type II zoning is simulated by convolution of a sawtooth-shaped filter with a series of randomly placed spikes. Spike heights are distributed normally, creating a range of peak amplitudes. The filter shape can be changed to match the characteristic shape of type II zones. Synthetic profiles in this study have been superposed on a normal zoning trend in the range An_{50} to An_{25}. Baseline trends can be determined from data sets using a low-order polynomial fit to the natural profiles.

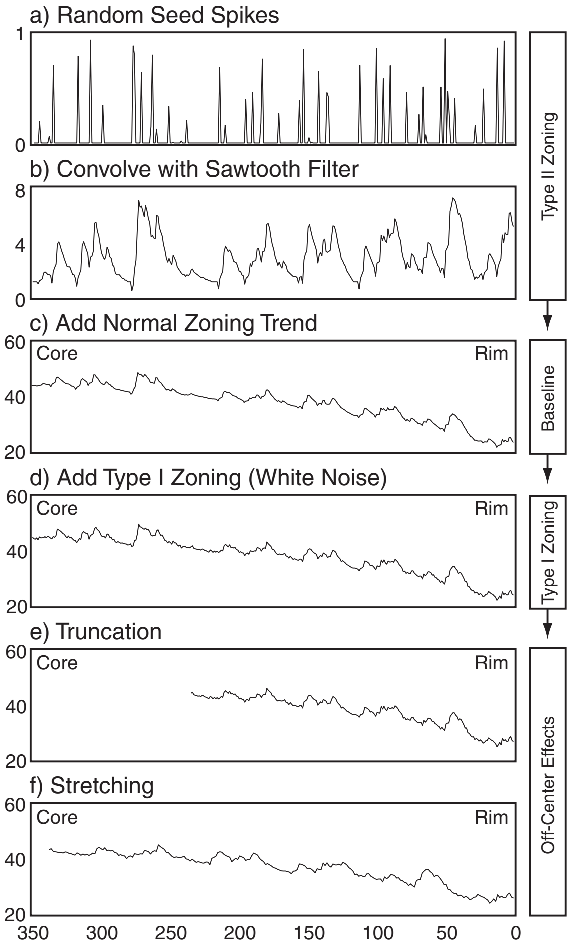

FIGURE 5. Significance levels for standard correlation and wavelet-based correlation (WBC) using normalization techniques outlined in text. Significance legend is at bottom of figure. Standard correlation techniques have the highest correlation levels for a given distortion index and percentile. Adaptive normalization gives the highest correlations with the WBC technique for a given distortion index and percentile; common length normalization gives the lowest. Increasing correlation with distortion index in WBC indicates decreasing reliability of the normalization routine with decreasing ideality of the section. Dashed lines are references at the 95th percentile for truncations of 0.1 and 0.4 for Figure 6.

Even with strict sampling criteria, natural zoning profiles are likely to have some degree of distortion because of the low probability of obtaining an ideal section. Consequently, synthetic profiles need to be modified to approximate varying degrees of non-ideality—they need to be stretched and truncated. A simplifying assumption is that sections are chosen to be within a given fractional distance from the core of the crystal and section orientation is not a sampling criterion. Truncation is treated as a simple removal of the near-core portion of the synthetic zoning profile. To simulate different sampling criteria, the amount of truncation from the near core part of the zoning profile is varied to different thresholds between 0 and 0.7 of the total profile length. For a truncation threshold of 0.6, the amount of truncation from the near-core part of the zoning profile is assigned randomly to be between zero and 60% of the profile length. Profiles are stretched by a random amount between 0.5 and 1.5 of the profile length to simulate the effects of misorientation; this approximates a tetragonal crystal with an aspect ratio of 2.8:1. This model for the distortion of synthetic profiles assumes that stretching of zoning patterns is evenly distributed along the profile. However, if zones in natural crystals are curved, the amount of stretching is no longer evenly distributed along the profile and is a function of the changing angle between the measured profile and growth faces. An appropriate stretching routine for curved zones in a spherical crystal is presented in Appendix I.

PROFILE SAMPLING REQUIREMENTS

Given that there may be multiple populations in a measured set of zoning profiles and that not all correlations within a population will be significant, there is a minimum population size that can be resolved from a limited number of profiles. The minimum fractional size of a population, x_{min}, in the total population that can be resolved with a given number of samples is a function of the total number of profiles, G, the smallest number of profiles in a population, G^*, and the fraction of correlations of a single population above the significance level, Q. Assuming that there is no selective bias during sampling, the probability of any individual crystal representing a given population is $P = x_{min}$. Note that if x_{min} is sampled significantly, and Q and G^* are constant for all populations, populations larger than x_{min} will be oversampled. Using this limiting case as a guide, the number of grains that must be sampled to resolve x_{min} is approximated as:

$$G = \frac{G^*}{x_{min}Q} \quad (8)$$

If Q is variable between populations, it may be necessary to calculate G for each sample according to the limiting case. Populations are not necessarily evenly distributed due to either inequalities in abundance or crystal size, which can introduce a systematic sampling bias in which populations made of large crystals are over represented (Russ and Dehoff 2000). For example, if populations are distributed evenly, x_{min} is 0.5, whereas for a 5:1 ratio in abundance between two populations, x_{min} is 0.2. Therefore, many profiles must be measured to resolve unevenly distributed populations than to resolve evenly distributed populations. For the Monte Carlo experiments in which a single population is analyzed, x_{min} is 1.0. Equation 8 also can be used to estimate the smallest population that can be resolved from a set of profiles.

RESULTS OF MONTE CARLO EXPERIMENTS

Monte Carlo experimental results for significance levels and single population correlations are presented in Figures 5 and 6. The 95th percentile significance levels vary between 0.35 and 0.98. Standard correlation reference distributions produce consistently higher significance levels than WBC. WBC significance levels are more variable and, except for common length normalization, increase with increasing truncation threshold. This increase in variability indicates a stronger dependence on non-ideality than other techniques that generally show little sensitivity to changes in truncation threshold. As the truncation threshold increases, there are fewer zones present in each profile, and the

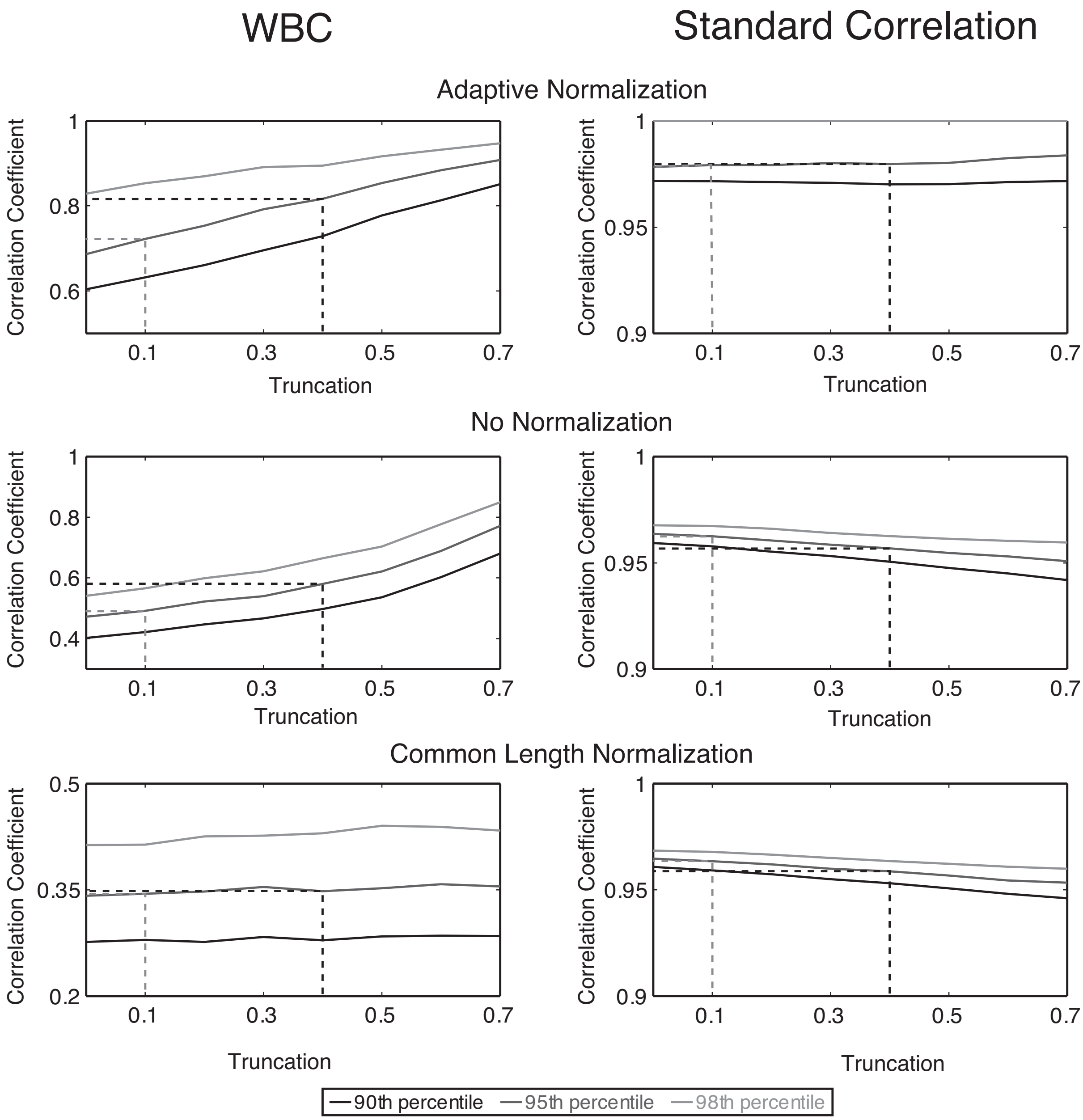

FIGURE 6. Correlations of a single population that has been stretched and truncated. Adaptive normalization produces the best results in WBC analyses. Dashed lines are the 95th percentile significance level for truncations of 0.1 (gray) and 0.4 (black), as in Figure 5. The percentile axis represents the percentage of the data that fall below the significance level for a corresponding significant correlation level from the **x**-axis. The fraction of significant correlations, Q, is the percentage the population with significant correlations (e.g., 40% for WBC with adaptive normalization at $T = 0.4$). The larger the fraction of significant correlations, the more effective the technique. Significance levels are from Monte Carlo results presented in Figure 5.

probability of a majority of those zones aligning increases. The resulting increase in weighting of individual zones on the correlation coefficient causes an increase in the significance level for WBC. Even though the same effects hold true for standard correlation, increases in correlation are buffered by increases in variance as the steeper part of the baseline trend becomes more dominant. Constant significance levels with increasing degrees of non-ideality indicate that sampling criteria will not strongly affect correlation significance in this data set. Trial Monte Carlo experiments with various synthetic profile configurations result in different reference distributions and significance levels, indicating that results of this study are only valid for profiles similar to the synthetic profile in Figure 7.

The fraction of significant correlations provides a benchmark for evaluating the effectiveness of different correlation and normalization techniques: the larger the significant fraction, the more effective the technique (Fig. 6). Adaptive normalization is consistently the most effective with a Q of 0.4, whereas common length normalization produces Q as low as 0.16. Common length and adaptive normalization Q values converge at low truncation thresholds. This convergence reflects an approach to ideal conditions for common length normalization (Table 1). Interestingly, despite the range of significance levels for adaptive normalization and no normalization, the techniques produce fairly constant Q over a range of truncation thresholds indicating that the effectiveness of each is more dependent on the underlying assumptions than the degree of truncation.

The number of profiles required to resolve populations is more dependent on normalization technique, than on correlation technique (Table 2). The number of profiles needed to resolve a single population ranges from 9 to 30 for adaptive normalization and common length normalization. Assuming identical Q for all populations, between 82 and 300 profiles may be needed to resolve a population represented by 10% of profiles.

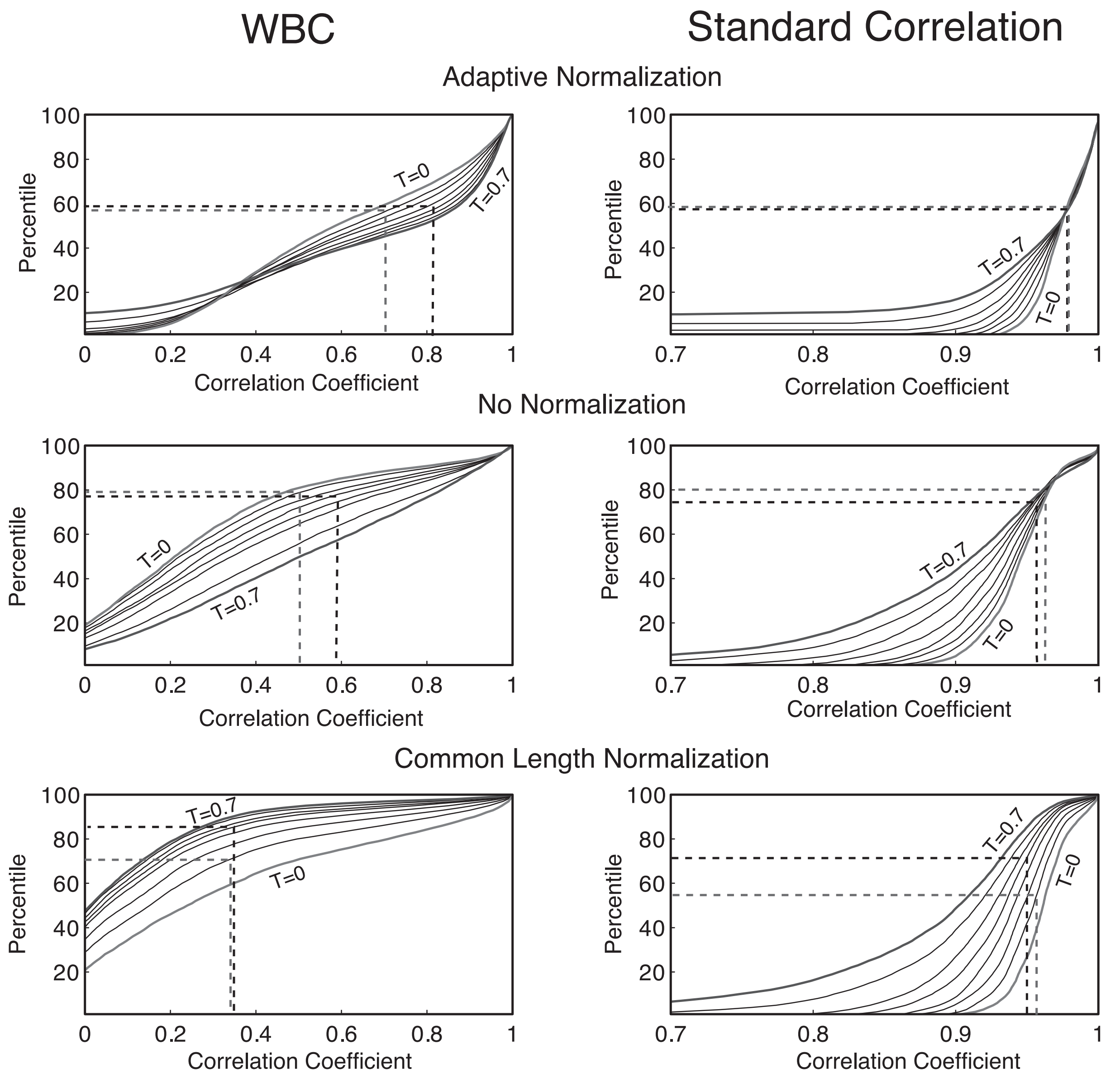

FIGURE 7. Construction of a synthetic plagioclase zoning profile, as discussed in text. Synthetic profiles are generated by the progressive addition of key zoning components. Type II zoning is simulated by the convolution of a sawtooth-shaped filter with a set of spikes with random height and distribution. The baseline trend is added as a smooth normal zoning trend. Different curves may be substituted to simulate reverse zoning, or other zoning trends. Type I zoning is simulated as white noise. Non-ideal geometries are simulated by truncation and stretching of the profile for off-center and misorientation. It is implicitly assumed that zones are parallel in the stretching routine used here. If zones are curved, a different routine must be used, such as the one presented in Appendix I for a hypothetical spherical crystal.

TABLE 2. Minimum number of profiles that must be analyzed to represent a population of crystals limited by a minimum population

Minimum	Adaptive normal.		No normalization		Common length normalization	
Population	Standard	WBC	Standard	WBC	Standard	WBC
0.1	82	86	116	120	250	300
0.2	41	43	58	60	125	150
0.3	28	29	39	40	84	100
0.4	21	22	29	30	63	75
0.5	17	18	24	24	50	60
0.6	14	15	20	20	42	50
0.7	12	13	17	18	36	43
0.8	11	11	15	15	32	38
0.9	10	10	13	14	28	34
1.0	9	9	12	12	25	30

Notes: A minimum population (x_{min}) is the smallest resolvable population fraction, as discussed in text. Sampling requirements are calculated from Equation 8 using Monte Carlo experimental results at the 95th percentile significance level and a truncation threshold of 0.7, as presented in Figure 7. normal. = normalization.

DISCUSSION

We have presented a Monte Carlo approach to determine statistical significance levels for the correlation of compositional zoning profiles and the effects of varying degrees of profile distortion and sampling criteria. The use of synthetic zoning profiles to build reference distributions allows significance levels to be determined for natural zoning profiles and different sampling criteria. However, because reference synthetic profiles are tailored to natural profiles, significance levels are valid only for profiles with similar characteristics. Sampling criteria should be based on a qualitative assessment of the distribution of populations based on petrographic inspections and a pilot set of Monte Carlo experiments to determine significance levels and sampling requirements. Monte Carlo experiments implicitly assume that there is no selective bias during measurement of zoning profiles. However, if populations are identified on a qualitative basis, smaller populations can be preferentially selected to reduce the total sampling requirements. If the amount of truncation can be estimated during sampling, significance levels can be assigned on a pair-by-pair basis from the appropriate reference distribution. Although minimum sampling requirements are appropriate only to their specific data set, they do indicate that large data sets are needed to resolve zoning populations. As more complex data sets are used for correlation, the number of profiles needed to resolve populations will increase, particularly for profiles with differences between baseline trends.

Rapid, high-resolution analytical techniques for measuring zoning profiles are needed to measure large numbers of profiles. Even though they may be faster to measure, low-resolution zoning profiles offer fewer points for correlation and are less amenable to wavelet analysis. Most optical methods like Nomarski differential interference contrast or a-normal profile comparison either offers no compositional information or lack adequate spatial resolution (Anderson 1983; Ginibre et al. 2002; Hibbard 1995). Microprobe point traverses are a common method of zoning profile measurement that offers excellent compositional resolution and a spatial resolution to 3–5 μm. However, many analysis points are required to characterize each profile, which can be time consuming. Laser interferometry coupled with an appropriate digitizing routine also has potential, but requires calibration by microprobe analysis (Pearce et al. 1987). Calibrated back-scattered electron (CBSE) imaging of zoning profiles offer spatial resolution to ~1 μm, and compositional resolution of 1–2% An when calibrated with microprobe analyses (Ginibre et al. 2002; Wallace and Bergantz 2002). CBSE imaging is perhaps the best available technique at present, because high-quality BSE images can be collected quickly, and require only a few calibration points.

Finding ways to reduce sampling requirements will increase the efficiency of techniques such as WBC. The most direct way to reduce sampling requirements is to increase the fraction of significant correlations for any population. The relatively simple adaptive normalization routine used in these Monte Carlo experiments improves efficiency by a minimum of 30% over other normalization techniques. If this is an indicator of the potential of adaptive normalization, further improvements in adaptive normalization techniques are also likely to increase efficiency. Adaptive normalization may be improved by including a wavelet basis similar to Fourier-based normalization, or by integrating multiple normalization techniques through neural networks to evaluate the best profile alignment.

CONCLUDING REMARKS

A precondition for the identification of crystal populations is the generation of an appropriate set of reference profiles for each set of natural profiles to distinguish significant correlations. Monte Carlo experiments are useful not only as a way to establish significance levels from reference populations, but also as a tool for establishing sampling guidelines when homogeneous populations are analyzed. Improvements in adaptive normalization and digital filtering have the potential to reduce sampling requirements. The large data sets that Monte Carlo experiments indicate are required to unravel zoning populations is daunting at first. However, recent advances in profile measurement coupled with the quantitative kinematic and chemical constraints that come from the correlation of crystals that are analyzed as both physical and chemical objects offer strong motivation for further work.

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APPENDIX I: NON-IDEAL SECTIONS IN A SPHERICAL GRAIN

A function that relates positions in oriented and misoriented profiles is needed to implement adaptive normalization routines and accurately distort synthetic profiles. For crystals with planar growth faces, the amount of stretching is distributed evenly in the profile because the angle between zones and profiles are constant from core to rim (Fig. A1a). However, for substances with curved growth faces the amount of stretching in an off-center section increases as the angle between the profile and the growth face decreases.

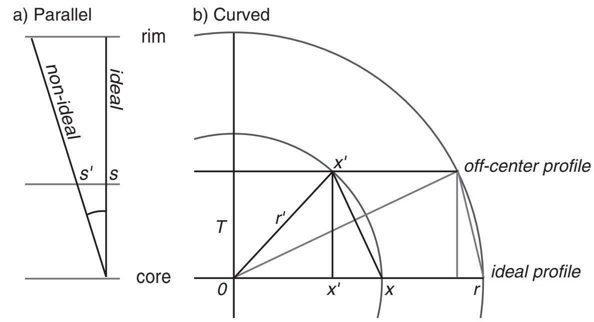

FIGURE A1. Relationship of points in non-ideal zoning profiles to ideal profiles for crystals with parallel and curved growth faces. **(a)** Where growth faces are planar, zones are parallel, and stretching is distributed evenly in misoriented profiles. **(b)** Where growth faces are curved, stretching is not distributed evenly and becomes more pronounced as profiles become tangential to zones.

For crystals where growth faces can be considered parallel (Fig. A1a), an arbitrary position in an oriented profile, *s*, can be mapped to a position, *s*', in a misoriented profile ϕ degrees from the ideal by:

$$s' = s \sec \phi \qquad \text{(A1)}$$

For a hypothetical spherical crystal, the amount of stretching in an off-center profile increases toward the apparent core as the profile becomes tangential to growth faces and zoning (Fig. A1b). In a spherical crystal, the amount of stretching at an arbitrary point in an off-center profile is a function of position in the profile and amount of truncation. Note that in a spherical crystal, the distance from the core controls both truncation and the distribution of stretching, so misorientation does not need to be considered independently. Points in ideal and off-center sections are connected by an arc between *x* and *x*' respectively. Using the properties of right triangles, the position in the ideal profile *x* can be mapped to the position in the off center section *x*' as:

$$x' = \sqrt{x^2 - T^2} \qquad \text{(A2)}$$

where *T* is the amount of truncation.