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Pankhurst, MJ, Walshaw, R orcid.org/0000-0002-8319-9312 and Morgan, DJ (2017) Major Element Chemical Heterogeneity in Geo2 Olivine Micro-Beam Reference Material: A Spatial Approach to Quantifying Heterogeneity in Primary Reference Materials. Geostandards and Geoanalytical Research, 41 (1). pp. 85-91. ISSN 1639-4488

https://doi.org/10.1111/ggr.12134

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Received Date : 19-Apr-2016

Revised Date : 27-Jun-2016

Accepted Date : 04-Jul-2016

Article type : Original Article

Major Element Chemical Heterogeneity in Geo2 Olivine Micro-Beam Reference Material: A Spatial Approach to Quantifying Heterogeneity in Primary Reference Materials

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A 270 spot-analysis study was conducted across a large (*ca*. 1200 µm x 1200 µm) chip of Geo2 olivine from a commercially available GEO Mk2 block (P and H Developments 2016) which revealed a 8.7% relative range in FeO abundance. Interleaved and overlapping grids of different resolutions were measured sequentially to prove spatial patterns are not due to drift or other external sources of error. Results were mapped and interpolated using commercially available geographical information system software, such that composition could be predicted according to location with high accuracy. The simple, systematic zonation pattern observed demonstrates that useful-sized regions of acceptable homogeneity do exist for some elements. This knowledge allows a user to target individual regions of a characterised chip for use as distinct measurement standards. As analysis times decrease and datasets grow, this approach may maximise laboratory efficiency by characterising large chips and extending time between standard block re-polish and coating, particularly in those cases where the avoidance of prior beam damage is a key concern.

Keywords: chemical mapping, olivine, natural mineral reference material, micro-beam, primary reference material, microanalysis, characterisation.

Analysis times of electron probe microanalysis (EPMA) single spots are becoming shorter as a result of both hardware and software improvements to systems such as increasing number of spectrometers on new instruments, development of large crystal and H-type spectrometers for increased counting efficiency (e.g., Jercinovic *et al.* 2008), and application of Mean Atomic Number defined backgrounds (Wark and Donovan 2011). These efficiency gains allow researchers and developers to generate larger datasets per unit time. This in turn places increasing pressure on the surfaces of matrix-matched reference material (RM) available for analysis before standard blocks must be re-polished and coated (e.g., Carpenter 2008). This also amplifies the potential impact of known issues with small heterogeneity in natural silicate RMs (e.g., Jarosewich *et al.* 1980, Rose *et al.* 2009, Fournelle 2012).

Common practice is to distribute analysis spots across RMs used as primary and secondary measurement standards, in part to minimise the possibility of prior beam effects influencing results, particularly where issues such as potential alkali mobility are important (Carpenter and Vicenzi 2012). Small chips of RM can therefore be quickly covered in beam damage or contamination and rendered unusable until re-polishing occurs (e.g., Carpenter 2008). Furthermore, long automated measurement runs involving numerous sets of standard analyses queued from an initial set of co-ordinates and using auto-incremented steps (e.g., Donovan *et al.* 2012) may be limited by the size of the RM chip (before the program would otherwise run outside the chip). Therefore large, homogeneous natural chips are increasingly desirable, as they promote maximum efficiency in EPMA (and LA-ICP-MS, SIMS etc.) laboratories.

In this contribution we demonstrate a compensatory approach. In this study, a large, chemically heterogeneous chip was spatially characterised using small, well-characterised RMs as primary and secondary measurement standards. Following this it was possible to divide the large chip into domains of acceptable homogeneity, and then employ each of these regions as a distinct measurement standard (with caveats discussed below).

The GEO Mk2 suite of samples, manufactured and distributed by P and H Developments, is one such set comprising generous chip(s) of reference materials, certainly with respect to olivine (Figure 1). In comparison, olivine RMs distributed by the Smithsonian National Museum of Natural History, Washington: Rockport (Fo_{00}), San Carlos ($Fo_{90.1}$); and Springwater meteorite (Fo_{83}) olivine, while probably peerless in terms of elemental characterisation (see Jarosewich *et al.* 1980, Fournelle 2011, and also Table 1), are composed of very small chips. This is necessary partly due to the desire to distribute material widely and prolong the use (and thus value) of the RMs, rather than for analytical reasons.

Motivation

To facilitate a very large study of natural olivine compositions at the University of Leeds, the Geo2 olivine chip was intended for use as an in-house reference material. Initially the chip performed well, yet when new areas of the chip were used, results from the natural olivine used as a secondary reference material, were found to be unacceptably different from known reference values and previously obtained analyses. Of particular note was a strong positive relationship between analysis totals and calculated FeO.

It was suspected at the time that due to the comparably low FeO content in Geo2 olivine (nominally ~ 4.67% *m/m*), even a small relative discrepancy between the reported and real FeO content would have a disproportionately large influence on the absolute calculated FeO from the natural samples (since FeO in olivine from basalts can vary from around 10–40% *m/m*, see Deer *et al.* 1982). A high-resolution back-scattered electron (BSE) image taken with very high contrast settings (see below for instrument details) revealed a subtle gradient in mean atomic number (Figure 1), visible when using a colour map with strongly graduated colour ramps (Rasband 2015). This observation is consistent with variable, systematic Fe abundance.

To investigate further, a qualitative map was made of legacy Geo2 olivine analyses (run as and secondary reference materials) in *Mapinfo* (Pitney Bowes 2015) and a pattern in Fo content appeared to correlate with the BSE response (not shown as it was superseded by the quantitative map shown in Figure 1). The systematic nature of this pattern suggested a solution could be found, and so it was decided to quantitatively characterise this chip in detail, utilising other reference materials. An approach was designed that is applicable to other RMs and other laboratories, which may be particularly useful where the chip(s) in question could be employed as a reference material(s) for more than one element of interest.

Experimental procedure

Analytical setup

A JEOL 8230 system with five wavelength dispersive spectrometers and Probe For EPMA (PFE) software (Donovan *et al.* 2012) interface housed at the University of Leeds Electron Microscopy and Spectroscopy Centre (LEMAS) was used to determine mass fractions of Fe, Mg, Si, Mn, Cr and Ni. While quantitative X-ray mapping was considered, spot analyses were chosen instead due to their superior precision and to ensure that analyses of Geo2 olivine and the other olivine reference material chips were directly comparable. A 20 kV, 40.0 nA beam was used on focused spots with auto focus used on each spot. Major elements were measured on multiple spectrometers and the counts summed to maximise precision. A TAP crystal for Mg and Si (40 s on-peak/30 s off-peak; cumulative 80/60 for Mg and Si respectively) was used, whereas TAPH was used for Mg (40/30), LIFL for Fe (40/30), Mn

(60/60) and Cr (20/20) and LIFH for Fe (40/30) and Ni (60/60). The data were collected in a single run of 23 hours duration.

The Springwater Meteorite Olivine USNM 2566 was used as a primary reference material for Fe and Mg, Geo2 Almandine (natural; Roxby, Connecticut) for Si, Geo2 Ni metal (pure) for Ni, Geo2 Rhodonite (natural; Broken Hill, New South Wales) for Mn and Geo2 Cr_2O_3 (synthetic) for Cr. Four blocks of three analyses of Smithsonian-distributed San Carlos Olivine USNM 111312/444 was used as a secondary reference material were distributed throughout the run, which recorded no evidence of significant drift (see online supporting information Appendix S1 for details of these analyses) and analyses reproduced published values within acceptable tolerance (*cf*. Jarosewich *et al.* 1980). Quantitative analyses (% *m/m* oxide) were produced using the Phi-Rho-Z matrix correction algorithm of Armstrong/Love Scott implemented within the Probe for EPMA (PFE) software package (Donovan *et al.* 2012).

Two outlying analyses from Geo2 olivine that were anomalous with very low totals of ~ 97 and ~ 78% *m/m* respectively, and one secondary RM analysis of San Carlos (total ~ 94% *m/m*) were rejected. Otherwise excellent stability of FeO, MgO and MnO was noted, and comparably less precise SiO_2, which dominated variance in the totals of the secondary RM analyses (99.09–100.20% *m/m*). Accordingly, it was believed that there was no reason to further correct or re-normalise the Geo2 olivine data.

Characterising the Geo2 olivine chip

Two, two-part rectangular grids (grid1aandb; grid2aandb), were programmed across overlapping regions of the chip of Geo2 olivine using PFE software (Donovan *et al.* 2012), (see Figure 1). Grid 1a and 1b were designed to, together, form a Cartesian grid across the majority of the chip, where the distance between points is 75 µm in the X direction and 65 µm in the Y. Grid 2a and 2b were designed to provide a high-resolution (13 µm in X, 45 µm in Y) strip, capturing a region that from previous analyses was determined likely to display compositional heterogeneity. While the polygonal grid function of PFE could have been employed, it was preferred to use two parts for each grid, analysed sequentially so that measurement repeatability could be constrained over time. In this way, any duplicated pattern of elemental abundance resulting from the combined grid could be confidently attributed to real variation, rather than subtle instrument drift. Conversely, if differences between the grids were observed, error propagation could then be constrained closely.

Data mapping and interpolation

Commercially available software *ioGAS* (REFLEX 2015) and *MapInfo* (Pitney Bowes 2015) was used to map the data. Both software packages are routinely utilised by geochemists in the mineral exploration community and contain a range of features that made them suitable for this task. For instance, we were able to modulate the spatial influence of each point in *ioGAS*, which provided considerable control over the weighting of each analysis spot, which in turn made the task of spatial geochemical mapping of the RM (see Bédard and Néron 2014 for an introduction to the concept) easily tailored to the user's requirements.

In Figure 1 a cell size of 20 µm is depicted (values were averaged in those instances where two analysis spots occupied the same cell), a search – and minimum smoothing radius – of four cells, and scaled the results linearly to produce domains of known variability. No evidence for inclusions was observed and, as such, nugget effects for the elements considered here were not anticipated (*cf*. Molloy and Sieber 2008). By geo-registering the high resolution BSE image of the chip of Geo2 olivine in *Mapinfo* (Pitney Bowes 2015) it was possible to locate all the analyses in order to compare grey-scale response with composition.

Results and discussion

Geo2 olivine chemical heterogeneity

Of the 268 accepted analyses from 270, a range in major element chemistry was observed, which was considered unacceptable (see Table 2). FeO abundance ranged from 4.66 to 5.11% *m/m*, a relative difference of ~ 8.7%. MgO and SiO_2 results returned a ~ 4% and ~ 3% relative difference respectively. Significant or systematic variations in trace element abundances were not observed, although it is important to note that we were concerned primarily with major element heterogeneity and designed our experiment accordingly (see Appendix S1).

Importantly, each part of grids 1 and 2 effectively duplicate one another. The same pattern was observed, and neighbouring points from each part-grid were within analytical error of each other. Thus it was possible to confidently ascribe the results to real variation, and not instrumental drift or another artefact imposed by the instrument.

An additional measure of heterogeneity can be statistically derived from the analytical data using a homogeneity index calculation. The homogeneity index (Boyd *et al.* 1967, Harries 2014) is an expression of the ratio between the standard deviation of the analytical dataset and the precision of the instrumental counting statistics, and its derivation is described in detail by Harries (2014). The homogeneity index provides a measure of the influence of external factors over the total analytical error budget.

A resultant index of 1, in which data variance equals counting precision is taken to signify perfect homogeneity, while an index of > 3 indicates significant chemical heterogeneity (or instrumental drift) within the data. Homogeneity indices for Fe, Mg and Si within our data all fell in the range 5–12 indicating a high degree of chemical heterogeneity within the analysed material. The derived homogeneity index values were exported from the Probe for EPMA software interface via its “sigma ratio” function.

The range in major element abundance confirmed the suspicion that a modest absolute difference in FeO in Geo2 olivine, used as a secondary Fe reference material, has the potential to impose an error upon seemingly “drift”-corrected calculated FeO in unknowns. When secondary reference material analyses were taken from areas where the real FeO abundance in Geo2 olivine was in fact higher than the nominal value, these resulted in an underestimation of FeO abundance in the unknowns. The effect led to the positive relationship between totals and FeO abundance, where the problem was first detected.

A systematic pattern, and creation of useful domains

The distribution of Fe and Mg in the chip of Geo2 olivine is shown to be systematic, and characterised by a linear gradient at ~ 45° to the chip boundaries (Figure 1), which are nearly square to the stage co-ordinates (at the time of analysis). As such, it is possible to divide the chip into ~ 45° strips of uniform composition that will return greater reproducibility than the dataset as a whole and could be referred as a sequence of measurement standards. To retain the utility of using large chips for long analytical runs, we now consider the chip as two roughly equal domains with their own composition described in Table 2.

Characterisation of large grains for use as primary measurement standards

Conventional characterisation of reference material uses statistically robust *in situ* measurements to define a material's variability from a mean value measured by bulk analysis (e.g., Jarosewich *et al.* 1980). Should the material be deemed to have acceptable variation, the bulk measurement is then conducted and adopted. Our approach differed, for we characterised the chemical variation in a chip already mounted by treating it as an unknown, using well-characterised matrix-matched primary reference materials. This is more akin to Eggins and Shelley (2002) who mapped elemental heterogeneity in a series of NIST glasses using LA-ICP-MS and were in a position to describe two-dimensional domains, and a mechanism for the observed heterogeneity. While using RMs to calibrate other RMs necessarily imposes an additional level of error – in our case from the error associated with the Smithsonian reference materials used – there are compelling advantages to the spatial approach (e.g., Bédard and Néron 2014).

For example, any wet chemical or indeed XRF analysis, despite the greatest care, must necessarily be composed of particles that hold the potential for heterogeneity which will be averaged by the sample preparation (e.g., Carpenter and Vicenzi 2012). In the case of olivine, the optical difference between particles that vary on the per cent level for FeO abundance is exceedingly small and is unlikely to be sorted visually or magnetically. Fournelle (2011) characterised twenty-five chips of the Smithsonian San Carlos olivine for a total of 236 points, and found that while the mean composition of Smithsonian-distributed San Carlos olivine did match the wet-chemical analysis, 18% of the analyses fell outside 2*s* of Fo90.1 (± 0.2). At present it is unclear how homogeneous individual chips were within Fournelle's (2011) study. All analyses of San Carlos olivine in this study were conducted on a single chip that contained no evidence for significant heterogeneity.

A spatial approach allows the user to define how intra-grain variation is distributed, and in turn allows for mass-balancing those analyses against the bulk value by weighting those analyses by area occupied (or volume as measured by emerging 3D techniques (or volume as measured by emerging 3D techniques, e.g., Pankhurst *et al.* 2014). This approach represents a deeper level of RM characterisation, which due to the ever-increasing requirement for greater precision at higher spatial resolutions, is likely to be warranted.

Towards an explanation for the observed pattern

The work raises questions as to why there is a reproducible gradient in the chemical analysis across this chip. A geologically plausible explanation may be that the chip is sectioned from a comparatively broad, diffused profile (Buening and Buseck 1973), or that an oxidation gradient is preserved that produces the observed % *m/m* shift (see Schaefer 1985), or that a crystallographic bending of some nature is affecting the WDS counts. In order to find a satisfying answer, however, one would (currently) need to use destructive techniques (e.g., micro-XANES Dyar *et al.* 1998), which in this particular case would undermine the original intention. We note that the GEO2 olivine is most likely to have been procured from the serpentinised shear zone within the Sumput Complex, Kohistan (Jan and Khan 1996). However, if genuinely gem quality as claimed, then after checking the Mindat.org entry (Mindat.org 2016), which features images of large, euhedral peridote crystals, this material seems *prima facie* unlikely to be deformed.

Conclusions and recommendations

The composition of Geo2 olivine is shown to be variable within this chip at a level of ~ 0.25% *m/m* FeO, and many analyses result in major element abundances that differ observably from the mean composition. In this study, a systematic distribution of Fe and Mg was described that allowed us to domain the chip into two useful-sized areas of acceptable major element homogeneity. Our approach of using overlapping grids and mapping software to interpolate and help calculate domain statistics could be adopted by other laboratories, for the basic method is not specific to our instrumentation.

In light of the results of this study, it is recommended that users of Geo2 olivine also characterise their chip(s) in order to improve confidence in those nominal compositions; it is not clear if our experience is typical or unlucky, but demonstrates that potential and measurable variability certainly exists in this reference material. The approach described herein could be adopted for use in any chip whose size makes it desirable for use during long measurement runs with internal standardisation. High-contrast BSE imaging and use of colour drapes such as the 3-3-2 RGB filter of *ImageJ* (Rasband 2015) may indicate problem chips, particularly those where chemical gradients are small, or define areas on chips for targeted characterisation.

Acknowledgements

The manuscript benefited from the thorough and constructive critiques, and we wish to thank the reviewers. MJP gratefully acknowledges the support of an AXA Research Fund Fellowship. Analyses for this work were supported by NERC grant NE/J024554/1 awarded to DJM.

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Supporting information

The following supporting information is available online:

Appendix S1.

This material is available as part of the online article from:
http://onlinelibrary.wiley.com/doi/10.1111/ggr.[00000]/abstract
(This link will take you to the article abstract).

Figure caption

Figure 1. Mapping systematic chemical variation in Geo2 olivine. (a) High contrast, high resolution Back Scattered Electron (BSE) image of Geo2 olivine (using beam settings of 20 kV, 30.0 nA), showing analysis spot locations and their respective grids. The overlapping grids allowed comparison of similar locations at different times in the run and to constrain subtle instrumental drift. The colour

table used is the 3-3-2 colour scheme that comes as part of the ImageJ software (Rasband 2015) and has been substituted for the default greyscale. This colour scheme uses a sequence of strongly graduated colour ramps to effectively highlight subtle gradients in variation that would otherwise be invisible to the unaided eye. Image is otherwise not manipulated from the original greyscale in any way other than to highlight domains and analyses. The greyscale profile is 100 pixels wide, and highlights an observed gradient in BSE brightness (qualitative measure of Z contrast). Note that the Y axis is reversed (corresponding to the stage co-ordinate system). The location of Domains 1 and 2 are shown, see text for details. (b) Distribution of forsterite content. A large number of bins are used here to illustrate the near-parallel gradients in this chip.

Table 1.
Compositions of olivine reference materials used in this study

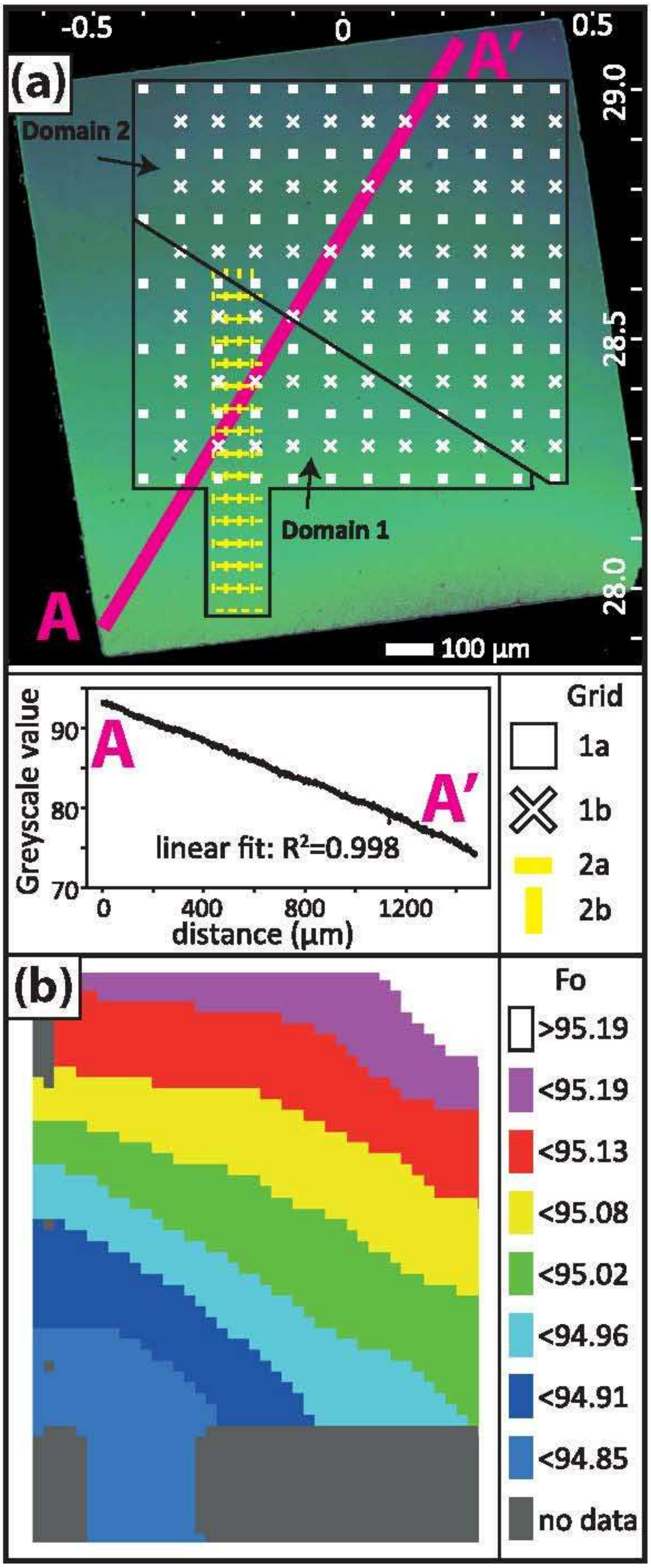
RM	Geo2 olivine	San Carlos olivine (USNM 111312/444)	Springwater Meteorite (USNM 2566)
Distributor	Commercially available	Smithsonian	Smithsonian
Fo*	~ 95.2	~ 90.1	~ 83.0
Oxide (% *m/m*)			
SiO_2	41.84	40.81	38.95**
Al_2O_3	nr	nr	nr
Cr_2O_3	nr	nr	0.02
FeO	4.67	9.55	16.62
MnO	0.12	0.14	0.3
MgO	53.02	49.42	43.58
CaO	nr	< 0.05	nr
NiO	0.19	0.37	nr

*Fosterite (the Mg end-member of the fosterite-fayalite solid-solution) was calculated as MgO/(MgO+FeO+MnO) on a molecular basis and expressed as between 0–100 where pure fosterite is Fo100

Table 2.
Major element summary statistics for entire Geo2 chip, and domains

	All *mean*	*n* = 268 2*s*	**Domain 1** *mean*	*n* = 168 2*s*	**Domain 2** *mean*	*n* = 100 2*s*
% m/m oxide						
FeO	4.91	0.22	4.99	0.12	4.79	0.12
MgO	53.47	0.61	53.33	0.51	53.72	0.45
NiO	0.20	0.06	0.20	0.07	0.21	0.01
MnO	0.15	0.01	0.15	0.01	0.15	0.01
SiO_2	41.59	0.50	41.65	0.50	41.49	0.44
Fo	94.95	0.25	94.87	0.13	95.09	0.14

NB: Further splitting domains results in an increase of precision (for a few iterations). This is not shown since what we wish to illustrate in its simplest form is that the approach of domaining a systematically zoned natural crystal results in higher precision, rather than show how we have solved a parochial issue.


-0.5
0
0.5
(a)
A′
29.0
Domain 2
28.5
Domain 1
A
28.0
100 µm
Greyscale value
90
80
70
A
A′
linear fit: R^2=0.998
0
400
800
1200
distance (µm)
Grid
1a
1b
2a
2b
(b)
Fo
>95.19
<95.19
<95.13
<95.08
<95.02
<94.96
<94.91
<94.85
no data