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REPRODUCIBILITY OF ELECTRON-MICROPROBE BULK ANALYSES OF FINE-GRAINED MEDIA: A CASE STUDY USING MODERN BONE CHINA

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ABSTRACT

The reproducibility of data on the bulk composition of very fine-grained media, and specifically the concentration of the major elements as established by electron-microprobe analysis, have been statistically assessed in order to establish criteria for analysis. Two sets of spot analyses, one using a beam diameter of 20 μm, the other of 40 μm, were undertaken on each of three fragments cut from a sample of modern bone china. Student's t-tests were run to determine if there was a significant difference (at 95% precision) between the two datasets. The results show that as few as 35 spot analyses need be averaged to provide a reliable indication of bulk composition, provided that the beam diameter is at least as large as the coarsest grains, and much larger than the average grain-size of the medium being analyzed.

Keywords: electron microprobe, analysis, porcelain, student's t-test, raster, statistics.

SOMMAIRE

Nous évaluons la précision statistique des données sur la composition globale de matériaux à granulométrie très fine, et particulièrement la concentration des éléments majeurs telle qu'établie par analyse à la microsonde électronique, afin d'obtenir les critères d'analyses. Nous avons effectué deux séries d'analyses, une avec un faisceau de 20 μm, l'autre de 40 μm de diamètre, sur chacun de trois fragments coupés d'un échantillon de porcelaine fine. Des tests t de student ont été faits afin de vérifier s'il y avait une différence significative (à une précision de 95%) entre les deux groupes de résultats. Aussi peu que 35 analyses ponctuelles suffisent pour obtenir une composition moyenne valable, mais il faut s'assurer que la taille du faisceau n'est pas inférieure au diamètre du grain le plus gros, et qu'elle dépasse la taille moyenne du matériau analysé.

(Traduit par la Rédaction)

Mots-clés: microsonde électronique, analyse, porcelaine, test t de student, balayage, statistique.

INTRODUCTION

Mineralogical and petrological research has been revolutionized by various microbeam methods of chemical analysis (Reed 1990). Ordinarily, the amount of sample is sufficient to allow the determination of major- and trace-element concentrations using a variety of methods, many of which (*e.g.*, inductively coupled plasma – mass spectrometry, ICP–MS) presently require that only a small amount of sample (*e.g.*, <1 g) be sacrificed. However, in some instances, sample size does become an issue (*e.g.*, as in the case of archaeological artifacts), and the researcher may be reluctant to powder even a tiny piece of the specimen if it can be avoided.

Although generally used to investigate the composition of minute subvolumes of individual grains, the electron microprobe has previously been used to determine the bulk composition of entire grains (*e.g.*, Bohlen & Essene 1977). However, there are few data governing practical aspects of this application, or its logical extension to measuring the bulk composition of fine-grained, polymineralic samples. Consequently, in this study, we report on the reproducibility of bulk, major-element electron-microprobe data for very fine-grained media. A sample of modern English bone china was chosen for this experiment; compared with many rock samples, this medium is relatively homogeneous and fine grained. As will be seen, it contains some of the same minerals found in some high-grade metamorphic rocks.

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Mineralogy of bone china

Bone china is a hybrid ware that was first derived in the 1790s by Josiah Spode, who combined ingredients used in the manufacture of two distinct types of porcelain: true porcelain and bone-ash porcelain. Both are derived from pastes containing quartz (or ground flint) and clay, but the former ware uses hydrothermally altered or weathered granite ("china stone") as a flux, whereas the latter contains bone ash. Bone-china pastes contain calcined bone ash [$Ca_3(PO_4)_2(OH)$], kaolinite, quartz and china stone. When fired, these ingredients react to produce high-temperature silica polymorphs (tridymite or cristobalite), whitlockite ($Ca_3P_2O_8$) or a compositionally and structurally similar phase (*e.g.*, β–$Ca_3P_2O_8$), anorthite and a melt phase. Whitlockite (or the β–$Ca_3P_2O_8$) is produced by the dehydration of bone ash. This process also liberates Ca (St. Pierre 1955), which can react with kaolinite to form anorthite (or gehlenite). However, other calcic phases, notably calcite ("whiting", in a ceramist's parlance), are also commonly used in ceramic pastes, and represent other possible sources of the Ca required to form anorthite.

ANALYTICAL METHODS

To monitor homogeneity, three cross-sections were cut at approximately 10-cm intervals from a large piece of bone china. These sections were mounted on glass, ground to a thin slab (30 μm), and polished on a lead lap for subsequent analysis with an electron microprobe.

The samples were analyzed with a JEOL 733 electron microprobe housed at Dalhousie University. This instrument is equipped with an Oxford Link eXL energy-dispersion system (EDS) and four wavelength-dispersion spectrometers. The EDS system was used during data acquisition. Natural and synthetic mineral (or glass) standards were used to calibrate the microprobe. Instrument precision assessed by replicate ($n = 10$) analysis of cobalt metal was found to be ±0.5% at one standard deviation. Accuracy for major elements (≥5 wt.% of relevant oxides) is approximately ±1.5 to 2.0% relative, but is lower for elements present in smaller concentrations. Count time was 20 seconds at each spot analysis, and the beam current remained the same (15 nA at 5 keV) for all analyses. The instrument was calibrated to measure the concentrations of Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, S, Pb and Co.

The bulk composition of the samples was determined by: (A) averaging the results of a large number of defocussed-beam spot analyses, and (B) rastering fields on each sample. Only data acquired by the former approach were statistically assessed; the raster data were collected solely for the purposes of comparison.

Two sets of spot analyses (method A) were undertaken on each sample, one at a beam diameter of ~20 μm, the other at ~40 μm. The spot analyses were obtained using a grid of an appropriate size (*i.e.*, as much of the sample that could fit into the grid) for a given number of analyses (*i.e.*, 40 by 30). A total of 1200 spot analyses were collected in each case. Each set of data required 8.3 hours of instrument time to acquire. Before processing the dataset, the data on Pb (originating from the secondary, metallic lead) were deleted, and all datasets with analytical totals less than 90% were excluded; the remaining datasets were then normalized to 100% to reduce the effect of variable totals owing to the inclusion of a secondary component (the Pb) on the statistical analysis. This resulted in two data sets of 1057 and 1079 spot analyses for 20 μm and 40 μm beam diameters, respectively. Consequently, the total area analyzed by this method was approximately 0.33 mm^2 and 1.36 mm^2, respectively. The analytical data were manipulated using SPSS, a statistical software program.

Phase proportions were determined by digitized back-scattered electron image (BSE) analysis. The BSE images were collected using the Oxford Link eXL system. Images were generated over a 256 × 256 pixel area at a magnification of 1200× and 2600×. Phase compositions were determined using a focused beam (1–2 μm in diameter) with a count time of 40 seconds.

The bulk compositions of the samples were also determined by raster-type analysis (method B). This technique consisted of a raster scan of a set grid-area at a magnification of 400×. The area consisted of 48 fields approximately 300 μm × 300 μm to give a total area of roughly 4.32 mm^2. These data took about 45 minutes of instrument time to acquire.

A glass pellet made from a powder prepared from the bone china object was also analyzed using the electron microprobe. The electron beam was defocussed to avoid alkali loss. The pellet was prepared using a lithium tetraborate ($Li_2B_4O_7$) flux in the ratio 5:1 (flux:powder), as well as 300 mg of lithium fluoride and 35 mg of lithium bromide to fuse the powder. The glass pellet was also analyzed by X-ray fluorescence using a Phillips 2400 spectrometer at the Geochemical Centre, Saint Mary's University.

SAMPLE DESCRIPTION

Mineralogy

The bone china contains silica polymorphs (*e.g.*, α-quartz, tridymite, cristobalite), a tricalcium phosphate phase, anorthite, and an inferred melt phase (Fig. 1). Phases were identified on the basis of their chemical composition.

There are two distinctive morphologies of the SiO_2 polymorphs: (1) relatively large (~25 μm), irregular grains of what is probably α-quartz, and (2) minute (μm- to sub-μm scale) grains of tridymite or cristobalite. The silica polymorphs occupy 5 vol.% of the sample. The phosphate constitutes approximately 37 vol.% of the sample, forming irregularly shaped grains ranging from 1 to ~25 μm across. Anorthite

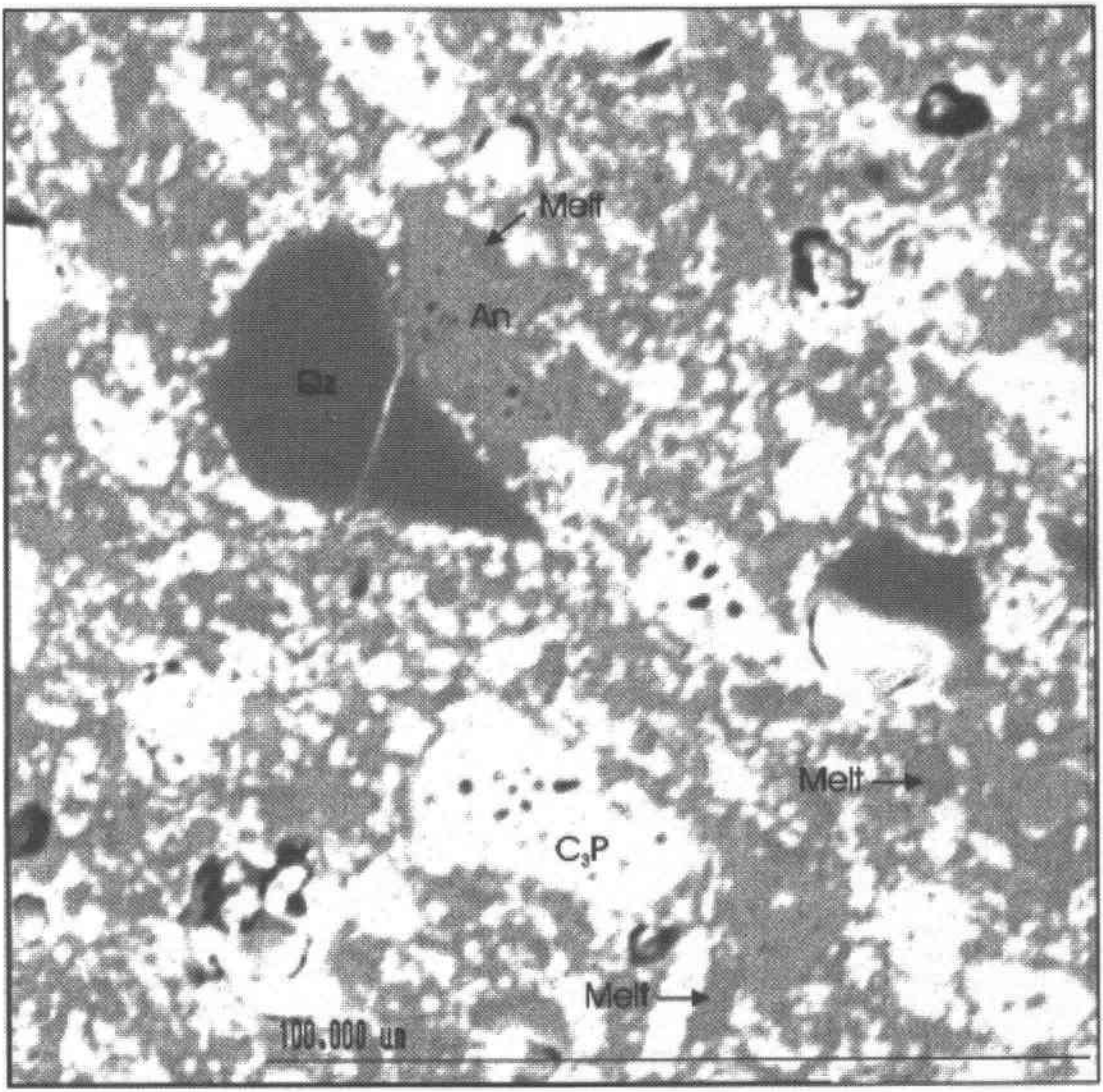

FIG. 1. Digitized back-scattered electron image of a sample of modern bone china. Scale bar: 100 μm.

occurs as 1–15 μm grains, and occupies approximately 40 vol.% of the sample. The remaining 17 vol.% of the sample is taken up by the melt phase. As will be seen, the significance of the volume and composition of the former melt can be assessed using appropriate phase diagrams.

Phase chemistry

Three phases in the sherds warranted analysis: the Ca phosphate, anorthite, and the former melt phase. Ideally, whitlockite has a CaO/P_2O_5 wt.% ratio of 1.18. The electron-microprobe analysis of the phosphate in the sherds, however, indicates a composition $Ca_{2.77}P_{1.99}O_8$ (*i.e.*, it has a lower CaO/P_2O_5 wt.% ratio of only 1.1, closer to that of bone ash). This implies that the dehydration of bone ash did not proceed to completion during firing. Furthermore, the phosphate contains traces of several extraneous components [*e.g.*, silicon (0.017 Si atoms per formula unit, *apfu*), aluminum (0.055 *apfu*), magnesium (0.117 *apfu*), and sodium (0.054 *apfu*): Table 1], although it should be noted that the whitlockite structure can accommodate various ions as well as vacancies (*cf.* Calvo & Gopal 1975). One spot analysis

TABLE 1. COMPOSITIONS OF SELECTED PHASES IN A SAMPLE OF MODERN BONE CHINA*

	Ideal An	Measured An	Ideal C_3P	Measured C_3P	Ideal Melt	Measured Melt
SiO_2 wt%	43.50	44.03		0.34	60.03	66.14
Al_2O_3	36.34	36.08		0.92	18.69	18.71
TiO_2		n.d.		n.d.		0.39
MgO		n.d.		1.54		n.d.
CaO	20.16	18.91	54.24	50.57	16.25	4.43
Na_2O		0.78		0.54		1.17
K_2O		0.20		0.17		7.00
P_2O_5			45.76	45.92	5.03	2.16
Total	100.00	100.00	100.00	100.00	100.00	100.00
		(98.06)		(99.95)		(96.91)

* Totals in brackets refer to actual measured total. The measured data given in the table have been normalized to 100 for ease of comparison with data on ideal phases.

indicated the presence of a small amount of Fe (0.34 wt.% FeO) in one grain. Similar deviations in the composition of this and other phases in ceramics have been noted by others (*e.g.*, Owen & Barkla 1997) and likely reflect (1) the incorporation of other components (*e.g.*, SO_4 within the phosphate where gypsum was used in the ceramic paste), (2) the entrainment of submicrometric grains of other phases (especially in melts; *cf.* Owen *et al.* 1998), or (3) the overlapping of grains by the beam during analysis.

The feldspar is anorthite ($An_{92–95}$; Table 2). No XRD traces were collected for the sample, so its structural state (*e.g.*, Daniel *et al.* 1995) is not known.

The matrix is interpreted as a former melt phase because (1) it forms the matrix to discrete mineral grains, and (2) its composition (Table 1) does not match that of any known mineral, and it has partitioned incompatible components, *e.g.*, Ti (0.38–0.53 wt.% TiO_2), Na (1–1.2 wt.% Na_2O), and K (6.4–6.8% K_2O). The SiO_2 content of the former melt ranges between 62 and 64.1 wt.%; the proportion of Al_2O_3 varies between 17.2 and 18.1 wt.%. It contains 4.3–4.5% CaO, implying that the Ca content of the paste exceeded the amount of Al required to form anorthite. The P_2O_5 content ranges between 2.1 and 2.8 wt.%. No discrete Ti- or K-rich phases were detected; consequently, these components are interpreted to be dissolved within the melt phase, or, alternatively, they might occur in submicrometric-scale crystallites that eluded detection.

BULK CHEMISTRY

Before discussing the bulk composition of the sample, the issue of homogeneity should be addressed. Although modern fine ceramics tend to be very homogeneous for the most part, it was considered important that the three separate sherds from the bone china object be analyzed to demonstrate this. Table 3 compares the bulk composition of each sherd as determined using defocused electron beams of 20 μm and 40 μm. It is quite clear from these data that the bone china object is very homogeneous.

The bulk composition of the bone china object (Table 4) was determined by four methods: (1) spot analysis by electron microprobe (method A), (2) raster approach (method B), (3) electron-microprobe analysis of a glass pellet prepared from the sample, and (4) X-ray fluorescence spectrometry.

Using a statistical program (SPSS), a student's t-test was run on the spot analysis electron-microprobe data to determine if there was a significant difference (at 95% precision) between the two data sets (*i.e.*, 20 *versus* 40 μm). Table 5 summarizes the results of this test for the major constituents of the sample and a few of its minor constituents, namely MgO, Na_2O, and K_2O. The statistical database consists of all spot analyses for both the

TABLE 2. BULK COMPOSITION OF THREE FRAGMENTS OF A SAMPLE OF MODERN BONE CHINA AS DETERMINED BY AVERAGING RESULTS OF DEFOCUSSED-BEAM ELECTRON-MICROPROBE SPOT ANALYSES (METHOD A)

	Beam diameter = 20 μm				Beam diameter = 40 μm			
	B3	B2	B1	Ave.	B3	B2	B1	Ave.
SiO_2 wt%	32.99	33.69	31.74	32.81	31.37	32.87	31.90	32.05
Al_2O_3	14.91	15.39	14.28	14.86	14.56	14.69	14.80	14.68
CaO	26.91	26.40	28.57	27.29	28.13	27.30	27.92	27.78
MgO	0.68	0.65	0.72	0.68	0.68	0.67	0.67	0.67
Na_2O	1.48	1.55	1.40	1.48	1.51	1.58	1.53	1.54
K_2O	1.91	2.00	1.81	1.91	2.00	2.10	1.97	2.03
P_2O_5	21.10	20.32	21.48	20.97	21.76	20.79	21.22	21.26
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

TABLE 3. COMPARISON OF THE COMPOSITIONS OF A SAMPLE OF MODERN BONE CHINA AS DETERMINED BY ELECTRON MICROPROBE AND XRF TECHNIQUES

	Average results of spot analyses		Raster	Glass NC	XRF
	20 μm	40 μm			
SiO_2 wt%	32.81	32.05	31.88	31.89	31.70
Al_2O_3	14.86	14.68	14.46	13.88	14.36
CaO	27.29	27.78	28.04	28.61	28.83
MgO	0.68	0.67	0.64	0.29	0.77
Na_2O	1.48	1.54	1.50	1.66	1.45
K_2O	1.91	2.03	1.98	1.86	1.93
P_2O_5	20.97	21.26	21.50	21.81	20.96
Total	100.00	100.00	100.00	100.00	100.00

NC: Normalized composition.

TABLE 4. SUMMARY RESULTS OF t-TEST
PERFORMED ON SPOT-ANALYSIS DATA (METHOD A)

	ALL DATA			~50% OF THE DATA		
	20 mm	40 mm	t-Test	20 mm	40 mm	t-Test
SiO_2 wt.%	32.31	31.30	S	32.80	31.21	S
Al_2O_3	14.63	14.35	NS	14.59	14.25	NS
CaO	26.92	27.16	NS	26.73	27.20	NS
MgO	0.67	0.66	NS	0.67	0.66	NS
Na_2O	1.45	1.50	S	1.46	1.50	NS
K_2O	1.88	1.98	S	1.91	1.97	NS
P_2O_5	20.67	20.79	NS	20.50	20.84	NS
	~25% OF THE DATA			~10% OF THE DATA		
SiO_2	31.89	31.11	NS	32.67	31.37	NS
Al_2O_3	14.73	14.27	NS	14.38	14.22	NS
CaO	27.18	27.14	NS	26.69	27.19	NS
MgO	0.67	0.66	NS	0.67	0.66	NS
Na_2O	1.45	1.51	NS	1.43	1.49	NS
K_2O	1.78	1.96	S	1.90	1.98	NS
P_2O_5	20.73	20.79	NS	20.43	20.84	NS
	~5% OF THE DATA			~3% OF THE DATA		
SiO_2	33.13	31.25	NS	33.83	32.43	NS
Al_2O_3	15.49	14.61	NS	15.12	15.13	NS
CaO	26.18	27.05	NS	26.60	26.56	NS
MgO	0.64	0.65	NS	0.64	0.63	NS
Na_2O	1.51	1.52	NS	1.48	1.50	NS
K_2O	1.89	1.94	NS	1.77	1.96	NS
P_2O_5	19.59	20.58	NS	20.33	19.04	NS

20 and 40 μm beam diameters, *i.e.*, 1057 points (20-μm beam) and 1079 points (40-μm beam). From this database, successively smaller subsets of the data were analyzed, *i.e.*, approximately 50%, 25%, 10%, 5% and 3%, as separate datasets. It should be noted that the subsets were randomly chosen by the program and that this particular test is relevant only to the precision of the data, and not its accuracy. T-test results (Table 5) show a significant difference for some components between the two beam diameters when run for all data, ~50% of the data, and ~25% of the data, but not for tests run on data subsets consisting of 10% or less of the original dataset. Even in this case, however, these perceived statistical differences may not be analytically significant given that the imprecision of the microprobe is ±1.5–2% relative, and this imprecision increases for constituents present at lower concentrations.

These statistical differences can be explained if one considers the beam diameter in relation to grain size. A significant difference for silica is likely due to the presence of grains of α-quartz that are larger than the beam diameter. As stated earlier, some grains of a silica polymorph exceed the 20-μm beam in diameter. Should the 20 μm beam hit a grain directly, it will give a reading of pure silica. Hitting even a few of these larger grains would skew the statistics of this component, but would have a negligible effect on the average if a large number of datasets are considered. Also one must keep in mind that comparing datasets of larger sizes, such as the two in question here, can result in statistically significant differences because larger datasets have lower t-values. The t-value is the number that must be overcome for a significant difference to exist between the datasets being compared. For example, the mean of a smaller dataset may have a t-value of 2.5 (*i.e.*, when comparing two smaller datasets, the means will have to vary by 2.5 in order for the difference to be significant between the two). On the other hand, a larger dataset may only have a t-value of 1.6. Obviously, the smaller the t-value, the greater the chance that there will be a significant difference between the datasets being compared. This is likely the reason for the statistically significant difference between the major components in the larger datasets. As for significant differences between minor components, this too can be explained. The smaller the numbers being compared, the more chance there will be a significant difference, *i.e.*, the imprecision increases. This is probably due to the imprecision of the instrument; as stated above, precision decreases for components present in lower concentrations.

TABLE 5. BULK COMPOSITION OF
A PHOSPHATIC NANTGARW PORCELAIN SHERD
AS DETERMINED BY ELECTRON-MICROPROBE ANALYSIS

wt.%	SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_4	Total
Spot Analysis	44.41	13.37	0.19	0.61	22.19	0.51	1.68	16.39	0.64	100.00
Raster	45.75	13.85	0.22	0.52	21.37	0.47	1.75	15.39	0.67	100.00

So what does this statistical evaluation of the spot analyses demonstrate? First, it shows that beam diameter is not as important a variable as was originally suspected, provided that it is as large or larger than the largest grains in the sample, and much larger than the average grain-size. Second, it indicates that the results of as few as 35 spot analyses (*i.e.*, ~3% of the dataset) can be averaged to reliably determine the bulk composition of a fine-grained medium. A visual comparison of the results of method A *versus* those of method B (Table 4) shows that the data correspond quite well. The XRF data also corroborate the electron-microprobe results, including the normalized stoichiometric microprobe-derived compositions of the glass pellet (Table 4).

DISCUSSION

Compared with many analytical instruments, the electron microprobe can be quickly and easily calibrated, and only a minute sample (a few millimeters in diameter; perhaps less than 0.5 g) is required for analysis. Method A (averaging results of spot analyses collected using a defocussed beam) has been used for some time. For example, Bohlen & Essene (1977) adopted this approach to re-integrate feldspar compositions for use in two-feldspar geothermometry. Owing to the coarse grain-size of the mesoperthite, this technique required a very large number of spot analyses (100–200 points per grain). This technique is more practical for the analysis of very fine-grained media (*e.g.,* volcanic rocks and fine ceramics such as porcelain). Data for both methods (A and B) have recently been reported in a number of publications despite the fact that there are few reliable criteria specifying, for example, the optimal number of analyses, beam diameter (in method A) or magnification (in method B) required to reliably determine the bulk composition of fine-grained rocks or ceramics. For example, after ensuring the reproducibility of replicate analyses of archeological potsherds, Owen (1997) elected to average results of ~100 spot analyses per sample to determine the composition of early (18th century) Worcester porcelain. Tite & Bimson (1991) apparently used the raster-type approach in their review of the composition of early British porcelains, but provided few details about their methodology.

Another issue to consider is what constitutes a reasonable or reliable analysis. The answer to this, of course, is dictated by the accuracy and precision of the data required to address the problem being investigated. For example, one experiment may require a 2σ tail of ±5%, whereas another may only need a 2σ tail of ±10%. This means that the data from one experiment may not be considered reliable for another that has more stringent analytical requirements.

Magnification is the variable of concern when using the raster-type approach for the analysis of fine-grained media, and has not been evaluated here. To obtain a reliable indication of the bulk composition of a fine-grained medium such as bone china, it is important to analyze a reasonably large area without jeopardizing the accuracy and precision of the data. It is for this reason that a magnification of 400× was chosen in the present study. A lower magnification would result in a geometrical problem, in which the beam hits at different intensities over the area being analyzed. This, in turn, results in lower totals (<100 wt.%), hence the data are less reliable. A higher magnification would avoid this problem, but at the expense of cost effectiveness, since a larger dataset is required to cover the same area of the sample being rastered. Furthermore, inhomogeneities in the sample, notably pores in volcanic rocks and fine ceramics, would be of greater concern.

The available data suggest that method B (rastering) may be just as reliable as the spot-analysis technique (method A). In fact, it may be a more cost-effective technique because it can cover a larger area in a much shorter period of time, and should be considered to be the method of choice for samples suspected (on the basis of petrography) to be somewhat heterogeneous on a thin-section scale. However, since the data will be less reliable for more porous samples, averaging the results of spot analyses (method A) may be the better approach for relatively porous and homogeneous samples because the points can be selected manually, and one can thereby avoid pores.

An obvious advantage of using the electron microprobe in analyzing fine-grained media is that both phase and bulk compositions can be determined. Furthermore, if it is equipped with a digitized back-scattered-electron imaging system, the proportions of phases also can be quantified. Collectively, these data can be used to assess various aspects of the petrology of the medium being investigated. For example, the proportion of the former melt phase (~17 vol.%) in the bone-china object described here is broadly consistent with the amount of minimum melt (~20–25 vol.%) that should form at a firing temperature of about 1290°C, as predicted (using the "lever rule" for plotted bulk compositions) according to the phase diagram for the system tricalcium phosphate – anorthite – silica (Fig. 2). This phase diagram is particularly relevant to bone china because (1) the sample contains all three phases that appear on the apices of this diagram, and (2) the bulk-composition data (Table 1) reveal that these constituents comprise >90 wt.% of the ware. Melt compositions, however, plot on neither the ternary minimum nor any cotectic, but rather form a linear array of points between the former and the SiO_2 apex (Fig. 2). This array suggests that the melt phase has been adulterated by the presence of submicrometric-scale SiO_2 crystallites (probably cristobalite or tridymite) (*cf.* Owen *et al.* 1998).

APPLICATION

In an effort to test the reliability of electron-microprobe-derived bulk analytical data, an early 19th century porcelain sherd from the Nantgarw factory site in southern Wales was analyzed by both methods in accordance with the guidelines put forth in this paper. In an attempt to be conservative, as many older, archeologically important porcelains may be somewhat coarser grained owing to the relatively crude milling technology of the day, 75 spot analyses (method A, 40 μm diameter of the beam) were performed instead of the recommended 35 for method A. Method B was performed at a magnification of 400×, covering an area of 4.32 mm^2. Table 5 clearly shows that the two datasets are quite comparable.

CONCLUSIONS

Statistical evaluation of results of a large set of defocussed-beam electron-microprobe analyses indicates that as few as 35 compositions need be averaged to produce a reliable indication of the bulk composition

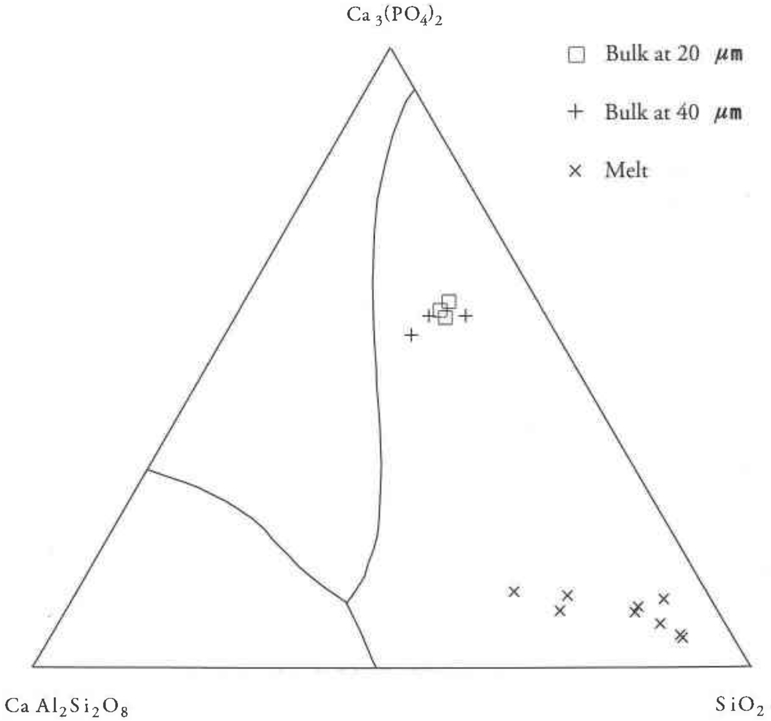

FIG. 2. Bulk- and melt compositions for a sample of modern bone china plotted in terms of the system tricalcium phosphate – anorthite – silica (St. Pierre 1956). The bulk compositions were determined by averaging results of electron-microprobe spot-analyses (see text).

of very fine-grained (compared with the diameter of the electron beam) media such as modern bone china (or, presumably, volcanic rocks). The data produced by rastering the same sample closely match these results, and may well be superior for relatively inhomogeneous or non-porous samples. Coupled with data on phase compositions and modal data, this application of the electron microprobe can provide a suitable database for comprehensive studies of rocks or materials using only polished thin sections.

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