



Evaluating effects of chemical weathering and surface contamination on the in situ provenance analysis of building stones in the Cuzco region of Peru with portable XRF

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ABSTRACT

As the only type of instrument capable of determining artifact geochemistry in a wide variety of settings, portable X-Ray Fluorescence (PXRF) may be frequently utilized as probably the best option for collecting data when removal of objects in part or in whole is unfeasible. However, using PXRF in circumstances where sample selection and preparation diverge from standards developed for lab-based instrumentation requires assessing the impact of new and potentially limiting factors to establish the validity of the method in these new contexts. Here we examine the effects of surface contamination and chemical weathering on the ability to assess provenance of igneous building stones used in the Cuzco region of Peru. Surface contamination was assessed through comparing low-impact cleaning methods on diorite and andesite blocks, and weathering was examined by comparing weathered vs. fresh surfaces of samples from two andesite quarries. In general, the lightest elements were most impacted by contamination and weathering while measurements of many of the heavier elements commonly used in provenance studies were relatively unaffected. Concentrations of Pb and Zn were problematic in the urban context of Cuzco because of pollution. Ability to determine provenance of building stones within those limitations (i.e., the validity of this application of PXRF) was demonstrated in a preliminary study by comparing measurements from uncleaned, exposed building stones in the region to fresh quarry samples.

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1. Introduction

Recent advances in the precision, limits of detection and affordability of Portable X-Ray Fluorescence (PXRF) instruments have greatly expanded our potential for non-destructive analyses. Primary advantages include the ability to measure objects in practically any context, from in situ finds to field laboratories and museums, and the ability to measure objects of large size without removing samples. These obviate the need to transport artifacts or damage them by removing samples for lab-based analysis, which may often be prohibited or require more onerous permits (Phillips and Speakman, 2009; Potts, 2008). Although PXRF technology has limitations and drawbacks (Liritzis and Zacharias, 2011; Nazaroff et al., 2010; Shackley, 2011; Speakman et al., 2011; Williams-Thorpe, 2008) and is not a complete substitute for lab-based XRF,

it has proven viable for a number of applications, such as obsidian provenance studies (e.g., Craig et al., 2007; Nazaroff et al., 2010; Phillips and Speakman, 2009).

The expansion in potential applications of PXRF necessitates development and assessment of field-based methodology for non-invasive in situ analysis in different contexts (Nazaroff et al., 2010: 885). This is particularly critical for those applications where PXRF is the only feasible method for collecting data. One major application encompasses provenance studies of igneous stone objects such as building stones and sculptures that are protected as components of standing architecture, museum collections, etc. (Williams-Thorpe, 2008). Because non-invasive analysis precludes exposing fresh surfaces and may limit cleaning, it is imperative we assess the validity of this application when taking measurements on exposed surfaces; i.e., we need to examine how much PXRF measurements are affected by weathering or contamination and if those effects are sufficient to impact our ability to match archaeological objects with geological sources.

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Here we address the effects of chemical weathering and surface contamination, two factors most likely to cause deviations in measured chemical composition when compared to fresh surfaces. Their potential effects are both variable and difficult to predict, so developing PXRF methodology for these applications requires assessing such effects for a range of materials and contexts. Because surface contamination and chemical weathering have only been partially explored, here we address their effects on building stone and quarry materials from the Cuzco area of Peru as generated over a 400–900 year time frame, with particular attention to igneous stone exposed in urban vs. rural contexts.

1.1. PXRF for *in situ* analysis of igneous stone objects

A number of factors can affect accuracy and therefore the applicability of XRF for geochemical provenance studies of igneous stone objects. These include individual sample size, grain size, surface irregularities, mineralogy, and chemical homogeneity, the effects of which have been studied by Davis et al. (1998), Liritzis and Zacharias (2011), and Williams-Thorpe et al. (1999), among others. But data for surface contamination and chemical weathering are limited because researchers have only begun addressing their effects. For example, Williams-Thorpe et al. (1999) and Potts et al. (2006) assessed weathering on rhyolite, microdiorite, and dolerite samples in the British Isles, Lundblad et al. (2008, 2011) examined weathering on Hawaiian basalt artifacts and geological samples, and Lundblad et al. (2011) also tested some effects of surface contamination on basalt artifacts. These effects are of less concern for lab-based analyses, which often allow for cleaning of samples to reduce effects of surface contamination, and for the choice of analyzing the least impacted surface or exposing fresh surfaces to reduce effects from chemical weathering. But they are more significant for non-invasive PXRF analyses restricted to exposed, unwashed surfaces, where surface contamination and chemical weathering could potentially alter the chemical composition of the outermost layer of a stone, enriching or depleting some of the elements being measured.

Effects can vary greatly, depending on type of stone, duration and conditions of exposure, types of surface contamination, and impacts of human activities. In addition, effects on measurement of specific elements are uneven due to the physics of Energy Dispersive XRF. Calculating the concentration of an element depends on detecting the characteristic energy of the fluorescent X-rays generated by atoms of that element when the instrument's X-ray beam penetrates the sample. The depth from which fluorescent X-rays can escape and be detected depends both on the energy of the X-rays and their absorption by the material. This is referred to as the critical penetration depth, which represents the thickness from which 99% of the fluorescent X-rays are generated. But the proportion of fluorescence detected is not constant through the depth of the sample, as the intensity of the emitted fluorescence is attenuated within the sample such that the majority of the signal is generated from shallower depths, e.g., 90% of the signal detected comes from a thickness equivalent to half the critical penetration depth (Potts et al., 1997).

Importantly, the critical penetration depth varies both by element, as the X-ray energy for a given type of X-ray line increases with atomic number (Z), and by the matrix through which the beam passes. Thus the signals for progressively lighter elements are generated from progressively shallower depths of the material. For the main type of stone considered here, andesite, Potts et al. (1997) calculated critical penetration depths ranging from 30 μm for K to 8555 μm for Ba. Thus for many elements XRF measurements derive from a relatively thin layer of the sample. Surface contamination and weathering could be problematic if they enrich or deplete

elements at or near the surface so that measured concentrations diverge from those of the sample as a whole (i.e., the bulk composition). The lighter elements tend to be most susceptible to these effects, as demonstrated in analyses of various igneous rocks (Lundblad et al., 2008, 2011; Potts et al., 2006; Williams-Thorpe et al., 1999). For the heavier mid- Z elements such as Rb, Sr, Y, Nb, and Zr, which have proven highly useful in sourcing, effects of weathering are less apparent. Some are less susceptible to geochemical changes than others, but in general the impact of weathering is greatly tempered by the deeper critical penetration depths for these elements.

The central question here is the extent to which surface contamination and chemical weathering impacts PXRF measurements of the composition of the andesites and other igneous stones used by the Incas for cut stone architecture. Specifically, in the subtropical highland climate of Cuzco, does chemical weathering over a time frame of ca. 400–900 years in combination with surface contamination in an urban context alter the near-surface chemical composition of these stones enough to affect measurements of elements of interest? Are the lighter elements all significantly altered, or are there some we can still use for provenance analysis? Will the heavier elements be relatively unaffected, as in other rock types? In essence, to what extent do these factors affect the validity (as described by Hughes, 1998) of this technique for determining geological provenance of these materials?

2. Provenance analysis of building stone in Cuzco

As Shackley (2002) advocates, we must gauge the level of precision and accuracy needed for specific applications of XRF. For those applications that require very high levels of precision and accuracy, even small effects of weathering could have a negative impact. But this should not be the case for the present application. Specifically, sourcing worked building stones does not always require as high a level of precision as some other artifact types because the potential number of quarries is often low. As used by the Incas and other complex societies, cut stone was typically quarried from limited occurrences of suitable stone. In other words, not every outcrop of andesite near Cuzco was a potential source of the andesite used for construction in the city. In contrast, any primary or secondary occurrence of stone of suitable qualities could be a potential source for small artifacts like flaked tools.

Often, potential sources of fine cut stone employed in significant quantities can be reduced to those showing direct evidence of quarrying, and further narrowed by comparing macroscopic properties, such as phenocrysts, color, etc. Such limits on the number of geological sources that must be included in the investigation can reduce the potential for overlaps in chemical composition between sources being compared. Of course, significant overlaps may occur in the case of quarrying of different outcrops of the same volcanic formation, and it is possible to have cases where we have not identified all of the physically distinct quarries from such outcrops. Such a case could mislead us to assign all building stones with similar geochemical composition to the know quarry; this issue is common to all lithic provenance analyses. But in general, provenance studies of building stone may be more amenable to analyses with lower levels of precision, such as PXRF, and effects of weathering or surface contamination, if minor, may not inhibit making source assignments.

2.1. Research setting

Extremely well-fitted stone masonry was a hallmark of the Inca Empire. Identifying the geological sources of the stone used in this

elite architecture can give us insights into access and control over quarries, organization and use of labor, and ideological dimensions of selecting and using stones from different sources. While there has been interest in matching Inca building stones to quarries (Gregory, 1916; Gomis, 2003; Heizer and Williams, 1968; Hunt, 1990; Protzen, 1983, 1993), geochemical analysis has only been used in one study to date (Ogburn, 2004). Because archaeologists are unlikely to be permitted to remove samples from standing walls in major Inca sites for lab-based analysis, PXRF opens the door for more studies.

For the Inca capital, Cuzco (Fig. 1), it has been long known that Rumiqlolqa was the primary quarry for the andesite used in many buildings (Gregory, 1916; Hunt, 1990; Squier, 1877). The Incas also quarried andesite from Huaccoto, which is from the same formation as Rumiqlolqa; these quarries represent two of the nine principal andesite outcrops to the east of Cuzco that comprise the late Pleistocene Rumicolca Formation (INGEMMET, 1999; we retain the INGEMMET spelling “Rumicolca” to refer to the geological formation to distinguish it from the quarry of Rumiqlolqa). Although there is variation in the appearance of the rock within both quarries, they are very similar in geochemistry (Ogburn, 2004) and petrology (Ixer et al., 2012). A number of other quarries also provided stone for Cuzco and other sites, with most royal sites in the region relying on local quarries supplemented by some stone from more distant sources (Gregory, 1916; Hunt, 1990; Protzen, 1993). Much of the stone quarried was igneous, including andesite, diorite, granite, and rhyolite, for which geochemical sourcing is potentially applicable. Most Inca cut stone architecture dates to the imperial period (ca. 1400–1532 AD), although some cut stone buildings may pre-date imperial expansion and Inca-style construction continued into the early colonial period. Thus, most quarried material has been exposed to surface contamination and weathering in Cuzco and surrounding sites for approximately 400–600 years, and perhaps several centuries more in some cases.

3. Weathering

Chemical weathering of rock begins at the very surface and penetrates into the material over time, forming a rind. The process

alters minerals through solution, oxidation, and other chemical reactions, and as minerals disintegrate some elements leach out, altering the geochemistry (Colman, 1982). Consequently, as the thickness of a weathering rind (and thus the extent of leaching) increases over time, it becomes more likely to affect the chemical composition of the layer analyzed by PXRF.

The effects of weathering on any particular rock are difficult to predict because they vary by the rock’s mineralogy and the conditions to which it has been exposed over time (Williams-Thorpe et al., 1999: 219), so it is necessary to study effects for a range of conditions and rock types. Most relevant here is the study by Colman and Pierce (1981), who analyzed andesites and basalts of various mineral compositions in the semiarid climate of the western US, conditions somewhat similar to the Cuzco region. Significantly, they determined that these rocks required at least 10,000 years to develop a 0.2 mm rind. The primary implication of that study is that andesites from around Cuzco should only develop very thin weathering rinds within the much shorter time frame treated here, even considering differences in mineralogy and conditions of exposure.

Nonetheless, shallow critical penetration depths for lighter elements suggest that even a minor weathering rind could affect XRF measurements. This is of particular concern because lighter elements tend to be the most mobile in chemical weathering, with the greatest potential effects on Si, Ca, Na, and K (Colman, 1982; Hendricks and Whittig, 1968; Oguchi, 2001; Sak et al., 2004). In contrast, the influence of a shallow surface rind should be much less apparent for the heavier trace elements such as Rb, Sr, Zr, and Ba (Williams-Thorpe et al., 1999).

3.1. Methods

To assess effects of chemical weathering, we analyzed weathered vs. fresh surfaces from spoils within the quarries of Rumiqlolqa and Huaccoto. We measured 19 samples from Rumiqlolqa and 10 from Huaccoto, taking paired readings of weathered and fresh surfaces from each. Previous analysis with WD-XRF (Ogburn, 2004) found that chemical variation within some individual building blocks of Rumiqlolqa andesite was minimal, with the concentrations of the

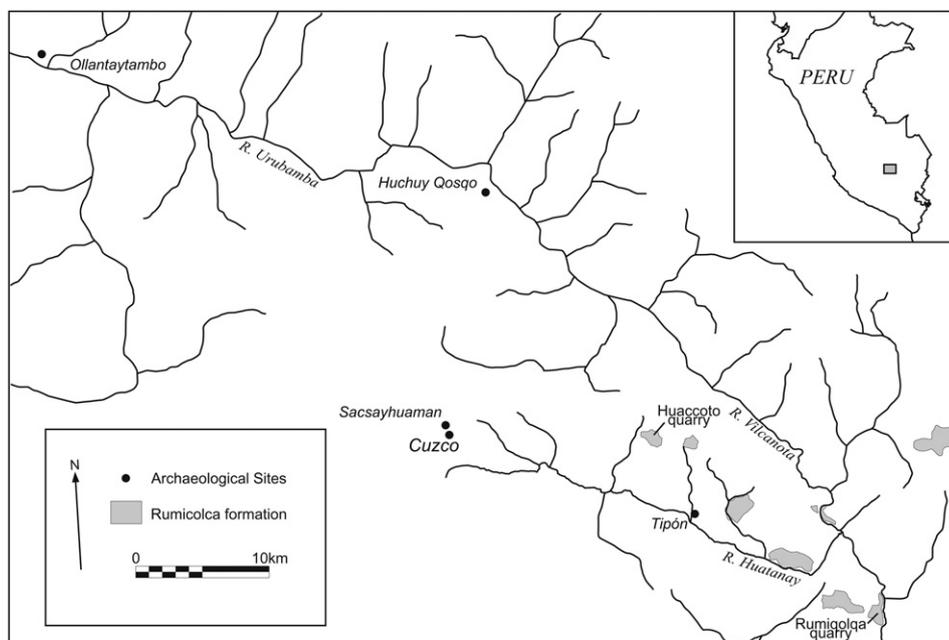


Fig. 1. Location of sites and quarries discussed in the text.

heavier elements differing by three percent or less between different samples from the same stone. Thus, we expect that significant differences in elemental concentrations between the weathered and fresh surfaces in this experiment should not result from variability within the source material. Surface contamination should not be a significant factor because the spoils were left on the surface and not subject to burial or affected by later human activities that could have left notable residues. The andesites from these quarries are fine-grained, and for measurement we selected surfaces that were flat and relatively smooth, so grain size and surface texture should not have a significant impact. Accordingly, discrepancies between measurements on weathered and fresh surfaces of the same sample, if significantly greater than instrument counting precision, should be primarily attributable to the effects of weathering.

Because these quarries were worked from pre-Inca times up to the present, it is difficult to precisely control for the age of weathering rinds on quarry materials, i.e., we cannot ensure that any individual piece had been chipped off during the Inca imperial era. To avoid under-representing the level of weathering, we aimed to collect samples that were most likely to have been quarried in pre-Columbian times by choosing those that exhibited the most visible weathering. These all included at least one surface with coloration clearly indicative of oxidation; these usually were distinct from other surfaces on the same sample and the majority of the surrounding spoils. As a result, the weathering should represent either earlier quarrying activity or surfaces that were naturally exposed over a longer geological time scale since the late Pleistocene, matching or exceeding the weathering expected in Inca imperial contexts.

Samples were measured for all tests in the field using an Innov-X Delta DP4000 PXRF with silicon drift detector and a rhodium tube. Measurements were made using the standard 3 beam soil mode operated at up to 50 kV for a 60 s total count time, with concentrations derived by Compton normalization. We analyzed a selection of 11 elements that have proven useful for provenance studies of igneous rocks. Under ideal conditions, instrumental limits of detection for the trace elements are in the range of 1–3 ppm for Rb, Sr, and Zr, 3–5 ppm for Zn, 15–30 ppm for Ba, and 2–4 ppm for Pb, according to the manufacturer. These limits are likely to be higher under field conditions, but concentrations of

those elements within the materials we analyzed were high enough that limits of detection should not be a concern, except for Pb.

Precision as well as stability of the instrument was checked through analysis of the NIST-2781 standard at the end of each session of measurements (Table 1). Using the standard deviation of those measurements as a percentage of the average of values, instrumental precision was primarily in the range of 2–4%, with a low of 1.3% for Mn and 6.7% for Ba. Precision of the method was evaluated through repeated measures of a quarry sample of Rumiqolqa andesite (Table 2). The surface was freshly exposed by chipping with a rock hammer, which avoided any potential effects of weathering or surface contamination. Each measurement was taken in approximately the same place on the sample, within a 1 cm radius of the center of the sample. Thus, the primary contributors to variability of the PXRF measurements should be limited to instrument error, surface morphology effects, and mineralogy. The repeated measurements show a low level of variability for most elements, with standard deviations in the range of 1–3% of the average. Zn was higher at 5.5%, and Pb at 14.8%; the imprecision of the latter may be due to concentrations that are close to the instrumental limits of detection. Overall, a single reading of a stone of this type under these parameters should yield a sufficiently precise measure of the bulk composition of the sample; following Potts et al. (1997), one measurement is sufficient to achieve a relative standard deviation of the mean of between 2 and 5% for each element, with the exception of Pb.

The instrument's factory calibration was used because this is a preliminary study to test the validity of this application, rather than absolute accuracy. Accuracy for some elements can be roughly gauged by comparing analysis for Rumiqolqa source samples in this study against those obtained by Wavelength-Dispersive XRF in a previous study (Table 3; Ogburn, 2004). The average elemental concentrations of the two sets of samples are fairly consistent, and the values for Mn, Sr, Zr, and Ba are quite close; values measured for the other elements should not be considered highly accurate. Given that the results of this current study are promising, an application-specific calibration with geostandards should be used in future fieldwork to ensure inter-instrument compatibility of the data (i.e., increased accuracy of the measurements).

Table 1
Elemental concentrations and instrumental uncertainty of NIST 2781 standard from 10 repeated measurements, with average value (ave.), standard deviation of group of measurements (s.d.), and minimum (min.) and maximum (max.) values; precision of PXRF instrument for each element can be gauged from \pm % (based on the range of values), the % of average value represented by the standard deviation (s.d. %), or the average absolute deviation (ave. abs. dev.%).

Measurement	Ca	\pm	Ti	\pm	Mn	\pm	Fe	\pm	Zn	\pm	Rb	\pm	Sr	\pm	Zr	\pm	Ba	\pm	Pb	\pm
1	58,083	661	4020	104	922	17	30,420	217	1214	14	32	1	224	3	265	3	855	52	195	4
2	58,833	675	4241	106	912	17	30,996	225	1237	14	30	1	222	3	252	3	784	52	206	5
3	58,083	661	4020	104	922	17	30,420	217	1214	14	32	1	224	3	265	3	855	52	195	4
4	58,031	664	4194	106	896	17	30,353	219	1224	14	32	1	225	3	256	3	767	52	188	4
5	57,901	669	4333	108	929	17	30,317	219	1215	14	30	1	220	3	260	3	794	53	195	5
6	56,720	654	4267	107	897	17	28,651	205	1154	13	29	1	212	3	255	3	792	52	183	4
7	60,364	688	4333	108	929	17	31,290	226	1246	14	33	1	223	3	252	3	828	53	207	5
8	57,120	673	4248	108	915	17	30,038	221	1204	14	33	1	225	3	256	3	685	52	186	5
9	57,902	663	4187	105	907	17	29,987	216	1204	14	30	1	217	3	258	3	752	51	196	5
10	57,529	657	4175	106	904	17	30,174	218	1202	14	32	1	225	3	262	3	844	52	198	5
Ave.	58,057		4202		913		30,265		1211		31.3		222		258		796		195	
S.d.	995		110		12.2		698		24.8		1.4		4.3		4.8		53.3		7.8	
Min.	56,720		4020		896		28,651		1154		29		212		252		685		183	
Max.	60,364		4333		929		31,290		1246		33		225		265		855		207	
\pm %	3.1		3.7		1.8		4.4		3.8		6.4		2.9		2.5		10.7		6.2	
S.d. %	1.7		2.6		1.3		2.3		2.0		4.5		1.9		1.9		6.7		4.0	
Ave. abs. dev. %	1.1		2.0		1.1		1.5		1.3		4.0		1.5		1.5		5.0		2.8	
Cert./rec. values	39,000		3200		n/a		28,000		1273		n/a		n/a		n/a		n/a		202.1	

Table 2

Data for 10 repeated measurements of a source sample of Rumiqlolqa andesite (RQA-7), including concentrations in ppm and instrument uncertainty; statistics include average (ave.), standard deviation of the group of measurements (s.d.), standard deviation as a percentage of the average (s.d. %), the standard deviation of the average (s.d. of ave.), percentage of the s.d. ave. relative to the average, and the number of measurements (*n*) necessary to attain a s.d. ave. relative to the mean of 1%, 2%, 5%, and 10%.

Measurement	K	±	Ca	±	Ti	±	Mn	±	Fe	±	Zn	±	Rb	±	Sr	±	Zr	±	Ba	±	Pb	±
1	45,760	844	28,421	407	4861	126	455	13	23,827	198	76	4	105	2	998	13	230	4	1305	63	24	3
2	44,466	825	28,181	402	4592	123	472	13	23,558	195	68	4	101	2	1015	13	233	4	1360	63	20	3
3	45,292	841	28,365	407	4820	126	447	13	23,784	198	78	4	106	2	1049	13	241	4	1315	63	19	3
4	45,032	833	28,368	405	4697	125	449	13	23,594	195	81	4	103	2	1002	13	234	4	1430	64	26	3
5	45,196	831	28,260	403	4732	124	468	13	24,074	200	81	4	108	2	1011	13	229	4	1284	62	17	3
6	43,709	821	28,450	407	4751	125	478	13	23,578	194	82	4	103	2	1025	13	236	4	1376	64	26	3
7	44,332	816	27,772	395	4752	124	472	13	23,842	197	82	4	106	2	1017	13	233	4	1372	63	19	3
8	45,074	832	28,180	403	4723	124	470	13	23,731	196	79	4	104	2	1004	13	235	4	1291	62	21	3
9	45,343	834	28,262	403	4647	124	465	13	23,859	198	76	4	105	2	1010	13	231	4	1396	64	19	3
10	46,075	843	28,354	405	4803	126	476	13	23,668	196	73	4	104	2	1030	13	237	4	1362	63	23	3
Ave.	45,426		28,509		4784		467.1		23,727		76.8		104.8		1016		234.8		1349		21.4	
S.d.	997		512		114		10.4		148		4.2		1.9		14		3.9		43		3.2	
S.d. %	2.2		1.8		2.4		2.2		0.6		5.5		1.8		1.4		1.7		3.2		14.8	
S.d. of ave.	315		162		36		3.3		47		1.3		0.6		4.4		1.2		14		1.0	
% rel. to ave.	0.69		0.57		0.76		0.71		0.20		1.73		0.57		0.43		0.52		1.01		4.68	
<i>n</i> (1%)	4.82		3.23		5.70		4.99		0.39		29.9		3.21		1.88		2.73		10.1		219	
<i>n</i> (2%)	1.20		0.81		1.43		1.25		0.10		7.47		0.80		0.47		0.68		2.53		54.8	
<i>n</i> (5%)	0.19		0.13		0.23		0.20		0.02		1.19		0.13		0.08		0.11		0.41		8.77	
<i>n</i> (10%)	0.05		0.03		0.06		0.05		0.00		0.30		0.03		0.02		0.03		0.10		2.19	

3.2. Results/discussion

The comparative results (Table 4, Fig. 2) for Rumiqlolqa samples showed notable differences in measured concentrations of most lighter elements, which were significant at the 5% level or lower according to Student's *t*-test (paired, two-tailed). The weathered faces tended to be depleted in K and Ca and enriched in Ti, Mn, Fe, and Zn, although there were some discrepancies and some samples did not show marked differences in fresh vs. weathered surfaces. Weathered surfaces also showed greater variability for K, Ca, and Mn, as indicated by the ratio of variance (*f*-test). Notably, measurements for Rb, Sr, Zr, or Ba were not significantly different, and in many cases the differences in paired readings were within the range of the reported instrument error. In contrast, Pb was significantly enriched for weathered surfaces, sometimes to twice the level measured for the fresh surfaces. Levels of Pb were also much more variable on weathered surfaces.

The Huaccoto samples produced similar results (Table 5, Fig. 2), with the notable differences being in mean concentrations for Ti, Sr, and Ba. These and other differences can be attributed mostly to the inclusion of three samples that showed extreme weathering, possibly dating back to the Pleistocene. Those outliers also produced the significant level of variability for Sr noted for weathered surfaces. Excluding those samples, the effect of weathering on the heavier elements is minimal. Also in contrast to Rumiqlolqa samples, Pb showed little difference on fresh vs. weathered surfaces in terms of concentration or variability.

For both quarries, the effects of weathering register to a greater extent for the lighter elements because of their shallow

critical penetration depths; heavier elements could have been impacted to some extent, but their measurements were not significantly distinct from fresh surfaces due to the deeper critical penetration depths. Notably, the differences for lighter elements are generally consistent with previous geological and archaeological studies of chemical weathering (e.g., Colman and Pierce, 1981; Oguchi, 2001; Williams-Thorpe et al., 1999). The effects on the lighter elements were less significant in this experiment than in Williams-Thorpe et al.'s (1999) study of weathering on prehistoric British artifacts of fine to medium grained rhyolite, dolerite and microdiorite, probably due to the much longer period during which the British artifacts were subjected to weathering. Given that we sampled surfaces that exhibited the most visible weathering, these results should generally represent the extremes in differences between fresh and weathered surfaces. Such extremes are unlikely to pertain to worked surfaces of Inca imperial stonework, except in rare cases where some of the original geologically exposed surface may have been left intact; for provenance analysis, measurement on such areas should therefore be avoided. Accordingly, it may be feasible to utilize some of the lighter elements in provenance studies of Inca stonework, and there is also the potential to derive a weathering factor to correct for these effects on some elements, as done by Potts et al. (2006).

It is also possible that chemical composition on the exposed surfaces was affected by the formation of rock (desert) varnish, a surface layer that results from the accretion of airborne particles over thousands of years (Dorn and Oberlander, 1982). Oxides of Mn and Fe are significant components of dark varnishes, which can

Table 3

Measured composition from Rumiqlolqa source samples, including minimum, maximum, average and standard deviation (all in ppm); taken from fresh surfaces of 36 samples, including the 19 samples included in the weathering comparison; average WDXRF values from 22 different Rumiqlolqa source samples from an earlier study (Ogburn, 2004) are provided for comparison, with Ti, Mn, and Fe values converted from oxide wt.% to ppm.

	K	Ca	Ti	Mn	Fe	Zn	Rb	Sr	Zr	Ba	Pb
Min.	44,637	24,925	4334	360	18,917	63	81	842	197	1144	15
Max.	53,518	31,623	6460	503	24,618	99	127	1068	231	1715	27
Ave.	48,786	28,063	5035	445	22,481	75	101	988	214	1385	21
S.d.	2394	1497	496	28	1348	8	7	48	8	142	3
WDXRF ave.	n/a	n/a	3875	445	25,520	n/a	120	977	214	1384	n/a

Table 4
Differences in fresh and weathered surfaces of andesite samples from the Rumiqlolqa quarry, including mean and arithmetic standard deviation of the group (s.d.), Student's *t*-test (paired, two-tailed), and *f*-test (ratio of variance of fresh vs. weathered, which is significant at the 0.05 level if >2.22).

Element <i>n</i> = 19	Fresh		Weathered		<i>t</i> -Test	<i>f</i> -test	Effects from weathering
	Mean	s.d.	Mean	s.d.			
K	48,445	2018	45,673	5354	0.0295	7.04	Depleted, increased variation
Ca	28,503	1565	25,703	2486	0.0000495	2.53	Depleted, increased variation
Ti	5008	501	5361	459	0.0634	1.19	Slightly enriched
Mn	451	22.9	713	356	0.00564	241	Enriched, increased variation
Fe	22,643	1082	24,311	1263	0.000882	1.36	Enriched
Zn	75.4	8.45	86.9	8.85	0.00117	1.10	Enriched
Rb	100.6	3.69	99.2	7.50	0.403	4.13	–
Sr	991	32.3	990	32.9	0.902	1.04	–
Zr	213.8	8.34	216.6	5.92	0.142	1.98	–
Ba	1364	144	1423	156	0.175	1.17	–
Pb	21.0	3.0	29.8	10.9	0.00321	13.1	Enriched, increased variation

also include Ca, K, Ti, Rb, Sr, and Ba as minor elements (Dorn and Oberlander, 1982; Garvie et al., 2008). Arid conditions are optimal for the formation of rock varnish, but it can form in almost any environment, albeit at a slower rate. In arid environments, the layer of varnish accumulates slowly, at rates from <1 to 40 μm per thousand years (Liu and Broecker, 2000), requiring about 10,000 years to form a solid coating (Elvidge and Iverson, 1983). Visually discernable varnishes are ca. 50 μm thick or greater (Liu and Broecker, 2000). Because of our bias toward sampling of rock with visibly distinct, weathered surfaces, it is quite possible that a number of the quarry samples were affected by the accretion of rock varnish, which could have been thick enough and enriched enough in Fe and Mn to account for the high concentrations of those elements in comparison to the fresh surfaces in many samples. Such varnishes would have accumulated over thousands of years, and thus would not have a significant impact on stones in Inca walls that were constructed around 500 years ago.

The elevated concentrations of Pb on weathered Rumiqlolqa samples are notable, and are much greater than could be caused by instrument error, which was ± 3 ppm (1σ) for all measurements (ranging from 20 to 64 ppm). Because measuring levels of Pb and other toxic metals is a primary application for PXRF, we would expect a high level of precision for this element. It seems probable that increased Pb readings result from airborne pollution from automobile exhaust (see below), an effect seen on weathered rock surfaces elsewhere (Potts et al., 2006). The differences between the quarries may result from location; compared to Rumiqlolqa, Huacoto is very distant from main roads and significantly higher in elevation than Cuzco, so much less airborne Pb would have reached that quarry.

4. Surface contamination

The effects of surface contamination could be much more variable over time than chemical weathering, as stones in standing walls can be subject to a wide range of contaminants such as air pollution, dirt, application and removal of coverings such as plaster and paint, and contact from humans and animals. These could be particularly marked in urban environments. Even though such contaminants may not be readily visible, they could potentially affect PXRF readings. As with chemical weathering, lighter elements are more likely to be affected by surface contamination because of their shallower critical penetration depths, while levels of heavier elements could be affected if contaminants are particularly enriched in those elements.

There is no doubt that a stone should be cleaned before analysis by PXRF if there are visible residues from contamination, unless such residues are of potential historical or cultural significance. However, if not visibly obvious, it is difficult to know whether surface contamination is sufficient to have an effect because its exact nature over time is difficult to establish for any specific context, and could conceivably vary across individual stones and between stones.

4.1. Methods

To examine the effects of surface contamination that is not visibly obvious, we tested the effects of low-impact cleaning and then compared those results to data from source material. Tests were carried out in the dense urban setting of Cuzco, where standing Inca exterior walls have been exposed to myriad possible contaminants for approximately five centuries.

Three walls were tested, including the northeast side of the Hatunrumiyoc structure, a segment of the Hatuncancha jutting into the sidewalk along Santa Catalina Angosta, and an exterior wall of Aqllawasi forming one side of the pedestrian path of Calle Loreto. Hatunrumiyoc was built from large polygonal blocks of green diorite extracted from the nearby San Blas area and the other two structures were built with rectangular andesite blocks from Rumiqlolqa (Gregory, 1916; Hunt, 1990). Although we obtained source samples for Rumiqlolqa, we were not able to locate a specific San Blas quarry during fieldwork in 2011, preventing comparison of the Hatunrumiyoc stones to source samples.

Ten different stones were selected, and six readings were taken on each. These comprised three paired readings before and after cleaning with different low-impact methods: water only, pH neutral soap rinsed with water, and isopropyl alcohol. Each spot was first measured with PXRF, then cleaned with one of the three liquids, scrubbed with a plastic brush for approximately 15 s, and allowed to dry before the second measurement. Small variations between before and after measurements are expected due to instrument error. Some variation could also result from heterogeneity within the material, as it is not possible to take both readings in exactly the same spot. Beyond that variability, a significant increase or decrease in the concentration of an element between unclean and cleaned surfaces should indicate the effects of removing surface contamination. Furthermore, differences between cleaned surfaces and quarry samples should indicate the extent to which surface contamination or weathering has affected the readings, i.e., if cleaned surfaces have significantly different concentrations from fresh quarry material, then the differences are

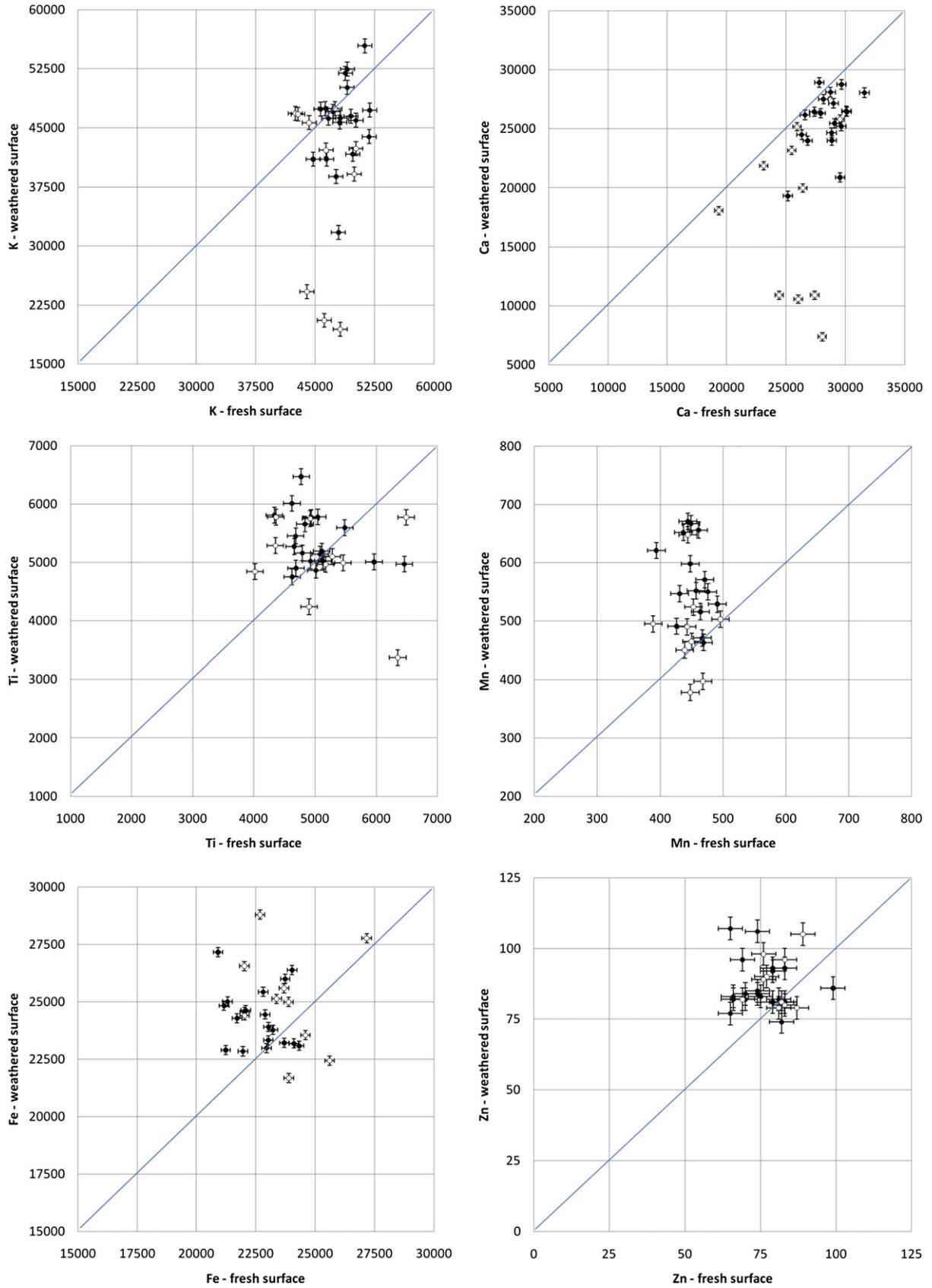


Fig. 2. Paired measurements of concentrations of elements (in ppm) from fresh (X axis) vs. weathered (Y axis) surfaces of the same sample, comparing Rumiqolqa (solid circles) and Huaccoto (open circles) andesites; error bars represent instrument counting error at one standard deviation.

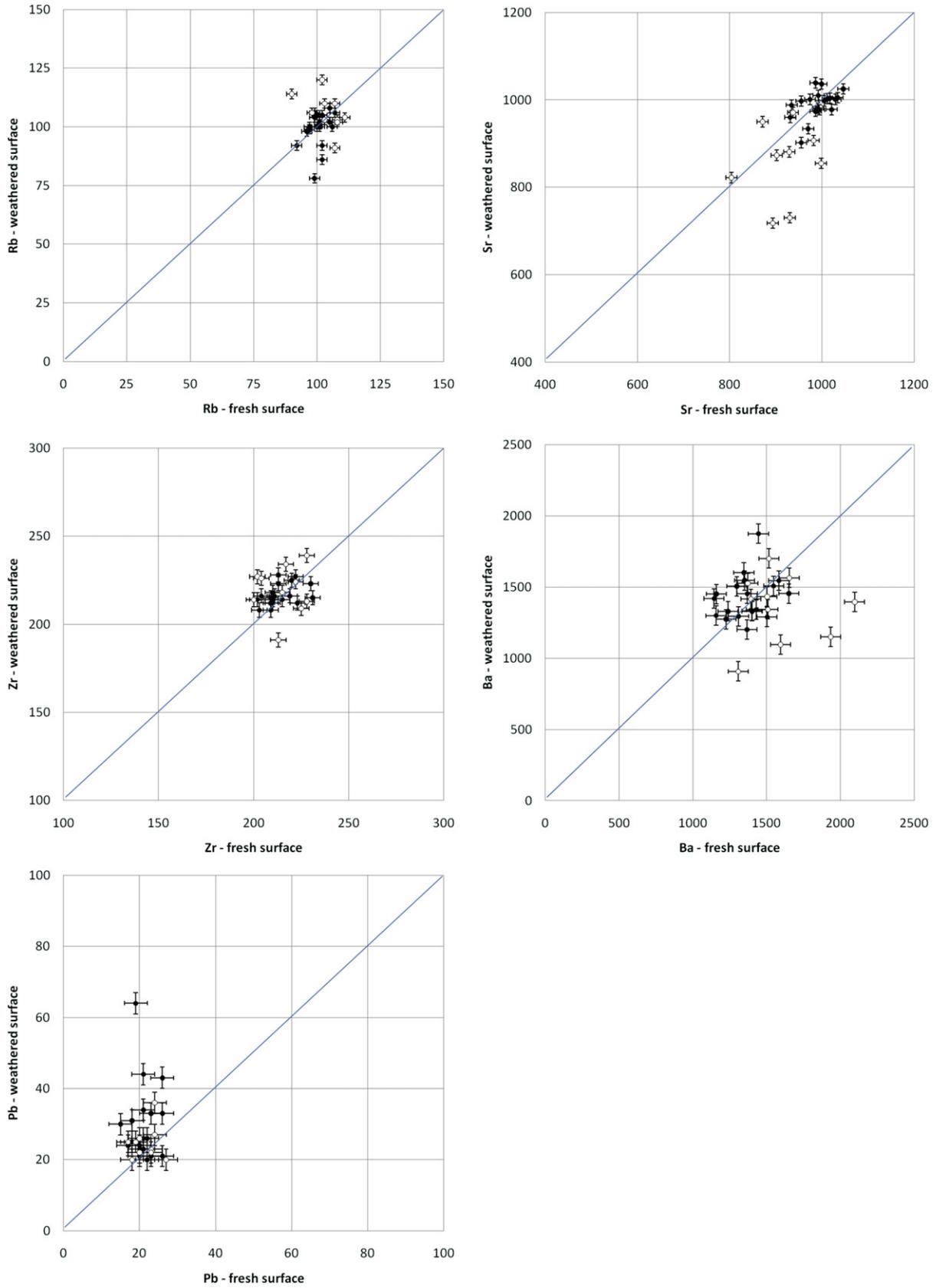


Fig. 2. (continued).

Table 5

Measurements of fresh and weathered surfaces of andesite samples from the Huaccoto quarry, plus mean, standard deviation (s.d.), Student's *t*-test (paired, two-tailed), and *f*-test (ratio of variance of fresh vs. weathered, which is significant at the 0.05 level if >3.18).

Element <i>n</i> = 10	Fresh		Weathered		<i>t</i> -Test	<i>f</i> -test	Effects from weathering
	Mean	s.d.	Mean	s.d.			
K	46,185	2628	37,448	10,841	0.049815	17.0	Depleted, increased variation
Ca	25,585	2694	17,388	6500	0.007542	5.82	Depleted, increased variation
Ti	5130	775	5010	715	0.769347	1.18	–
Mn	455	33.4	605	371	0.232664	123	Increased variation
Fe	23,893	1516	25,088	2118	0.219138	1.95	–
Zn	80.3	5.60	87.9	8.77	0.041111	2.45	Enriched
Rb	103.7	5.80	106.3	7.44	0.514339	1.65	–
Sr	923	56.0	798	193	0.113994	11.9	Depleted, increased variation
Zr	215.4	10.0	219.5	13.1	0.458737	1.69	–
Ba	1588	237	1358	227	0.058684	1.10	Depleted
Pb	21.5	3.01	24.6	4.43	0.096324	2.17	Somewhat enriched

likely to derive from some combination of weathering or contamination that was not removed by our cleaning.

4.2. Results/discussion

In comparing the different cleaning methods for the andesite blocks of the Aqllawasi and Hatuncancha, the results suggest no solvent is markedly more effective than the others in changing measurements for the elements considered; this was also observed for the Hatunrumiyuq material. Aggregating the results for the andesites (Table 6) of all three solvents allows statistical gauging of the differences of surfaces cleaned by any method versus unclean surfaces. Student's *t*-test indicates that cleaning resulted in a significant difference in levels of K and Ca, while the change in Zn was close to the 5% level of significance. The difference for Ba is statistically significant, but is not really meaningful because it falls within the range of instrument error (60–70 ppm). Cleaning had some effect on Mn, but had little impact on Fe and Ti and none on Rb, Sr, Zr, or Pb. For most elements, cleaning did not affect the variability, as reflected in the ratio of variance (*f*-test): variation was only significantly reduced for Mn, but curiously increased with Pb.

Graphs plotting the before and after measurements of the same spot (Fig. 3) are generally consistent with the statistics. Points tend to cluster around the 1:1 line for many elements, illustrating the minimal impact of cleaning. In those cases, the small differences between before and after measurements may be in part attributed to heterogeneity in the material or to instrument error. In contrast, clustering away from the 1:1 line indicates an impact from cleaning: K appears somewhat enriched by cleaning, while Ca is reduced.

There are some outliers for Mn that seem to be reduced through cleaning. Pb and Zn exhibit unusual patterns, as discussed below.

Comparing these results (Table 6) to quarry data (Table 3) demonstrates how the building stones vary from source material and whether that can be attributed primarily to surface contamination or to weathering. Surface contamination and cleaning had no effect on Rb, Sr, and Zr; all those measurements were within the range for fresh source samples, which represents the range of variability within the source material. Ba was similar, although a few measurements fell just below the range for both fresh and weathered quarry materials. Concentrations for Mn, Ti, and Fe on both unclean and cleaned surfaces fall mostly within the range noted for weathered surfaces on quarry samples, suggesting that surface contamination cannot totally account for deviations from fresh source material. K and Ca deviate the most from source material. K mostly falls below the range for fresh source material but within the weathered range, and cleaning tends to bring measurements closer to the fresh range. Ca ranges widely, tending significantly higher than quarry material and cleaning only slightly reduces levels toward the source range. The high concentrations cannot be attributed to weathering; they could possibly be residues from plaster or other materials previously applied to the surface. This appears to be the greatest impact from surface contamination in this context, and as with impacts of weathering, the shallow critical penetration depths for these elements mean that these differences are highlighted with XRF.

The results are less clear for the Hatunrumiyuq diorite (Table 7). Several elements are more highly variable than in the andesite stones, especially K, Ti, Fe, Rb, and Sr. But without source samples it

Table 6

Comparison of changes in measured concentrations of 11 elements after cleaning andesite stones in standing walls in Cuzco, including mean and standard deviation (s.d.) in ppm, Student's *t*-test (paired, two-tailed), and *f*-test (ratio of variance of bare vs. cleaned, which is significant at the 0.05 level if >2.27).

Element <i>n</i> = 18	Bare		Cleaned		<i>t</i> -Test	<i>f</i> -test	Effects from cleaning
	Mean	s.d.	Mean	s.d.			
K	41,243	2302	42,776	2696	0.034	1.37	Increased concentration
Ca	41,860	11,181	36,367	7477	0.00094	2.24	Reduced concentration
Ti	4920	529	4930	710	0.91	1.80	–
Mn	588	212	513	97	0.099	4.77	Slightly reduced concentration, reduced variation
Fe	23,856	1919	23,477	1566	0.42	1.50	–
Zn	178	88.3	156	71.3	0.057	1.54	Reduced concentration
Rb	98	3.9	100	4.0	0.10	1.02	–
Sr	958	39.8	972	30.8	0.15	1.67	–
Zr	208	6.33	209	8.35	0.75	1.74	–
Ba	1204	77.3	1258	95.7	0.037	1.53	Increased concentration
Pb	46.4	25	62.5	61.1	0.19	5.80	Increased variation

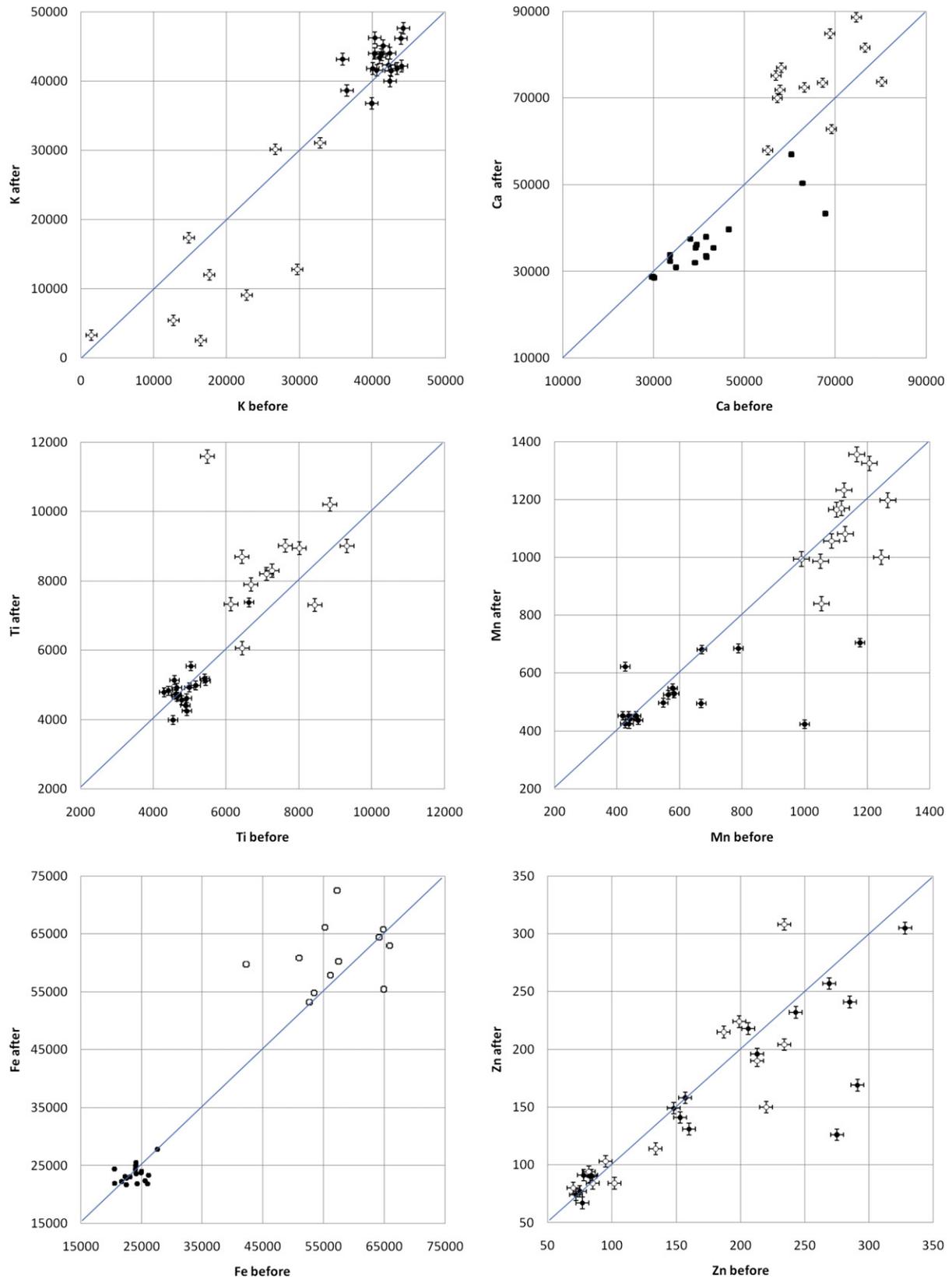


Fig. 3. Paired measurements of concentrations of elements (in ppm) before (X axis) and after (Y axis) cleaning surfaces of the same building stone, including Rumicolqa andesite blocks (solid circles) and diorite (open circles); error bars represent instrument counting error at one standard deviation.

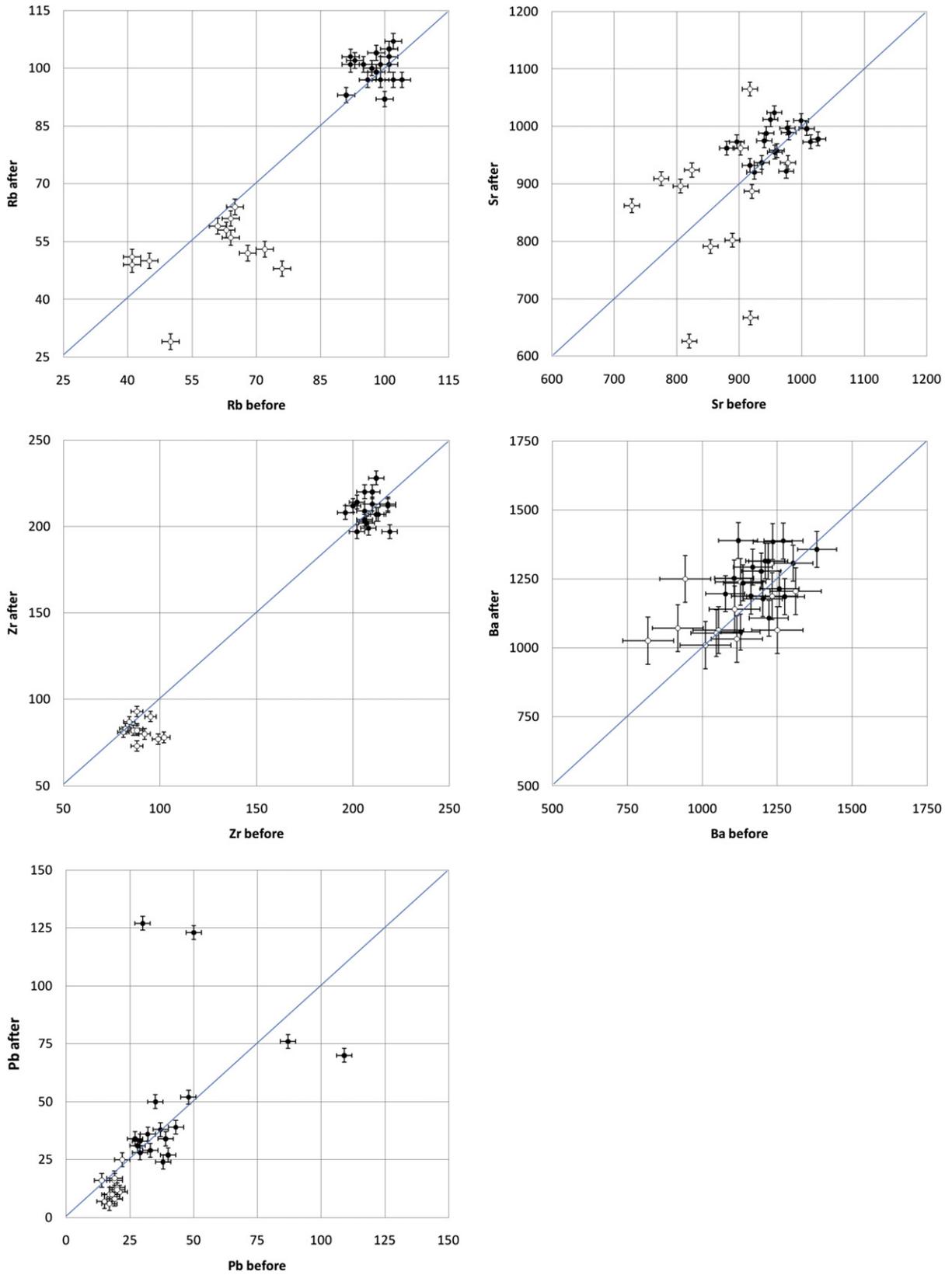


Fig. 3. (continued).

Table 7
Comparison of changes in measured concentrations of 11 elements after cleaning diorite stones in standing walls in Cuzco, including mean and standard deviation (s.d.) in ppm, Student's *t*-test (paired, two-tailed), and *f*-test (ratio of variance of bare vs. cleaned, which is significant at the 0.05 level if >2.98).

Element <i>n</i> = 12	Bare		Cleaned		<i>t</i> -Test	<i>f</i> -test	Effects
	Mean	s.d.	Mean	s.d.			
K	14,954	11,876	9904	11,580	0.051	1.05	Reduced concentration
Ca	65,440	8620	74,124	8564	0.0054	1.01	Increased concentration
Ti	7317	1166	8544	1427	0.038	1.50	Increased concentration
Mn	1129	81.7	1117	152	0.76	3.44	Increased variation
Fe	57,112	7033	61,179	5544	0.098	1.61	Slightly increased concentration
Zn	155	65.6	154	73.4	0.97	1.25	
Rb	59	12	53	9	0.082	1.78	
Sr	861	72	861	123	0.99	2.92	Increased variation
Zr	89	6.5	82	5.5	0.026	1.37	Decreased concentration
Ba	1078	144	1112	87	0.42	2.73	
Pb	18.4	2.4	12.6	5.3	0.0014	5.07	Decreased concentration, increased variation

is difficult to gauge the chemical variability within and between stones as distinguished from the effects of contamination. Heterogeneity within this material may be more of an issue because the diorite has a larger grain size (ca. 3 mm) than the Rumiqolqa andesite, and this could produce significant variation between measurements of the same stone. If so, data for provenance studies could be obtained through averaging multiple readings taken on each stone (Potts et al., 1997). As it stands, it is difficult to know to what extent the differences in readings for unclean vs. cleaned surfaces were caused by heterogeneity of the material versus the removal of surface contamination. The ratio of the variance before and after (*f*-test, Table 7) does not indicate much change, except for Mn, Sr, and Pb, so cleaning generally did not reduce the range of variability. The variance of Sr was impacted by two outliers and Pb had a high variance because levels were closest to the limits of detection, but it is unclear why variability in measurements of Mn increased with cleaning.

Despite that obstacle, some useful observations can be made. K was problematic, as measurements were extremely variable and sometimes close to the level of instrument error; this element appears unsuitable for PXRF studies of this particular stone type. In contrast to the andesite blocks, Ca, Ti and Fe tended to increase after cleaning. Mn and Zn were not significantly affected by cleaning, nor were the heavier elements. Although *t*-tests for Rb, Zr, and Pb suggest some effect, concentrations were in the lower range (<100 ppm) where the level of instrument error (~2–4 ppm) and internal chemical variability likely account for the apparent differences.

These measurements of Pb and Zn may represent special cases. Most of the andesite blocks had elevated Pb, up to four times the average for fresh quarry samples. As suggested above, these levels likely result from airborne contamination from leaded gasoline, in use in Peru until 2005. Highest concentrations were on the wall directly exposed to vehicle traffic, Santa Catalina Angosta, a typical pattern for Pb contamination (Markus and McBratney, 2001). They did not seem elevated for Hatunrumiyoq, which is isolated from traffic. Whether these Pb levels were elevated is difficult to gauge without source samples, but it is notable that they were not significantly reduced through cleaning. Overall, Pb appears unsuitable for PXRF-based provenance analysis in this type of urban environment.

Zn levels were likewise elevated in many andesite blocks, and while cleaning did reduce concentrations in some cases, it did not reduce them to source levels. Automobile traffic is one possible source of Zn contamination, perhaps from wearing of tires or brake linings (e.g., Amusan et al., 2003; Hopke et al., 1980; Yetimoglu et al., 2007). But here Zn was highest along the streets restricted to pedestrian traffic, Calle Loreto and Hatunrumiyoq, suggesting

automobiles were not the primary cause. Notably, levels of Zn tended to be highest in the stones lower toward ground level. It is possible that urination (human and animal) may be increasing the concentration of Zn on walls, as it is naturally passed through urine, and public urination has been common in Cuzco. As with Pb, Zn may be of limited use in this type of environment, though both may be useful in sites more distant from dense automobile traffic and with more controlled access.

5. Field testing: standing walls

In light of the above findings, we examined the validity of using PXRF to establish provenance for building stones in situ. This relies on being able to achieve two things: 1) making a close geochemical match between building stones and quarry materials and 2) distinguishing different geological sources based on their geochemistry.

The first was assessed by measuring unprepared stones in various Inca contexts in Cuzco and the surrounding region to see how closely stones assumed to derive from Rumiqolqa actually matched samples from that quarry. The second is a more complex question that revolves around the degree to which potential sources are chemically distinct from each other. Individual sources of igneous rocks will contain an internal range of variability, but are relatively homogeneous compared to other rock types. Assigning provenance geochemically depends on being able to separate sources based on differences in concentrations of multiple elements (either individually or as ratios). The level of chemical heterogeneity within sources can vary, but this is not an issue as long as the concentrations of the distinguishing elements do not all overlap, and the precision of the method is sufficient to reflect those distinctions in measurements. As noted, the Huaccoto and Rumiqolqa andesites are closely related and are challenging to distinguish chemically, even with lab-based XRF. That task will need to be addressed elsewhere, but building stones from those quarries can often be distinguished by physical characteristics. Some other andesites are easily distinguished chemically, such as the pinkish andesite used at Pisac, which has markedly high levels of Fe, Sr, and Ba. The critical test is distinguishing stone from sources with chemical composition closer in range to the Rumiqolqa material; this was assessed by measuring a range of other gray andesite blocks to determine if other types could be identified.

5.1. Methods

For these tests, PXRF measurements were taken from standing walls, intact features, and loose blocks in Inca imperial contexts at the sites of Cuzco, Sacsayhuaman, Ollantaytambo, Huchuy Qoqso,

and Tipón (Fig. 1). Contexts included exterior and interior building walls, water features, and a large basin. Limitation to Inca imperial sites controlled for duration of chemical weathering, while the variety of contexts sampled allowed for a wider variety of possible contaminants than in the cleaning experiments. A single reading was taken for each stone, on unprepared flat surfaces that appeared relatively clean (i.e., no obvious build-up of residues); this allowed for testing the potential for totally non-invasive analyses. A large number of the stones measured were chosen based on physical resemblance to Rumiqolqa andesite to provide data to compare to the composition of quarry samples. We also measured a selection of other blocks of andesite or closely related materials to determine whether other geological sources could be distinguished chemically from in situ analysis.

5.2. Results/discussion

Overall, the blocks presumed to be from Rumiqolqa based on appearance produced results (Fig. 4) consistent with observations on weathering and surface contamination for Rumiqolqa material. Compared to the range of elemental concentrations of fresh quarry samples, the lighter elements deviate the most; K tended to be depleted, and Ca tended to be enriched. Mn, and to a lesser extent Fe were enriched in some stones (Fig. 4), likely from weathering. Ti was enriched in some cases and depleted in others. In the protected

interior of the Coricancha, concentrations Mn and Fe were always within the source range, but Ca was significantly enriched, likely due to residues of historic period plastering.

The heavier elements Rb, Sr, and Zr all fell within the Rumiqolqa quarry range, which is well-illustrated in Fig. 4; a few readings for Ba were slightly below the minimum for source samples. The results indicate that PXRF measurements for these four elements are reliable for making source assignments under these conditions, provided they can also be used to distinguish material from other sources.

Zn and Pb are again problematic, being enriched for a number of stones in exposed walls in Cuzco, likely due to surface contamination. In contrast, the interior stones in the Coricancha were mostly unaffected, as were walls more distant from heavy automobile and urban foot traffic (e.g., Ollantaytambo, Sacsayhuaman, and Huchuy Qosqo).

It also appears that we can distinguish other sources of andesite within the parameters of these tests. Specifically, andesites from at least two unidentified sources (referred to as types X and Y) can be identified based on bivariate plots of Rb, Sr, Zr, and Ba (Fig. 4). The blocks tend to be lighter colored than Rumiqolqa stones used by the Incas in Cuzco, but because they do resemble the coloration seen in some parts of the Rumiqolqa quarry (Fig. 5), it is essential to be able to identify them chemically. This can be easily achieved, as Rumiqolqa and the two unidentified types fall into distinct groups (with

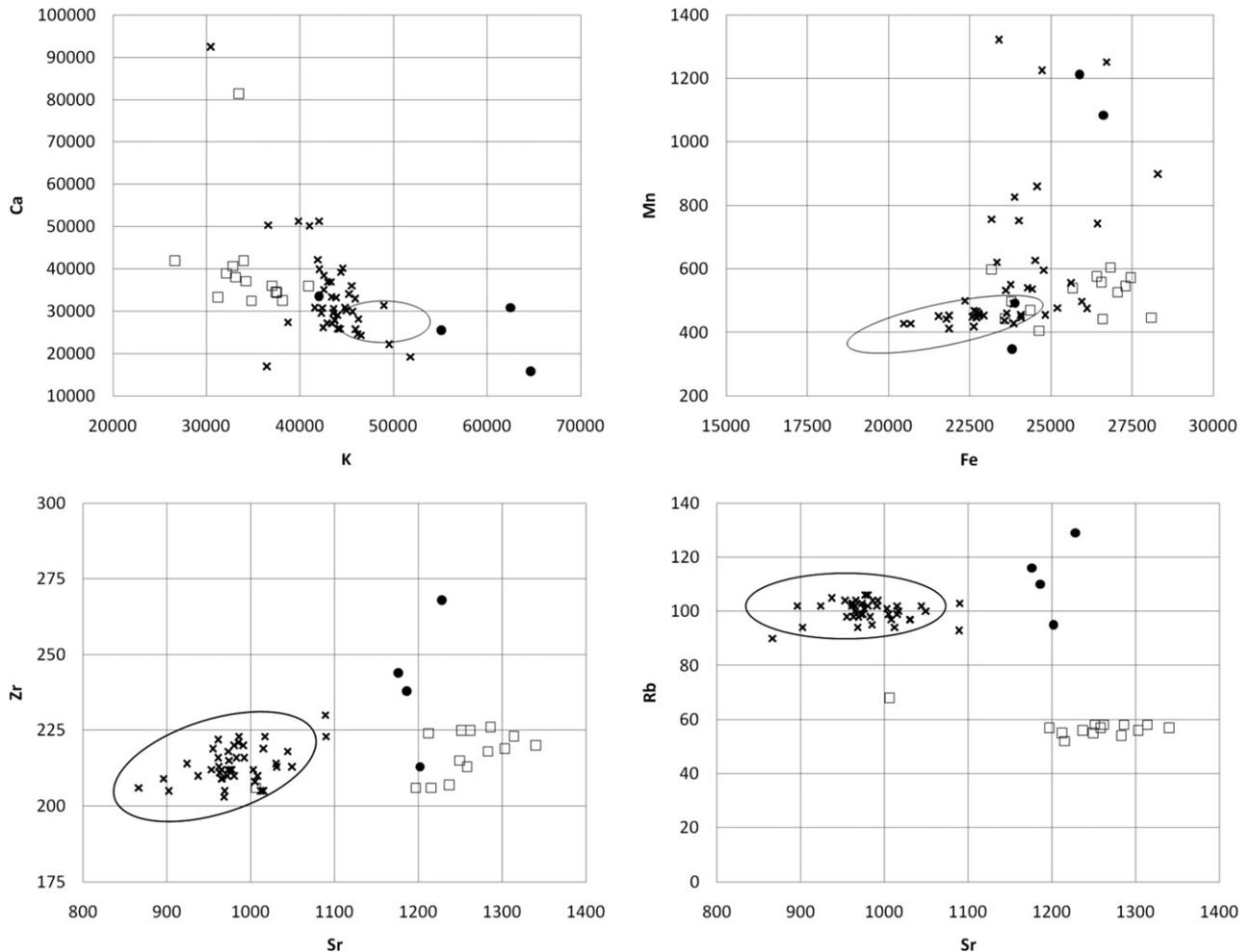


Fig. 4. Bi-variate plots of K vs. Ca, Fe vs. Mn, Sr vs. Zr, and Sr vs. Rb (in ppm) for andesite building stones from the Cuzco region, including stones assigned to the Rumiqolqa quarry (x) and the unidentified andesite X (open squares) and Y (filled circles) sources; the oval indicates the range of variation of fresh surfaces of Rumiqolqa quarry samples; error bars are not included because they would have been smaller than the individual points.



Fig. 5. Fresh surfaces of samples from the Rumiqlolqa quarry, showing the range of variation in physical appearance seen in the material.

one outlier of type X) in a basic bivariate plot of Sr vs. Rb. As with the Rumiqlolqa material, there is some variability of elemental concentrations in these unknown sources, but this is not problematic because they do not overlap significantly with each other.

6. Conclusions

These tests have provided insights into the utility and limitations of PXRF for provenance studies of building stones. In general, surface contamination and weathering had the most impact on the lightest elements. The greatest effects are seen with K and Ca, as concentrations measured on exposed surfaces seldom fell within the range of fresh quarry material, and non-invasive cleaning did not offer improvement; these two elements appear least suitable for this type of provenance analysis. Impacts were much less severe for Ti, Mn, and Fe, while the heavier elements Rb, Sr, Zr, and Ba were not significantly impacted, as their X-ray responses emanated from a greater volume of the material owing to their greater critical penetration depths. This indicates that PXRF can be successfully employed for non-invasive provenance studies of Inca building stones made of fine-grained volcanic stone when geological sources can be distinguished based on a limited number of heavier elements.

Such analyses could possibly be made more robust by the inclusion of other heavy elements such as Th, Y and Nb, which are often valuable for sourcing studies. Apart from K and Ca, some lighter elements might also be incorporated by developing correction factors to compensate for the effects of chemical weathering. Correction factors would be unsuitable for compensating for surface contamination, because such effects were much more variable. But for stones that do not exhibit significant visible contamination, low-impact cleaning seems to make little difference in terms of reducing deviations in concentrations in lighter elements as compared to source material. In cases where they cannot be avoided, it is always advisable to clean surfaces that are obviously dirty, though we cannot specify a preferred low-impact cleaning procedure.

Zn and Pb were found to be enriched in exposed surfaces in this investigation because of specific sources of contamination in Cuzco's urban environment; these are likely to affect other urban areas in the Andes and elsewhere. This contamination is not readily removed by low-impact cleaning, so these elements cannot be used in provenance analysis in this context. However, they may be useful for studies of stones in protected interior spaces or in more rural, low traffic settings. Also, the identification of these surface contaminants suggests the potential for using PXRF to identify residues of some ancient activities.

While this study focused on the specific geological and archaeological context of stones quarried by the Incas, the results should be applicable to similar contexts. It may be reasonable to expect objects of similar fine-grained volcanic material of up to 1000 or 1500 years old to yield similar results, although increased chemical weathering may require developing different correction factors for lighter elements. Also, the results should pertain to analysis of other types of objects made from similar materials within that time frame, e.g., sculptures, grinding stones, and weapons.

Overall, while PXRF is not yet equal to lab-based instruments in terms of precision, it can be considered valid for application to provenance studies of building stones, as we could successfully match Inca building stones to geological source and distinguish different sources within the parameters tested here. Thus, PXRF can be a viable tool when we are restricted to non-invasive analysis, as issues of chemical weathering and surface contamination do not necessarily prevent the collection of fingerprinting data suitable for confidently making source assignments.

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