

Evaluation of the Niton XL3 X-ray Fluorescence Analyzer

The following summarizes the results of a series of measurements made with the Thermo Scientific Niton XL3 Analyzer during IODP Expedition 330. The goal was to see whether this portable X-ray fluorescence (XRF) instrument, which had recently been installed on the ship, would be of value for distinguishing magmatic units reliably and relatively rapidly. At the beginning of the expedition, internal (measurement) error was assessed by analysis of three pieces of the ODP Site 1203 cores that were present aboard the ship (**Table 1**). These rocks are similar in composition to those that were expected for Expedition 330, and subsequently recovered. For a number of elements, the internal error is reasonably low (e.g., Sr, Zr, TiO₂, Al₂O₃, CaO, SiO₂, Fe₂O₃). For others (e.g., Ni, Cu, Nb, Ba), it is too high for them to be useful, at least for rocks of broadly basaltic composition.

Because no solid rock standards were available on the ship, and before any ICP-AES (inductively coupled plasma – atomic emission spectrometer) data for the first site, Site U1372, were available, we next analyzed powders of four rock standards, three basalts and one andesite. The first column in **Table 2** lists the percent difference between the XRF value and the recommended value for these standards. The second column lists two standard deviations (2 s.d.) of the range of XRF values. For these powders, the XRF instrument yielded values for several elements that are reasonably close to the recommended values (e.g., CaO, K₂O, SiO₂). For many of the other petrologically useful elements, however, the differences are great. Nevertheless, for some of these elements, the machine gave rather consistent values (i.e., although values were way off the recommended values, the *range* of the differences was relatively small; e.g., Zr, Sr, TiO₂), suggesting that in some cases these elements might still be useful.

The first two columns in **Table 3** list the *range* (as 2 s.d.) of the difference between XRF values and ICP-AES values measured for ten Site U1372 basalts. The first column is for XRF measurements of powders and the second is for slabs of rock. The goal here was to check for consistency of XRF measurements (regardless of whether they were high or low). Powders yielded somewhat better results overall (e.g., for SiO₂, Al₂O₃, CaO). For Zr, it can be seen that the range of differences for the powders was smaller (4%) than for the slabs (10%). For TiO₂ and Sr, the slabs gave slightly smaller ranges (7% vs. 5% and 13% vs. 11%, respectively). For several petrologically important elements and element ratios, the measured levels of consistency would be useful for distinguishing between units of certain rock suites (e.g., volcanic sequences where, say, basalts, and more evolved rocks like andesites and dacites are all present). They also might be useful for studies of certain sedimentary sequences (e.g., the Bengal Fan).

What about the utility of the instrument for distinguishing magmatic units during Expedition 330? The third column in **Table 3** lists the standard deviation of ICP-AES values measured for all of the Site U1372 samples (i.e., not just the ten analyzed by XRF). In order to reliably distinguish different units at this site, the values in columns 1 and 2 should be at least three times less (preferably even smaller) than the values in column 3. It can be seen that only Zr and K₂O measured on powders meet this criterion. For slabs, TiO₂ comes close. However, as is often the case for submarine lava suites, most of the variation in K₂O at Site U1372 is caused by alteration, so K₂O is not very useful for distinguishing different magmatic types in such suites. For comparison, column 4 in **Table 3** shows the percent difference between the ICP values for the BHVO-2 standard, which was run as an unknown with the Site U1372 samples, and the recommended values. Of course, the ICP instrument determines most (but not all) of the elements at levels well below the values in column 3.

Do multiple XRF measurements of a small area of a sample make a substantial difference? **Table 4** presents the results of multiple measurements of five Site U1372 samples. The sawn faces of pieces of core were used for these analyses. In each case, seven different spot analyses were made and averaged. Between each spot analysis, the piece was moved slightly. Column 1 is equivalent to the second column in **Table 3**. Column 2 is the same as the fourth column in **Table 3**. It can be seen that averaging several measurements made at slightly different locations in a piece of rock does not help overall and in some cases can increase the range of variation (e.g., SiO₂, MgO, Al₂O₃). This is probably a result of sample heterogeneity from spot to spot, which is one of the main reasons why research XRF laboratories measure finely ground powders and glasses rather than slabs of rock.

Multiple measurements were subsequently made on several additional Site U1372 core pieces, bringing the total to eleven. In **Table 5**, the results are divided according to the level of alteration of the samples, into “less altered” and “more altered” categories. The less-altered group of five samples includes four aphyric samples and one highly phyrlic (>10% phenocrysts) sample, and the results are shown both with and without results for the highly phyrlic sample (columns 1 and 2, respectively). The five samples of the more-altered group (column 3) were all aphyric. Some of the values in columns 1-3 are higher, and some lower, than those in column 2 of **Table 3**, but in general the values in columns 1-3 are again too large for reliably distinguishing different units at Site U1372. Overall, the less-altered samples yielded somewhat more consistent results for several elements (e.g., SiO₂, Al₂O₃, CaO), whereas the more-altered group gave more consistent results for several other elements (e.g., TiO₂, Zr, Sr). The 7% value for Zr and the 4% value for Sr

for the more-altered aphyric samples (column 3) are “too good”; that is, the measurement (internal) error for each element is as large or larger (8% for Zr and 4% for Sr; see **Table 1**). These two results appear to be a fortuitous consequence of the relatively small number of samples in the group. The same applies for the relatively low value for MgO (8%) in column 2, given the 12% measurement error for MgO (**Table 1**) and the 25% range measured for finely ground powders of rock standards (**Table 2**).

Summarizing the results of all the tables, the elements that are both useful for distinguishing lava units and also are measured most reproducibly by the instrument on slabs of variably altered submarine rock are TiO₂, Zr, and Sr. The reproducibility for these elements is larger (poorer) than needed to reliably distinguish units at sites similar to Site U1372. However, the instrument could be useful for sites with substantially greater compositional variation, or for sites where the goal is to identify “spikes” or extremes in composition.

The above experiments with basaltic samples suggested to us that the instrument might be particularly useful in a different type of application: material identification. Both macroscopic and microscopic inspection often fail to identify certain materials that may be present in sedimentary deposits and zones of alteration, such as ferromanganese oxide, which can be difficult to distinguish from dark clay, and phosphate, which can be difficult to identify when it co-occurs with carbonate, zeolites, ferromanganese, or clay. Such phases can have important implications regarding redox, paleoclimatic, and paleoceanographic conditions. X-ray powder diffraction can be used to identify these kinds of phases, but requires both sufficient amounts of material and time (in addition to the time of the analysis, the material must be separated from the bulk rock and then powdered). In contrast, the Niton XL3 Analyzer is capable of relatively rapid analysis of spots as small as 3 mm.

In the second half of Expedition 330, we evaluated this application of the instrument by making measurements of material exposed on core faces in sedimentary intervals. The instrument’s small beam mode, which uses an X-ray beam 3 mm in diameter, was employed. The results were very encouraging. **Figure 1A** summarizes the results for one sedimentary interval (Interval 330-U1374A-3R-1W, 66.5-70.5 cm), for which 21 different spots were analyzed. For the shipboard sedimentologists and paleontologists, the primary interest was to determine whether or not the dark material occurring in a rather complicated association with carbonate, volcanic clasts, and pieces of bioclastic sandstone was ferromanganese oxide (see “330-U1374A-C-Sedimentology” and “330-U1374A-D-Paleontology”, Expedition 330 Scientists, 2011). The analysis was qualitative rather than quantitative, because no suitable standards were available on the ship and

the dark layers were thin relative to the X-ray spot size. Our measurements showed that markedly higher levels of Fe₂O₃, MnO, Ni, Pb, and As are present in the large dark area and a smaller dark area to its right (**Fig. 1A**) than in the surrounding areas, indicating that both dark areas contain a large proportion of ferromanganese material. The larger area also has relatively high concentrations of phosphorus. In addition, the thin dark zones along the edges of carbonate clasts below the two dark areas were identified as ferromanganese coatings. Enrichment in phosphorus was discovered in the interior of one of the carbonate clasts (spots outlined in purple, **Fig. 1A**), indicating that the carbonate had been phosphatized. The overall association suggests phosphatization followed by ferromanganese deposition.

Measurements of eight additional sedimentary core pieces from Sites U1372, U1375, U1376 and U1377 (Intervals 330-U1372A-5R-1W, 0-4 cm; -U1372A-5R-1W, 24-27 cm; -U1375A-2R-1A, 0-7cm; -U1375A-2R-1A, 17-32 cm; -U1376A-3R-3W, 85-101cm; -U1376A-4R-3A, 45-52 cm; -U1376A-4R-3A, 89-98 cm; and -U1377A-2R-1A, 0-10.5 cm) identified ferromanganese oxide and calcium carbonate. Ferromanganese phases were ruled out as the very dark material in another core piece (Interval 330-U1376A-3R-3W, 111-120 cm). In addition, phosphate was identified within the carbonate in Intervals 330-U1372A-5R-1W, 24-27 cm (**Fig. 1B**), -U1375A-2R-1A, 0-7cm, -U1375A-2R-1A, 17-32 cm (**Fig. 1C**), and -U1377A-2R-1A, 0-10.5 cm. In Intervals 330-U1376A-4R-3A, 45-52 cm, and -U1376A-4R-3A, 89-98 cm (**Fig. 1D**), spatial variation in Fe content was observed within the carbonate. Moreover, the degree of phosphatization or Fe enrichment in these intervals appeared to correlate with the color of the carbonate. We emphasize that the phosphatization of the carbonate in the core pieces of **Figure 1B** and **C** and in Interval 330-U1377A-2R-1A, 0-10.5 cm, was not, and could not be, detected by visual observation alone; the presence of the phosphate was revealed by the XRF instrument.

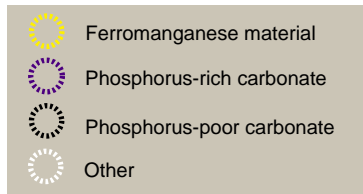
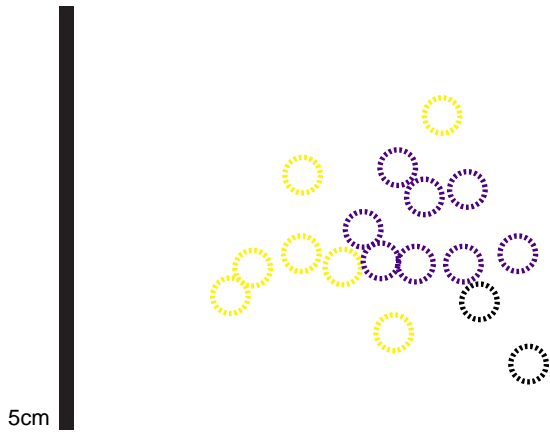
Reference

Expedition 330 Scientists, 2011. Site U1374. In Koppers, A.A.P., Yamazaki, T., Geldmacher, J., and the Expedition 330 Scientists, *Proc. IODP*, 330: Tokyo (Integrated Ocean Drilling Program Management International, Inc.).

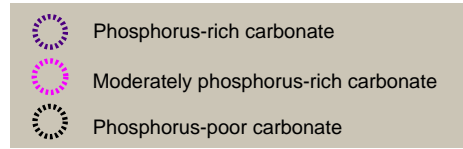
Figure captions

Figure 1. Photographs of Intervals 330-U1374A-3R-1W, 66.5-70.5cm (**A**), -U1372A-5R-1W, 24-27 cm (**B**), -U1375A-2R-1A, 17-32 cm (**C**), and -U1376A-4R-3A, 89-98 cm (**D**). The spots analyzed were all 3 mm in diameter and are indicated by dashed circles.

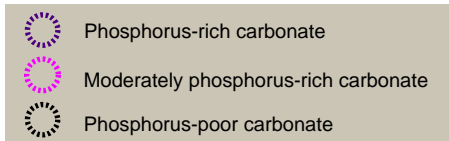
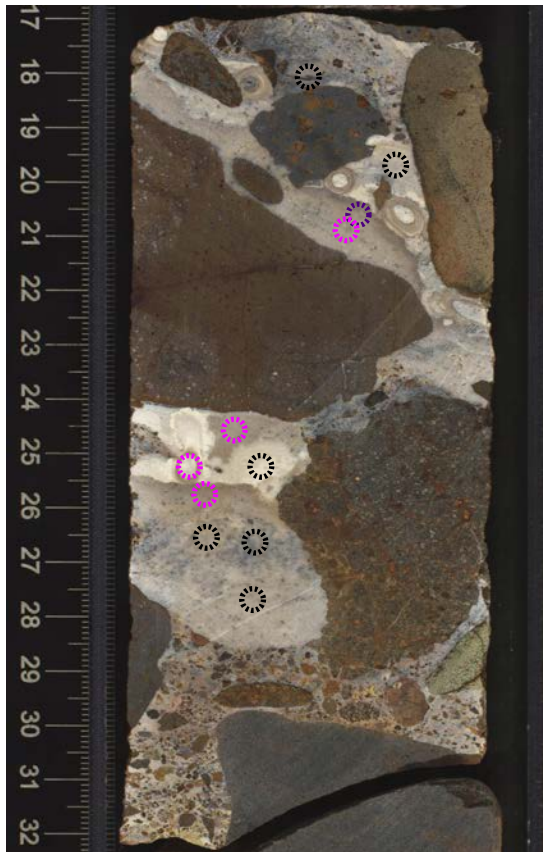
(A) Interval 330-U1374A-3R-1W, 66.5-70.5cm



(B) Interval 330-U1372A-5R-1W, 24-27 cm



(C) Interval 330-U1375A-2R-1A, 17-32 cm



(D) Interval 330-U1376A-4R-3A, 89-98 cm

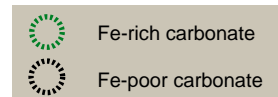
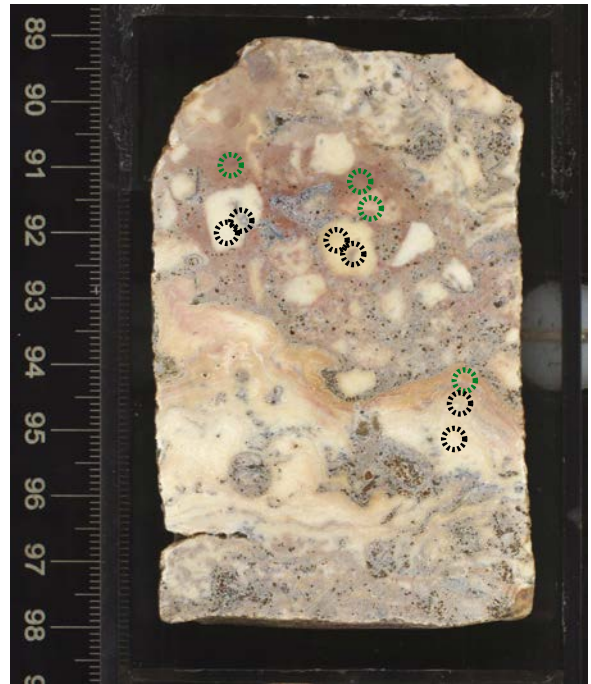


Figure 1

Table 1. Average Internal (Measurement) Error (2 s.d.) on Three Pieces of Site 1203 Cores

SiO ₂	1.00%
TiO ₂	2.80%
Al ₂ O ₃	2.60%
Fe ₂ O ₃ ^T	1.60%
MgO	12%
MnO	16%
CaO	1.60%
K ₂ O	8%
P ₂ O ₅	44%
Ba	38%
Nb	48%
Zr	8%
Sr	4%
Zn	30%
Cu	46%
Ni	126%
Cr	20%
V	18%
Ti/Zr	8%
Sr/Zr	9%
Nb/Zr	49%
K ₂ O/Zr	11%
K ₂ O/TiO ₂	8%
Al ₂ O ₃ /TiO ₂	4%
CaO/Al ₂ O ₃	3%
MgO/Fe ₂ O ₃ ^T	12%

Each piece was measured three to five times in one spot for 150 seconds each time. Fe₂O₃^T is total iron as ferric iron.
s.d. = standard deviation.

Table 2. XRF Measurements of Powder Pellets of Four Rock Standards

	Diff. from recommended (%)	Range of deviation (2 s.d.)
SiO ₂	-3 to +2 %	4%
TiO ₂	-27 to -20 %	5%
Al ₂ O ₃	-5 to -24 %	15%
Fe ₂ O ₃ ^T	-1 to +183 %	170%
MgO	-43 to -75 %	25%
MnO	-8 to +9 %	12%
CaO	-8 to +6 %	11%
K ₂ O	0 to -10 %	10%
P ₂ O ₅	-28 to +33 %	44%
Ba	-37 to +828 %	747%
Nb	-36 to +15 %	37%
Zr	-28 to -18 %	8%
Sr	-35 to -27 %	5%
Zn	-6 to -25 %	16%
Cu	-100 to +8 %	109%
Ni	-100 to +19 %	95%
Cr	+1 to +1092 %	968%
V	+22 to +120 %	69%
Ti/Zr	-3 to +4 %	6%
Sr/Zr	-15 to -2 %	10%
Nb/Zr	-12 to +40 %	38%
K ₂ O/Zr	+12 to +27 %	12%
K ₂ O/TiO ₂	+14 to +27 %	10%
Al ₂ O ₃ /TiO ₂	-1.5 to +21 %	19%
CaO/Al ₂ O ₃	+12 to +20 %	7%
MgO/Fe ₂ O ₃ ^T	-86 to -42%	37%

The standards were BHVO-2, BCR-2, JA-2, and BAS-140. (BAS-140 was not used for K₂O, P₂O₅, or Nb in the calculations above, because its values for these for these elements are low.) Each powder-pellet measurement is an average of three 150-sec. spot analyses. Fe₂O₃^T is total iron as ferric iron. s.d. = standard deviation.

Table 3. Comparison of XRF Data for Powders and Slabs with ICP Data for Ten Site U1372 Basalts

	Range (2 s.d.), diff. from ICP		Std. dev. of ICP values, Site U1372	BHVO-2 run as an unknown, ICP <i>Diff. from recommended</i>
	<i>Powders</i>	<i>Slabs</i>		
SiO ₂	5%	7%	3%	0.3%
TiO ₂	7%	5%	14%	1%
Al ₂ O ₃	7%	12%	8%	-2%
Fe ₂ O ₃ ^T	5%	7%	9%	1%
MgO	21%	21%	54%; 24 % within Unit VI***	0.8%
MnO	14%	55%	11%	7%
CaO	10%	24%	10%*	-0.5%
K ₂ O	8%	18%	40%**	16%
P ₂ O ₅	16%	29%	19%	5%
Ba	81%	72%	20%	8%
Zr	4%	10%	17%	7%
Sr	13%	11%	11%	5%
Cu	91%	229%	42%	-1.7%
Ni	103%	60%	92%	3.3%
Cr	72%	76%	82%	0.8%
V	10%	11%	15%	-0.3%
Ti/Zr	8%	11%	7%	-7%
Sr/Zr	16%	23%	17%	-2%
K ₂ O/Zr	7%	12%	23%**	9%
K ₂ O/TiO ₂	13%	23%	40%**	15%
Al ₂ O ₃ /TiO ₂	10%	16%	13%	-3%
CaO/Al ₂ O ₃	13%	20%	17%	2%
MgO/Fe ₂ O ₃ ^T	19%	18%	51%; 28% within Unit VI***	-0.3%

Note: A rough rule of thumb is that you want the 2 s.d. (standard deviation or std. dev.) value on your measurements to be at least three times better than the 1 s.d. range of a given quantity. Each XRF measurement was an average of three individual measurements (each 150 sec). Column 4: BHVO-2 was run as an unknown with the Site U1372 batch analyzed by ICP.

*Excludes two highly altered Site U1372 samples.

**Variation at Site U1372 is largely due to alteration of K₂O contents.

***For MgO and MgO/Fe₂O₃^T, the within-unit variation in Unit VI was a substantial portion of the total range.

Table 4. Multiple Measurements (7) of Five Site U1372 Basalts (Core Pieces)

	Range (2.s.d.), diff. from ICP	Std. Dev. of ICP values, Site U1372
SiO ₂	18%	3%
TiO ₂	5%	14%
Al ₂ O ₃	38%	8%
Fe ₂ O ₃ ^T	10%	9%
MgO	42%	54%; 24% within Unit VI
MnO	27%	11%
CaO	8%	10%*
K ₂ O	11%	40%**
P ₂ O ₅	17%	19%
Ba	31%	20%
Zr	8%	17%
Sr	5%	11%
Cu	34%	42%
Ni	130%	92%
Cr	34%	82%
V	10%	15%
Ti/Zr	6%	7%
Sr/Zr	8%	17%
K ₂ O/Zr	18%	23%**
K ₂ O/TiO ₂	21%	40%**
Al ₂ O ₃ /TiO ₂	56%	13%
CaO/Al ₂ O ₃	33%	17%
MgO/Fe ₂ O ₃ ^T	39%	51%; 28% within Unit VI

Each XRF measurement was an average of seven individual spot analyses. The spot analyses were in different spots in the same area of the core piece. The pieces were fine grained, free of amygdules or vesicles, and aphyric. Std. dev. and s.d. = standard deviation.

*Excludes values for two highly altered Site U1372 samples.

**Variation at Site U1372 is mainly due to alteration of K₂O contents.

Table 5. Multiple Measurements (7) on Eleven Site U1372 Basalts (Core Pieces)

	<i>Range (2 s.d.) of difference from ICP</i>			Std. Dev., ICP values, Site U1372
	Less alt. all (5)	Less alt. aphyric (4)	More alt. aphyric (5)	
SiO ₂	4%	5%	18%	3%
TiO ₂	13%	14%	6%	14%
Al ₂ O ₃	11%	9%	36%	8%
Fe ₂ O ₃ ^T	9%	8%	13%	9%
MgO	33%	8%	38%	54%; 24 % within Unit VI
MnO	21%	23%	35%	11%
CaO	6%	3%	11%	10%*
K ₂ O	21%	17%	11%	40%**
P ₂ O ₅	25%	15%	23%	19%
Ba	62%	38%	24%	20%
Zr	11%	12%	7%	17%
Sr	13%	12%	4%	11%
Cu	61%	68%	131%	42%
Ni	87%	95%	113%	92%
Cr	201%	207%	140%	82%
V	10%	10%	15%	15%
Ti/Zr	13%	12%	5%	7%
Sr/Zr	14%	13%	8%	17%
K ₂ O/Zr	34%	32%	16%	23%**
K ₂ O/TiO ₂	37%	35%	19%	40%**
Al ₂ O ₃ /TiO ₂	36%	39%	51%	13%
CaO/Al ₂ O ₃	12%	8%	34%	17%
MgO/Fe ₂ O ₃ ^T	27%	5%	35%	51%; 28% within Unit VI

Each XRF measurement was an average of seven individual measurements (each 150 sec). The spot analyses were in different spots in the same area of the core piece. The pieces were fine grained and free of vesicles or amygdules. In the less-altered (alt.) group, four samples were aphyric, one was highly phyric. The more-altered samples were aphyric. Std. Dev. and s.d. = standard deviation.

*Excludes values for two highly altered Site U1372 samples.

**Variation at Site U1372 is mainly due to alteration of K₂O contents.