APPLICATION NOTE
XE-2012-3172

Xenemetrix
The Power to Change Energy Into Information

Quantitative analysis of CaO, MgO in Limestone & Dolomite & Al_2O_3, SiO2 and Fe2O3 in Iron Ores

by X-Calibur SDD Analyzer

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ABSTRACT
Quantitative analysis of geological samples, Limestone, Dolomite and Iron ores, was performed with X-Calibur SDD detector.
More specifically:

- Quantitative analysis of CaO and MgO in Limestone
- Quantitative analysis of CaO and MgO in Dolomite
- Quantitative analysis of Al2O3, SiO2 and Fe2O3 in Iron Ores
- For dolomites: Static precision study with 9 consecutive acquisitions to evaluate the precision of the X-Calibur SDD analyzer; Reproducibility test to evaluate the distribution of CaO and MgO among the Baljee sample in crude stone and milled forms
- For Limestone: study the effect sample preparation (crushing and milling) on the repeatability of unknown sample results.

GOALS

1. Quantitative analysis of CaO and MgO in Dolomite and Limestone
2. Quantitative analysis of Al2O3, SiO2 and Fe2O3 in Iron Ores
3. Static precision to evaluate instrument performance
4. Evaluate element distribution in Dolomite stone sample form
5. comparison of crude native samples to milled samples for Limestones.

BACKGROUND
Energy Dispersive X-ray Fluorescence (EDXRF) is a fast and non-destructive, non invasive, quick, technique that can quantify any type of sample solid, powder and liquid from. EDXRF is an ideal method for a quick and simple elemental analysis for industrial control purposes offering the following advantages: 1.) Fast and minimal sample preparation, 2.) Automated analysis process, 3.) Limited or no exposure to corrosive reagents used by other analytical techniques, 4.) Ease of use for operation by non-technical or non-specialized personnel. These advantages have made XRF as the method of choice among diverse industries including mineral and mine sectors.

ANALYTICAL CONFIGURATIO N

Table 1: Analytical Configuration

Instrument	X-Calibur SDD EDXRF Bench top Spectrometer System.
Excitation	Rh-Anode X-ray Tube, 50KV 50W
Detector	High Performance Silicon Drift Detector SDD
Analysis Time	300-450 second
Type of analysis	Quantitative method using regression, precision test, repeatability test.
Environment	vacuum
Sample preparation	The samples and standards were analyzed as obtained from the customers, in some cases analysis was done with crushed-milled samples. All samples were analyzed in X-ray cups with X ray-film support.

EXPERIMENTALS

Three sets of geological standards and corresponding samples were provided (table 2). Analysis was performed in X ray cups with special 4µm thick prolene thin film support followed by slight tapping of the cup in order to compact the soil and eliminate the air voids. The spectra was acquired at 8KV energies and 10KeV low energy range in vacuum in order to stress the low Z elements. It is necessary to eliminate the oxygen in the X-ray beam path since otherwise Oxygen absorbs the signal emitted by the light elements.
Calibration methods were established for each of the 3 sets. Since only few standards were provided for Dolomite and Limestone, several portions were taken from each standard pack.
Limestone standards were mixed with powder mixer. Both Dolomite and Limestone standards were "diluted" 50% W/W with H_3BO_3 (*) to produce additional low concentration standards.
(*) ED XRF transparent substance used to dilute samples for EDXRF analysis)

Table 2: Elemental standard concentrations in Dolomite, Limestone and Iron ore with the corresponding list of unknown samples

Dolomite	Type	CaO	MgO
standard-1	Standard	30.84	17.34
standard-2	Standard	31.12	16.53
standard-3	Standard	28.89	16.93
standard-4	Standard	29.72	17.54
Balajee	sample unknown	----	----

Limestone	Type	CaO	MgO
standard-1	Standard	49.91	2.02
standard-2	Standard	46.82	1.41
standard-3	Standard	45.42	2.02
standard-4	Standard	48.51	2.02
S.B.S.Refractories	sample unknown	----	----
Oswal	sample unknown	----	----

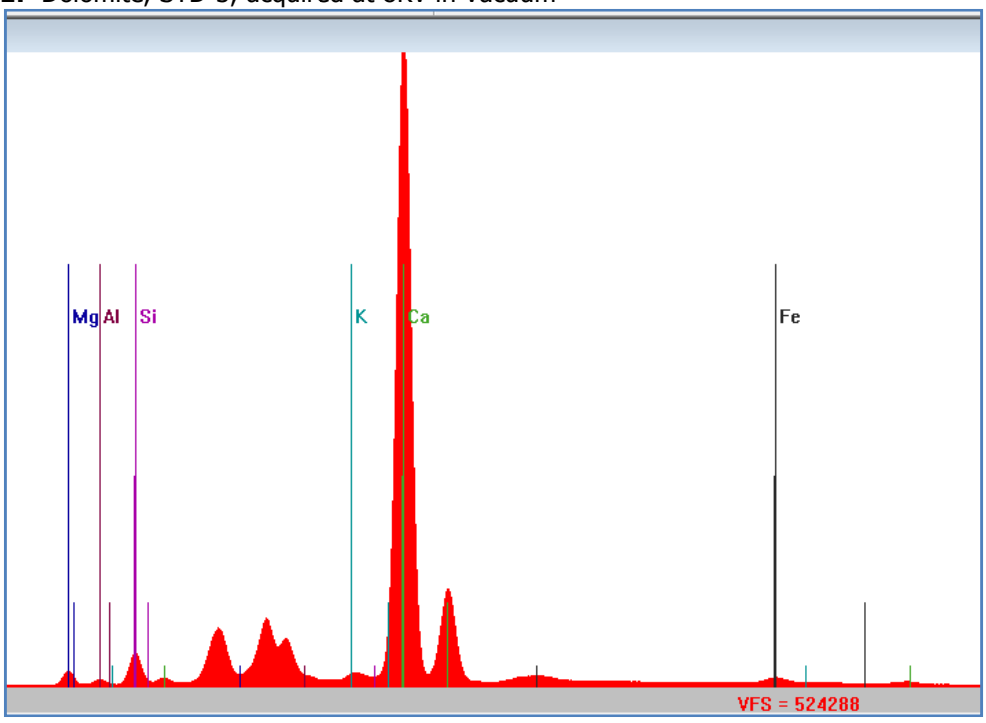
Iron ore	Type	Fe2O3	SiO2	Al2O3
standard-1	Standard	61.1	5.47	2.36
standard-2	Standard	65.35	3.05	1.64
standard-3	Standard	64.43	3.46	2.02
standard-4	Standard	64.14	2.4	2.36
standard-5	Standard	63	3.33	2.02
standard-6	Standard	62.34	4.39	2.32
standard-7	Standard	65.22	2.83	1.66
standard-8	Standard	62.65	3.64	2.18
standard-9	Standard	65.47	2.75	1.48
standard-10	Standard	64.51	3.31	1.63
standard-11	Standard	63.28	3.65	2.04
standard-12	Standard	64.61	3.14	1.85
K.J.S.Aluwalia	sample unknown	----	----	----
Sushant minerals	sample unknown	----	----	----
R.P.Sao S.N.M.M	sample unknown	----	----	----
B.I.CO Rungta	sample unknown	----	----	----
Essel Mining	sample unknown	----	----	----

Precision study
In order to show the repeatability of the X-CaliburSDD, dolomite calibration standard underwent static precision study: single sample was analyzed 10 times without being moved between the acquisitions. The mean result together with standard deviation and relative standard deviation (RSD) were calculated for CaO and MgO (table 4).
Reproducibility study
Six different portions from the same pack of crude native Balajee dolomite were poured into XRF cups and analyzed separately. Similar procedure was held with 4 portion of milled Balajee (table 4).
For Limestone samples, both crude (native) and milled samples were analyzed and the results processed statistically (Table 6 and 7).

RESULTS and DISCUSSIONS

1. DOLOMITE

Low molecular weight elements in the geological samples of Dolomite are shown in figures 1.
Figure 1: Dolomite, STD-3, acquired at 8KV in Vacuum

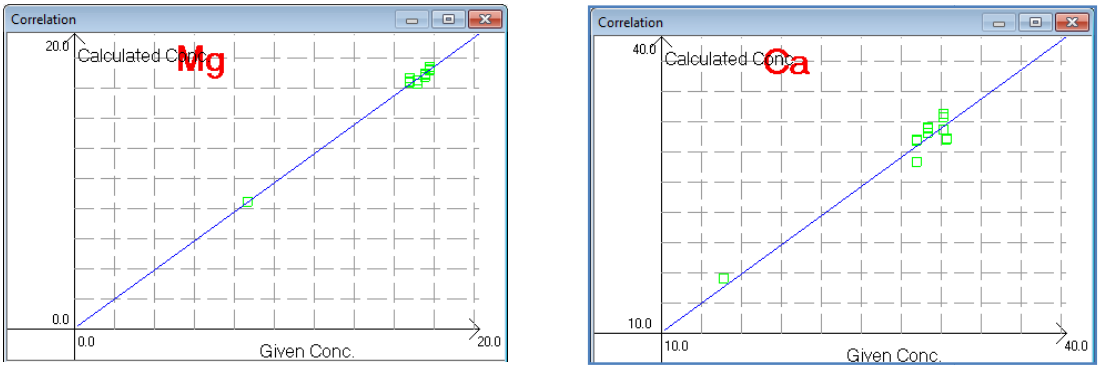


Quantitative method for CaO and MgO in Dolomite
Quantitative analysis was performed by regression analysis with certified standards. Three portions from each standard pack were used to calibrate the instrument (table 3, figure 2 and result report 1). One standard was diluted 50% W/W with Boric acid; transparent substance in EDXRF. It is advised to use standards with broader range of element concentration, particularly is unknown samples are due to be analyzed.
Since Mg concentration range was narrow, 16.53-17.54, it was decided to dilute one of the sample by 50% to add to the existing calibration curve. It is advises to use independent standards if such are available. Yet, a compromise was taken here.

Table 3: Calibration data of MgO and CaO in Dolomite.

Sample ID	MgO Standard deviation=0.21 correlation =0.9955			CaO Standard deviation=1.12 correlation =0.9647		
	Given Conc.	Averaged Calc. Conc.	Rel.Dev.	Given Conc.	Averaged Calc. Conc.	Rel.Dev.
STD1	17.34	17.17	0.17	30.84	31.52	-0.68
STD2	16.53	16.81	-0.28	31.12	29.56	1.56
STD3	16.93	16.73	0.20	28.89	28.69	0.20
STD4	17.54	17.63	-0.09	29.72	30.53	-0.81

Figure 2: MgO and CaO in Dolomite, concentration versus intensity



REPRODUCIBILITY STUDY

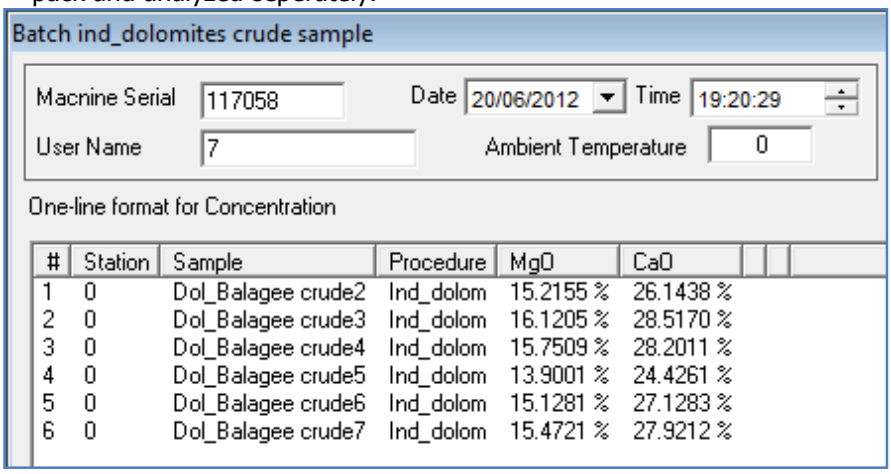
The reproducibility test is aimed to show the distribution of the elements in the sample. Comparison was done between crude Balajee sample is it native stone form and pre-treated by crushing and milling.

Six different portions from the same pack were analyzed separately for crude sample (result report 1). After Balajee sample was crushed and milled, the pile was divided into 4 portions and analyzed separately in 4 X ray cups (result report 2). For each of the sets, crude and milled, the average (mean) and relative standard deviations (RSD) were calculated and compared (tabel 4). The RSD values, for CaO and MgO, in the milled Balajee were considerabley smaller than those obrtained for the native untreated form. This proves that CaO and MgO were more evenly distribution in the milled from of Balajee. It is a commonly used practive to use identical sample preparation for both standards and samples. Therefore following the customer's standard preparation procedure of milling Balajee stones into powder, at Xenemetrix application lab, produced a more reproducible and precise results than with crude native stone form (table 4).

Table 4: statistical results for MgO and CaO in crude and milled Balajee.

	MgO		CaO	
	Mean	% RSD	Mean	% RSD
Crude Balajee; stone form (6 portions taken)	15.3	4.9	27.1	5.7
Crushed and milled into powder Balajee (4 portions)	17.7	1.0	31.1	0.5

Result report 1: Result report for Balagee sample in stone form; 6 portions taken from the same sample pack and analyzed seperately.



Batch ind_dolomites crude sample

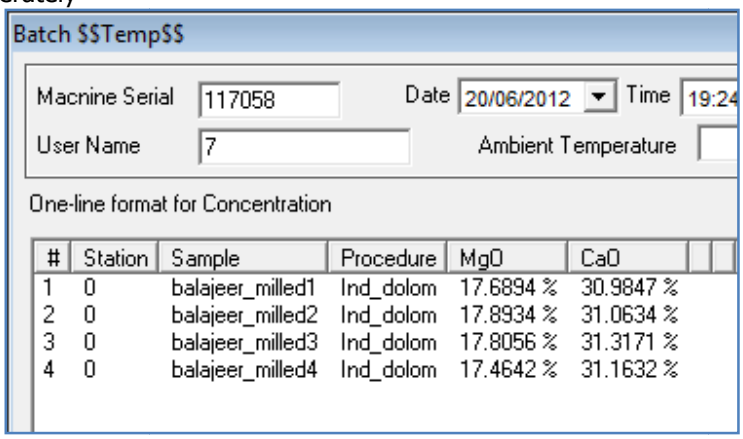
Macnine Serial 117058 Date 20/06/2012 Time 19:20:29

User Name 7 Ambient Temperature 0

One-line format for Concentration

#	Station	Sample	Procedure	MgO	CaO
1	0	Dol_Balagee crude2	Ind_dolom	15.2155 %	26.1438 %
2	0	Dol_Balagee crude3	Ind_dolom	16.1205 %	28.5170 %
3	0	Dol_Balagee crude4	Ind_dolom	15.7509 %	28.2011 %
4	0	Dol_Balagee crude5	Ind_dolom	13.9001 %	24.4261 %
5	0	Dol_Balagee crude6	Ind_dolom	15.1281 %	27.1283 %
6	0	Dol_Balagee crude7	Ind_dolom	15.4721 %	27.9212 %

Result report 2: Report for milled Balajee sample 4 portions taken from the sample pack and analyzed seperately



Batch $$Temp$$

Macnine Serial 117058 Date 20/06/2012 Time 19:24

User Name 7 Ambient Temperature

One-line format for Concentration

#	Station	Sample	Procedure	MgO	CaO
1	0	balajeer_milled1	Ind_dolom	17.6894 %	30.9847 %
2	0	balajeer_milled2	Ind_dolom	17.8934 %	31.0634 %
3	0	balajeer_milled3	Ind_dolom	17.8056 %	31.3171 %
4	0	balajeer_milled4	Ind_dolom	17.4642 %	31.1632 %

STATIC PRECISION

In order to show the repeatability of the X-CaliburSDD, nine repeated acquisitions were performed for a single milled Balajee sample without moving the sample between the consecutive acquisitions. The intensity of each element was extracted from spectral data and the precision was calculated as % relative standard deviation for MgO and CaO. The results demonstrate good repeatability of the X-CaliburSDD device (table 5, result report 3).

Table 5: Static precision for MgO and CaO in milled Balajee.

	Mean value	% RSD
MgO	17.9	1.1
CaO	31.2	1.0

Result report 3: Static precision results for nine consecutive spectra acquisition same milled Balajee sample without movement from measuring place

atch static precision

Macnine Serial 117058 Date 21/06/2012 Time 12:09:52

User Name 6 Ambient Temperature 0

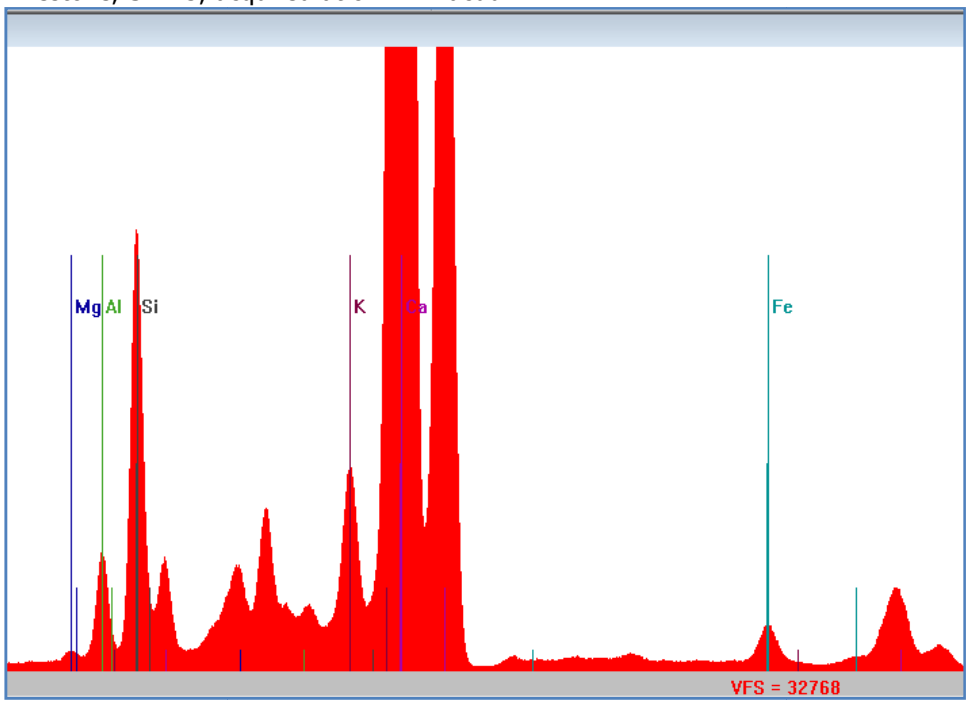
One-line format for Concentration

#	Station	Sample	Procedure	MgO	CaO
1	0	balajeer_milled1-2	Ind_dolom	17.5789 %	30.8424 %
2	0	balajeer_milled1-3	Ind_dolom	17.5989 %	30.8433 %
3	0	balajeer_milled1-4	Ind_dolom	17.9637 %	31.2245 %
4	0	balajeer_milled1-5	Ind_dolom	17.9167 %	31.1770 %
5	0	balajeer_milled1-6	Ind_dolom	17.9023 %	30.8323 %
6	0	balajeer_milled1-7	Ind_dolom	18.0845 %	31.5544 %
7	0	balajeer_milled1-8	Ind_dolom	18.0575 %	31.5637 %
8	0	balajeer_milled1-9	Ind_dolom	18.0823 %	31.5491 %

2. LIMESTONE

Low molecular weight elements in the geological samples of Limestone are shown in figures 3

Figure 3: Limestone, STD-3, acquired at 8KV in Vacuum



Quantitative method for CaO and MgO in Limestone

Two portions from each pack of standard were used to calibrate the instrument (table 6). Since the reference values for MgO in three of the standards were identical (table 2) and 2 standard calibration hardly suffice for

powder samples, standard dilution (50% W/W) with Boric acid H_3BO_3 was done. Although the addition of such standard does not contribute to sample variation, in such case it became beneficial (table 6, figure 4 and result report 5). In addition it was found that Mg is not evenly distributed among the Limestone standards. Example is shown by superimposition of Mg characteristic peaks acquired from different portions of STD1 using same acquisition conditions. Even mixing the soil with a dedicated powder mixer (8000 mixer mill, Certiprep made) did not provide a complete solution.

Figure 4: Superimposed spectra of different portions of Standard 1 limestone, showing variation in Mg peak among samples from the same pack.

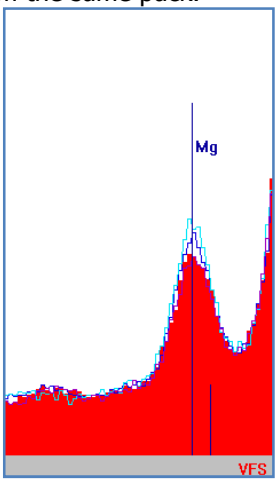
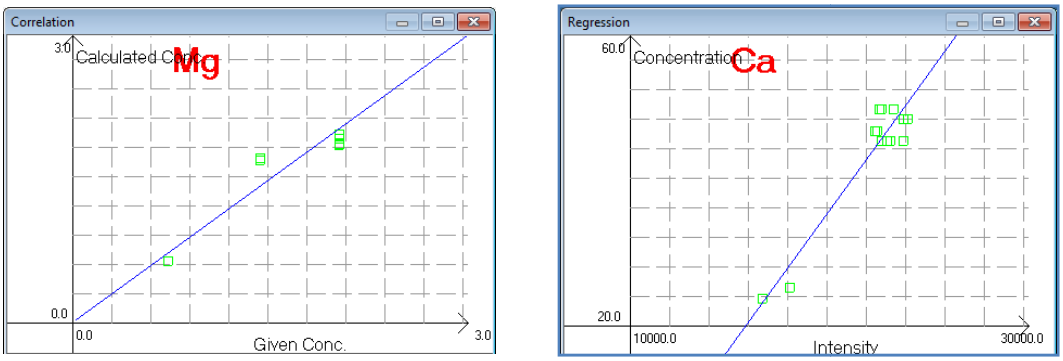


Table 6: Calibration data of MgO and CaO in Limestone.

	MgO Standard deviation=0.18 correlation =0.9204			CaO Standard deviation=4.7 correlation =0.9491		
	Given Conc.	Averaged Calc. Conc.	Abs.Dev.	Given Conc.	Averaged Calc. Conc.	Abs.Dev.
LS_STD1-2-mix.str	2.02	1.86	0.16	49.91	45.74	4.17
LS_STD1-3mix.str	2.02	1.92	0.11	49.91	48.59	1.31
LS_STD2-1-mix.str	1.41	1.70	-0.30	46.82	45.36	1.46
LS_STD2-2-mix.str	1.41	1.68	-0.27	46.82	45.02	1.80
LS_STD4-1-mix.str	2.02	1.96	0.06	48.51	51.47	-2.96
LS_STD4-2-mix.str	2.02	1.85	0.17	48.51	50.56	-2.05
LS_STD2 dill.str	0.71	0.62	0.08	23.41	22.47	0.94
LS_STD1 dill.str	1.01	0.93	0.06	24.95	28.00	-3.05
LS_STD3-2-mix.str	2.02	2.45	0.43	45.42	47.92	-2.50
LS_STD3-2.str	N/A	N/A	N/A	45.42	46.21	-0.79
LS_STD3-4.str	N/A	N/A	N/A	45.42	47.41	-1.99
LS_STD3-2-mix.str	N/A	N/A	N/A	49.91	45.74	4.17

Generally it recommended to use more standards with broader concentration range of the elements of interest. This results is a more reliable and robust calibration method. However in this work a "compromise" was taken to use more portions from the same standard and used dilutions to extend the concentration curve. As mentioned before since this approach does not contribute to method variability and robustness it is not recommended as a general practice.

Figure 5: MgO and CaO in Limestone, concentration versus intensity



Analysis of unknown Limestone samples.

Two unknown limestone samples were provided for analysis: S.B.S and Oswal; both as small stone form. Since the standards are in powder form, it was decided to analyze the samples both in native (stone form) and pre-treated by grinding and milling into powder. *Ie:* treated like the standards.

Again, several portions were taken from each pack for native form (Black in table 7) and milled form (blue in table 7). Average, standard deviation and relative standard deviation (RSD) were calculated for each set to evaluate the variations among samples. Although less milled samples were analyzed for S.B.S and Oswal (table 7) smaller RSD values were obtained for the milled forms. Sample preparation was shown to improve distribution of MgO and CaO among the samples and thus the repeatability results.

Yet, samples can be analyzed also in their native form, it all depends on the customer's specifications and required accuracy. As expected, higher values of MgO% and CaO% were obtained for the milled form than for the native stone form. The reason lies in the packing of the powder comparing to air voids among in the stone form.

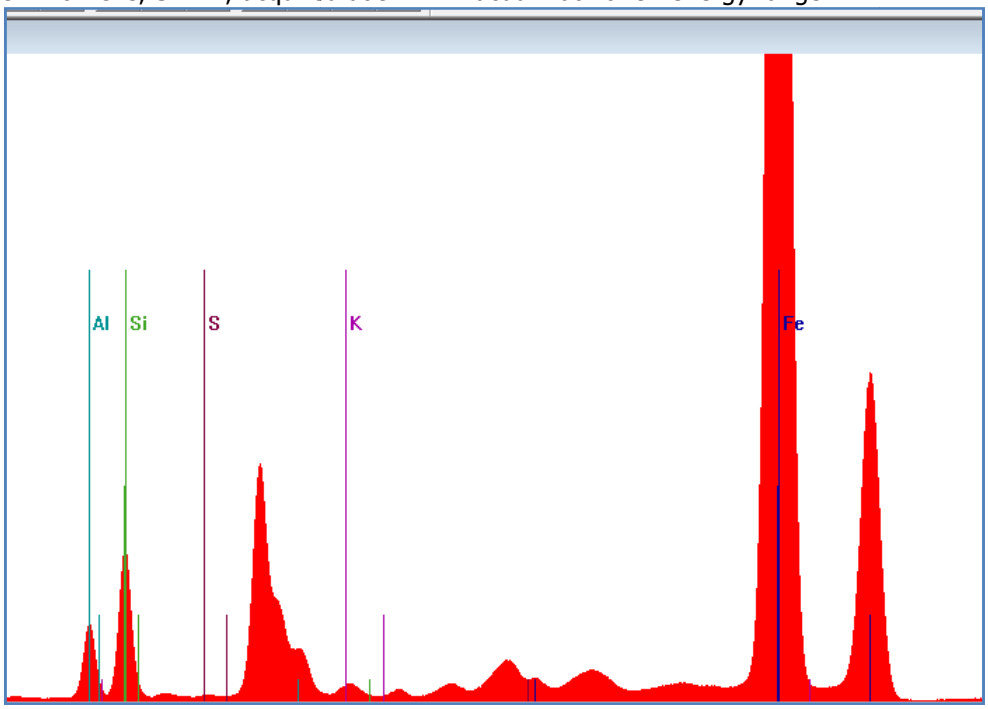
Table 7: Analysis result for unknown Limestone samples: Oswal and SBS in the native and milled form.

			MgO			CaO		
Sample	MgO	CaO	Average results	Standard deviation	Relative standards deviation (RSD)	Average results	Standard deviation	Relative standard deviation (RSD)
LS_Oswal_native-1	**1.42%**	**39.50%**	**1.48%**	**0.00**	**0.07**	**42.44%**	**0.03**	**0.07**
LS-oswal2	**1.34%**	**40.71%**						
LS_Oswals-native 3	**1.60%**	**46.26%**						
LS_Oswals-native 4	**1.55%**	**45.49%**						
LS_Oswals-native 5	**1.53%**	**43.19%**						
LS_Oswals-Milled 3	**1.69%**	**47.99%**	**1.71%**	**0.00**	**0.00**	**47.04%**	**0.02**	**0.03**
LS_Oswals-Milled 4	**1.69%**	**47.85%**						
LS-SBS- native-2	**1.76%**	**45.28%**	**1.89%**	**0.00**	**0.05**	**47.69%**	**0.03**	**0.06**
LS-SBS-native-3	**1.97%**	**49.17%**						
LS_SBS-native-4	**2.01%**	**50.78%**						
LS_SBS-native-5	**1.84%**	**46.34%**						
LS_SBS-native-6	**1.82%**	**46.23%**						
LS_SBS_Native	**1.95%**	**48.33%**						
LS_SBS_Milled-2	**2.18%**	**53.77%**	**2.10%**	**0.00**	**0.05**	**52.36%**	**0.02**	**0.04**
LS_SBS-Milled-3	**2.02%**	**50.94%**						

3. Iron Ore

The main elements in the geological samples of Dolomite are shown in figures 1-3.

Figure 6: Iron Ore, STD-1, acquired at 9KV in Vacuum at 10KeV energy range.

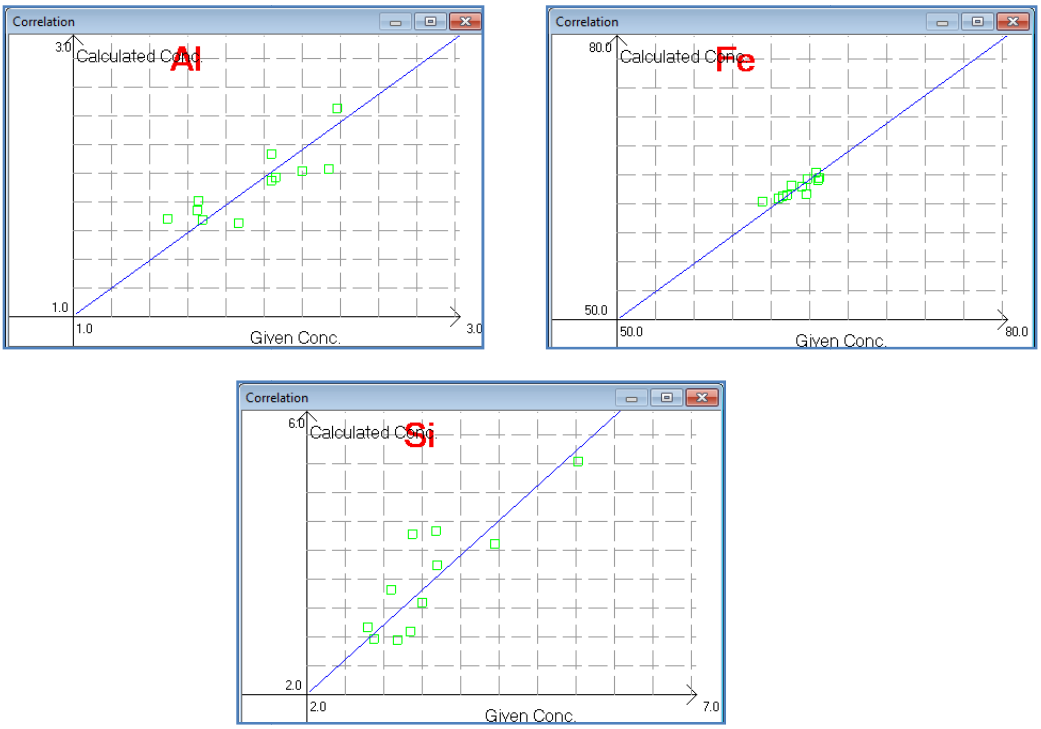


Quantitative analysis was performed with regression analysis based on 12 certified standards (table 7 and figure 7).

Table 7: Calibration data of Al2O3, SiO2 and Fe2O3 in Iron Ores

Sample ID	Al2O3 Standard deviation=0.15 correlation =0.8401			SiO2 Standard deviation=0.38 correlation =0.9787			Fe2O3 Standard deviation=0.67 correlation =0.8788		
	Given Conc.	Calc. Conc.	Abs.Dev.	Given Conc.	Calc. Conc.	Abs.Dev.	Given Conc.	Calc. Conc.	Abs.Dev.
IO-STD-1	2.36	2.48	-0.12	5.47	5.28	0.19	61.1	62.26	-1.16
IO-STD-2	1.64	1.81	-0.17	3.05	3.46	-0.41	65.35	64.62	0.73
IO-STD-3	2.02	1.95	0.07	3.46	3.28	0.18	64.43	63.08	1.35
IO-STD-4	2.36	1.88	0.48	2.4	3.70	-1.30	64.14	63.96	0.18
IO-STD-5	2.02	2.15	-0.13	3.33	4.25	-0.92	63	62.98	0.02
IO-STD-6	2.32	2.04	0.28	4.39	4.11	0.28	62.34	62.70	-0.36
IO-STD-7	1.66	1.68	-0.02	2.83	2.75	0.08	65.22	65.36	-0.14
IO-STD-8	2.18	2.03	0.15	3.64	4.30	-0.66	62.65	62.89	-0.24
IO-STD-9	1.48	1.68	-0.20	2.75	2.92	-0.17	65.47	64.88	0.59
IO-STD-10	1.63	1.74	-0.11	3.31	2.86	0.45	64.51	64.76	-0.25
IO-STD-11	2.04	1.98	0.06	3.65	3.81	-0.16	63.28	64.02	-0.74
IO-STD-12	1.85	1.65	0.20	3.14	2.75	0.39	64.61	62.43	2.18

Figure 7: Calibration of Al2O3, SiO2 and Fe2O3 in Iron Ores, concentration versus intensity



Analysis of unknown Iron Ore samples.

Two portions were analyzed from each unknown Ion Ore samples**.** The results (results report 5) show good agreement with little variations among samples from to the same pack**.**

No sample preparation was performed since both standards a and sample came in powder form after being pre-trated in identical way at customer's lab. Therefore tandards and samples were analyzed as obtainer from the customer.

Result report 4: Result report; Analysis for unknown Ion Ore samples. Two independent portions were analyzed for each unknown sample pack.

Batch limestone unknown samples

Macnine Serial 117058 Date 21/06/2012 Time 17:20:49

User Name 6 Ambient Temperature 0

One-line format for Concentration

#	Sample	Procedure	Al2O3	Fe2O3	SiO2
1	IO-SUSHANT-1	Ind_IronOres	1.3470 %	60.0364 %	0.9184 %
2	IO-SUSHANT-2	Ind_IronOres	1.3472 %	60.1213 %	0.9261 %
3	IO-BICO-1	Ind_IronOres	1.6058 %	60.1878 %	1.8549 %
4	IO-BICO-2	Ind_IronOres	1.6075 %	60.2692 %	1.8575 %
5	IO-ESSEL-1	Ind_IronOres	1.8953 %	58.8058 %	3.5572 %
6	IO-ESSEL-2	Ind_IronOres	1.8987 %	58.8420 %	3.5556 %
7	IO-RPSao-1	Ind_IronOres	1.3896 %	60.8717 %	0.9533 %
8	IO-RPSao-2	Ind_IronOres	1.3842 %	60.8942 %	0.9519 %
9	IO-KJS1	Ind_IronOres	1.4330 %	59.8236 %	1.1934 %
10	IO-KJS2	Ind_IronOres	1.4249 %	60.5138 %	1.1999 %

CONCLUSIONS

This report shows the superior performance of X-Calibur SDD EDXRF analyzer for analysis of powder and stone samples. In a very short time one can get an overview of most elements in the standards (not performed in this work) and assess the element distribution within powder standards. Reproducibility studies with Dolomites showed less variations and better reproducibility when analysed in powder form than as crude native stones.
Successful calibration methods were established for Dolomites, Limestone and Iron Ores and unknown samples were analyzed quantitatively. In the case of Limestone, not enough standards were provided for MgO and thus a compromise was taken to prepare diluted standards with Boric acid. Yet, it is recommended to add more standards, as in the case of Iron Ores, to produce a robust reliable calibration.

Based on this report X-Calibur EDXRF provided the necessary tools for analysis of all sorts of geological samples both in stone and powder form.