RAPID CHARACTERIZATION OF DRILLED TEST
EARTH CORES BY X-RAY ENERGY DISPERSIVE
ANALYSIS

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RAPID CHARACTERIZATION OF DRILLED TEST EARTH CORES BY X-RAY ENERGY DISPERSIVE ANALYSIS

INTRODUCTION

The objective of this work was to make an evaluation of a rapid method of characterizing drilled test earth cores. This evaluation has been made by directly comparing the standard technique of wavelength-dispersive x-ray analysis (WLX) with the faster alternative technique of energy-dispersive x-ray analysis (EDX). The analysis of core constituents on a micro-scale provides identification of contained minerals. These data taken at potential geothermal energy sites provide a basis for the evaluation of pollution hazards associated with geothermal energy production.

EXPERIMENTAL PROCEDURE

Six geothermal energy site core samples were obtained. They were taken from positions in the core that corresponded to depths ranging from 280 feet to 1332 feet. The samples were cut, mounted, polished and made electrically conductive by vacuum deposition of a 700 Å thick layer of gold. Each specimen was placed in an electron microprobe where specimen current and elemental x-ray images of a 725 μm x 950 μm area were photographed (Figure 1). The x-ray images were used to classify the mineral types present in the photographed areas. In each of the six areas photographed a crystal of each mineral type present was analyzed by both the normal wave length dispersive x-ray (WLX) analysis method and also by the energy dispersive x-ray (EDX) method.

There were eight different mineral types found in the samples. One crystal of each type was selected for determining the precision of the two methods. This was done by analyzing each of these crystals

a total of six times by both methods. The replicate analyses were performed by first analyzing each crystal once and then repeating the process starting with the original crystal until each of the eight crystals had been analyzed a total of six times. As a consequence the replicate analyses were not always performed at the identical position on the minerals. Thus, inhomogeneity could account for some spread in replicate results. Table I compares the analytical results obtained by the two methods. The table is arranged in order of mineral types and the results are reported in weight percent of the oxides. Table II shows the precision of the two methods for six analyses by each method on a single crystal. Table III shows how the precision of the two methods vary with change in the weight percent of the measured oxide.

DISCUSSION OF RESULTS

The analyses by the two methods are in good agreement. The precision of both methods is also good. Table III shows that for elemental oxides present in quantities less than 5 percent the precision of the methods is about the same and for those present in quantities greater than 5 percent the wavelength-dispersive method usually produced a slightly more precise result, nominally 1-2 percent better. A more intense beam with a greater diameter was used for the wavelength dispersive analysis (WLX); thus a larger spot on the sample was analyzed by this method. Normally there are some composition changes from one area to the next on a given crystal. Thus the use of a larger spot size would usually reduce the impact of these differences and produce closer agreement between replicate analyses.

The 612-3, 612-7, 923-4, 923-6, 1332-2, and 1332-3 crystals were found to be very inhomogeneous and the results reflect this condition. Inhomogeneities often reveal alterations that are taking place and enable the geologist to predict the stability of the rock system and the possible contaminants in the ground water.

There appears to be a significant bias in the measurement of Si in quartz, Ca in apatite and Fe in the iron oxide specimens. In the quartz and apatite analyses the energy-dispersive analysis is nearer to the expected result and is probably the better analysis. The bias probably reflects the need for recalibration for the wavelength-dispersive method inasmuch as older standardization values were used with these measurements. The mineral type was obvious in spite of any bias.

The use of carbon rather than gold for coating the samples would improve the results by reducing the corrections needed for the absorption of the x-rays. The use of well standardized crystals of minerals as standards rather than the use of elemental standards would also improve the results of the method. In this study pure elements and stoichiometric compounds were used for standardization. Therefore, large corrections to the x-ray intensities were necessary because of differences between the sample matrix and the standards.

CONCLUSION

The usability of electron microprobe analysis employing x-ray energy-dispersive measurements for the characterization of core specimens was demonstrated. The EDX method produced comparable results to the WLX method. The cost per analysis by EDX is approximately 20 percent that of WLX. The EDX method identified the minerals, revealed alteration of the minerals and can form a basis for predicting possible pollutants associated with use of the geothermal energy site.

TABLE I
COMPARISON OF ANALYTICAL RESULTS OBTAINED
BY EDX AND WDX METHODS

Elements	Weight Percent		Weight Percent	
	EDX	WLX	EDX	WLX
Mineral Type: Potassium Feldspar				
Analysis Number:	280-1 *		448-3	
Na ₂ O	---	---	1.3	---
Al ₂ O ₃	18.0	18.1	18.2	17.7
SiO ₂	61.3	62.5	62.3	62.8
K ₂ O	16.3	16.5	12.4	17.5
CaO	---	---	0.5	---
FeO	---	---	0.2	---
BaO	1.9	1.7	0.9	0.6
Mineral Type: Sodium Feldspar				
Analysis Number:	448-5*		612-1	
Na ₂ O	7.8	8.1	7.7	8.4
Al ₂ O ₃	21.0	22.6	20.6	22.2
SiO ₂	62.6	62.5	63.9	60.6
K ₂ O	0.2	0.2	0.3	0.1
CaO	5.5	5.2	7.5	5.8
FeO	0.3	0.2	0.3	0.1
BaO	---	---	---	---

TABLE I. continued

-5-

Elements	Weight Percent		Weight Percent	
	EDX	WLX	EDX	WLX
Mineral Type: Sodium Feldspar				
Analysis Number:	803-1		923-1	
Na ₂ O	8.1	8.5	6.8	7.9
Al ₂ O ₃	21.0	23.3	23.7	25.3
SiO ₂	62.8	61.6	58.3	59.2
K ₂ O	---	0.2	0.2	0.2
CaO	6.9	5.6	8.3	7.8
FeO	0.4	0.1	0.2	0.2
BaO	---	---	---	---

Analysis Number:	1332-4	
Na ₂ O	6.7	7.1
Al ₂ O ₃	23.3	23.8
SiO ₂	59.1	60.5
K ₂ O	---	0.1
CaO	7.3	6.8
FeO	0.3	0.2
BaO	---	---

Mineral Type: Sphene

Analysis Number:	280-8*		448-7	
Al ₂ O ₃	1.6	1.1	1.6	1.2
SiO ₂	31.5	32.5	31.0	31.5
CaO	30.6	31.0	28.4	29.4
TiO ₂	36.1	35.0	35.1	32.8
FeO	1.1	1.0	2.2	2.9

TABLE I. continued

-6-

Elements	Weight Percent		Weight Percent	
	EDX	WLX	EDX	WLX
Mineral Type: Sphene				
Analysis Number:	612-4		923-3	
Al ₂ O ₃	1.3	1.1	1.2	---
SiO ₂	32.6	33.1	31.0	32.3
CaO	32.0	32.0	30.5	31.2
TiO ₂	37.8	35.6	35.3	33.2
FeO	1.2	0.6	1.2	0.6

Mineral Type: Apatite

Analysis Number:	280-7 *		448-4	
P ₂ O ₅	47.7	47.2	44.3	47.3
CaO	54.8	58.0	53.8	59.6

Analysis Number: 803-3

P ₂ O ₅	49.8	49.2
CaO	52.8	60.1

Mineral Type: Zircon

Analysis Number: 280-6 *

SiO ₂	36.3	39.2
FeO	0.9	0.8
ZrO ₂	59.8	60.5
Hf	0.8	0.6

TABLE I. continued

-7-

Elements	Weight Percent		Weight Percent	
	EDX	WLX	EDX	WLX
Mineral Type: Quartz				
Analysis Number:	280-4*		448-6	
Al ₂ O ₃	---	----	----	----
SiO ₂	100.3	92.8	101.0	94.3
FeO	0.4	0.4	0.2	0.3
Analysis Number:	612-5		923-5	
Al ₂ O ₃	---	---	---	---
SiO ₂	105.6	95.2	101.7	91.8
FeO	0.2	---	---	0.1
Mineral Type: Iron Oxide				
Analysis Number:	280-5*		448-1	
MgO	---	---	1.7	1.1
Al ₂ O ₃	1.7	---	1.1	---
SiO ₂	---	0.3	---	0.7
FeO	80.6	86.2	78.2	83.2
Analysis Number:	803-4		923-4	
Al ₂ O ₃	1.2	---	1.1	0.2
SiO ₂	---	0.8	5.0	3.5
FeO	81.0	82.1	23.3	15.6
TiO ₂	---	---	56.6	71.1

TABLE 1. continued

-8-

Elements	Weight Percent		Weight Percent	
	EDX	WLX	EDX	WLX
Mineral Type: Iron Oxide				
Analysis Number: 1332-1				
Al ₂ O ₃	---	---		
SiO ₂	---	0.3		
FeO	78.2	85.2		

Mineral Type: Biotite

Analysis Number: 280-2 *

448-2

MgO	10.7	11.2	12.4	12.2
Al ₂ O ₃	15.5	15.2	15.0	15.9
SiO ₂	39.7	38.6	40.0	40.7
K ₂ O	11.8	12.1	11.1	11.0
TiO ₂	1.7	1.2	2.0	1.7
MnO	0.5	0.3	0.5	0.3
FeO	16.7	16.7	15.5	16.2

Analysis Number: 612-2

803-2

MgO	12.5	12.3	10.8	10.7
Al ₂ O ₃	16.3	14.3	16.1	15.5
SiO ₂	42.0	38.6	41.0	38.4
K ₂ O	11.8	11.7	12.2	13.0
TiO ₂	2.2	1.5	2.1	1.5
MnO	---	---	0.8	0.5
FeO	17.6	16.3	17.3	17.4

TABLE I. continued

-9-

Elements	Weight Percent		Weight Percent	
	EDX	WLX	EDX	WLX
Mineral Type: Biotite				
Analysis Number:	923-2		1332-3	
MgO	11.6	12.1	9.3	10.7
Al ₂ O ₃	15.4	15.0	16.2	14.8
SiO ₂	39.4	38.8	43.5	38.6
K ₂ O	11.8	12.6	7.8	12.2
TiO ₂	2.2	1.7	1.9	12.2
MnO	---	---	---	---
FeO	15.0	16.1	14.1	16.1
Mineral Type: Miscellaneous				
Analysis Number:	280-3		612-3	
MgO	---	---	19.4	18.5
Al ₂ O ₃	22.4	22.4	21.7	19.1
SiO ₂	42.5	40.0	33.2	27.8
K ₂ O	---	---	1.0	---
CaO	23.5	25.4	0.4	---
TiO ₂	---	---	0.5	---
MnO	---	---	0.6	0.3
FeO	12.1	12.5	20.5	18.9

TABLE I. continued

-10-

Elements	Weight Percent		Weight Percent	
	EDX	WLX	EDX	WLX
Mineral Type: Miscellaneous				
Analysis Number:	612-6		612-7	
MgO	11.9	11.9	---	---
Al ₂ O ₃	8.6	7.6	19.4	22.7
SiO ₂	51.8	49.2	64.7	39.8
K ₂ O	1.0	0.9	---	---
CaO	12.6	13.1	8.1	24.8
TiO ₂	0.9	0.8	---	---
MnO	0.4	0.2	---	---
FeO	15.1	14.8	3.3	11.7
Analysis Number:	803-5		923-6	
MgO	---	---	12.9	12.2
Al ₂ O ₃	21.2	19.5	9.6	15.4
SiO ₂	50.2	50.0	20.1	28.6
K ₂ O	---	---	1.7	---
CaO	17.5	21.5	5.8	---
TiO ₂	---	---	1.3	1.4
MnO	0.4	---	0.6	0.5
FeO	8.0	8.9	25.9	26.9

TABLE I. continued

-11-

Elements	Weight Percent		Weight Percent	
	EDX	WLX	EDX	WLX
Mineral Type: Miscellaneous				
Analysis Number: 1332-2				
MgO	6.9	9.9		
Al ₂ O ₃	25.9	26.0		
SiO ₂	46.3	41.0		
K ₂ O	0.5	0.3		
CaO	0.7	0.3		
FeO	8.8	12.6		

* Average of six analyses; all other analytical results in this table are from single measurements.

TABLE II

Measurement Precision Based Upon Six Separate Analyses
By EDX and WLX Methods

	EDX			WLX		
	$\bar{x}$	σ	$100\sigma/\bar{x}$	$\bar{x}$	σ	$100\sigma/\bar{x}$
Sample Number: 280-1						
Al ₂ O ₃	18.0	0.65	3.61	18.1	0.43	2.36
SiO ₂	61.3	0.88	1.44	62.5	0.79	1.26
K ₂ O	16.3	0.24	1.45	16.5	0.47	2.85
BaO	1.9	0.24	12.64	1.7	0.28	16.50
Sample Number: 280-2						
MgO	10.7	0.61	5.69	11.2	0.18	1.64
Al ₂ O ₃	15.5	0.55	3.53	15.2	0.24	1.55
SiO ₂	39.7	1.01	2.55	38.6	0.33	0.86
K ₂ O	11.8	0.30	2.57	12.1	0.70	5.80
TiO ₂	1.7	0.12	7.20	1.2	0.23	19.50
FeO	16.3	0.26	1.62	16.7	0.55	3.31
Sample Number: 280-4						
SiO ₂	100.3	2.23	2.23	92.8	2.04	2.20
FeO	0.4	0.12	30.60	0.4	0.04	10.2
Sample Number: 280-5						
Al ₂ O ₃	1.7	0.51	30.2	---	---	---
SiO ₂	---	---	---	0.3	0.12	38.97
FeO	80.6	1.95	2.42	86.2	1.58	1.64
Sample Number: 280-6						
SiO ₂	36.3	1.24	3.41	39.2	0.20	0.52
FeO	0.9	0.40	44.25	0.8	0.13	16.60
ZrO ₂	59.8	1.66	2.77	60.5	0.82	1.35
Hf	0.8	0.12	15.14	0.6	0.20	32.80

TABLE II Continued

	EDX			WLX		
	$\bar{x}$	σ	$100\sigma/\bar{x}$	$\bar{x}$	σ	$100\sigma/\bar{x}$
Sample Number: 280-7						
P ₂ O ₅	47.7	1.72	3.61	47.2	1.31	2.78
CaO	54.8	0.60	1.09	58.0	0.54	0.93
Sample Number: 280-8						
Al ₂ O ₃	1.6	0.24	15.2	1.1	0.18	16.7
SiO ₂	31.5	0.29	0.93	32.5	0.10	0.32
CaO	30.6	0.47	1.87	31.0	0.49	1.59
TiO ₂	36.1	0.38	1.06	35.0	0.64	1.83
FeO	1.1	0.23	21.1	0.95	0.08	8.81
Sample Number: 448-5						
Na ₂ O	7.8	0.19	2.40	8.1	0.48	5.93
Al ₂ O ₃	21.0	0.71	3.39	22.6	0.19	0.86
SiO ₂	62.6	0.36	0.58	62.5	0.47	0.75
K ₂ O	0.2	0	0	0.2	0	0
CaO	5.5	0.075	1.37	5.2	0.08	1.45
FeO	0.25	0.055	21.90	0.2	0.052	25.82

TABLE III

ANALYTICAL PRECISION FOR EDX AND WLX METHODS

Oxide Weight Percent	Average Precision	
	EDX (100 $\sigma/\bar{x}$)	WLX (100 $\sigma/\bar{x}$)
0- 1	22.4	19.0
1- 5	17.3	17.6
5-10	1.9	3.7
10-20	3.1	2.5
20-30	3.4	0.9
30-40	2.0	1.0
> 40	2.0	1.6

SPECIMEN CURRENT
IMAGE
A

POTASSIUM X-RAY
EMISSION IMAGE
B

SILICON X-RAY
EMISSION IMAGE
C

IRON X-RAY
EMISSION IMAGE
D

MAGNESIUM X-RAY
EMISSION IMAGE
E

TITANIUM X-RAY
EMISSION IMAGE
F

PHOSPHOROUS X-RAY
EMISSION IMAGE
G

CALCIUM X-RAY
EMISSION IMAGE
H

ALUMINUM X-RAY
EMISSION IMAGE
I

FIGURE 1. PHOTOMICROGRAPHS OF THE POLISHED EARTH CORE SPECIMEN FROM THE 448 FOOT LEVEL. SHOWN ARE A SPECIMEN CURRENT IMAGE A AND X-RAY EMISSION IMAGES. MAGNIFICATION IS 100X.

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