APPLICATION NOTE

XRD and XRF investigation of Martian analog basalt from terrestrial craters

Introduction

Terrestrial analogs to Martian geologic conditions are being employed in combination with data collected over the various Martian rover and satellite expeditions ongoing since the 1960's to characterize the physiological and chemical properties of Mars. Such materials are being used to study a wide range of topics, from general geochemistry to the potential for human missions to Mars. X-ray diffraction (XRD) and X-ray Fluorescence (XRF) are considered to be gold standard methods for material analysis. In the geologic sector, from mining to research, these two synergistic techniques have found many uses and applications.

Modern applications in research, require fast and accurate instruments with limited downtime. Such improvements allow central laboratories to streamline data collection and analysis.

Instruments

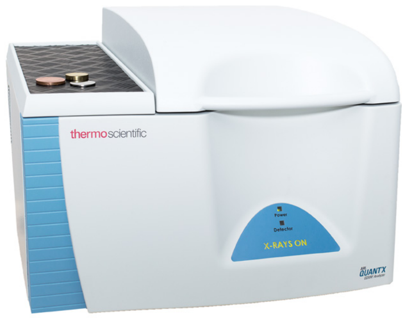
The Thermo Scientific™ ARL™ EQUINOX 100 X-ray diffractometer (Figure 1) employs a custom-designed Cu (50 W) or Co (15 W) micro-focus tube with mirror optics. The low wattage consumed by the unit allows it to be completely portable, not requiring an external water chiller. The same unit is capable of being transported between laboratories without the need for special infrastructure.

The ARL EQUINOX 100 instrument provides very fast data collection times when compared to other diffractometers due to its unique curved position sensitive detector (CPS) that measures all diffraction peaks simultaneously and in real time and is therefore well suited for both reflection and transmission measurements.

The Thermo Scientific™ ARL™ QUANT'X Energy Dispersive X-ray fluorescence (EDXRF) spectrometer (Figure 2) employs primary filtered radiation for sample excitation causing fluorescence of constituent elements. With a set of eight filters plus unfiltered tube excitation specifically designed to optimize the peak-to-background ratio for elements from Na to U, the ARL QUANT'X is a versatile research-grade instrument that can be easily adapted to any application or range of elements. The use of a combination of filter and voltage (kV) is referred to as the "excitation condition" resulting in a unique spectrum representative of the sample. A multi-element analysis typically employs several excitation conditions providing the most efficient excitation for a suite of elements. In EDXRF terminology, the complete set of conditions form the basis of the analytical "method" for a particular sample matrix.

Figure 1: ARL EQUINOX 100 X-ray diffractometer

Figure 2: ARL QUANT'X EDXRF spectrometer



Experimental

XRD

A sample of basalt collected from craters of the Moon National Monument, Idaho, USA was studied by grinding the bulk material and placing it in a reflection sample holder. The sample was analyzed from 0-115° 2θ under Co Kα (1.78897 Å) radiation for 30 minutes, with the sample rotating during the analysis to reduce the effects of preferred orientation. Raw data evaluation was performed with I_MAD. Data processing, consisting of whole pattern fitting Rietveld refinement (WPF) was performed using MDI JADE 2010 equipped with the Crystallographic Open Database (COD) and AMCSD.

XRF

The same sample was analyzed using the UniQuant standard-less fundamental parameters (FP) software package. The spectrometer employed a 50 W Rh source, operating at voltages up to 50 kV, equipped with an 8 mm beam collimator. Data is collected using a digital pulse processor on an electronically cooled SDD with, 140 eV resolution and 30 mm^2 x 0.45 mm active volume.

XRF Results		
Compound	**m/m %**	**Std Err**
SiO_2	43.25	0.24
Fe_2O_3	19.30	0.44
Al_2O_3	15.75	0.19
CaO	7.16	0.13
TiO_2	3.00	0.17
MgO	3.00	0.09
Na_2O	2.68	0.08
K_2O	2.25	0.03
P_2O_5	2.21	0.10
ZrO_2	0.371	0.019
MnO	0.281	0.021
SO_3	0.281	0.017
Co_3O_4	0.174	0.045
BaO	0.139	0.007
SrO	0.0486	0.0024
ZnO	0.0286	0.0012
Y_2O_3	0.0243	0.0012
Cl	0.0203	0.0031
Nb_2O_5	0.0148	0.0007

Table 1: XRF results

Results

The XRF data presented in Table 1, suggests a high P basalt primarily comprised of plagioclase and potassic feldspars. Along with a relatively low silica content, SiO2 = 43.25%, the sample is enriched in both Fe, Fe_2O_3 = 19.30%, and P, P2O5 = 2.21% roughly 2x and 10x terrestrial normal respectively (Adcock et al., 2018).

The XRD raw data (Figure 3) was analyzed using MDI JADE 2010. The dataset underwent a WPF Rietveld refinement to achieve a quantitative phase analysis (QPA) of the sample. The final refinement (Figure 4) had an Rwp = 6.21, with GooF = 1.25, and identified the following phases: plagioclase feldspars (anorthite, albite), k-spars (orthoclase, microcline and sanidine), hematite, augite, apatite, pyroxene, and olivine (forsterite).

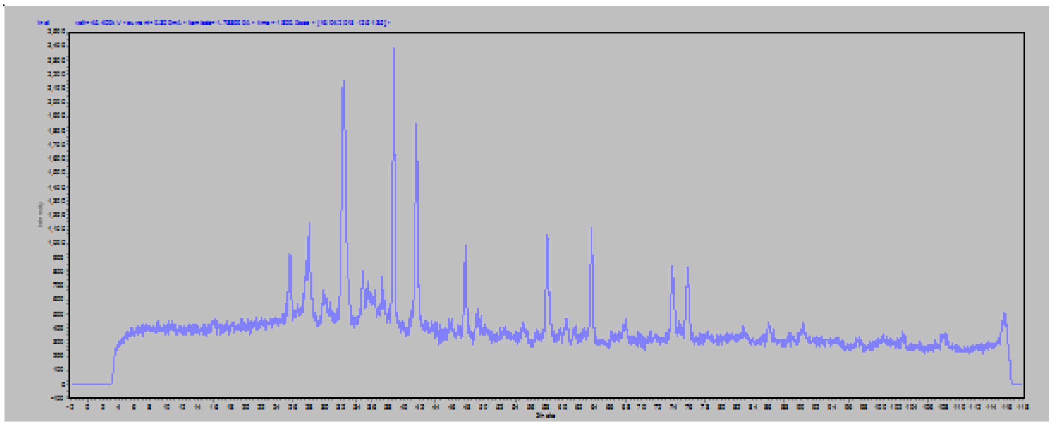


Figure 3: 30 minute raw dataset

Phase assemblage results for all scans are presented in Table 2. The trend of the phases correlates well with the XRF results. Plagioclase feldspars account for 40.9% of the sample while potassic feldspars comprise another 17.1%. The rest of the sample is comprised of hematite = 21.9%, pyroxenes = 10.7% and olivine = 1.4%.

Conclusion

The resolution and speed of the ARL EQUINOX 100 diffractometer enables the ability to fully analyze geologic materials from qualitative phase assemblages to full QPA. A 30 minute measurement time was chosen to maximize intensities of minor phases. Paired with the ARL QUANT'X EDXRF spectrometer elemental information, a complete synergistic analysis of the alkaline basalt sample can be obtained. Therefore, the ARL EQUINOX 100 benchtop diffractometer and ARL QUANT'X benchtop EDXRF spectrometer are an ideal combination of analytical instruments for geologic research and process applications.

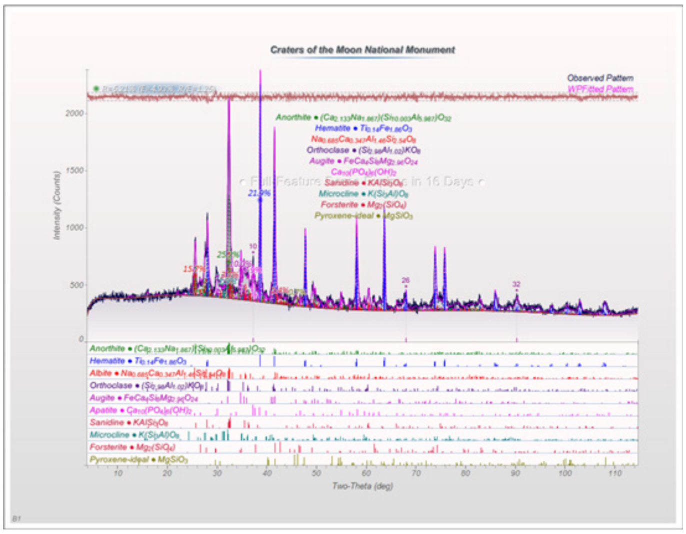


Figure 4: Refined data from 4-114° 2θ **using MDI JADE 2010**

Phase Assemblage			
Phase	**Formula**	**WT%**	**ESD**
Anorthite	$(Ca_{0.533},Na_{0.467})(Si_{2.501},Al_{1.499})O_8$	25.2	1.7
Hematite	$(Fe_{1.86},Ti_{0.14})O_3$	21.9	0.7
Albite	$(Na_{0.685},Ca_{0.315})(Si_{2.54},Al_{1.46})O_8$	15.7	1.6
Orthoclase	$K(Si_{2.98},Al_{1.02})O_8$	11.5	1.1
Augite	$Ca(Mg_{0.75},Fe_{0.25})Si_2O_6$	10.0	0.6
Apatite	$Ca_5(PO_4)_3(F,OH,Cl)$	7.9	0.4
Sanidine	$KAlSi_3O_8$	3.7	0.7
Microcline	$KAlSi_3O_8$	1.9	0.5
Forsterite	$Mg_2(SiO_4)$	1.4	0.4
Pyroxene	$MgSiO_3$	0.7	0.3

Table 2: XRD phase assemblage

References

Adcock et al, 2018. Craters of the Moon National Monument Basalts as Unshocked Compositional and Weathering Analogs for Martian Rocks and Meteorites. American Mineralogist. In Press.

Acknowledgements

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Find out more at **www.thermofisher.com/xrd**