

Application Note SC-XRD 522

A Day at the Beach with a Fast Diffractometer

- Mineral identification and structure determination of Lake Michigan sand grains using a single crystal D8 QUEST diffractometer

Introduction

Kohler-Andrae State Park on the shore of Lake Michigan is one of the treasures of Wisconsin's Sheboygan County that can be enjoyed all year round. With majestic dunes, no land on the horizon and the crystal-clear water of Lake Michigan, the beach feels like it's on the ocean. Walking along the beach, one will most certainly come across

stretches that have patches of black sand — definitely not pollution, despite what a lot of beach-goers think (Picture 1). The black sand will stick to a magnet, so we always assumed that it was magnetite. To find out for sure, we decided to take some sand to the X-ray lab for further investigation.

A study conducted in 2004 confirms that magnetic sands are found at several Wisconsin beaches. Small concentrations of black sands are common on the Great Lakes. On the Wisconsin shoreline of Lake Michigan, the sands are primarily composed of high-density oxide and silicate minerals such as magnetite, ilmenite, hematite, amphiboles, pyroxenes, and garnets. These minerals are common constituents of igneous and metamorphic rocks and may become part of the sand from the mechanical weathering of the source rocks during glaciation or from the abrasion of rocks in the surf zone. Black sands concentrate in the near-shore because higher density particles have different hydraulic properties in the surf zone than the less dense quartz and feldspar. These concentrations are essentially lag deposits or placer deposits.^[1]



Picture 1: Beach at Kohler-Andrae State Park with patches of black sand deposits

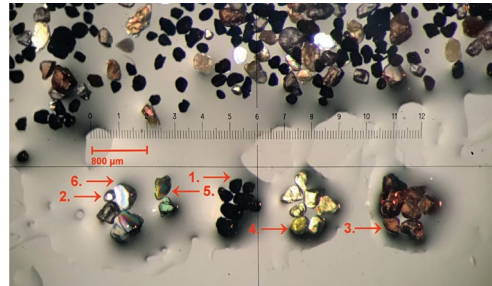
Sample Preparation

Black sand was collected from the beach and air dried. Even with the naked eye it was easy to see that the sample was a mixture of different materials of varying grain sizes with predominantly black material. (Picture 2). A small amount of the sample was spread out on a microscope slide and visually inspected under an optical microscope. Grain sizes were mostly in the 200 micrometer to 500 micrometer range with a good variety of color and transparency. The dominant species were black opaque grains. Potential candidates for crystallographic investigation were selected and separated by color and appearance. (Picture 3). To better judge the quality of the samples, the grains were covered with Parabar 10312TM oil that also served as adhesive



Picture 2: Sample of dried black sand

to affix the crystals to the sample holder. Samples were mounted using Mitegen MicroMountsTM with an aperture size of 100 micrometers. Samples used for X-ray experiments are labeled on Picture 3.



Picture 3: Samples on microscope slide separated by color

X-ray diffraction experiments

Crystallographic data were acquired using a D8 QUEST diffractometer equipped with a molybdenum sealed tube source and a TRIUMPH monochromator, a FIXED-CHI goniometer and a PHOTON III mixed-mode detector (Picture 4). The experiments were performed at room temperature.

Mineral identification from X-ray data

Data for mineral identification were collected using a fast scan – a 180° phi scan with the detector positioned at 5 cm distance and 2θ at 0°. In continuous scan mode 180 shutterless images (1°/s) were acquired to cover a complete sphere of data to about 0.8 Å resolution in 3 minutes. Data for sample 4, which turned out to be polycrystalline, were acquired with a single 30°/60s omega scan (Picture 5). These data were sufficient to index and identify all minerals. Indexing and Bravais-class determination were performed using APEX3 software. All minerals, with the exception of sample 4,



Picture 4: D8 QUEST diffractometer

were identified with a cell parameter and symmetry search against the *American Mineralogist Crystal Structure Database*^[2]. Sample 4 was matched using phase analysis from a powder pattern with the XRD software DIFFRAC.EVA and the Crystallography Open Database.

Table 1 lists the mineral name, cell parameters and Bravais lattice for the crystalline samples. (Refer to picture 3 for sample identification).

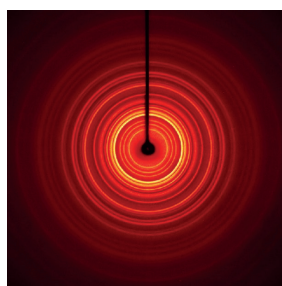
Sample	Mineral	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]	Bravais lattice
1.	Hematite	5.037	5.037	13.743	90	90	120	Hexagonal R
2.	Zircon	6.611	6.611	5.987	90	90	90	Tetragonal I
3.	Garnet	11.599	11.599	11.599	90	90	90	Cubic I
4.	Epidote	8.98	5.65	10.22	90	115.4	90	Monoclinic P
5.	Hornblende	9.871	18.079	5.340	90	104.979	90	Monoclinic C
6.	Quartz	4.914	4.914	5.402	90	90	120	Hexagonal P
7.	Diopside	9.772	8.941	5.260	90	105.730	90	Monoclinic C

Table 1: Mineral identification from unit cell parameters (samples 1 - 3, 5 - 7) and phase analysis (sample 4)

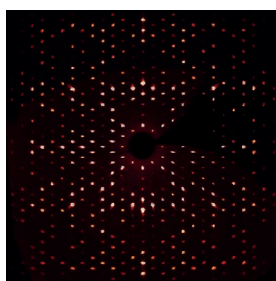
Structure determination

Data for all single-crystal samples were collected to 0.7 Å with a combination of omega and phi scans and exposure times varying from 1 to 10 seconds for 1° scans. Total experiment times varied from 15 minutes to 2 hours. Quality of the diffraction patterns varied considerably, with some samples showing sharp reflections and low mosaicity (Picture 6), while other samples showed broad reflections (Picture 7) and signs of twinning (Picture 8). In total all data were collected in less than 4 hours.

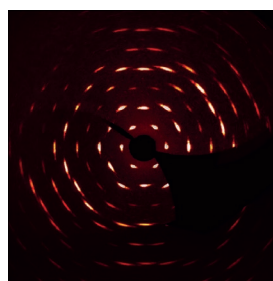
Data processing, including integration and scaling of intensities, as well as structure solution and refinement, used APEX3 software. Sample 1. (Hematite) was treated as a 2-component non-merohedral twin. Sample 6. (Quartz) was refined as a merohedral twin. The structure all refined with good reliability criteria. A few selected parameters are listed in Table 2.



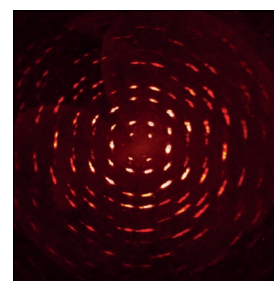
Picture 5: Debye rings for polycrystalline Epidote (sample 4)



Picture 6: Sharp, low mosaicity reflections for Hornblende hk0 layer (sample 5)



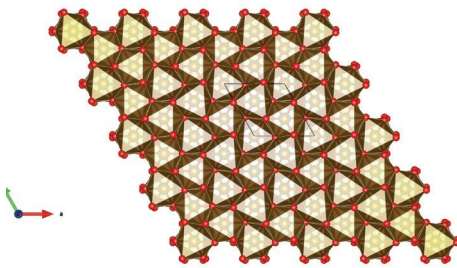
Picture 7: High mosaicity diffraction spots for Quartz hk0 layer (sample 6)



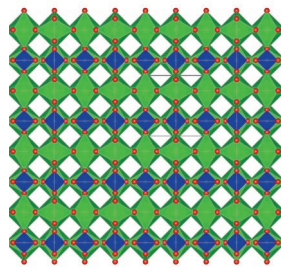
Picture 8: High mosaicity and signs of twinning for Hematite 1kl layer (sample 1)

Sample	Mineral	R1 [%]	wR2 [%]	R_{int} [%]	Completeness [%]	Observed [%]	Residuals [Å ⁻³]	Space-group
1.	Hematite	1.40	4.58	3.97	100.0	97.7	0.413/-0.390	R-3c
2.	Zircon	1.41	3.78	3.89	100.0	100.0	0.334/-0.846	I41/amd
3.	Garnet	1.31	4.77	4.92	100.0	96.4	0.266/-0.243	Ia-3d
5.	Hornblende	2.06	5.94	3.57	99.4	97.5	0.415/-0.353	C2/m
6.	Quartz	2.16	5.81	5.68	100.0	100.0	0.315/-0.207	P3221
7.	Diopside	1.68	4.41	2.78	99.3	96.7	0.389/-0.337	C2/c

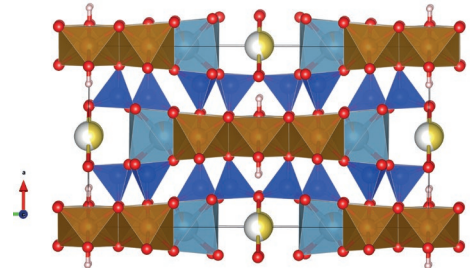
Table 2: Selected crystallographic parameters of minerals from Lake Michigan



Picture 9: Structure of Hematite^[3]



Picture 10: Structure of Zircon^[3]



Picture 11: Structure of Hornblende^[3]

Crystal structures

Hematite, Fe_2O_3 , is an iron oxide that has the same crystal structure as corundum. In the lattice of hematite, the oxygen atoms form a hexagonal close packing, in which two-thirds of the gaps between the octahedra are occupied by iron ions (Picture 9).

Zircon, ZrSiO_4 , is an orthosilicate in which isolated SiO_4 tetrahedra share corners and edges with ZrO_8 dodecahedra. The ZrO_8 dodecahedra share edges with each other to form chains along the a-axis. (Picture 10).

Garnet, $\text{Fe}_{2.8}\text{Mg}_{0.2}\text{Al}_2\text{Si}_3\text{O}_{12}$, is an orthosilicate that forms an octahedral/tetrahedral framework with SiO_4 anions occupying the tetrahedra.

Hornblende, $(\text{Ca}_2(\text{Mg}, \text{Fe}, \text{Al})_5(\text{Al}, \text{Si})_8\text{O}_{22}(\text{OH})_2)$, is an isomorphous mixture of several silicates. Hornblende has a more complex silicate structure, in which the SiO_4 tetrahedra are linked to form a continuous chain twice the width of the pyroxene $\text{Ca}, \text{Mg}, \text{Fe}(\text{Si})_2\text{O}_6$ chains. For this reason, they are often referred to as double-chain silicates. Without elemental analysis at hand, the structure refined best as an isomorphous mixture of calcium-iron-magnesium silicate and iron-magnesium silicate (Picture 11).

Quartz, SiO_2 , forms a continuous framework of SiO_4 tetrahedra, with each oxygen shared between two tetrahedra.

Diopside ($\text{CaMgSi}_2\text{O}_6$) forms a structure that consists of chains of corner-linked SiO_4 tetrahedra, bonded to metal-oxygen octahedra.

Conclusion

Single-crystal diffraction on a Bruker D8 QUEST provides an extremely fast and unambiguous method for mineral identification. The excellent hardware is complemented by excellent software: APEX3 for data collection and data processing of single crystal and twinned data, and DIFFRAC.EVA for handling the Debye rings.

To our surprise, we discovered that the sand collected from a Lake Michigan beach contains mostly single crystal grains of a variety of minerals. The only iron oxide mineral that was identified was Hematite with several black opaque grains investigated. A good collection of other minerals of igneous origin was identified with data collected in a few minutes, and their unit cells referenced against the American Mineralogist Crystal Structure Database. High-quality data sets were collected in short experiment times, and yielded structures with impressively good reliability criteria.

The accessibility of this experiment lends itself to demonstrating the power of single crystal X-ray diffraction for the identification of unknown materials.

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- [1] Kean, W. F. (2004) Distribution of magnetic sands on Lake Michigan beaches near Milwaukee, Wisconsin. The Free Library. Michigan Academy of Science Arts & Letters.
- [2] Downs, R.T. and Hall-Wallace, M. (2003) The American Mineralogist Crystal Structure Database. American Mineralogist 88, 247-250.
- [3] Momma, K. and Izumi, F. (2011), VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, J. Appl. Crystallogr., 44, 1272-1276.

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