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# MicroXRD: Small Area Analysis of Single Grains of Sand

**MicroXRD can help you solve challenging problems that require the analysis of small areas or volumes.**

## Background

Lately, we've been thinking a lot about beach sand. While your image may be of a beautiful white beach that is likely composed of either quartz ($SiO_2$) or two polymorphs of calcium carbonate ($CaCO_3$) depending on whether the sand was produced by the ocean pulverizing granite or a big pile of seashells, a lot of beaches are much more heterogeneous. Figure 1 is a microscope image of some sand taken from a beach where the source of the sand is weathered volcanic rock. As you can see, there are a wide variety of shapes and sizes of sand grains. As bulk samples, diffraction patterns from sands like these can be very complex.

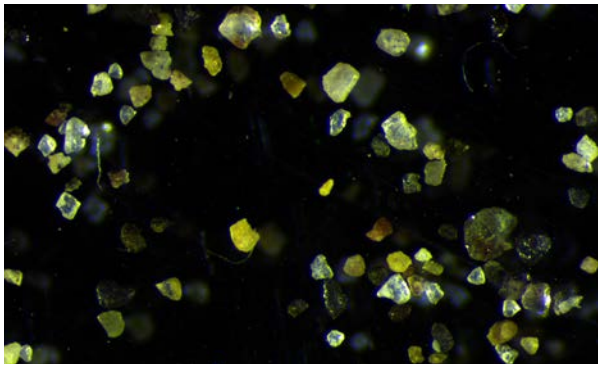

*Figure 1: Microscope image of sand*

Figure 2 shows the phase identification results for sand from Pfeiffer Beach in Big Sur, CA. This beach is unique because it has pink sand due to the erosion of garnet ($X_3Y_2(SiO_4)_3$ where X=(Ca, Mg, Fe or Mn)$^{+2}$ and Y=(Al, Fe or Cr)$^{+3}$). At least 12 crystalline phases were identified, often based on just a single weak peak. Data were collected on a ground sample packed into a bulk sample holder and measured on a traditional diffractometer. This got us wondering whether we could analyze individual grains of sand by microdiffraction.

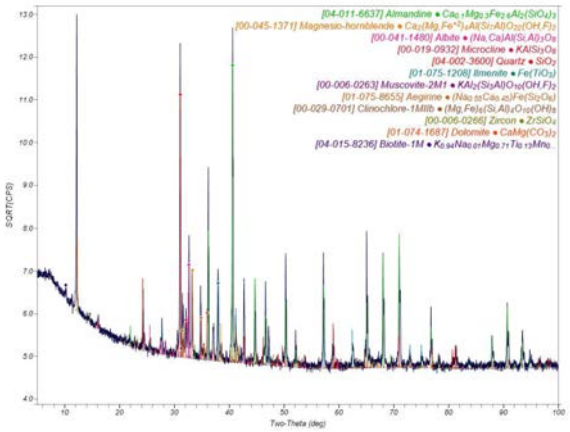


*Figure 2: Phase identification results for Pfeiffer beach sand*

Figure 3 shows a picture of the microdiffractometer used for this work. There are three features that set it apart from a standard diffractometer. The first is a combination of changes to the X-ray source and the introduction of collimation to dramatically reduce the size of the incident beam. While it is possible to simply put a very small collimator in front of a standard X-ray tube, this typically results in a huge intensity loss. Instead, most microdiffractometers use microfocus X-ray sources. The X-ray source used in this app note only operates at 50 watts compared to 1800 watts for a conventional X-ray tube. To make up for this loss in power, a special two-dimensional parabolic mirror monochromator is placed next to the source. This monochromator takes the divergent X-rays from the source and make them parallel both vertically and horizontally. The efficiency of the monochromator is maximized by placing it as close

to the filament as possible. The result is that even though the X-ray source produces many fewer X-rays, the collimator greatly increases the fraction of X-rays that make their way from the X-ray source to the actual sample.

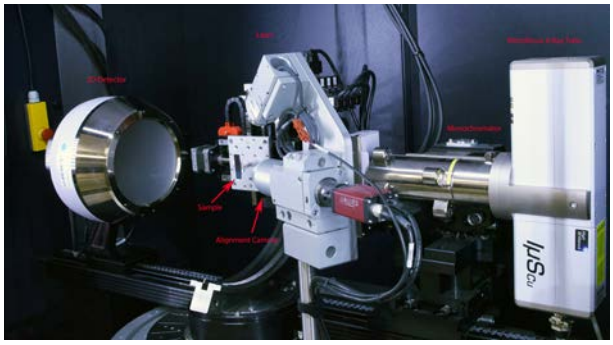

*Figure 3: Microdiffractometer*

The second feature that sets the microdiffractometer apart is the 2D detector. The 2-Theta range covered simultaneously by the detector is as large as 70 degrees and as small as 5 degrees depending on how close the detector is to the sample. Not only does this detector allow simultaneous data acquisition, but it also brings crystallites into diffracting conditions that are inclined by up to +/- 30 degrees with respect to the X-ray beam. Typical diffractometers are only looking at crystallites that are parallel to the sample surface. This greatly increases the percentage of crystallites that come into diffracting conditions which allows the microdiffractometer to compensate for the low X-ray tube power and very small volume of material analyzed.

Finally, there is a crossed laser and alignment microscope used to bring the area of interest into the X-ray beam. The alignment is correct only when the area of interest and the laser are both in the center of the alignment image.

## Microdiffraction of Individual Sand Grains

Using a microscope, a few interesting grains of sand were selected and placed on a Si wafer coated with a thin layer of Vaseline so that the grains would stay in one place. Figure 4 shows the first step of analyzing materials by microdiffraction. The sample stage is moved until a grain is centered in the camera and the sample height is adjusted until the laser is also centered. The scale indicates that this reddish grain is about 500 µm wide and 600 µm tall. A 500 µm pinhole collimator is used, which results in an oval-shaped irradiated area that is approximately 500 um high and variable in width depending on the 2-Theta position (wider at low angle, narrower at high angle).

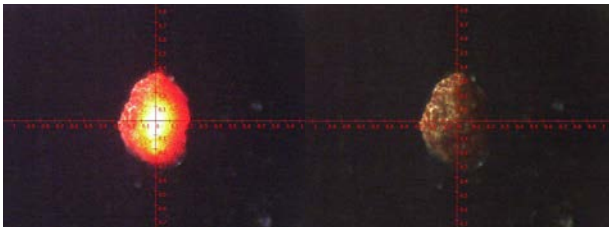

*Figure 4: Alignment image of red sand grain with and without laser*

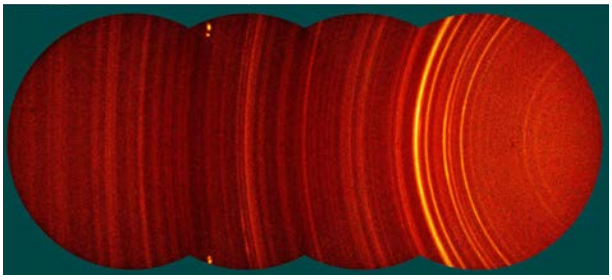

*Figure 5: 2D frames acquired on the red sand grain. Note 2-Theta goes from right to left.*

At its normal distance from the sample, the 2D detector covers about 30 degrees at a time so to cover an entire full diffraction pattern, a series of overlapping frames are acquired. Figure 5 shows the four 2D frames acquired on this grain. A considerable amount of information is present in a 2D detector frame. In each frame image, 2-Theta increases from left to right in these images. Each arc represents a constant 2-Theta and varying Chi (tilt) angle belonging to a specific reflection (hkl) and d-spacing. The overall appearance of a diffraction pattern produced in this manner can provide quite a lot of information, even before the data are analyzed:

1. With 2D area detectors, fine-grained, randomly oriented crystalline materials like this reddish sand grain will generate a smooth, uniform intensity, with continuous arcs at 2-theta values that satisfy Bragg's law.
2. Slightly larger-grained materials can generate arcs that are spotty along their length but, on average, the arc is still relatively uniform in intensity.

3. Very large-grained materials may generate only a few bright spots along an arc and a single crystal will generate only one spot on the arc.
4. Texture (i.e., preferred orientation) will produce arcs that are not uniform in intensity and tend to be more intense in specific directions. Strong texture may produce only a short arc tilted with respect to the horizontal centerline.
5. Amorphous materials will produce broad, diffuse arcs and usually with relatively low intensity.

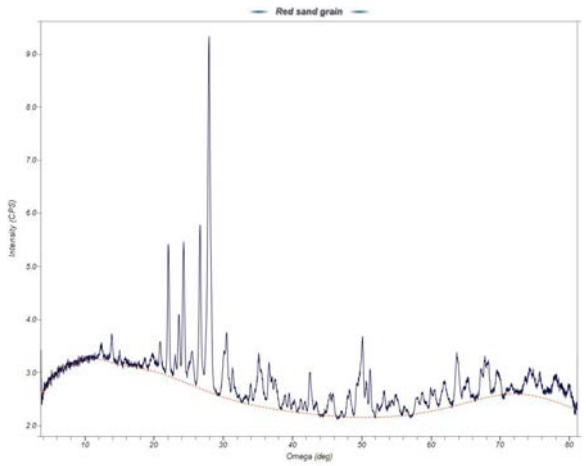


*Figure 6: Standard diffractogram after chi integration of 2D frames*

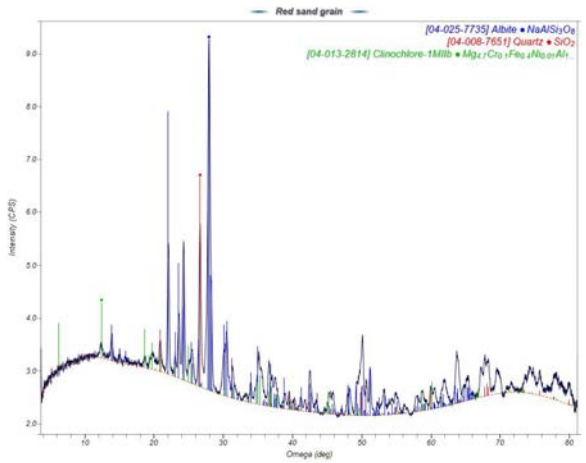


*Figure 7: Phase identification for the red sand grain*

Figure 6 shows the standard diffractogram obtained after integrating the 2D frames in the chi (tilt) direction. Note that while each pixel in the 2D frames may contain only a few counts, by integrating along each arc, a significant number of counts are acquired. This compensates for the extremely small analysis volume and low power of the X-ray source. From this point, analysis of the diffraction data occurs exactly the same way as if it were acquired with a point detector.

Figure 7 shows the best matches for this reddish grain after comparing the data to the ICDD diffraction database. The best matches are albite, which is a type of feldspar, clinochlore which is a member of the chlorite family and quartz which may be the most common mineral on earth. Despite the large number of peaks in this pattern, these three phases account for almost all of the peaks.

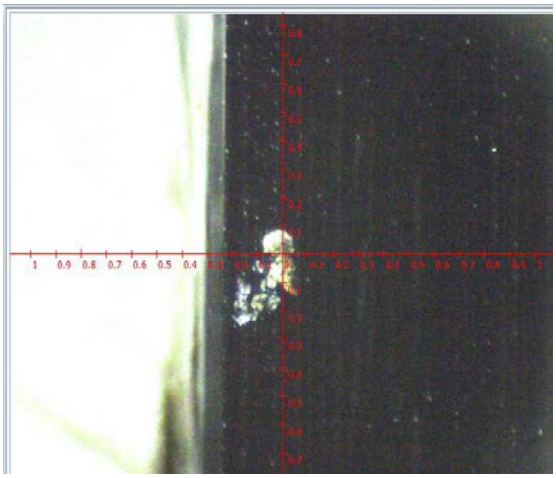

*Figure 8: Image of composite sand grains*

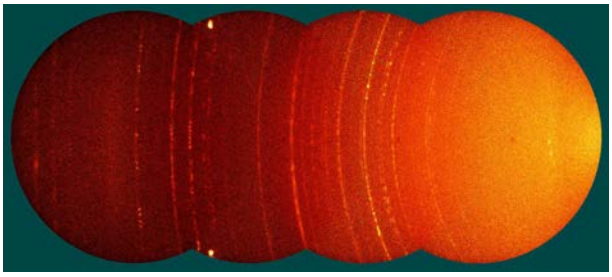

*Figure 9: 2D frames acquired on the composite sand grains. Note 2-Theta goes from right to left.*

Figure 8 is an assemblage of transparent and smaller grains near the edge of the Si substrate. Figure 9 shows the 2D frames for this sample. Note that unlike the previous example, some of these arcs are becoming spotty with brighter and darker areas along some of the arcs. This is due to the presence of larger crystallites. The chi-integrated

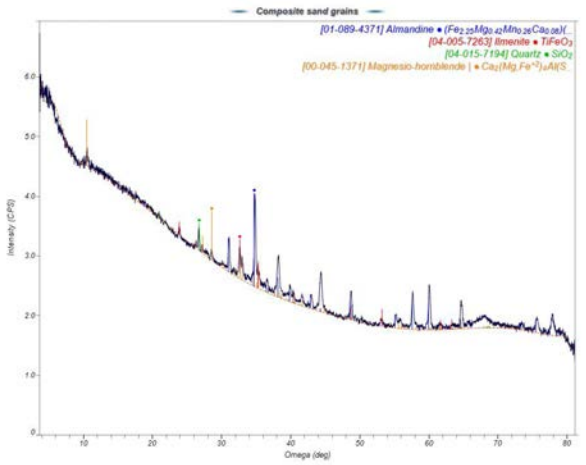


*Figure 10: Phase identification for the composite sand grains*

data, modeled background, and best matches are shown in Figure 10. The phases present in this small pile of grains are totally different from the first example. The major phase is almandine which belongs to the garnet family. In fact, the trace amounts of manganese in this mineral are what gives the sand at Pfeiffer Beach a distinct pink or purple hue. Magnesio-hornblende is an amphibole mineral and ilmenite is a common accessory mineral. The presence of these minerals indicate that the parent rock was likely metamorphic or igneous in nature.

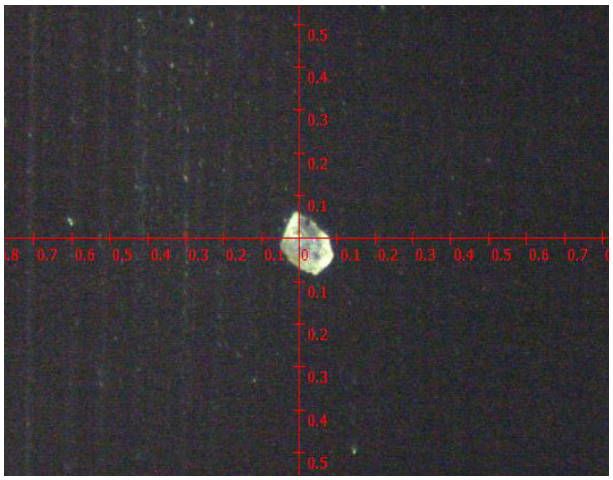

*Figure 11. Image of single clear sand grain*

Unlike our previous examples, our next grain of sand (Figure 11) looks like a single crystal. This observation turned out to be true when the initial sets of 2D frames had only 2 small dots. This was not enough information to identify the mineral, so data were reacquired while oscillating the sample in both the chi (tilt) and phi (rotation) directions. The idea here is to bring more crystal planes into diffracting conditions. Figure 12 shows the resulting 2D frames. Due to the oscillations, we now have many dots that form into a series of arcs. Figure 13 shows the chi-integrated pattern and that this pattern is also due to almandine. Note that in this case, there are large differences between the observed peak heights and the ICDD marker heights which are based on randomly oriented material. This is because not all crystal planes can be brought into diffracting conditions. However, there are more than enough peaks to identify the mineral.

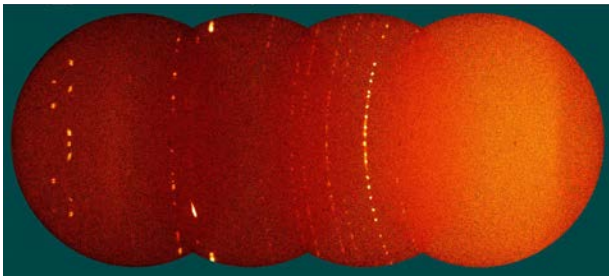

*Figure 12: 2D frames acquired on the single clear grain. Note 2-Theta goes from right to left.*

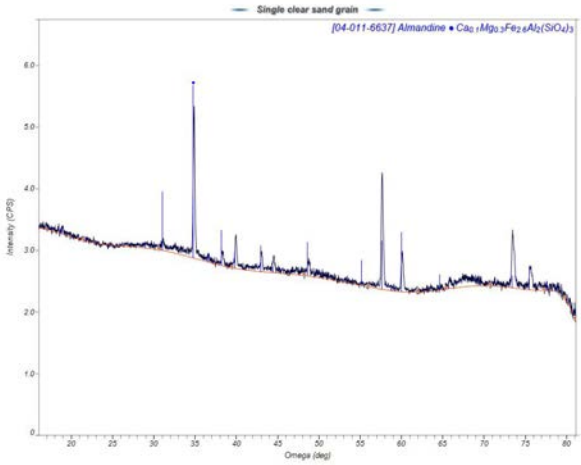


*Figure 13: Phase identification for the single clear sand grain*

Our last example is a small, darker crystallite (Figure 14). The 2D frames are shown in Figure 15 and the chi-integrated data and best match are shown in Figure 16. This is also a single crystal grain with the exception of a couple very weak arcs from polycrystalline material. But in this case, there are wide differences between the experimental peak intensities and the ICDD marker heights which are

based on a fine-grained, randomly oriented sample. In fact, the expected strongest magnesio-hornblende peak near 29 degrees 2-Theta is barely detected at all. Depending on the mineral and how it is oriented on the sample holder, it may not be possible to bring all of the crystalline planes into diffracting conditions. Nevertheless, there are enough peaks detected to clearly identify the mineral despite the sand grain being only about 100 x 150 µm in size.

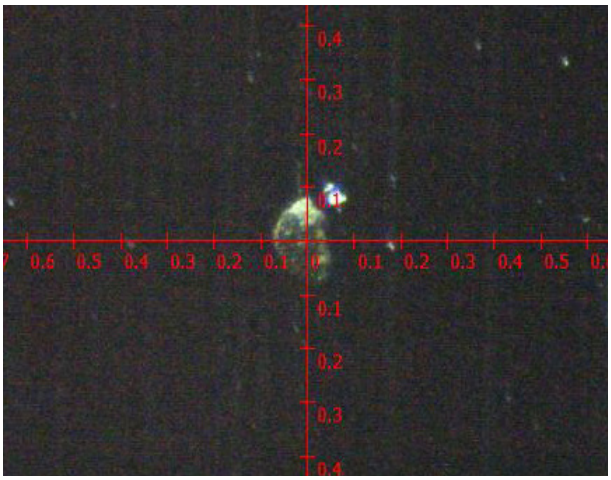


*Figure 14: Image of smaller dark sand grains*

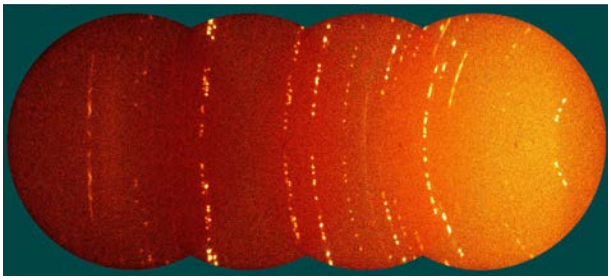

*Figure 15 - 2D frames acquired on the smaller dark sand grain. Note 2-Theta goes from right to left.*

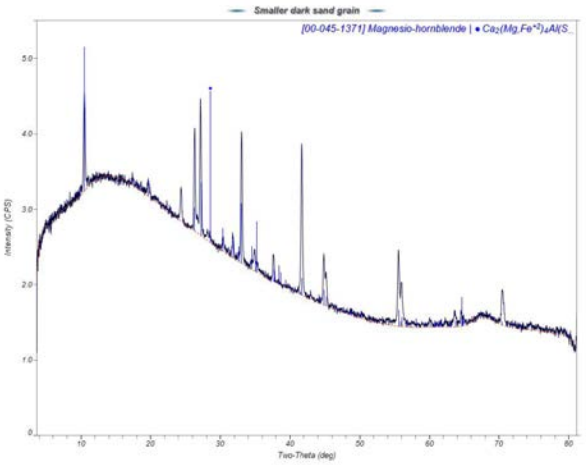


*Figure 16: Phase identification for the smaller dark sand grain*

## Conclusion

The combination of microfocus X-ray source, narrow pinhole collimator and 2D detector makes it possible to make diffraction measurements on areas as small as ~30µm diameter areas (~1000 µm$^2$) in a reasonable amount of time. Few, if any people reading this application note have any need to identify the mineralogy of individual grains of sand; but there are many, many scientific and technology-based applications where you might want to identify the crystalline material in a very small area or volume. For example, microdiffraction can be used to identify crystalline inclusions in glass, look at film texture in a test pad on an integrated circuit, identify a single particle found in an air filter, or to identify the phosphor used in an LED. And while this application note involved phase identification, microdiffraction can generally be used to perform any type of XRD analysis that is typically done on a standard diffractometer whether that be crystallite size analysis, % texture analysis or residual stress analysis.

At Eurofins EAG, our XRD team has collectively many decades of XRD expertise. We have a collaborative group coming from different backgrounds, industries and research specialties. With our recent addition of a Small Spot XRD tool along with our extensive instrument base, we offer a wide variety of analytical options that can be tailored specifically to our clients' needs. Contact us today to learn how we can help with your next project.