eurofins

EAG
Laboratories

Characterization of Beach Sand Using WDXRF and XRD

WDXRF and XRD are complementary techniques that are often used together for the characterization of unknown materials from a wide variety of industries.

Introduction

Anyone who has visited beaches around the world is aware of how sand comes in a wide variety of colors and textures. Sand has such a wide variability due to the processes involved in its formation. While most sand originates due to weathering of rocks and minerals on land, shells and coral in the ocean also can contribute to the composition of sands. Since beach sand is typically created from the local surroundings, the compositions constitute a unique fingerprint.

Wavelength Dispersive X-ray Fluorescence spectroscopy (WDXRF) and X-ray Diffraction (XRD) are two powerful tools that allow us to obtain detailed characterization of materials, covering both the elemental composition and crystalline phases present. For this reason, applying these two techniques to the characterization of beach sand provides a window into the local geology and processes that produce the sand in different parts of the world.

Discussion

Part 1: WDXRF Results

A simple compositional analysis can usually be accomplished using WDXRF without the need of matched standards by using Fundamental Parameters (FP), a “standardless” method relying on sensitivity factors derived from pure elements. By analyzing different types of certified reference materials, the relative accuracy for the FP method can be evaluated. For major and minor elements, the relative accuracy is typically in the range of 10% down to less than 5%. The FP method is routinely used to analyze specific alloy, ceramic or glass samples with sufficient accuracy to identify the specific class of these materials.

Mineralogical materials are often very complex and may contain some major elements in multiple phases (such as Si in quartz and aluminosilicate

Table 1: Quantification of Beach Sand by WDXRF (in Wt%)

	Lanikai Beach	Clearwater Beach	Pfieffer Beach
Location	Oahu, HI	Clearwater, FL	Big Sur, CA
Sand color	Off-white/orange	White	Purple
Na_2O	0.16	0.19	0.51
MgO	3.21	0.067	3.81
Al_2O_3	0.11	0.31	13.8
SiO_2	0.58	95.0	32.7
P_2O_5	0.088	0.19	0.098
SO_3	0.41	0.047	0.047
Cl	0.023	-	-
K_2O	0.014	0.12	0.30
CaO	50.4	1.94	3.34
TiO_2	0.025	0.056	6.86
V_2O_5	-	-	0.028
Cr_2O_3	-	0.070	0.22
MnO	0.013	-	1.48
Fe_2O_3	0.22	0.48	36.1
NiO	0.008	0.015	0.021
CuO	-	0.006	-
ZnO	-	-	0.020
SrO	0.40	0.014	0.009
Y_2O_3	-	-	0.045
ZrO_2	-	-	0.46
BaO	-	-	0.14
WO_3	-	-	0.027
LOI*	44.3	1.5	-

* loss on ignition

phases). To eliminate potential inaccurate quantification due to such "mineralogical effects" geological materials are typically prepared for XRF analysis using borate fusion, whereby the material is fired to remove volatile species, followed by fusing with lithium borate. The analytical sample will consist of simple oxides homogeneously dispersed into a glass disk.

Table 1 shows results from sand collected at three beaches from diverse locations: Lanikai Beach (Oahu, HI), Clearwater Beach (Clearwater, FL) and Pfeiffer Beach (Big Sur, CA). Significant compositional differences are immediately evident and can also be seen in overlays of spectra of the major elements (Figure 1). The Clearwater Beach sand is nearly entirely composed of SiO_2, while the Lanikai Beach sand is primarily composed of calcium oxide along with a high loss on ignition after firing. The Pfeiffer Beach sand has a notably greater degree of complexity. These data demonstrate that WDXRF is a powerful tool for measuring the full composition of materials from major matrix species down to trace elements in the ~10-100ppm range, or lower with a tailored analysis.

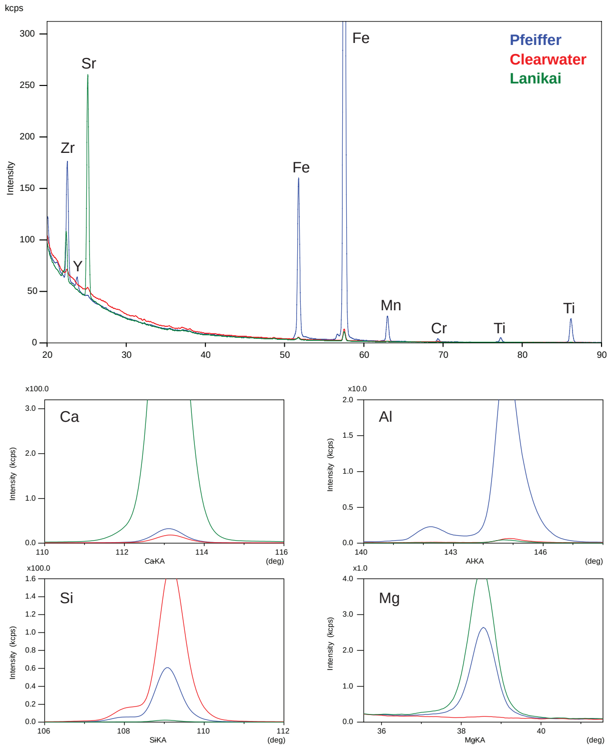


Figure 1: Selected XRF spectra showing notable differences between locations.

While XRF does not provide chemical state information, some preliminary interpretations can be made from the measured compositions and available literature. Since the Lanikai sand is principally composed of calcium oxide and volatile species (the LOI, or loss on ignition) such as carbonates, the data suggest that this sand is largely composed of calcium carbonate from shells and possibly coral. A literature search indicates that much of the sand on Florida beaches consists of quartz that has washed down from land masses such as the Appalachian Mountains, which is consistent with the ~95% SiO_2 composition. As noted, the Pfeiffer Beach sand is much more complex and gets its color from the local geology, primarily manganese garnet, which gives it its purple color. However, the results indicate that this sand also has a large fraction from iron oxide based minerals. In order, to delve more deeply into the complex chemistry of these sands, they were also analyzed using x-ray diffraction and these results are discussed in the next section.

Part 2: XRD Results

While XRF can clearly differentiate sands from these three beaches, so much more can be learned by adding X-ray diffraction (XRD). Let's start with Lanikai beach on the island of Oahu in Hawaii. Figure 2 shows the experimental XRD data, the modeled background and the best reference pattern matches from the International Centre for Diffraction Data (ICDD) powder diffraction database. This database contains more than a quarter of a million reference patterns on different crystal structures

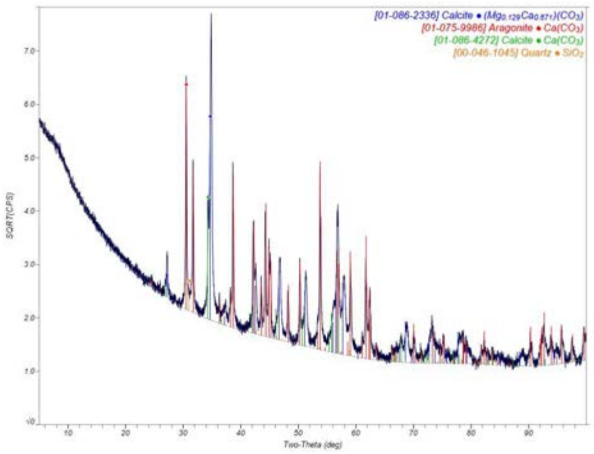


Figure 2: Phase identification results for the Lanikai beach sample

including nearly all mineral species. The results show that like many of the world's most beautiful white beaches, Lanikai is composed almost exclusively of pulverized coral, mollusks and other sea creatures that produce protective calcium carbonate shells. Each crystal structure has a unique XRD fingerprint so, for example, it is quite easy to differentiate the various forms of calcium carbonate. Figure 3 is an expanded view of part of this pattern. Calcite and aragonite are the two most common forms of calcium carbonate and in this figure, aragonite is represented by the red markers and calcite is represented by the green markers. In addition, there is a third strong phase in blue (magnesiocalcite) which is a form of calcite with a significant amount of magnesium substituted for the calcium. Note that while the aragonite markers line up nearly exactly with the experimental peaks, the calcite and magnesiocalcite markers are shifted. This indicates that there is a small amount of magnesium in the peaks assigned to calcite and an incorrect amount of magnesium in the peaks assigned to magnesiocalcite. In addition to these three phases, there is a very small amount of quartz (SiO_2) which is one of the world's most common minerals.

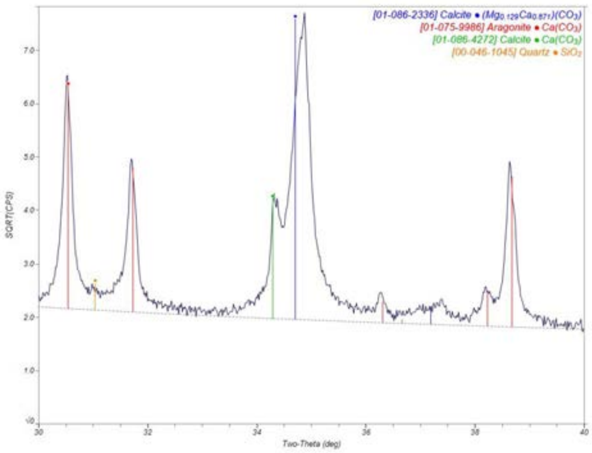
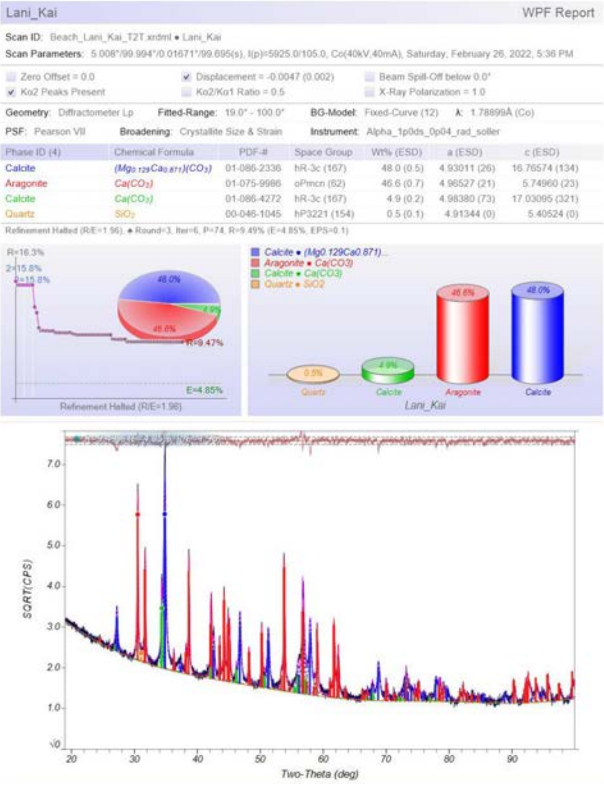


Figure 3: Phase identification results for the Lanikai beach sample - expanded view

The ratio of aragonite to calcite produced in a seashell depends on the water temperature. This makes seashells or calcium carbonate deposits a valuable source of information for people who try to reconstruct the earth's climate history. The most accurate way to determine the amount of each phase is a process called whole pattern fitting (WPF). In WPF, the ICDD reference pattern "fingerprints" are given realistic peak shapes and combined to minimize the overall differences between the experimental data and the sum of the simulated profiles. Figure 4 shows the WPF process for this sample. The results indicate that this sample contains 48.0% Magnesiocalcite, 46.6% Aragonite, 4.9% Calcite and 0.5% Quartz. The pink curve at the top of the plot of the experimental data shows the difference between the experimental data and the sum of the model profiles. The R value for this fit is 9.47% which indicates quite a good fit between the experimental data and the simulated pattern. When discussing quantitative XRD, it is important to note that there are a half dozen factors that influence peak intensity that have nothing to do with composition; most notably, texture, crystallite size and changes in phase composition. For this reason, WPF is often referred to as semi-quantitative analysis to differentiate it from the kind of accuracy and precision expected from elemental analysis techniques like XRF.


Lani_Kai WPF Report

Scan ID: Beach_Lani_Kai_T2T.xrdml • Lani_Kai
Scan Parameters: 5.008°/99.994°/0.01671°/99.695(s), I(p)=5925.0/105.0, Co(40kV,40mA), Saturday, February 26, 2022, 5:36 PM

☐ Zero Offset = 0.0
☑ Kα2 Peaks Present
☑ Displacement = -0.0047 (0.002)
☐ Kα2/Kα1 Ratio = 0.5
☐ Beam Spill-Off below 0.0°
☐ X-Ray Polarization = 1.0

Geometry: Diffractometer Lp **Fitted-Range:** 19.0° - 100.0° **BG-Model:** Fixed-Curve (12) **λ:** 1.78899Å (Co)
PSF: Pearson VII **Broadening:** Crystallite Size & Strain **Instrument:** Alpha_1p0ds_0p04_rad_soller

Phase ID (4)	Chemical Formula	PDF-#	Space Group	Wt% (ESD)	a (ESD)	c (ESD)
Calcite	$(Mg_{0.129}Ca_{0.871})(CO_3)$	01-086-2336	hR-3c (167)	48.0 (0.5)	4.93011 (26)	16.76574 (134)
Aragonite	$Ca(CO_3)$	01-075-9986	oPmcn (62)	46.6 (0.7)	4.96527 (21)	5.74960 (23)
Calcite	$Ca(CO_3)$	01-086-4272	hR-3c (167)	4.9 (0.2)	4.98380 (73)	17.03095 (321)
Quartz	SiO_2	00-046-1045	hP3221 (154)	0.5 (0.1)	4.91344 (0)	5.40524 (0)

Refinement Halted (R/E=1.96), ♣ Round=3, Iter=6, P=74, R=9.49% (E=4.85%, EPS=0.1)

Figure 4: Whole pattern fitting for the Lanikai beach sample

Figure 5 shows the raw data, background and matching phases for a sample from Clearwater beach near Tampa, Florida. Unlike a calcium carbonate beach like Lanikai, Clearwater beach is nearly completely composed of quartz. However, the inset shows that there are several very weak peaks from other phases. Many crystalline phases share at least a single common peak position so trying to identify a phase from a single peak is very speculative at best. The best matches were selected by limiting the possibilities using the XRF elemental data. Figure 6 shows the WPF results for this sample. The results indicate that the sample is 96.4% quartz. Where all this quartz came from was a geological mystery for a while because the Florida peninsula is essentially a big pile of seashells. It is now believed that the quartz is from weathering of the Appalachian Mountains far to the north.

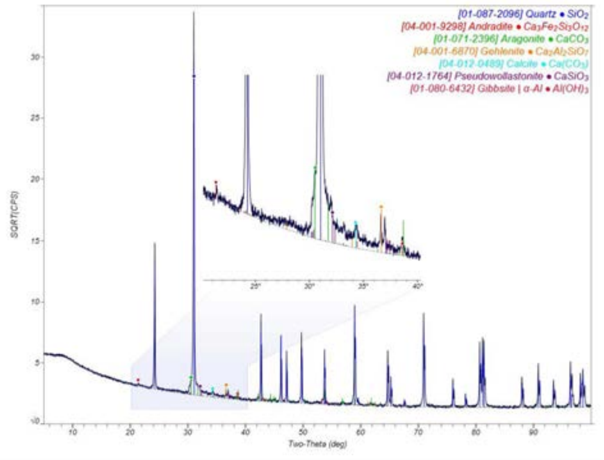
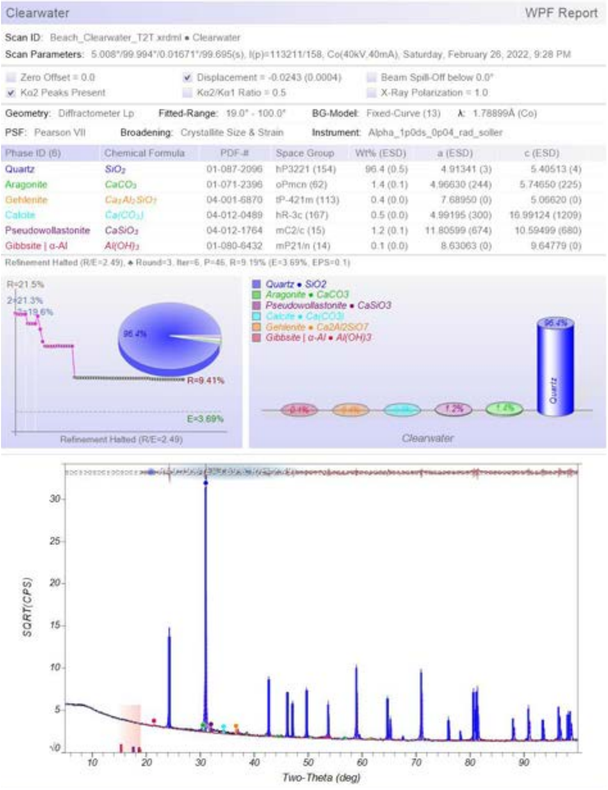


Figure 5: Phase identification results for the Clearwater beach sample



Clearwater — WPF Report

Scan ID: Beach_Clearwater_T2T.xrdml • Clearwater

Scan Parameters: 5.008°/99.994°/0.01671°/99.695(s), I(p)=113211/158, Co(40kV,40mA), Saturday, February 26, 2022, 9:28 PM

☐ Zero Offset = 0.0
☑ Displacement = -0.0243 (0.0004)
☐ Beam Spill-Off below 0.0°
☑ Kα2 Peaks Present
☐ Kα2/Kα1 Ratio = 0.5
☐ X-Ray Polarization = 1.0

Geometry: Diffractometer Lp **Fitted-Range:** 19.0° - 100.0° **BG-Model:** Fixed-Curve (13) **λ:** 1.78899Å (Co)

PSF: Pearson VII **Broadening:** Crystallite Size & Strain **Instrument:** Alpha_1p0ds_0p04_rad_soller

Phase ID (6)	Chemical Formula	PDF-#	Space Group	Wt% (ESD)	a (ESD)	c (ESD)
Quartz	SiO_2	01-087-2096	hP3221 (154)	96.4 (0.5)	4.91341 (3)	5.40513 (4)
Aragonite	$CaCO_3$	01-071-2396	oPmcn (62)	1.4 (0.1)	4.96630 (244)	5.74650 (225)
Gehlenite	$Ca_2Al_2SiO_7$	04-001-6870	tP-421m (113)	0.4 (0.0)	7.68950 (0)	5.06620 (0)
Calcite	$Ca(CO_3)$	04-012-0489	hR-3c (167)	0.5 (0.0)	4.99195 (300)	16.99124 (1209)
Pseudowollastonite	$CaSiO_3$	04-012-1764	mC2/c (15)	1.2 (0.1)	11.80599 (674)	10.59499 (680)
Gibbsite | α-Al	$Al(OH)_3$	01-080-6432	mP21/n (14)	0.1 (0.0)	8.63063 (0)	9.64779 (0)

Refinement Halted (R/E=2.49), ♣ Round=3, Iter=6, P=46, R=9.19% (E=3.69%, EPS=0.1)

Figure 6: Whole pattern fitting for the Clearwater beach sample

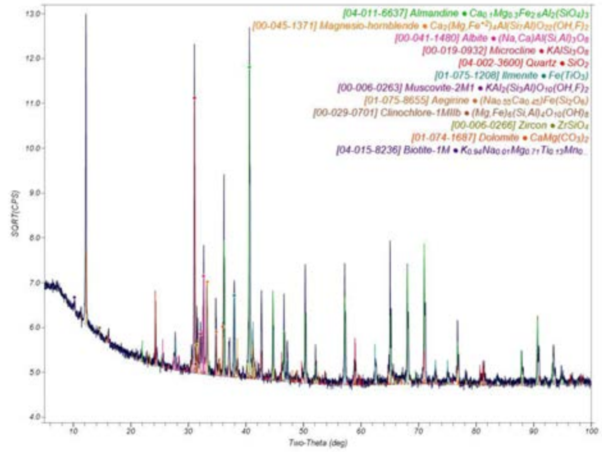
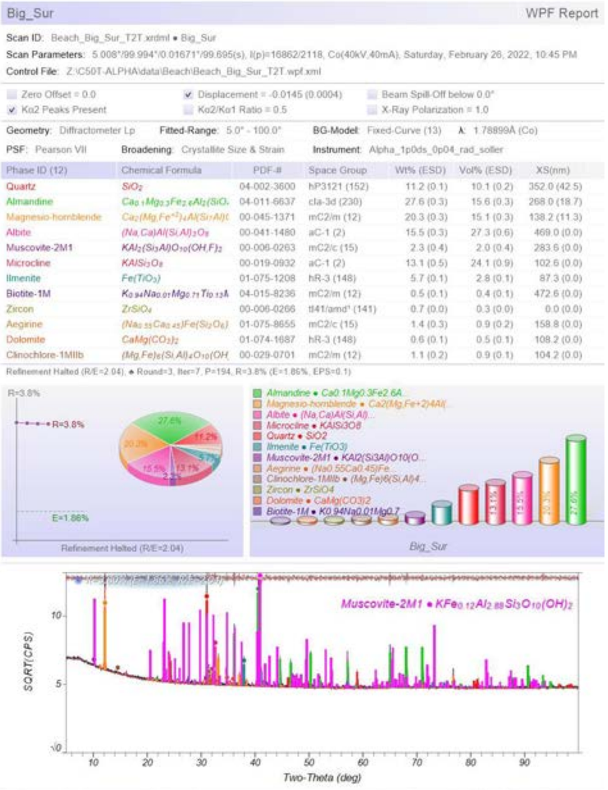


Figure 7: Phase identification results for the Pfeiffer beach sample

Our final example comes from Pfeiffer beach near Big Sur, California. This beach is known for its purple sand. While it is easy to conclude from the XRF results alone that Lanikai beach is mostly calcium and magnesium carbonate and Clearwater beach is mostly quartz, Pfeiffer beach sand is totally different with iron, silicon, aluminum, titanium, magnesium, calcium and manganese all present at 1% or higher on an oxide basis. Figure 7 shows that the diffraction pattern for this sample is very complex. In XRD, the more diffraction peaks there are in the pattern, the more matches there will be. So, XRF is crucial for providing elemental constraints on the potential matches. The results indicate that almandine, magnesio-hornblende, albite, microcline, quartz and ilmenite are the major mineral phases. All of these phases point to either metamorphic or igneous rocks being the source of the sand. The reason for the unusual color of the sand at Pfeiffer beam is the almandine (the phase with the green markers in the figure). Almandine is a reddish/brown member of the garnet family with a nominal chemical formula of $Fe_3Al_2Si_3O_{12}$. However, the XRF results indicate that this sand contains about 1.5% MnO. Manganese replaces some of the iron in the almandine structure and this changes the color to purple. As with the trace phases in the Clearwater beach sample, XRF is also used here to find specific minerals that may better explain the XRD results. In particular, the large amount of titanium in this sample is due to ilmenite ($FeTIO_3$) and the zirconium is due to zircon ($ZrSiO_4$). Figure 8 shows the WPF results for this sample. The R value of 3% indicates excellent agreement between the experimental data and the simulated pattern despite the complexity of the data.


Big_Sur — WPF Report

Scan ID: Beach_Big_Sur_T2T.xrdml • Big_Sur
Scan Parameters: 5.008°/99.994°/0.01671°/99.695(s), I(p)=16862/2118, Co(40kV,40mA), Saturday, February 26, 2022, 10:45 PM
Control File: Z:\C50T-ALPHA\data\Beach\Beach_Big_Sur_T2T.wpf.xml

☐ Zero Offset = 0.0
☑ Kα2 Peaks Present
☑ Displacement = -0.0145 (0.0004)
☐ Kα2/Kα1 Ratio = 0.5
☐ Beam Spill-Off below 0.0°
☐ X-Ray Polarization = 1.0

Geometry: Diffractometer Lp **Fitted-Range:** 5.0° - 100.0° **BG-Model:** Fixed-Curve (13) **λ:** 1.78899Å (Co)
PSF: Pearson VII **Broadening:** Crystallite Size & Strain **Instrument:** Alpha_1p0ds_0p04_rad_soller

Phase ID (12)	Chemical Formula	PDF-#	Space Group	Wt% (ESD)	Vol% (ESD)	XS(nm)
Quartz	SiO_2	04-002-3600	hP3121 (152)	11.2 (0.1)	10.1 (0.2)	352.0 (42.5)
Almandine	$Ca_{0.1}Mg_{0.3}Fe_{2.6}Al_2(SiO$	04-011-6637	cIa-3d (230)	27.6 (0.3)	15.6 (0.3)	268.0 (18.7)
Magnesio-hornblende	$Ca_2(Mg,Fe^{+2})_4Al(Si_7Al)($	00-045-1371	mC2/m (12)	20.3 (0.3)	15.1 (0.3)	138.2 (11.3)
Albite	$(Na,Ca)Al(Si,Al)_3O_8$	00-041-1480	aC-1 (2)	15.5 (0.3)	27.3 (0.6)	469.0 (0.0)
Muscovite-2M1	$KAl_2(Si_3Al)O_{10}(OH,F)_2$	00-006-0263	mC2/c (15)	2.3 (0.4)	2.0 (0.4)	283.6 (0.0)
Microcline	$KAlSi_3O_8$	00-019-0932	aC-1 (2)	13.1 (0.5)	24.1 (0.9)	102.6 (0.0)
Ilmenite	$Fe(TiO_3)$	01-075-1208	hR-3 (148)	5.7 (0.1)	2.8 (0.1)	87.3 (0.0)
Biotite-1M	$K_{0.94}Na_{0.01}Mg_{0.71}Ti_{0.13}A$	04-015-8236	mC2/m (12)	0.5 (0.1)	0.4 (0.1)	472.6 (0.0)
Zircon	$ZrSiO_4$	00-006-0266	tI41/amd¹ (141)	0.7 (0.0)	0.3 (0.0)	0.0 (0.0)
Aegirine	$(Na_{0.55}Ca_{0.45})Fe(Si_2O_6)$	01-075-8655	mC2/c (15)	1.4 (0.3)	0.9 (0.2)	158.8 (0.0)
Dolomite	$CaMg(CO_3)_2$	01-074-1687	hR-3 (148)	0.6 (0.1)	0.5 (0.1)	108.2 (0.0)
Clinochlore-1MIIb	$(Mg,Fe)_6(Si,Al)_4O_{10}(OH$	00-029-0701	mC2/m (12)	1.1 (0.2)	0.9 (0.1)	104.2 (0.0)

Refinement Halted (R/E=2.04), ♠ Round=3, Iter=7, P=194, R=3.8% (E=1.86%, EPS=0.1)

Figure 8: Whole pattern fitting for the Pfeiffer beach sample

Conclusion

WDXRF is a powerful tool for measuring the composition of practically any solid and coupled with borate fusion it is an ideal technique for analyzing geological materials such as sand. However, due to the often complex mineralogy of these materials an elemental composition only provides part of the complete picture. We can gain a deeper understanding of geological materials and their history by measuring the crystalline phases using XRD. Both the XRF compositional data and the International Centre for Diffraction Data (ICDD) powder diffraction database provide the tools to comprehensively characterize even very complex diffraction data as was specifically demonstrated here with the Pfeiffer Beach sand. WDXRF and XRD are complementary techniques that are often used together for the characterization of unknown materials from a wide variety of industries. The example of the sands here is analagous to identifying unknown material from a chemical process or to identifying a deposit left over in semiconductor process chamber, to name but two examples. Contact us today to learn how we can help with your next project.