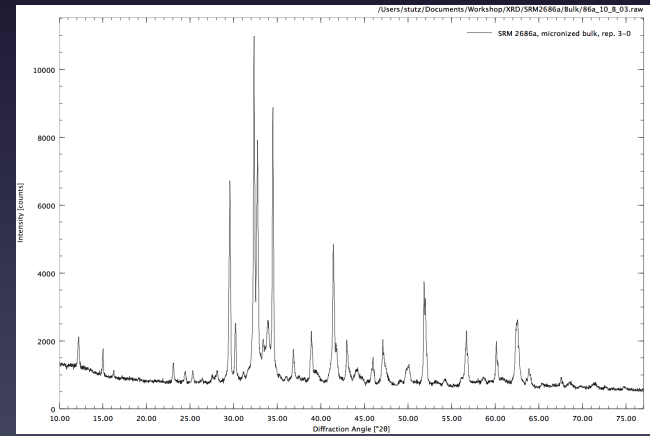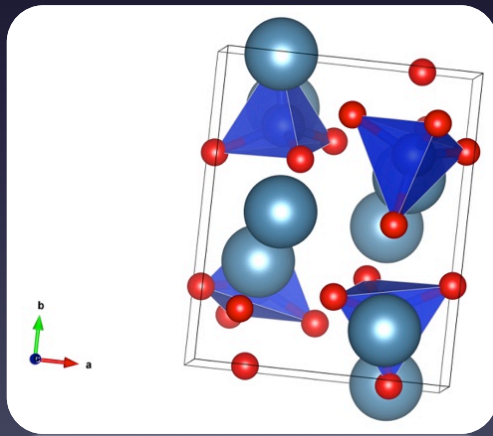# Cements Materials Characterization Workshop

Specimen Preparation for X-Ray Powder Diffraction

Phase Identification for Cementitious Materials

ASTM C1365

No detailed procedure, providing flexibility

- Qualification approach based upon each user's analysis of SRM clinkers

- Precision and accuracy criteria based upon an inter-laboratory study

- Four cements compounded using SRM clinkers and lab-prepared calcium sulfates

- Rietveld and traditional methods are acceptable

- Some guidance provided for phase identification and analytical procedures

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Designation: C 1365 – 06

Standard Test Method for
Determination of the Proportion of Phases in Portland Cement and Portland-Cement Clinker Using X-Ray Powder Diffraction Analysis[1]

This standard is issued under the fixed designation C 1365; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers direct determination of the proportion by mass of individual phases in portland cement or portland-cement clinker using quantitative X-ray (QXRD) analysis. The following phases are covered by this standard: alite (tricalcium silicate), belite (dicalcium silicate), aluminate (tricalcium aluminate), ferrite (tetracalcium aluminoferrite), periclase (magnesium oxide), gypsum (calcium sulfate dihydrate), bassanite (calcium sulfate hemihydrate), anhydrite (calcium sulfate), and calcite (calcium carbonate).

1.2 This test method specifies certain general aspects of the analytical procedure, but does not specify detailed aspects. Recommended procedures are described, but not specified. Regardless of the procedure selected, the user shall demonstrate by analysis of certified reference materials (CRM's) that the particular analytical procedure selected for this purpose qualifies (that is, provides acceptable precision and bias) (see Note 1). The recommended procedures are ones used in the round-robin analyses to determine the precision levels of this test method.

Note 1—A similar approach was used in the performance requirements for alternative methods for chemical analysis in Test Methods C 114.

1.3 The values stated in SI units shall be regarded as the standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazards, see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

C 114 Test Methods for Chemical Analysis of Hydraulic Cement
C 150 Specification for Portland Cement
C 183 Practice for Sampling and the Amount of Testing of Hydraulic Cement
C 219 Terminology Relating to Hydraulic Cement
C 670 Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials
E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions are in accordance with Terminology C 219.*
3.2 *Phases* (1):[3]
3.2.1 *alite, n*—tricalcium silicate (C_3S)[4] modified in composition and crystal structure by incorporation of foreign ions; occurs typically between 30 to 70 % (by mass) of the portland-cement clinker; and is normally either the M_1 or M_3 crystal polymorph, each of which is monoclinic.
3.2.2 *alkali sulfates, n*—arcanite (K_2SO_4) may accommodate Na^+, Ca^{2+}, and CO_3 in solid solution, aphthitalite (K_{4-x},Na_x)SO_4 with x usually 1 but up to 3), calcium langbeinite ($K_2Ca_2[SO_4]_3$) may occur in clinkers high in K_2O, and thenardite (Na_2SO_4) in clinkers with high Na/K ratios (1).
3.2.3 *aluminate, n*—tricalcium aluminate (C_3A) modified in composition and sometimes in crystal structure by incorporation of a substantial proportion of foreign ions; occurs as 2 to 15 % (by mass) of the portland-cement clinker; is normally cubic when relatively pure and orthorhombic or monoclinic when in solid solution with significant amounts of sodium (2).
3.2.4 *anhydrite, n*—calcium sulfate ($C\bar{S}$) and is orthorhombic (see Note 2).

Note 2—Calcium sulfate is added to the clinker during grinding to control setting time, strength development, and volume stability. Several phases may form as a result of dehydration of gypsum. The first 1.5

[3] The boldface numbers in parentheses refer to the list of references at the end of this standard.
[4] When expressing chemical formulae, C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, M = MgO, $\bar{S}$ = SO_3, and H = H_2O.

Errors in Powder Diffraction

Relative Importance of Errors

scale	d- Measurement Errors	I – Instrument Errors	Type
10	**Displacement**		**S**
9			
8			
7		**Preferred Orientation**	**R**
6	d-spacing		R
	d-reporting		R
		Stress/Strain	R
5	Axial Divergence		S
	Zero Angle		S
		I – Reporting	R
4	Flat Specimen		S
	Transparency		S
	2:1	2:1	S
3	Spec.-Rec Slit Distance		S
	Broad Lines		S
	Counting Statistics	Counting Statistics	R
2	Beam Uniformity		R
	alpha-2 influence		
	cocked slits		
	mechanical		
1			
0	Temperature Variations		
	wavelength CuK$_{alpha}$		

S = Systematic Error   R = Random Error

- Specimen displacement has little effect on intensities

- Preferred orientation continues to present problems, particularly with the top-loaded specimens commonly used today,

- After displacement, round off error in d-spacing reporting is most significant

- Alignment errors may be identified and corrected via external standards (zero error, 2:1)

- Zero error and specimen displacement are highly correlated over short 2-theta distance

- Displacement and orientation errors will affect phase identifications

- Incorrect phase identification introduces bias

These focus on data collection, analysis is another aspect of the test procedure

Careful phase identification and refinement procedure improves the possibility of a success

Preferred Orientation: Alite

Ground to – 10 µm
Specimen pressed to induce preferred orientation (red trace)

Minimal preferred orientation

Peak Intensity Ratio
29.3/30.1   32.1/32.7
2.6   1.2 OK
2.6   1.5 not OK

29.3 30.07   32.1 32.7   34.2

Intensity (Counts)

Degrees Two-Theta   Cu Kalpha
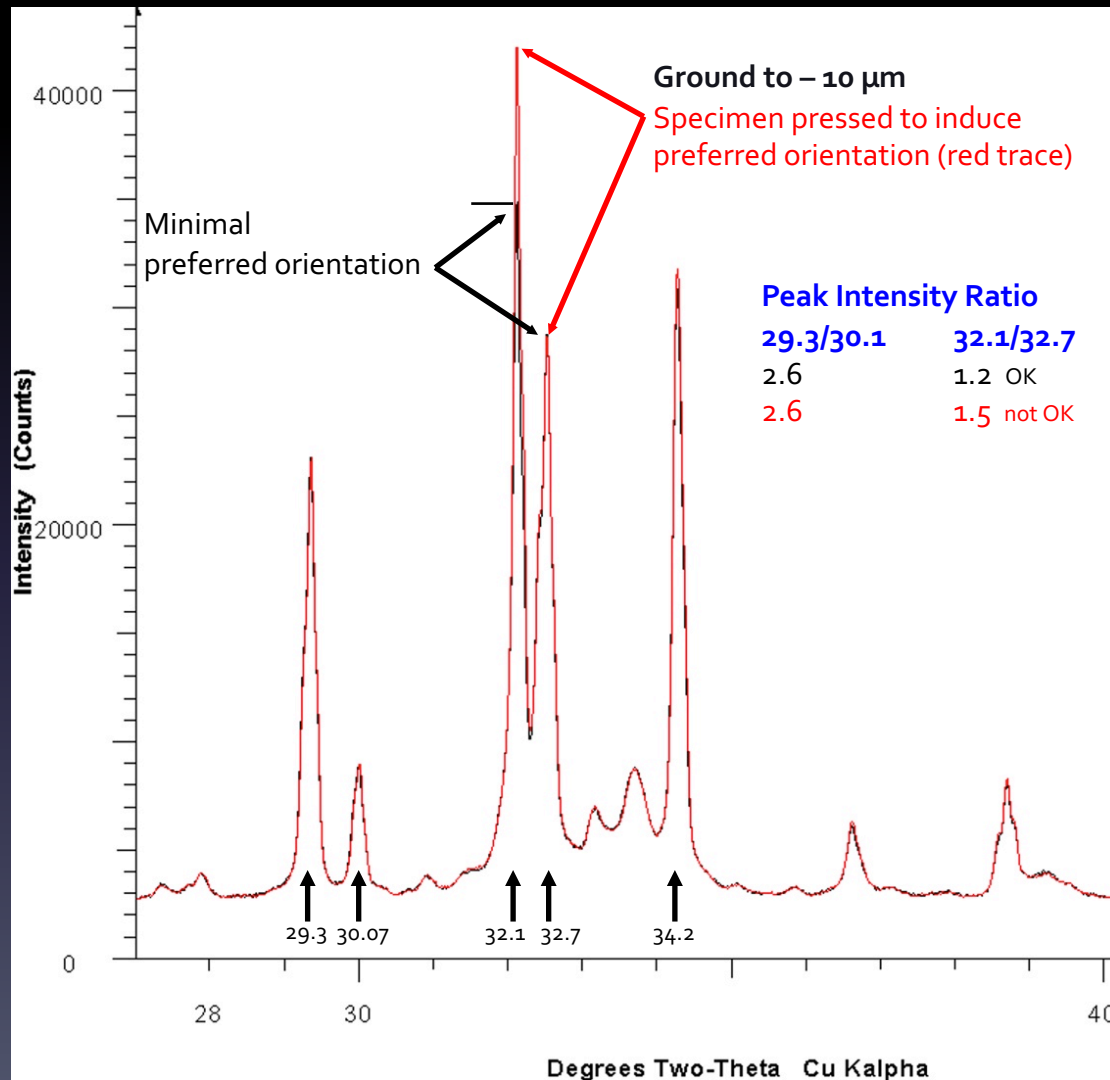
Coarse-ground samples, like cement from the finish mill, can be susceptible to preferred orientation.

Phases that exhibit strong cleavage like alite, calcite, gypsum are prone to orientation, particularly with top-loaded specimens.

For alite this is most apparent with the diffraction peak occurring at 32.1 degrees.

Fine-grinding, careful specimen loading and pressing minimize these tendencies, though for some phases with strong cleavage we rarely eliminate orientation

Orientation corrections are possible but seem to work best in quantitative analysis when orientation is not too severe.

Specimen Preparation

Modern instruments today obtain results in a fraction of the time required in 1930 but are still subject to sample preparation and mounting artifacts that may affect the analysis,

Grinding reduces particle size, improves representative sampling and particle statistics, reduces preferred orientation tendencies, and improves packing characteristics,

The packed powder mount ideal characteristics present a representative sampling of bulk material, a homogeneous volume, and smooth surface.

✓ Cement phase solid interaction volume is roughly 15 μm at 40 degrees 2-theta

✓ Sampling is improved by specimen rotation, bringing more particles into the beam footprint

✓ Many particles are multi-phase with individual crystals smaller than the particle

Cement: As-Received

Cement: hand-ground, mortar and pestle

Cement: 70% <10 um
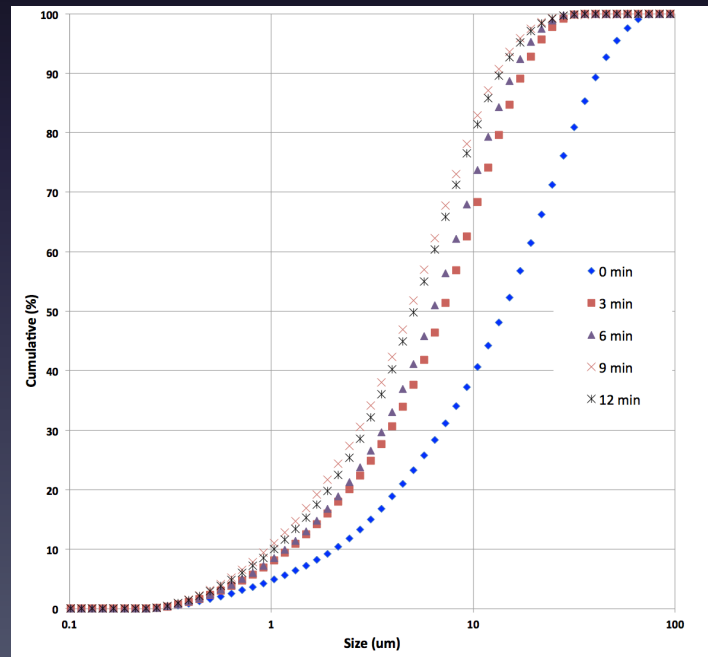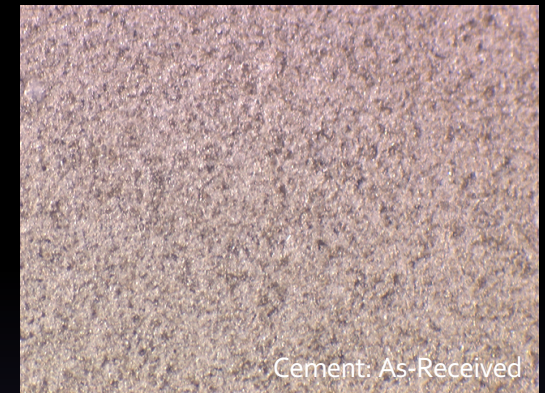
Preparing Powders

Jaw Crusher – down to mm-sized fragments
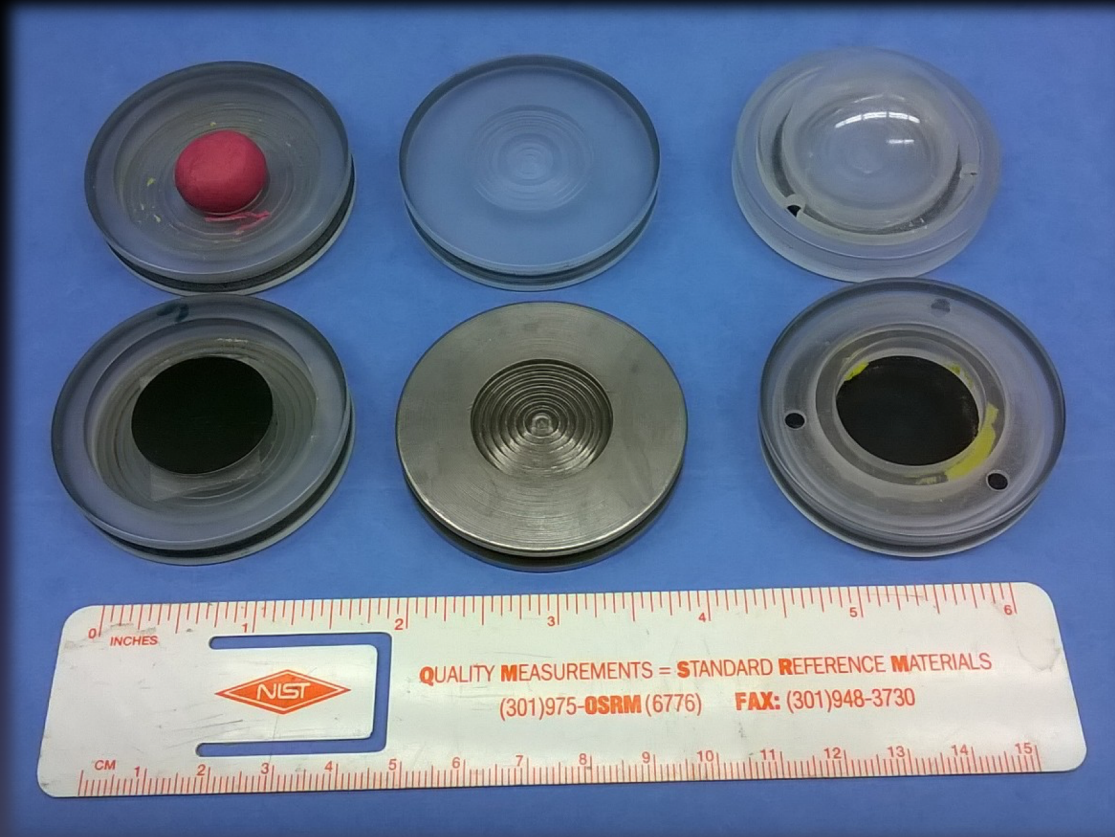

Mortar and Pestle – to -50 um

to -10 um

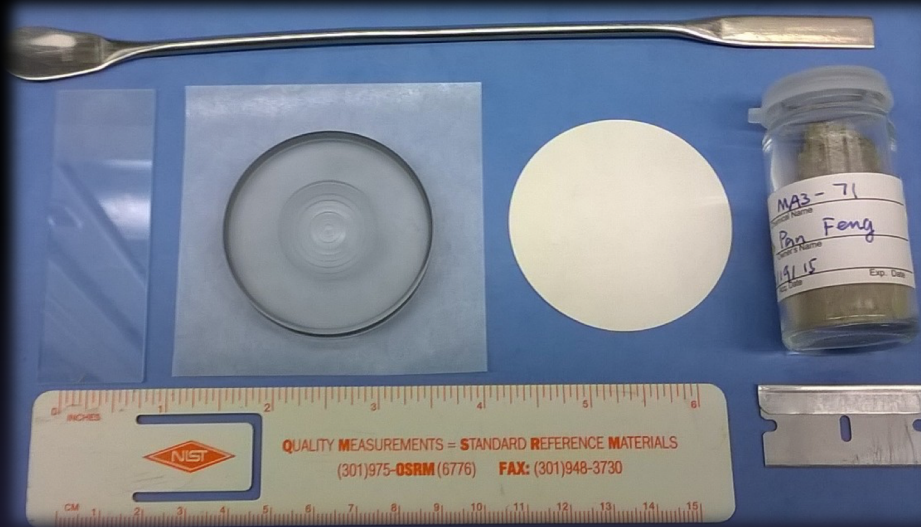Splitter for subsampling

Preparing Specimen Mounts

A wide range of specimen mounts are available for normal and specialized applications
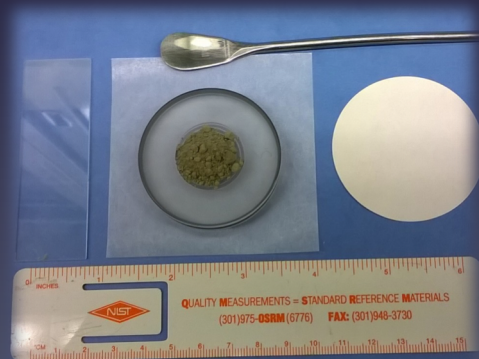
Preparing Powder Mounts

- Spatula
- Microscope slide
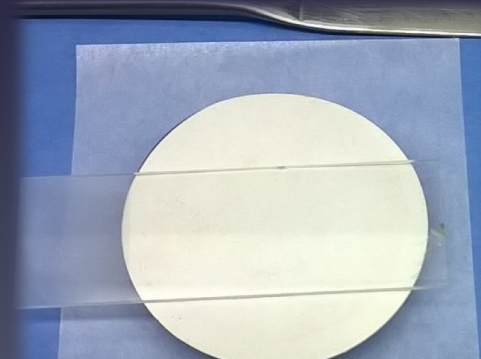- Cavity holder
- Weighing paper

Determine the approximate amount to make a compact specimen mount. For these holders, about 1.2 g is sufficient.

Level the surface by cutting with the spatula and gently tapping the mount, press it flush using the weighing paper and glass slide.
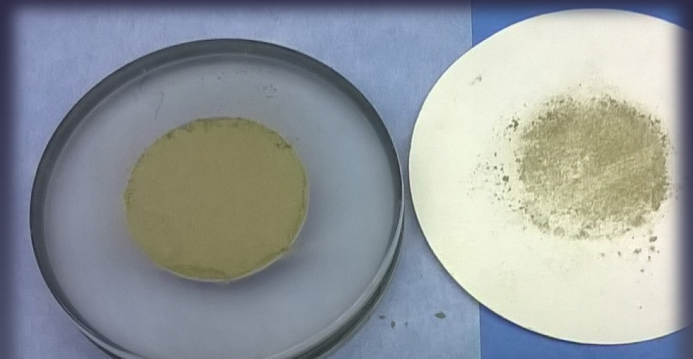
Pour approximate volume, level

Gently press with slide and paper
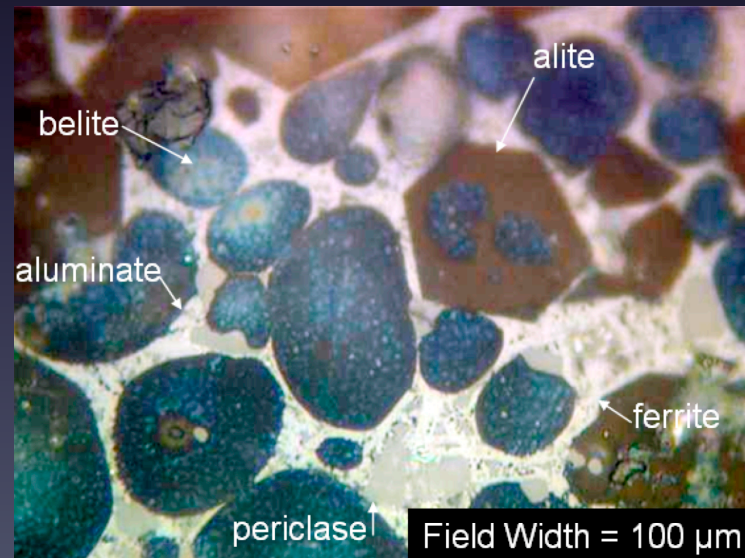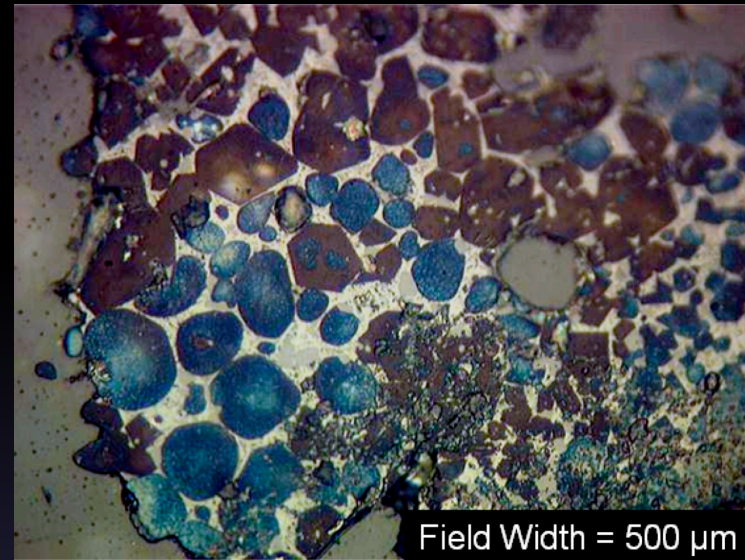

Examine surface for smoothness and uniformity

Powder on the holder surface will result in height displacement!

Clinker Phases

Clinker is comprised of a three-dimensional framework of alite and belite crystals and a matrix of aluminate and ferrite, crystallized from a molten liquid, periclase dispersed throughout as equant to dendritic crystals, alkali sulfates, which are typically located along fractures and pore walls. Finally, porosity may also be considered a component of the microstructure.

The phase texture, size and distribution reflect the history of the raw materials preparation, firing (clinkering), and cooling.

Field Width = 500 μm

belite, alite, aluminate, ferrite, periclase

Field Width = 100 μm

HFW Taylor, Cement Chemistry
DH Campbell, Microscopical Examination and Interpretation of Portland Cement and Clinker

Silicate Phases

Alite (Ca_3SiO_5): comprises 40 % to 70 % of a clinker, has triclinic, and monoclinic forms; impurities of up to about 4% stabilizes the monoclinic form; magnesium and aluminum may substitute for silicon and other substitutions include iron and sodium; distinct (idiomorphic) crystals exhibiting six-sides; density may range from 3.13 g/cm3 to 3.22 g/cm3

Belite (Ca_2SiO_4): comprises 10 % to 30 % of a clinker as a series of orthorhombic and monoclinic solid solution phases; impurities of up to 6 % as Mg, K, Na, Al, Mn, P, Fe and S may stabilize the polymorphs such as the beta form (most common), alpha, alpha-prime, gamma; as idiomorphous, rounded grains often exhibiting a lameller texture due to twinning; density (beta form) is 3.28 g/cm3

Field Width = 500 μm

alite
belite
aluminate
ferrite
periclase
Field Width = 100 μm
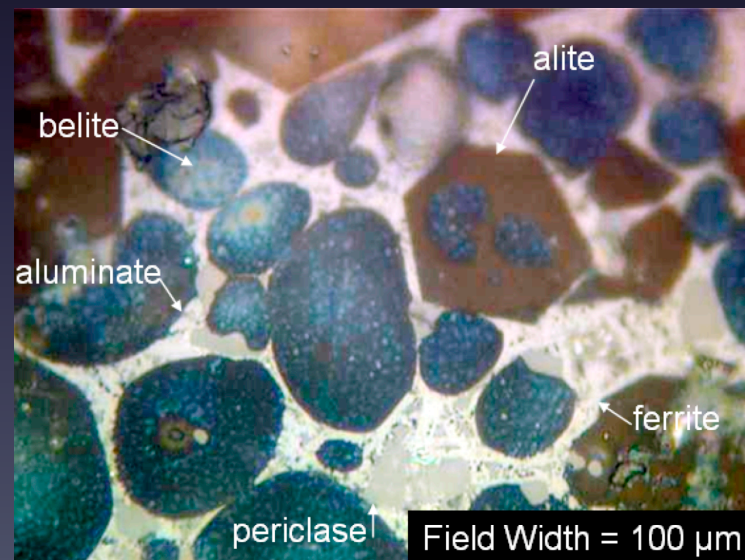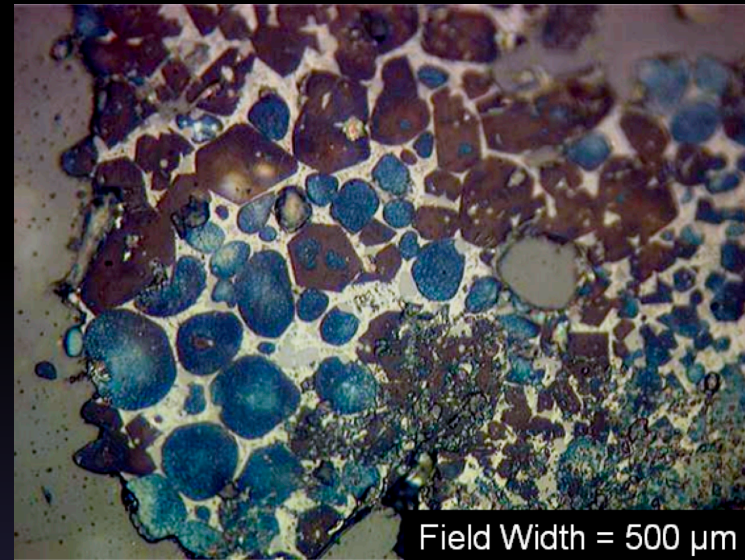
Interstitial Phases

Aluminate ($Ca_3Al_2O_6$): comprises up to 18 % of a clinker as xenomorphic or anhedral (no distinct form) crystals intermixed with the ferrite phase has cubic, orthorhombic, and monoclinic forms; impurities of up to about 10 % include Mg, Si, K, and Na; alkali aluminate is typically orthorhombic and monoclinic, may exhibit a lath-like texture; density around 3.064 g/cm^3 for the cubic form and 3.052 g/cm^3 for orthorhombic

Ferrite ($Ca_4Fe_4O_{10}$ to $Ca_4FeAl_3O_{10}$): is an orthorhombic solid solution comprises about 14 % of a clinker; impurities of up to 13 % as Mg, K, Na, Al, Mn, and Ti; exhibiting a lath-like (slow cooling) to dendritic (rapid cooling) texture; density is 3.77 g/cm^3

HV 10.0 kV | WD 12.13 mm | 10 µm

ferrite (dendritic)
void
belite
aluminate
alite
Field Width = 100 µm
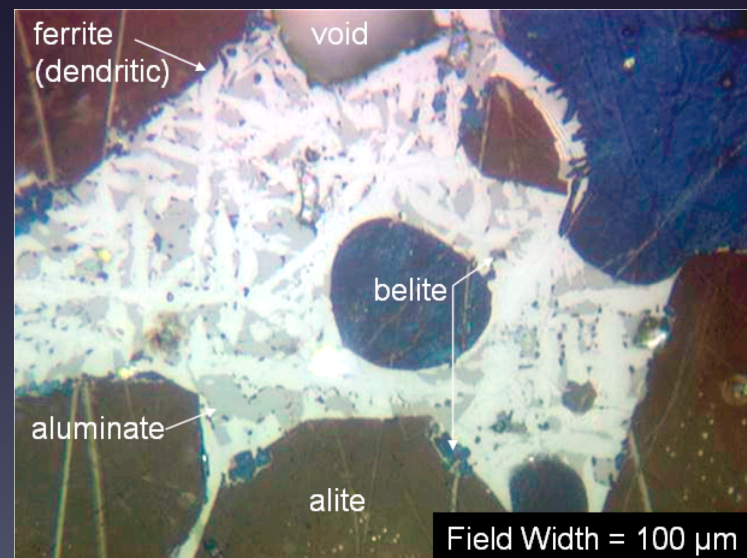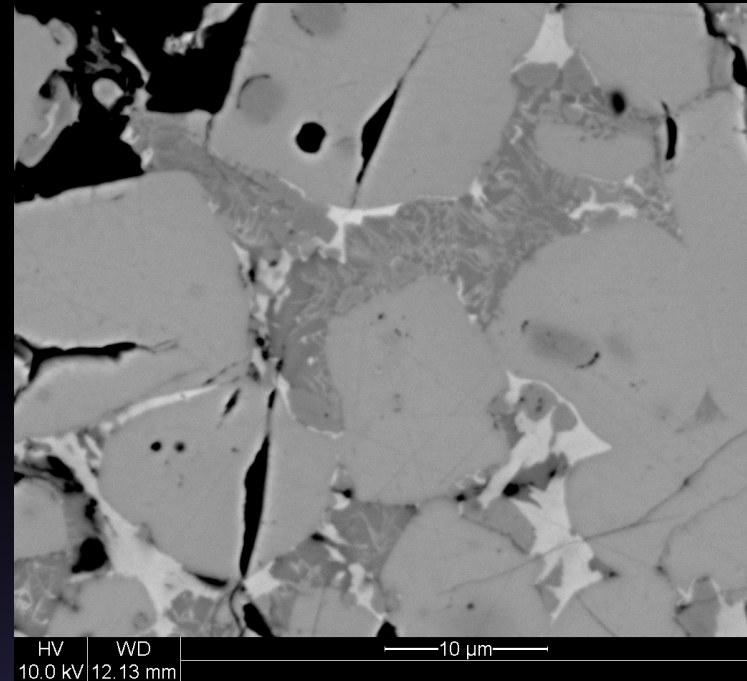
Dispersed Phases

Free Lime (CaO): Cubic, rounded, idiomorphous grains, sometimes agglomerated and retaining the shape of the parent limestone fragment; density of 3.32 g/cm^3

Periclase (MgO): Cubic, euhedral (equiaxed),rounded to dendritic grains free within the clinker and as inclusions in the silicates and interstitial phases, comprising up to 7 % of a clinker; density of 3.58 g/cm^3

Na and K sulfates may only comprise up to a few percent of the clinker but can affect early hydration as they typically form along pore and fracture surfaces and have a high solubility.
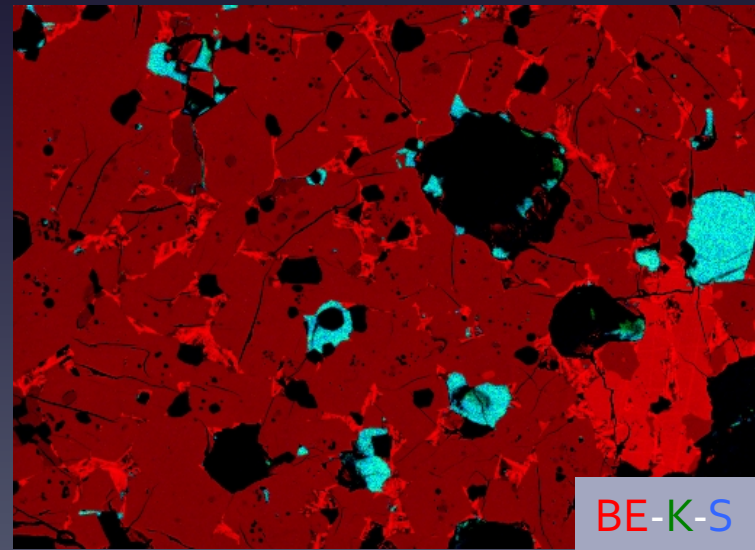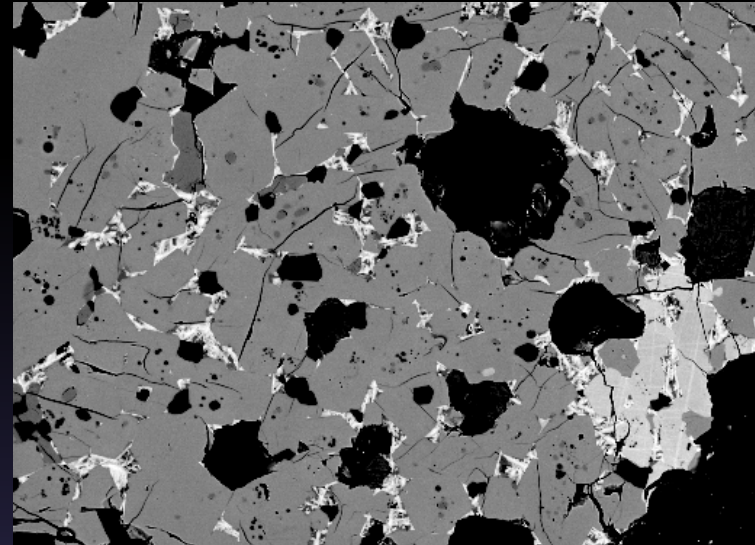
Arcanite (K_2SO_4); orthorhombic; density of 2.67 g/cm^3

Aphthitalite (($K_2Na)_2SO_4$); trigonal; density of 2.66 to 2.71 g/cm^3

Ca Langbeinite (K_2SO_4 $2CaSO_4$); cubic; density of 2.87 g/cm^3

Thenardite (Na_2SO_4) ; orthorhombic; density of 2.67 g/cm^3

Syngenite ($K_2Ca(SO_4)_2$ H2O; monoclinic, secondary product in cements density of 2.6 g/cm^3

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Mn_2O_3	Fe_2O_3
alite	0.1	1.1	1.0	25.2	0.1	0.1	0.1	71.6	0.0	0.0	0.7
belite	0.1	0.5	2.1	31.5	0.1	0.2	0.9	63.5	0.2	0.0	0.9
aluminate (cubic.)	1.0	1.4	31.3	3.7	0.0	0.0	0.7	56.6	0.2	0.0	5.1
ferrite	0.1	3.0	21.9	3.6	0.0	0.0	0.2	47.5	1.6	0.7	21.4
aluminate (orthorhombic)	0.6	1.2	28.9	4.3	0.0	0.0	4.0	53.9	0.5	0.0	6.6
aluminate (low Fe)	0.4	1.0	33.8	4.6	0.0	0.0	0.5	58.1	0.6	0.0	1.0
ferrite (low Al)	0.4	3.7	16.2	5.0	0.0	0.3	0.2	47.8	0.6	1.0	25.4

Typical chemical compositions for the primary phases in cement clinkers. Taylor, 1997

BE-K-S

Clinker and Cement Phase Identification Cheat Sheet

Clinker

Alite (Ca_3SiO_5): M1, M3
Belite (Ca_2SiO_4): β, $\boldsymbol{\alpha}$, $\boldsymbol{\alpha'}$, γ
Aluminate ($Ca_3Al_2O_6$): cubic, orthorhombic
Ferrite ($Ca_4Fe_4O_{10}$ to $Ca_4FeAl_3O_{10}$)
Free Lime (CaO)
Periclase (MgO)
Arcanite (K_2SO_4)
Aphthitalite (($K_2Na)_2SO_4$)
Ca Langbeinite (K_2SO_4 $2CaSO_4$)
Thenardite (Na_2SO_4)

Cement

Anhydrite ($CaSO_4$)
Bassanite ($CaSO_4$ 0.5 (H_2O))
Gypsum ($CaSO_4$ 2(H_2O))
Calcite ($CaCO_3$)
Quartz (SiO_2)

Hydration Products

Syngenite ($K_2Ca(SO_4)_2$ H_2O
Portlandite ($Ca(OH_2)$)
Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$ $26H_2O$)

Phase Identification: 1

d-Spacing	Two-Theta	I/I100
2.432	36.93	9
2.106	42.90	100
1.489	62.29	44
1.270	74.66	5

Traditional methods - manual search-match using the Hanawalt method.

- Identify significant peak positions and relative intensities
    - correction for displacement errors would requite some kind of internal standard.
        - otherwise, keep in mind the need for some flexibility in peak locations
    - relative intensity is useful but secondary to peak position and the collective set of peaks

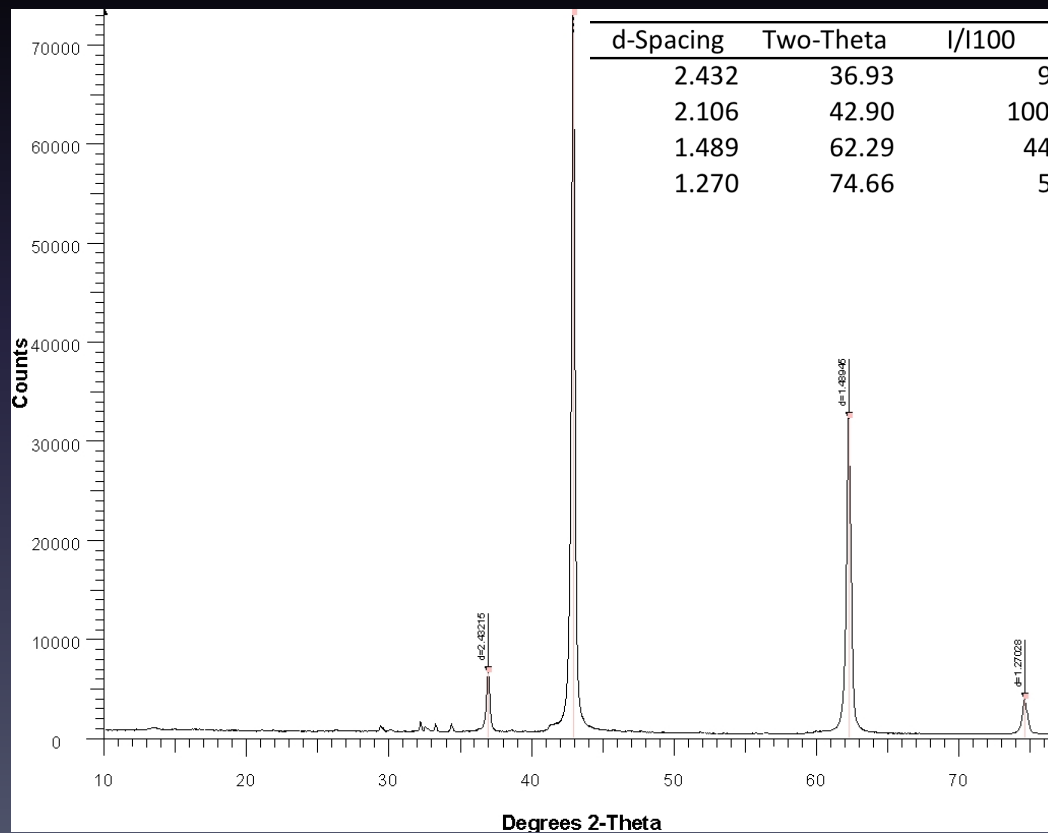- List peak d&I in order of relative intensity

Phase Identification: 1

Traditional methods - manual search-match using the Hanawalt method.

- List peak d&I in order of relative intensity

- Search on strongest peak followed by second and third strongest.

- Each entry is listed three times to account for relative intensity error

Any guesses?

d-Spacing	Two-Theta	I/I100
2.432	36.93	9
2.106	42.90	100
1.489	62.29	44
1.270	74.66	5

Computer-Aided Search-Match

- Mark peak positions and relative intensities
- Set negative and positive chemistry
- set subfiles; user-created subfile if possible

Computer-Aided Search-Match
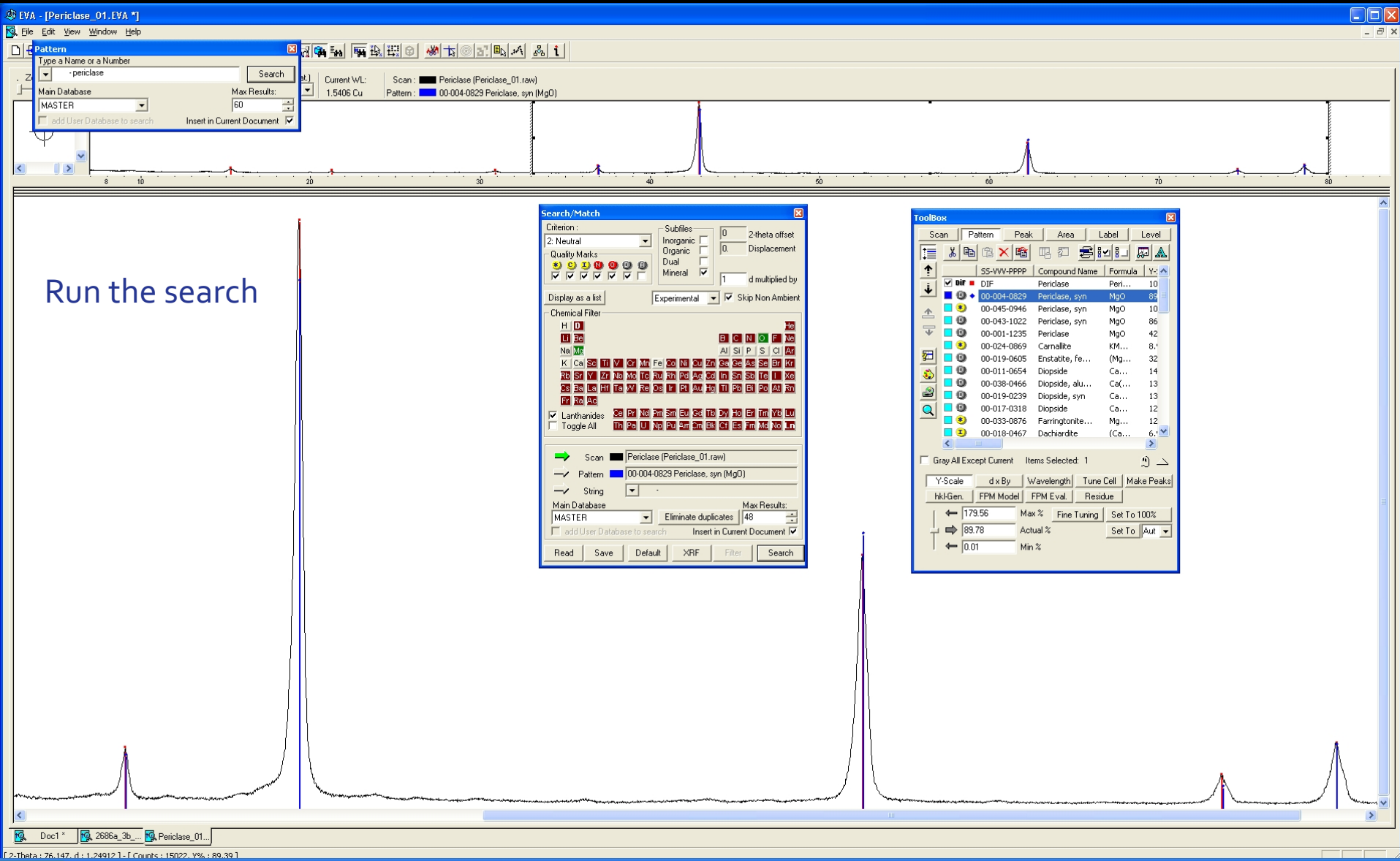
Computer-Aided Search-Match

Computer-Aided Search-Match

Check the stick figures against the pattern; consider the plausibility of the chemistry

Some are close!
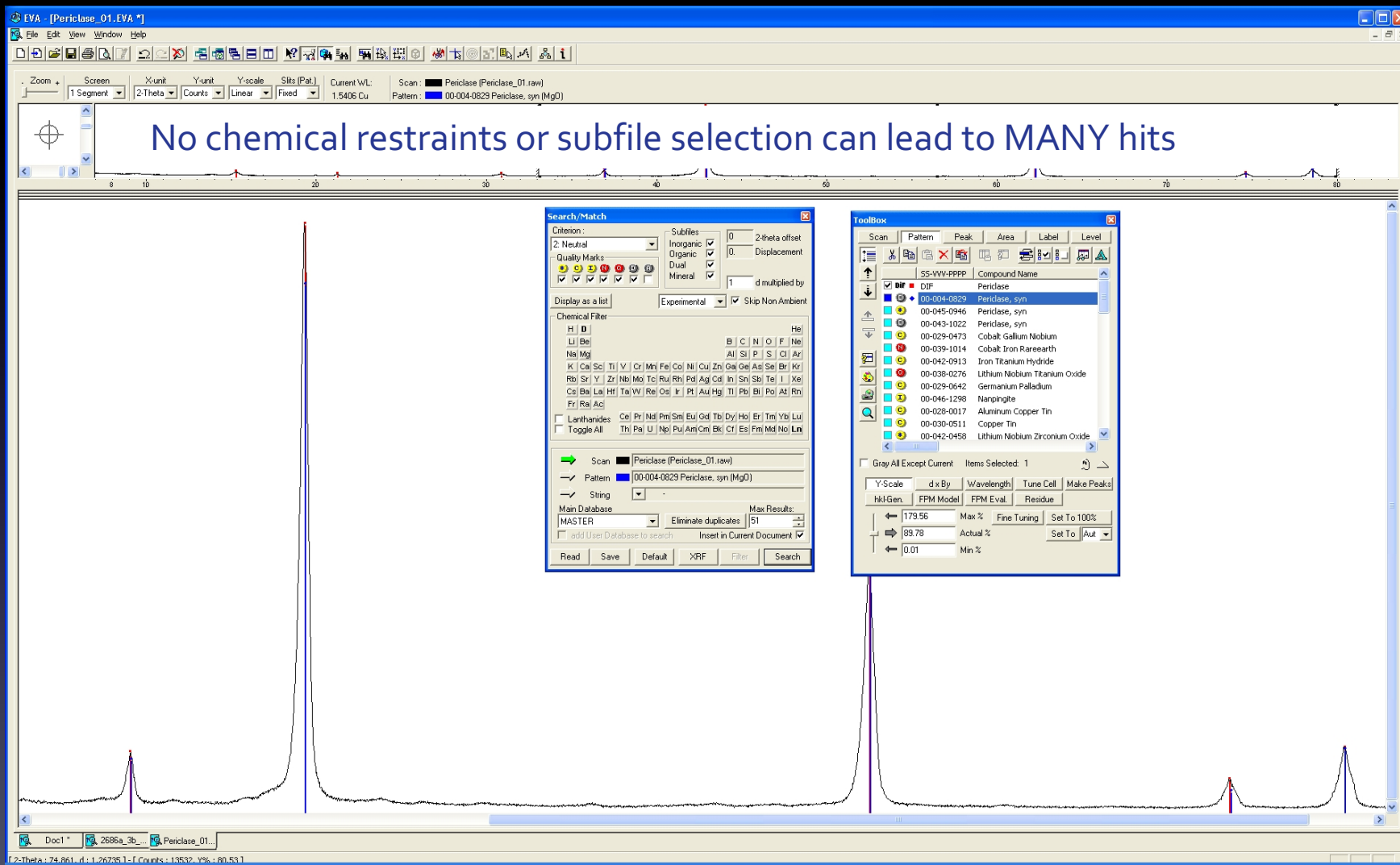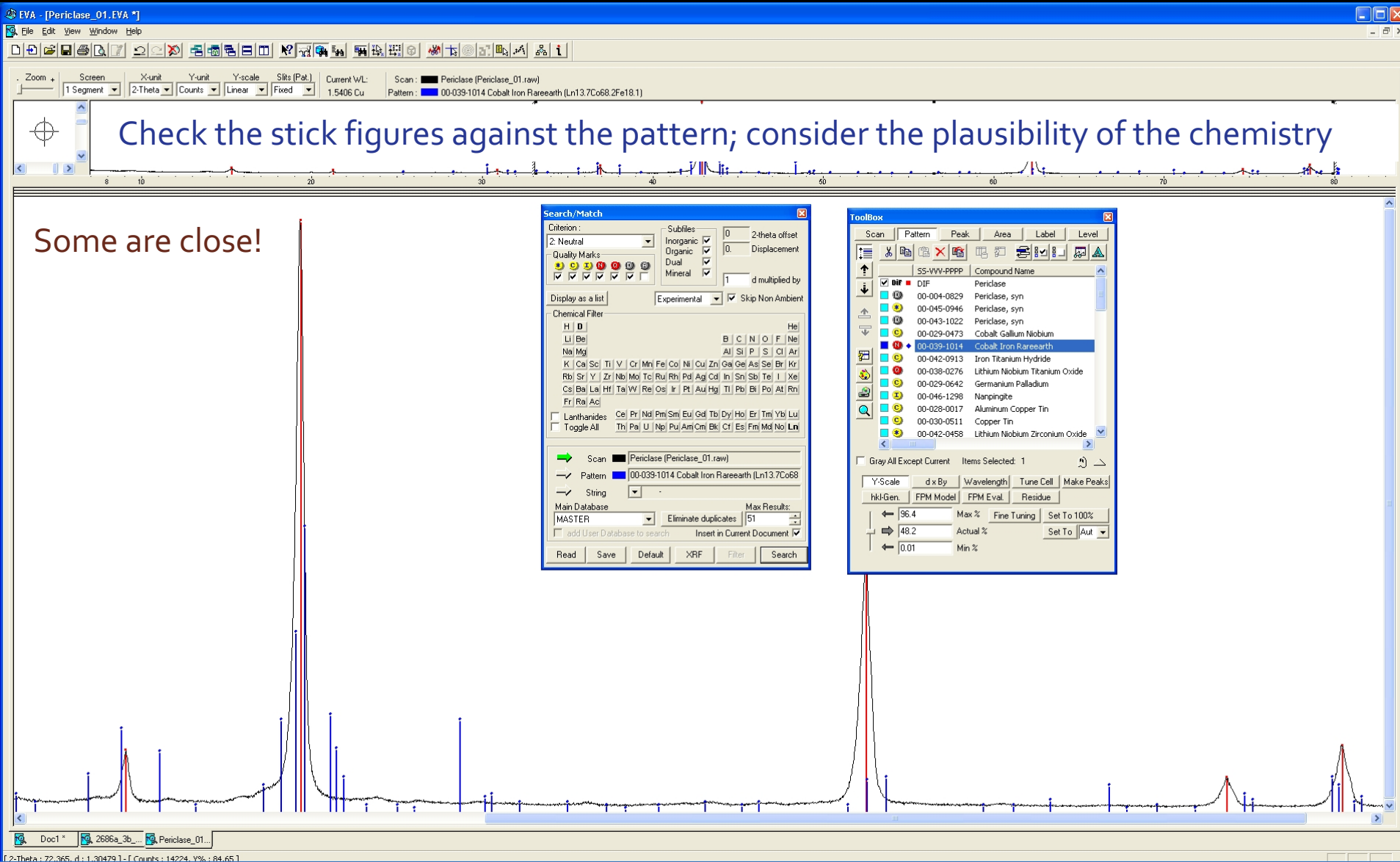
Computer-Aided Search-Match
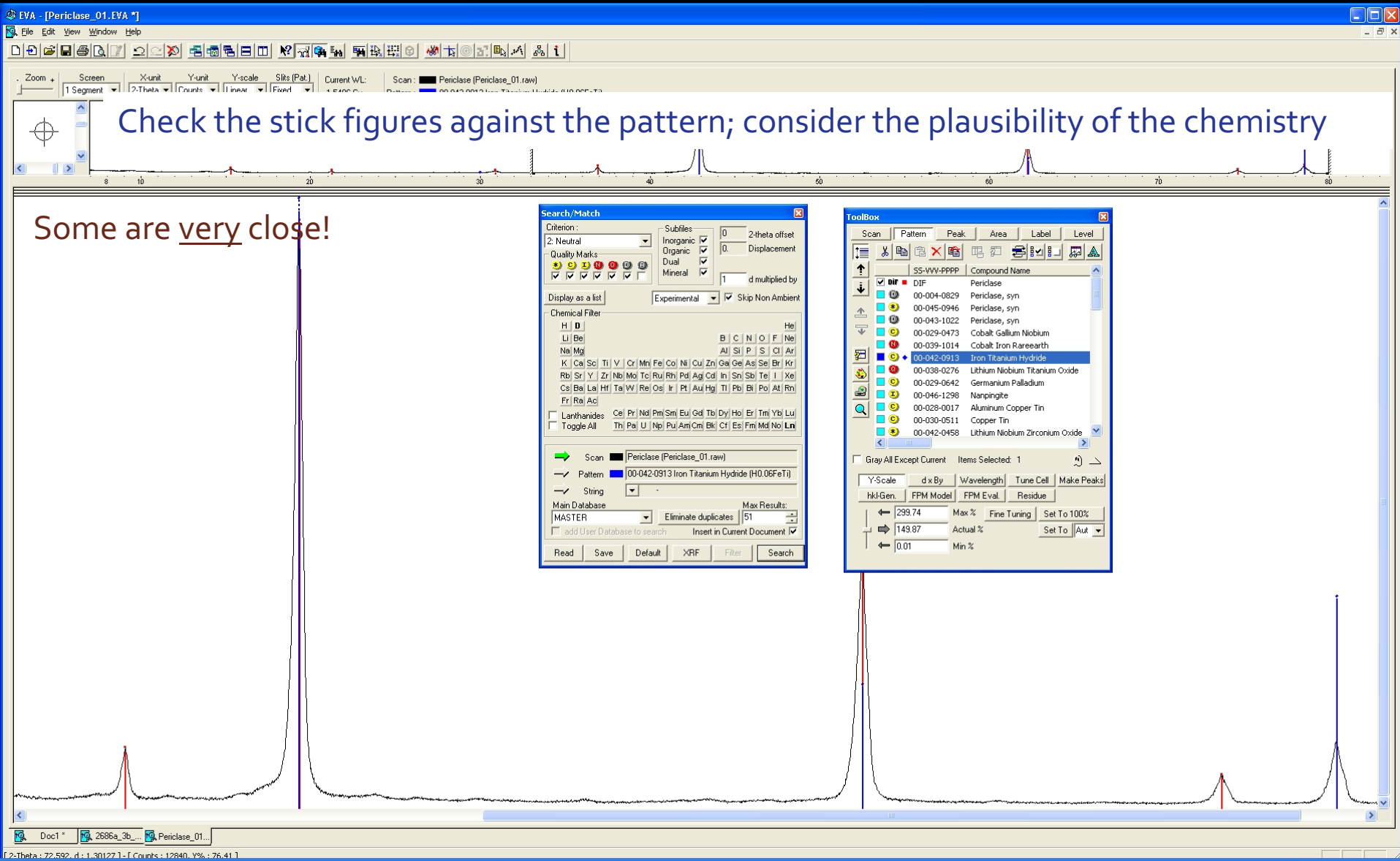
Check against the ICDD Database Card Files using either the D & I values or a graphical representation as a stick figure against the diffraction pattern.

Recall that the specimen displacement error is the greatest so expect some peak shifting.

For clinker phases, chemical substitution will also affect the peak positions.

The high degree of pattern overlap and the number of phases also complicates identification. Therefore, an alternative is to look for the key resolvable peaks and then check the cards.

Peaks not assigned to a phase may be from some new phase

Larnite, syn
Ca2 Si O4   <Colorles

Radiation: CuKa1	Lambda= 1.540598	Filter=
Calibration: Internal(Si)	d-Cutoff=	I/Ic(RIR)=

Ref: Natl. Bur. Stand. (U.S.) Monogr. 25, 19 29 (1982)

Monoclinic (?), P21/n(14)   Z= 4   mp=
Cell= 9.310x6.7565x5.5059<94.46>   Pearson: mP28 (?)
Dx= 3.313   Dm= 3.280   Mwt= 172.24   Vol= 345.29   F(30)=51.6(.0135,43)
Ref: Ibid.

Strong Line: 2.78/X 2.79/X 2.75/8 2.19/5 2.61/4 2.72/3 1.98/2 2.81/2 2.28/2 2.88/2

The sample was prepared by heating Ca C O3 and Si O2 with 0.5% B2 O3 at 900 C for 20 minutes, raised to 1450 C over 45 minutes, heated for 20 minutes and air quenched. Pattern taken at 25 C. Chemical analysis (wt.%): Si O2 34.56, CaO 64.24, minor Al2 O3, Fe2 O3, S O3, Na2 O, K2 O, Ti O2, B2 O3. Optical data on specimen from Larne, Ireland, UK. To replace 9-351 and 24-37 and validated by calculated pattern 29-371.

#	d(A)	I(f)	I(v)	h	k	l	2-Theta	Theta	1/(2d)
1>	4.8920	3	2	-1	0	1	18.119	9.059	0.1022
2>	4.6410	9	5	2	0	0	19.108	9.554	0.1077
3>	3.8240	5	4	2	1	0	23.242	11.621	0.1308
4>	3.7860	5	4	1	1	1	23.478	11.739	0.1321
5>	3.3780	7	6	0	2	0	26.362	13.181	0.1480
6>	3.2410	6	5	-2	1	1	27.498	13.749	0.1543
7>	3.1760	5	4	1	2	0	28.072	14.036	0.1574
8>	3.0490	9	8	2	1	1	29.267	14.633	0.1640
9>	2.8770	21	20	0	2	1	31.059	15.530	0.1738
10>	2.8140	22	22	3	1	0	31.773	15.886	0.1777
11>	2.7900	97	97	-3	0	1	32.054	16.027	0.1792
12>	2.7830	100	100	-1	2	1	32.136	16.068	0.1797
13>	2.7450	83	84	0	0	2	32.594	16.297	0.1821
14>	2.7180	30	31	1	2	1	32.926	16.463	0.1840
15>	2.6100	42	45	3	0	1	34.330	17.165	0.1916
16>	2.5450	9	10	0	1	2	35.235	17.618	0.1965
17>	2.4480	12	14	-2	0	2	36.680	18.340	0.2042
18>	2.4330	9	10	3	1	1	36.915	18.457	0.2055
19>	2.4100	13	15	1	1	2	37.280	18.640	0.2075
20>	2.4030	18	21	2	2	1	37.392	18.696	0.2081
21>	2.3230	2	2	4	0	0	38.730	19.365	0.2152
22>	2.3010	4	5	-2	1	2	39.116	19.558	0.2173
23>	2.2810	22	27	3	2	0	39.473	19.736	0.2192
24>	2.1890	51	65	1	3	0	41.206	20.603	0.2284
25>	2.1650	13	17	2	1	2	41.683	20.842	0.2309
26>	2.1290	7	9	0	2	2	42.422	21.211	0.2349
27>	2.1030	1	1	-1	2	2	42.972	21.486	0.2378
28>	2.0910	6	8	-4	1	1	43.231	21.616	0.2391
29>	2.0830	6	8	0	3	1	43.406	21.703	0.2400
30>	2.0500	14	19	1	2	2	44.141	22.070	0.2439

Key Lines for Cement Phase Identification using XRD

d-Spacing	Two-Theta	Phase
7.627	11.593	gypsum (100)
7.249	12.200	C4AF (45)
5.997	14.759	bassanite (80)
5.970	14.827	triclinic C3S (12)
5.953	14.869	triclinic C3S (12)
5.927	14.935	triclinic C3S (12)
5.927	14.935	mono. C3S (12)
5.610	15.784	γC2S (19)
5.107	17.350	C3Ao (10)
4.917	18.026	aphthitalite (10)
4.659	19.033	thenardite (71)
4.640	19.112	α'C2S (30)
4.316	20.561	γC2S (45)
4.284	20.717	gypsum (100)
4.253	20.869	langbeinite (30)
4.235	20.959	C3Ac (6)
4.222	21.024	langbeinite (25)
4.188	21.197	langbeinite (16)
4.175	21.264	arcanite (28)
4.158	21.352	arcanite (23)
4.091	21.706	aphthitalite (30)
4.079	21.770	C3Ac (12)
4.059	21.879	γ C2S (20)
3.900	22.783	αC2S (20)
3.886	22.866	triclinic C3S (10)
3.855	23.052	calcite (9)
3.838	23.156	thenardite (17)
3.817	23.285	γC2S (509)
3.810	23.328	α'C2S (30)
3.799	23.397	gypsum (17)
3.764	23.617	γC2S (119)
3.744	23.745	arcanite (18)
3.670	24.231	aphthitalite (20)
3.653	24.346	C4AF (16)
3.497	25.450	anhydrite (100)
3.468	25.666	bassanite (40)
3.462	25.711	langbeinite (12)
3.424	26.002	C3Ao (11)
3.385	26.307	arcanite (13)
3.379	26.354	γC2S (25)
3.370	26.426	α'C2S (30)
3.313	26.889	langbeinite (95)
3.271	27.241	langbeinite (80)
3.263	27.309	langbeinite (80)
3.225	27.637	langbeinite (100)
3.180	28.036	thenardite (52)
3.153	28.281	langbeinite (18)
3.114	28.643	langbeinite (18)
3.077	28.995	thenardite (55)
3.065	29.111	gypsum (75)
3.056	29.198	triclinic C3S (60)
3.045	29.306	bassanite (10)
3.038	29.375	M1 C3S (50)
3.036	29.400	calcite (100)
3.036	29.395	mono C3S (40)
3.034	29.415	m1 C3S (50)
3.025	29.504	triclinic C3S (65)
3.025	29.504	mono C3S (75)
3.011	29.645	γC2S (80)
3.002	29.736	bassanite (80)
3.000	29.756	arcanite (77)
2.985	29.909	triclinic C3S (25)
2.974	30.022	triclinic C3S (18)
2.972	30.043	M1 C3S (20)
2.968	30.084	mono C3S (12)
2.968	30.084	M1 C3S (20)
2.965	30.115	triclinic C3S (20)
2.961	30.157	mono C3S (25)
2.940	30.378	aphthitalite (75)
2.902	30.785	arcanite (100)
2.894	30.872	γC2S (25)
2.886	30.960	arcanite (53)
2.880	31.026	langbeinite (18)
2.876	31.070	βC2S (21)
2.872	31.115	gypsum (45)
2.870	31.137	α'C2S (30)
2.850	31.361	anhydrite (29)
2.843	31.440	calcite (2)
2.838	31.497	aphthitalite (100)
2.813	31.784	βC2S (22)
2.813	31.784	bassanite (100)
2.810	31.819	αC2S (80)
2.790	32.053	βC2S (97)
2.788	32.077	triclinic C3S (100)
2.788	32.077	gypsum (10)
2.786	32.101	langbeinite (45)
2.784	32.124	C4AF (25)
2.784	32.124	thenardite (100)
2.782	32.148	βC2S (100)
2.776	32.220	free lime (36)
2.775	32.231	M1 C3S (100)
2.775	32.231	langbeinite (50)
2.773	32.255	mono C3S (85)
2.767	32.327	triclinic C3S (70)
2.754	32.484	triclinic C3S (65)
2.750	32.533	γC2S (70)
2.750	32.533	langbeinite (45)
2.747	32.569	mono C3S (45)
2.747	32.569	M1 C3S (40)
2.745	32.593	βC2S (83)
2.743	32.618	M1 C3S (60)
2.743	32.618	langbeinite (45)
2.740	32.655	α'C2S (100)
2.737	32.691	mono C3S (75)
2.736	32.704	triclinic C3S (60)
2.717	32.939	βC2S (30)
2.714	32.976	C3Ao (65)
2.714	32.976	bassanite (10)
2.710	33.026	αC2S (100)
2.698	33.178	C3Ac (100)
2.692	33.254	C3Ao (100)
2.684	33.356	gypsum (35)
2.680	33.407	α'C2S (75)
2.673	33.497	C4AF (35)
2.647	33.836	thenardite (52)
2.644	33.875	C4AF (100)
2.618	34.222	triclinic C3S (60)
2.612	34.303	triclinic C3S (90)
2.610	34.330	βC2S (42)
2.607	34.371	M1 C3S (70)
2.605	34.398	M1 C3S (80)
2.603	34.425	mono C3S (100)
2.590	34.604	γC2S (14)
2.576	34.798	C4AF (17)
2.517	35.640	arcanite (13)
2.514	35.684	γC2S (25)
2.499	35.906	arcanite (15)
2.495	35.968	calcite (15)
2.494	35.980	gypsum (11)
2.458	36.526	triclinic C3S (12)
2.458	36.526	aphthitalite (15)
2.455	36.572	γC2S (17)
2.448	36.680	βC2S (12)
2.442	36.774	aphthitalite (16)
2.430	36.962	periclase (10)
2.422	37.088	arcanite (25)
2.409	37.296	βC2S (13)
2.405	37.360	free lime (100)
2.402	37.408	βC2S (18)
2.385	37.685	arcanite (13)
2.374	37.866	arcanite (17)
2.360	38.100	α'C2S (30)
2.339	38.455	triclinic C3S (15)
2.329	38.627	triclinic C3S (20)
2.329	38.627	thenardite (25)
2.329	38.627	aphthitalite (14)
2.328	38.644	anhydrite (20)
2.325	38.696	γC2S (15)
2.323	38.725	M1 C3S (10)
2.319	38.800	M1 C3S (20)
2.315	38.870	triclinic C3S (25)
2.315	38.870	mono C3S (10)
2.285	39.408	calcite (20)
2.280	39.491	βC2S (22)
2.280	39.491	triclinic C3S (11)
2.270	39.672	α'C2S (10)
2.268	39.709	bassanite (10)
2.230	40.415	α'C2S (30)
2.220	40.605	αC2S (40)
2.218	40.643	gypsum (15)
2.209	40.816	anhydrite (20)
2.205	40.893	C3Ao (20)
2.205	40.893	arcanite (14)
2.203	40.932	C3Ac (10)
2.196	41.068	langbeinite (12)
2.195	41.088	triclinic C3S (75)
2.189	41.206	βC2S (51)
2.184	41.304	M1 C3S (40)
2.181	41.364	mono C3S (60)
2.180	41.383	α'C2S (30)
2.179	41.403	triclinic C3S (17)
2.179	41.403	M1 C3S (40)
2.171	41.563	triclinic C3S (11)
2.169	41.603	M1 C3S (10)
2.166	41.663	M1 C3S (10)
2.164	41.704	βC2S (13)
2.164	41.704	mono C3S (15)
2.163	41.724	triclinic C3S (11)
2.162	41.744	M1 C3S (10)
2.136	42.276	bassanite (20)
2.109	42.844	langbeinite (18)
2.105	42.930	periclase (100)
2.094	43.157	calcite (15)
2.093	43.188	langbeinite (20)
2.088	43.297	arcanite (25)
2.085	43.362	gypsum (25)
2.082	43.428	arcanite (25)
2.073	43.626	gypsum (15)
2.051	44.118	C4AF(35)
2.050	44.141	βC2S (14)
2.041	44.346	aphthitalite (45)
2.036	44.461	langbeinite (14)
2.026	44.692	βC2S (25)
2.024	44.738	γC2S (13)
2.020	44.832	α'C2S (30)
2.019	44.855	βC2S (15)
2.017	44.902	langbeinite (20)
2.009	45.091	langbeinite (14)
1.994	45.449	triclinic C3S (10)
1.982	45.740	M1 C3S (10)
1.981	45.764	βC2S (20)
1.973	45.960	mono C3S (10)
1.940	46.788	αc2s (60)
1.937	46.865	M1 C3S (10)
1.933	46.968	M1 C3S (10)
1.930	47.045	α'C2S (30)
1.930	47.045	mono C3S (13)
1.928	47.097	C4AF(35)

d-Spacing	Two-Theta	I/I100
2.432	36.93	9
2.106	42.90	100
1.489	62.29	44
1.270	74.66	5

d-Spacing	Two-Theta	Phase	d-Spacing	Two-Theta	Phase
7.627	11.593		3.036	29.400	calcite (100)
7.249	12.200	C4AF (45)	3.036	29.395	mono C3S (40)
5.997	14.759	bassanite (80)	3.034	29.415	m1 C3S (50)
5.970	14.827	triclinic C3S (12)	3.025	29.504	triclinic C3S (65)
5.953	14.869	triclinic C3S (12)	3.025	29.504	mono C3S (75)
5.927	14.935	triclinic C3S (12)	3.011	29.645	γC2S (80)
5.927	14.935	mono. C3S (12)	3.002	29.736	bassanite (80)
5.610	15.784	γC2S (19)	3.000	29.756	arcanite (77)
5.107	17.350	C3Ao (10)	2.985	29.909	triclinic C3S (25)
4.917	18.026	aphthitalite (10)	2.974	30.022	triclinic C3S (18)
4.659	19.033	thenardite (71)	2.972	30.043	M1 C3S (20)
4.640	19.112	α′C2S (20)	2.968	30.084	mono C3S (12)
4.316	20.561	γC2S (45)	2.968	30.084	M1 C3S (20)
4.284	20.717	gypsum (100)	2.965	30.115	triclinic C3S (20)
4.253	20.869	langbeinite (30)	2.961	30.157	mono C3S (25)
4.235	20.959	C3Ac (6)	2.940	30.378	aphthitalite (75)
4.222	21.024	langbeinite (25)	2.902	30.785	arcanite (100)
4.188	21.197	langbeinite (16)	2.894	30.872	γC2S (25)
4.175	21.264	arcanite (28)	2.886	30.960	arcanite (53)
4.158	21.352	arcanite (23)	2.880	31.026	langbeinite (18)
4.091	21.706	aphthitalite (30)	2.876	31.070	βC2S (21)
4.079	21.770	C3Ac (12)	2.872	31.115	gypsum (45)
4.059	21.879	γ C2S (20)	2.870	31.137	α′C2S (30)
3.900	22.783	αC2S (20)	2.850	31.361	anhydrite (29)
3.886	22.866	triclinic C3S (10)	2.843	31.440	calcite (2)
3.855	23.052	calcite (9)	2.838	31.497	aphthitalite (100)
3.838	23.156	thenardite (17)	2.813	31.784	βC2S (22)
3.817	23.285	γC2S (509)	2.813	31.784	bassanite (100)
3.810	23.328	α′C2S (30)	2.810	31.819	αC2S (80)
3.799	23.397	gypsum (17)	2.790	32.053	βC2S (97)
3.764	23.617	γC2S (119)	2.788	32.077	triclinic C3S (100)
3.744	23.745	arcanite (18)	2.788	32.077	gypsum (10)
3.670	24.231	aphthitalite (20)	2.786	32.101	langbeinite (45)
3.653	24.346	C4AF (16)	2.784	32.124	C4AF (25)
3.497	25.450	anhydrite (100)	2.784	32.124	thenardite (100)
3.468	25.666	bassanite (40)	2.782	32.148	βC2S (100)
3.462	25.711	langbeinite (12)	2.776	32.220	free lime (36)
3.424	26.002	C3Ao (11)	2.775	32.231	M1 C3S (100)
3.385	26.307	arcanite (13)	2.775	32.231	langbeinite (50)
3.379	26.354	γC2S (25)	2.773	32.255	mono C3S (85)
3.370	26.426	α′C2S (30)	2.767	32.327	triclinic C3S (70)
3.313	26.889	langbeinite (95)	2.754	32.484	triclinic C3S (65)
3.271	27.241	langbeinite (80)	2.750	32.533	γC2S (70)
3.263	27.309	langbeinite (80)	2.750	32.533	langbeinite (45)
3.225	27.637	langbeinite (100)	2.747	32.569	mono C3S (45)
3.180	28.036	thenardite (52)	2.747	32.569	M1 C3S (40)
3.153	28.281	langbeinite (18)	2.745	32.593	βC2S (83)
3.114	28.643	langbeinite (18)	2.743	32.618	M1 C3S (60)
3.077	28.995	thenardite (55)	2.743	32.618	langbeinite (45)
3.065	29.111	gypsum (75)	2.740	32.655	α′C2S (100)
3.056	29.198	triclinic C3S (60)	2.737	32.691	mono C3S (75)
3.045	29.306	bassanite (10)			

d-Spacing	Two-Theta	Phase	d-Spacing	Two-Theta	Phase
2.736	32.704	triclinic C3S (60)	2.268	39.709	bassanite (10)
2.717	32.939	βC2S (30)	2.230	40.415	α′C2S (30)
2.714	32.976	C3Ao (65)	2.220	40.605	αC2S (40)
2.714	32.976	bassanite (10)	2.218	40.643	gypsum (15)
2.710	33.026	αC2S (100)	2.209	40.816	anhydrite (15)
2.698	33.178	C3Ac (100)	2.205	40.893	C3Ao (20)
2.692	33.254	C3Ao (100)	2.205	40.893	arcanite (14)
2.684	33.356	gypsum (35)	2.203	40.932	C3Ac (10)
2.680	33.407	α′C2S (75)	2.196	41.068	langbeinite (12)
2.673	33.497	C4AF (35)	2.195	41.088	triclinic C3S (75)
2.647	33.836	thenardite (52)	2.189	41.206	βC2S (51)
2.644	33.875	C4AF (100)	2.184	41.304	M1 C3S (40)
2.618	34.222	triclinic C3S (60)	2.181	41.364	mono C3S (60)
2.612	34.303	triclinic C3S (90)	2.180	41.383	α′C2S (30)
2.610	34.330	βC2S (42)	2.179	41.403	triclinic C3S (35)
2.607	34.371	M1 C3S (70)	2.179	41.403	M1 C3S (40)
2.605	34.398	M1 C3S (80)	2.171	41.563	triclinic C3S (11)
2.603	34.425	mono C3S (100)	2.169	41.603	M1 C3S (10)
2.590	34.604	γC2S (14)	2.166	41.663	M1 C3S (10)
2.576	34.798	C4AF(17)	2.164	41.704	βC2S (13)
2.517	35.640	arcanite (13)	2.164	41.704	mono C3S (15)
2.514	35.684	γC2S (25)	2.163	41.724	triclinic C3S (11)
2.499	35.906	arcanite (15)	2.162	41.744	M1 C3S (10)
2.495	35.968	calcite (15)	2.136	42.276	bassanite (20)
2.494	35.980	gypsum (11)	2.109	42.844	langbeinite (18)
2.458	36.526	triclinic C3S (12)	2.105	42.930	periclase (100)
2.458	36.526	aphthitalite (10)	2.094	43.157	calcite (15)
2.455	36.572	γC2S (17)	2.093	43.188	langbeinite (20)
2.448	36.680	βC2S (12)	2.088	43.297	arcanite (25)
2.442	36.774	aphthitalite (16)	2.085	43.362	gypsum (20)
2.430	36.962	periclase (10)	2.082	43.428	arcanite (25)
2.422	37.088	arcanite (25)	2.073	43.626	gypsum (15)
2.409	37.296	βC2S (13)	2.051	44.118	C4AF(35)
2.405	37.360	free lime (100)	2.050	44.141	βC2S (14)
2.402	37.408	βC2S (18)	2.041	44.346	aphthitalite (45)
2.385	37.685	arcanite (15)	2.036	44.461	langbeinite (14)
2.374	37.866	arcanite (17)	2.026	44.692	βC2S (35)
2.360	38.100	α′C2S (30)	2.024	44.738	γC2S (13)
2.339	38.455	triclinic C3S (15)	2.020	44.832	α′C2S (30)
2.329	38.627	triclinic C3S (20)	2.019	44.855	βC2S (20)
2.329	38.627	thenardite (25)	2.017	44.902	langbeinite (20)
2.329	38.627	aphthitalite (14)	2.009	45.091	langbeinite (14)
2.328	38.644	anhydrite (20	1.994	45.449	triclinic C3S (10)
2.325	38.696	γC2S (20)	1.982	45.740	M1 C3S (10)
2.323	38.725	M1 C3S (10)	1.981	45.764	βC2S (20)
2.319	38.800	M1 C3S (20)	1.973	45.960	mono C3S (10)
2.315	38.870	triclinic C3S (20)	1.940	46.788	αc2s (60)
2.315	38.870	mono C3S (20)	1.937	46.865	M1 C3S (10)
2.285	39.408	calcite (20)	1.933	46.968	M1 C3S (10)
2.280	39.491	βC2S (22)	1.930	47.045	α′C2S (30)
2.280	39.491	triclinic C3S (11)	1.930	47.045	mono C3S (13)
2.270	39.672	α′C2S (10)	1.928	47.097	C4AF(35)

Practicum 2

Using the file <u>Cement Key Lines.pdf,</u> identify the single phases and simple mixture phases found in the folder XRD Phase Identification

Each folder contains
- an image of the pattern (.JPG),
- a .RAW powder diffraction data file (.RAW) that may be read into Profex,
- and a text file providing peak d-spacings, two-theta positions, and relative intensities

Work on identifying the file using the key lines and knowledge that it diffraction pattern is from a phase that is related to portland cement

Work in pairs if you wish

While most examples are of a single phase, one or more may be a mixture

Analysis of Clinker and Cements Using Selective Extractions

Phase Identification

Cement phases are a challenge and can be difficult to identify using the traditional methods

Tentative identification is made using diagnostic peaks for each phase rather than the traditional methods (three major peaks); confirmation uses the ICDD powder diffraction database
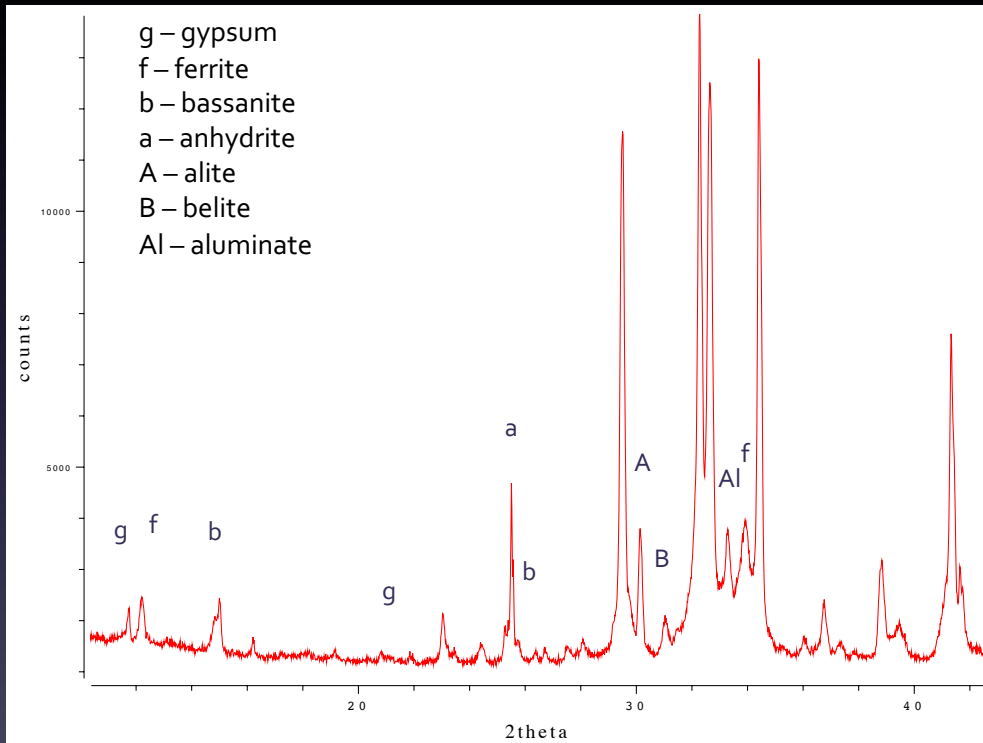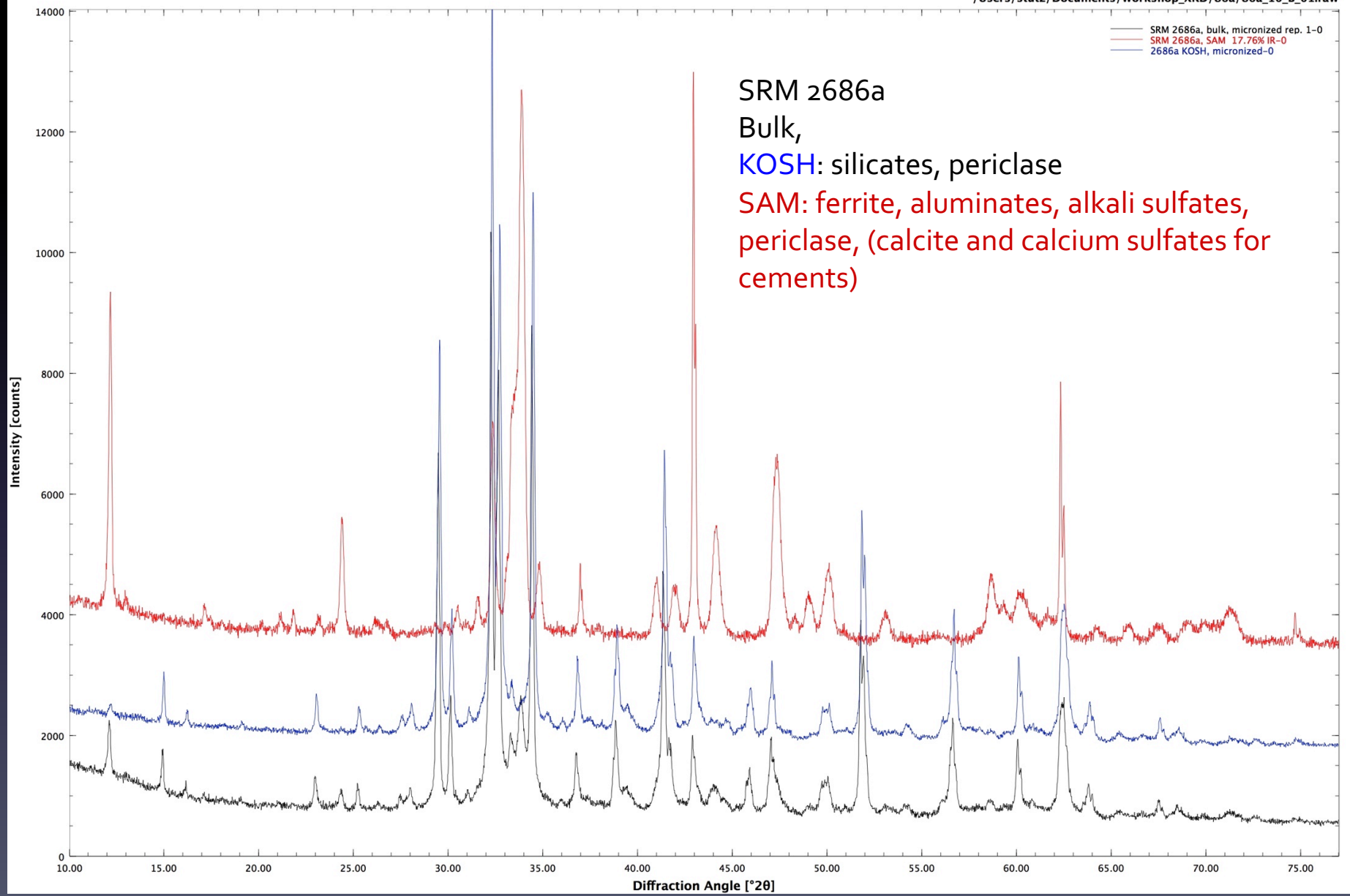
g – gypsum
f – ferrite
b – bassanite
a – anhydrite
A – alite
B – belite
Al – aluminate

Table X1.1 of ASTM C1365 lists peaks by descending d-spacing that have minimal interference. ICDD card numbers allow recalling the entire pattern.

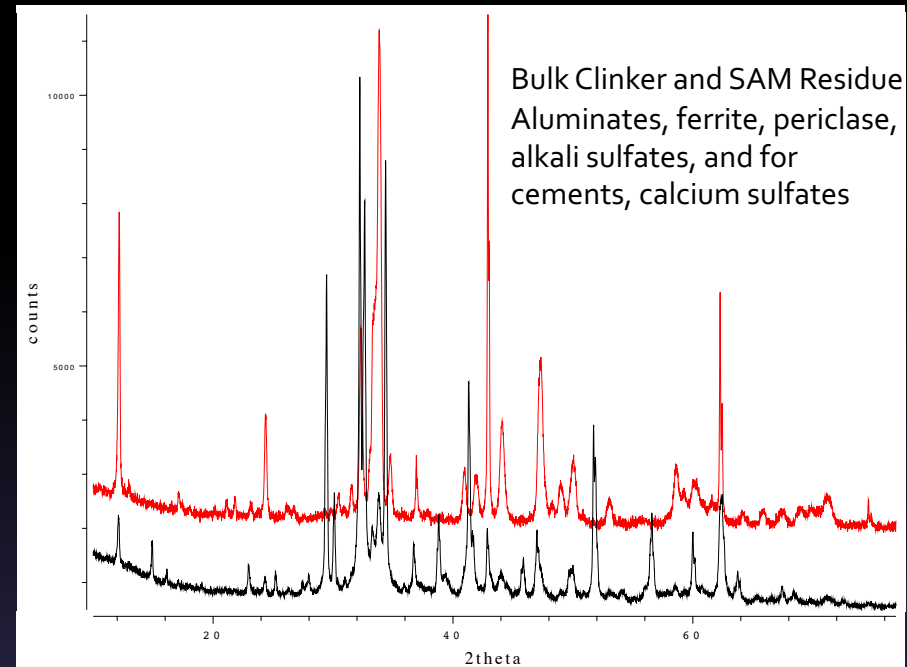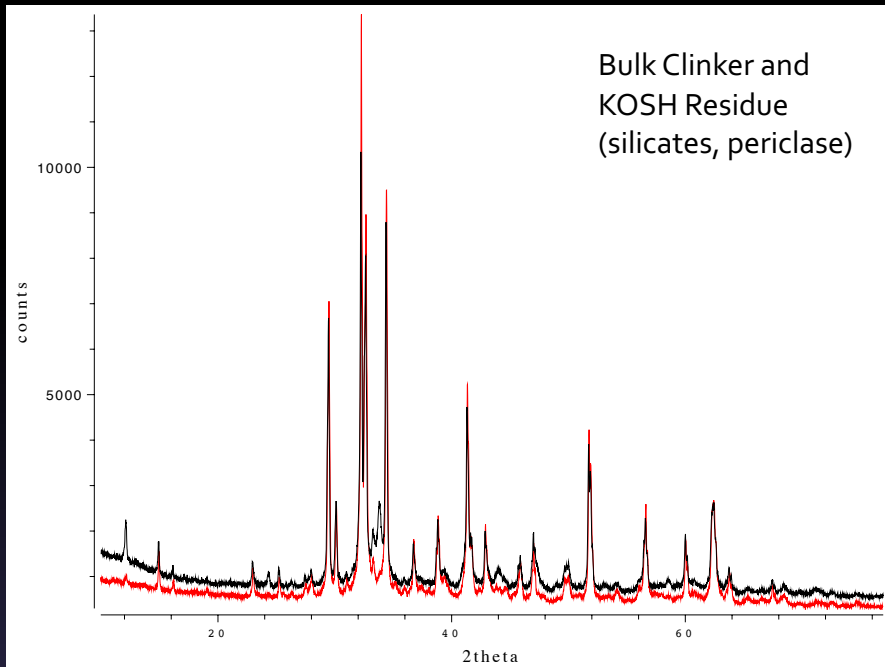**TABLE X1.1 Diagnostic Peaks and ICDD Entry Number for Common Cement Phases (15)**

d-spacing (nm)	Two-Theta (CuKα)	Phase (rel. I)	ICDD No.
0.7627	11.593	gypsum (100)	33-311
0.7249	12.200	ferrite (45)	30-226
0.5997	14.759	bassanite (80)	41-224
0.4284	20.717	gypsum (100)	
0.4235	20.959	aluminate, cubic (6)	38-1429
0.4175	21.264	arcanite (28)	5-613
0.4158	21.352	arcanite (23)	
0.4079	21.770	aluminate, cubic (12)	
0.3799	23.397	gypsum (17)	
0.3670	24.231	aphthitalite (20)	20-928
0.3653	24.346	ferrite (16)	
0.3497	25.450	anhydrite (100)	37-1496
0.3468	25.666	bassanite (40)	
0.3313	26.889	langbeinite (95)	19-975
0.3271	27.241	langbeinite (80)	
0.3263	27.309	langbeinite (80)	
0.3225	27.637	langbeinite (100)	
0.3065	29.111	gypsum (75)	
0.3040	29.355	alite, triclinic (55)	31-301
0.3036	29.395	alite, monoclinic (40)	42-551
0.3025	29.504	alite, triclinic (65)	
0.3025	29.504	alite, monoclinic (75)	
0.3002	29.736	bassanite (80)	
0.3000	29.756	arcanite (77)	
0.2985	29.909	alite, triclinic (25)	
0.2974	30.022	alite, triclinic (18)	
0.2965	30.115	alite, triclinic (20)	
0.2961	30.157	alite, monoclinic (25)	
0.2940	30.378	aphthitalite (75)	
0.2902	30.785	arcanite (100)	
0.2880	30.960	arcanite (53)	
0.2886	31.026	langbeinite (18)	
0.2876	31.070	belite, β-form (21)	33-302
0.2838	31.497	aphthitalite (100)	
0.2784	32.124	ferrite (25)	
0.2714	32.976	aluminate, orthorhombic (65)	
0.2710	33.026	belite α-form (100)	23-1042
0.2698	33.178	aluminate, cubic (100)	
0.2692	33.254	aluminate, orthorhombic (100)	26-957
0.2644	33.875	ferrite (100)	
0.2610	34.330	belite, β-form (42)	
0.2405	37.360	free lime (100)	37-1497
0.2220	40.605	belite, α-form (40)	
0.2110	42.920	periclase (100)	4-829
0.1940	46.788	belite, α-form (60)	
0.1764	51.783	alite, monoclinic (55)	
0.1757	52.004	alite, monoclinic (30)	

ASTM C1365: Standard Test Method for Determination of the Proportion of Phases in Portland Cement and Portland-Cement Clinker Using X-ray Powder Diffraction, *Annual Book of ASTM Standards*, ASTM Int., West Conshohocken, PA, 2013.

Selective Extractions

Bulk Clinker and KOSH Residue (silicates, periclase)

Bulk Clinker and SAM Residue Aluminates, ferrite, periclase, alkali sulfates, and for cements, calcium sulfates

Provide a clearer picture of phase groups to facilitate identification, refinement of their characteristics (peak shape, lattice parameters), and an additional sample set for quantitative analysis.

1) KOH-Sucrose: 7.5 g KOH, 7.5 g sucrose, 75 ml water. Heat to 95 C, stir in 2 g ground cement for one minute. Vacuum filter, wash residue with 20 ml water followed by 50 ml of methanol

2) Salicylic Acid / Methanol: 20 g salicylic acid in 300 ml methanol. Stir 5 g ground cement in SAM solution for 2 h, vacuum filter, wash residue with methanol, dry below 60 C, weigh residue

3) Nitric Acid / Methanol: 10 g of ground clinker or cement in 500 ml of 7 % nitric acid in methanol for 30 minutes to produce residue of ferrite and periclase (if present).

Analytical Approach

- **Bulk Analysis**
  - detection limits due to dilution by silicates make them difficult to identify – but certain diagnostic peaks are evident even in low concentrations. An alternative is to perform a selective extraction to concentrate the intersitital phases, calcium sulfates, and alkali sulfates

- **SAM extraction residue**
  - quantitative extraction, QXRD and re-calculation of phases on a whole-cement basis

- **KOSH Extraction Residue**
  - can be a difficult extraction but will provide an improved pattern of the silicate phases and identification of belite and alite forms
  - Generally not quantitative but still useful

Common Sulfate Phases in Clinkers and Cements

Some sulfate is substituted in the silicates (below 1% for low-sulfate and 2% for high-sulfate clinkers. Some may also be found in the aluminates and ferrite.

SO3 to alkali ratio of up to 0.5 occurs as alkali sulfates. Higher SO3 levels, there is insufficient alkali dissolved to balance the sulfate and that sulfate may be present in other phases – calcium langbeinite, anhydrite, silicates

- arcanite (K_2SO_4) may accommodate Na+, Ca2+, and CO3 in solid solution

- aphthitolite (K_4-x,Nax)SO_4 with x usually 1 but up to 3)

- calcium langbeinite ($K_2Ca_2[SO_4]_3$) may occur in clinkers high in K_2O and SO_3

- anhydrite *(rare)* ($CaSO_4$) in clinkers with high SO_3 (>2%)

- thenardite: *(rare)* (Na_2SO_4) in clinkers with high Na/K ratios

these phases are generally found along silicate crystal boundaries – though

sometimes too as inclusions

Cement Sulfates

- gypsum: $CaSO_4\ 2[H_2O]$

- bassanite: (hemihydrate, plaster) $2CaSO_4\ H_2O$, or $\gamma\text{-}CaSO_4$

- anhydrite: $CaSO_4$

- syngenite: $(K_2Ca_2SO_4\ [H_2O])$ formed by reaction of gypsum and potassium sulfate - reacts rapidly on mixing.

Calcium Sulfates

- Gypsum ($CaSO_4$ $2H_2O$) – moderate solubility. Dehydrates around 100 C to bassanite (hemihydrate or plaster) $CaSO_4$ ½ H_2O and at higher temperatures to anhydrite ($CaSO_4$). Both dehydration products exhibit different solubility than gypsum

- Bassanite hydration to gypsum during mixing may result in paste stiffening – false set

The SAM extraction enhances detection limits by eliminating the dilution effect of the calcium silicates. Be careful however, to dry the residue at low enough temperature that dehydration does not alter the forms

Aluminate Forms: Cubic and Orthorhombic

cubic – two peaks around 21 and 21.8 degrees; single peak at 33.2 degrees. The 21 degree peak has half the intensity of the 21.8 degree peak

orthorhombic: the 33.2 degree peak is split and there is no peak at 21.8 degrees.

There is an overlap with the 21 degree cubic form peak. If the 21 degree peak is greater than half the intensity of the 21.8 degree peak, you may conclude that there is some orthorhombic aluminate in the sample

This is best observed in a SAM extraction residue
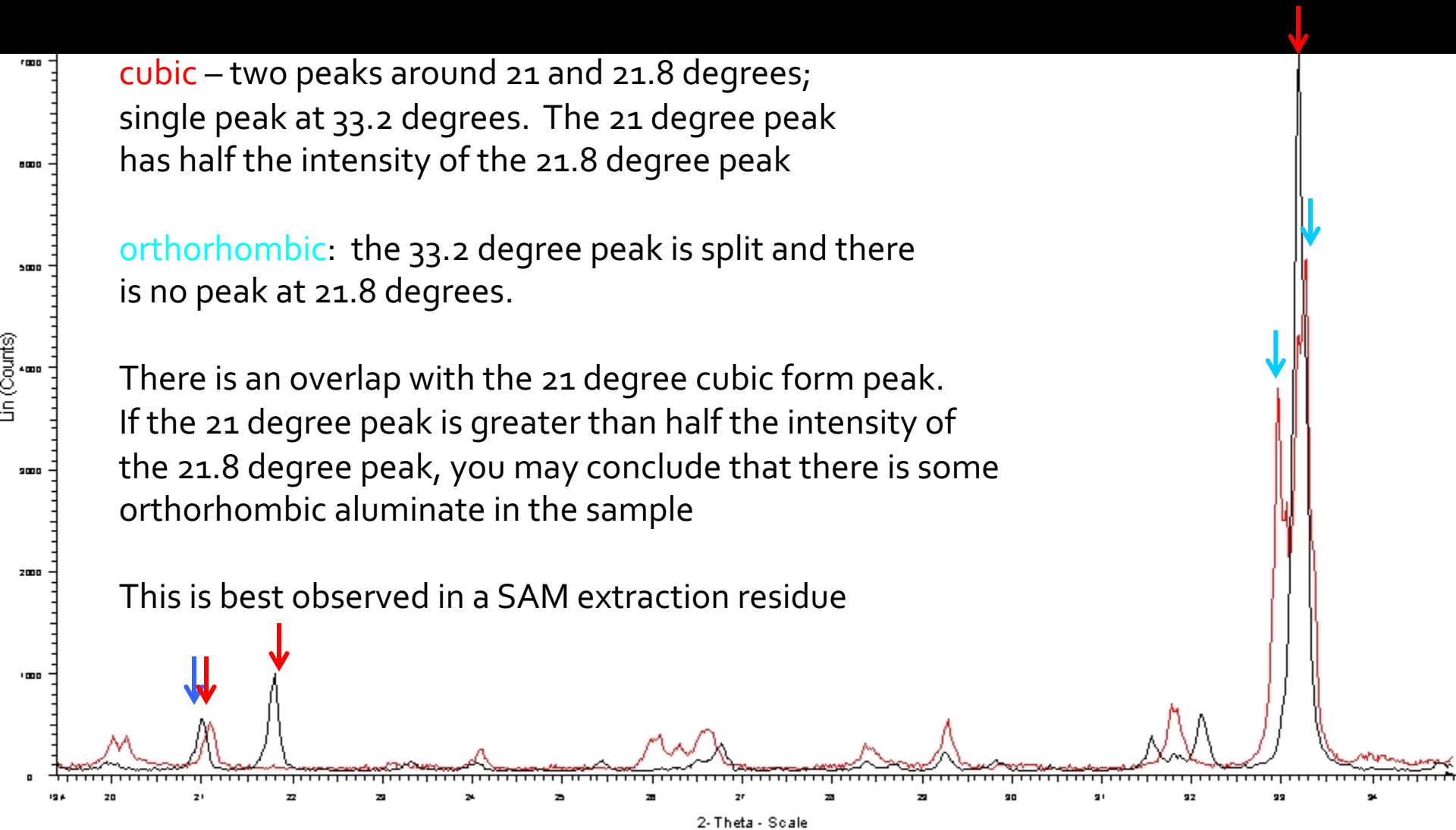
Cubic Aluminate 8299 - File:c3acubb.RAW - Type:2Th/Th locked - Start:14.951 ° - End: 119.975 ° - Step:0.020 ° - Step time:4.s - Temp.: 25 °C (Room) - Time Started: 0 s - 2-Theta: 14.951 ° - Theta:7.500 °
Operations: Displacement 0.094 | Displacement 0.167 | Import
Orthorhombic C3A, CTL NC8A3 RR preparation - File:c3aort.RAW - Type:2Th/Th locked - Start 15.000 ° - End: 120.000 ° - Step:0.020 ° - Step time:4.s - Temp.: 25 °C (Room) - Time Started:0 s - 2-Theta:15
Operations: Y Scale Mul 0.792 | Y Scale Mul 1.750 | Import

triclinic vs. monoclinic alites

the 51 degree region is relatively clear of other peaks and is a good place to look – especially in the KOSH residue
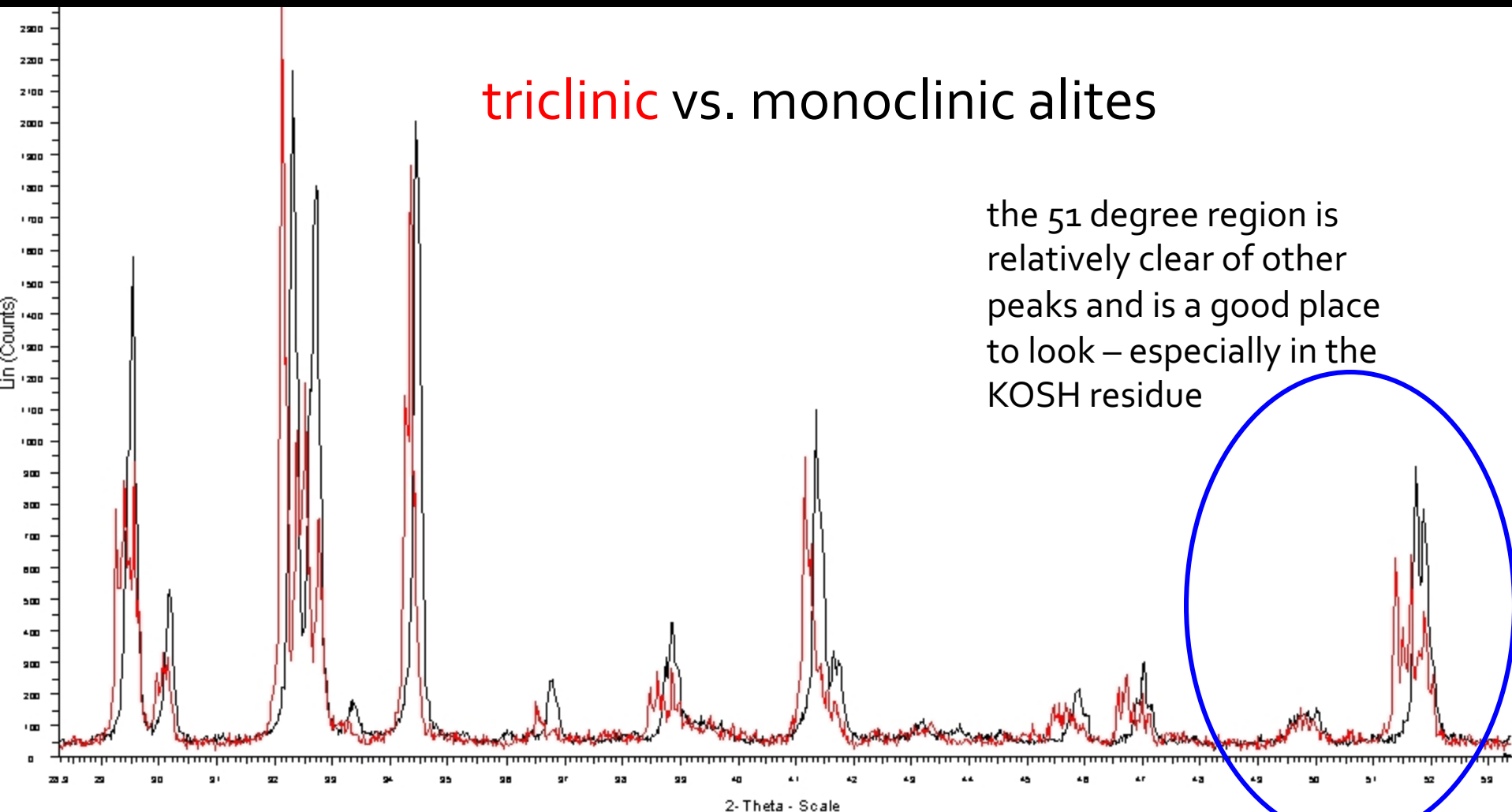
Monoclinic C3S, Alite, ASTM RR Prep.- File: Alite.RAW - Type: 2Th/Th locked - Start: 15.000 ° - End: 120.000 ° - Step: 0.020 ° - Step time: 4. s - Temp.: 25 °C (Room) - Time Started: 0 s - 2-Theta: 15.000 ° - Th
Operations: Import

sum of Triclinic C3S PCA 8414 - File: c3stric_Add_Scans.RAW - Type: 2Th/Th locked - Start: 18.000 ° - End: 120.000 ° - Step: 0.020 ° - Step time: 4. s - Temp.: 25 °C (Room) - Time Started: 0 s - 2-Theta: 18.00
Operations: Y Scale Mul 2.250 | Add Scans | Import

Calcite in Cement

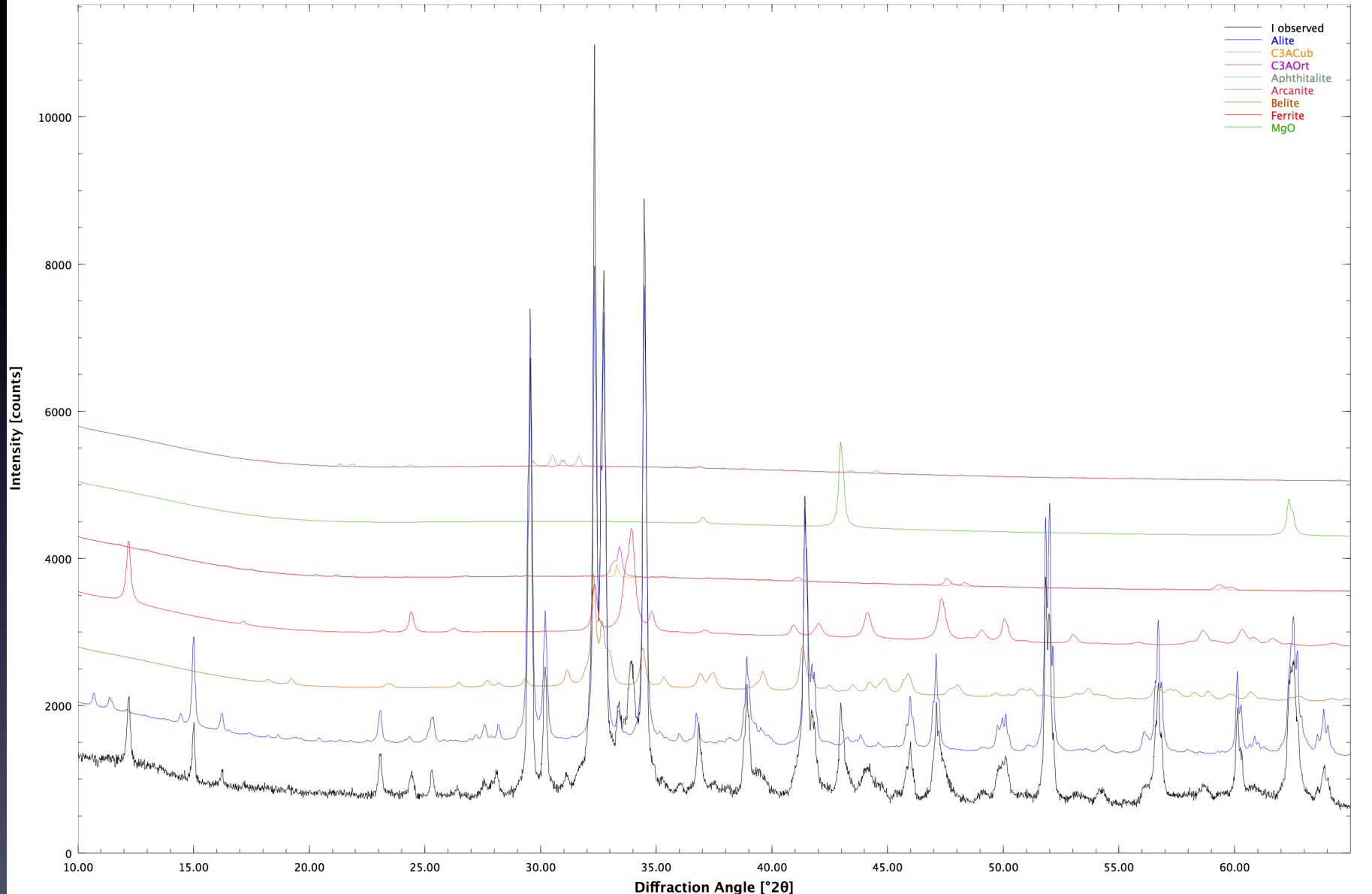**Peak Intensity Ratio**
29.3/30.1: 2.6
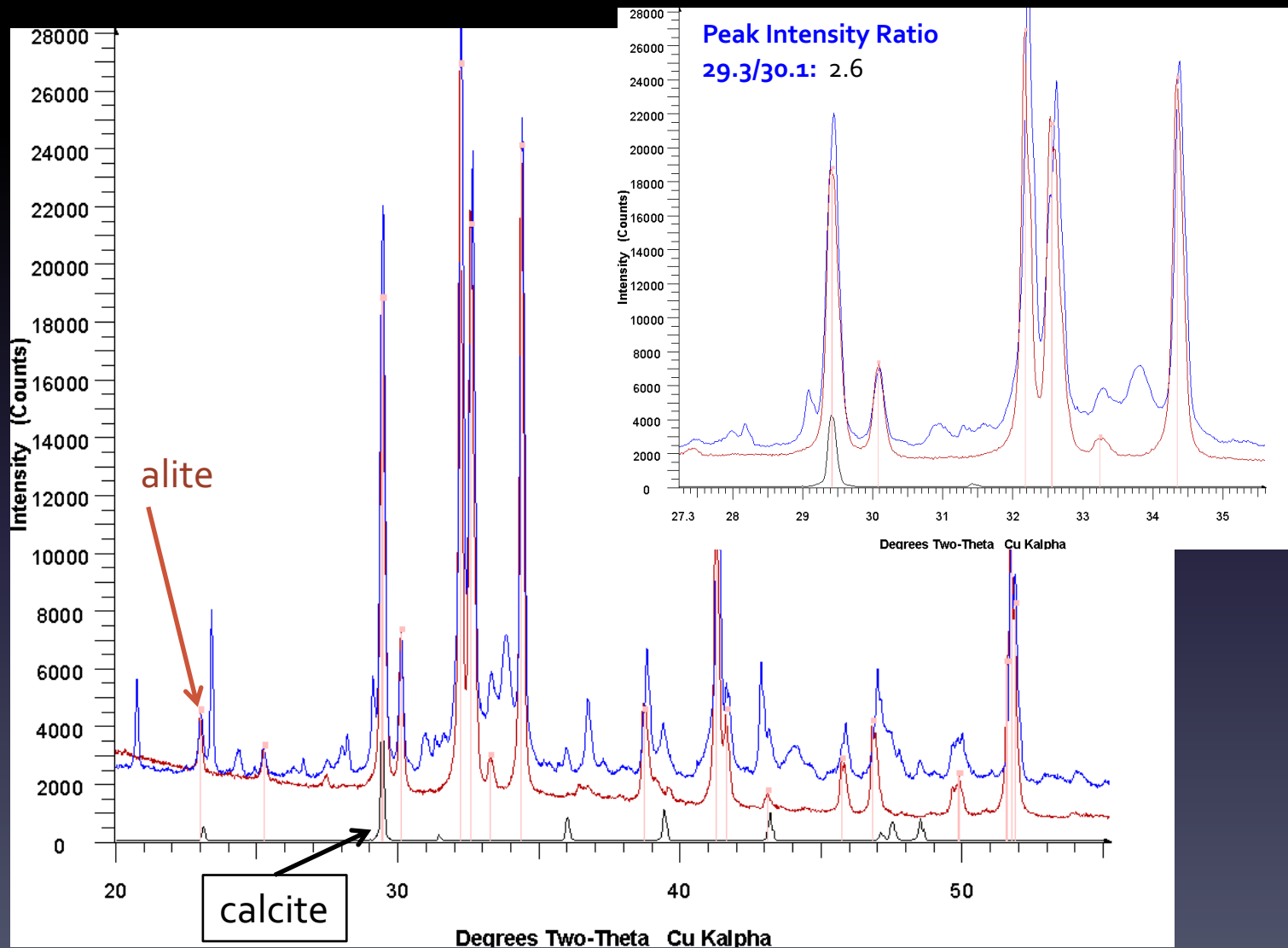
The primary calcite peak (104) overlaps the alite peak at 29.3 degrees

Peak ratios in excess of 3 suggest an overlap from calcite

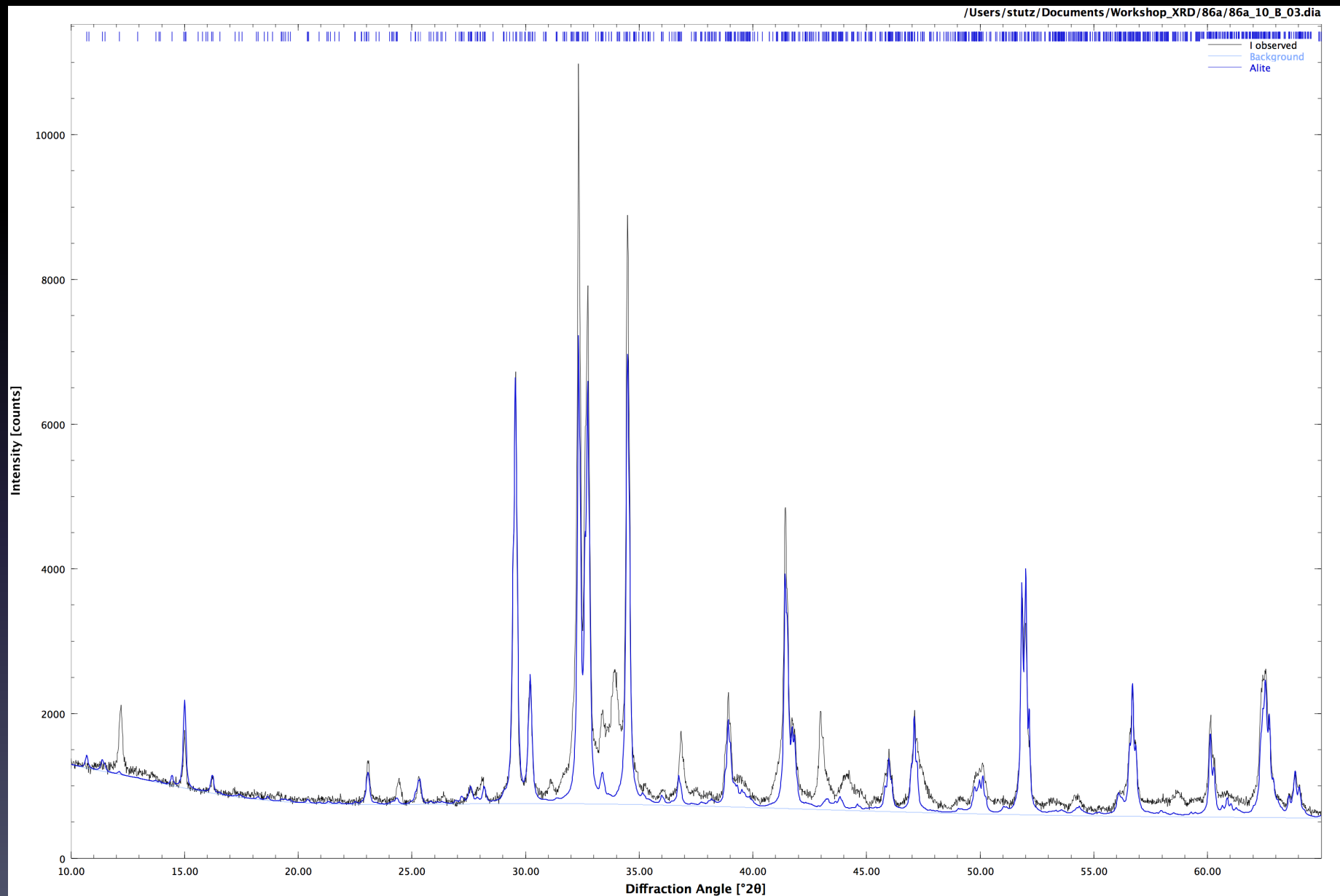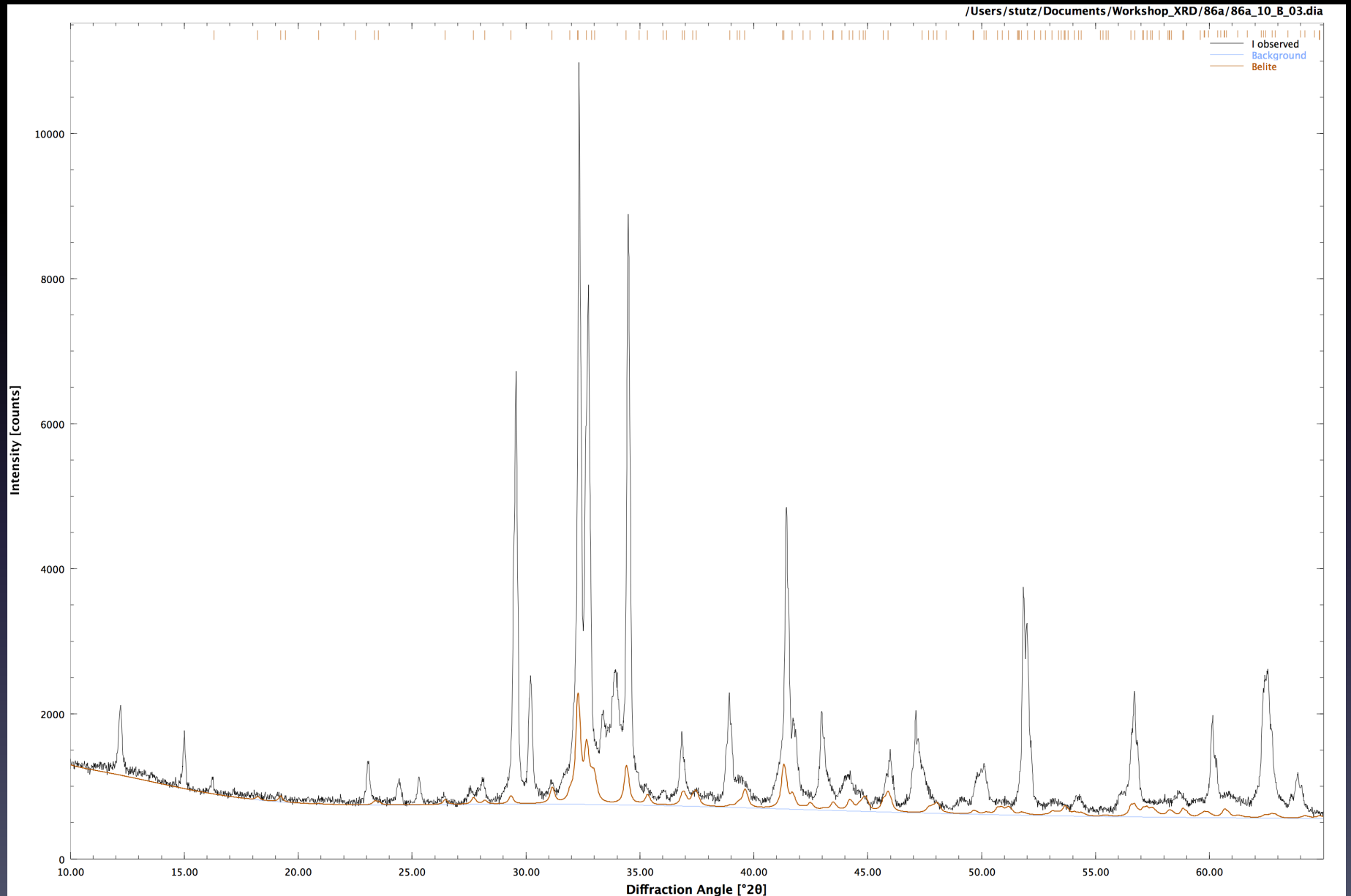Confirm from SAM and KOHS extraction residue

Composite Pattern 2686a

Alite

Belite
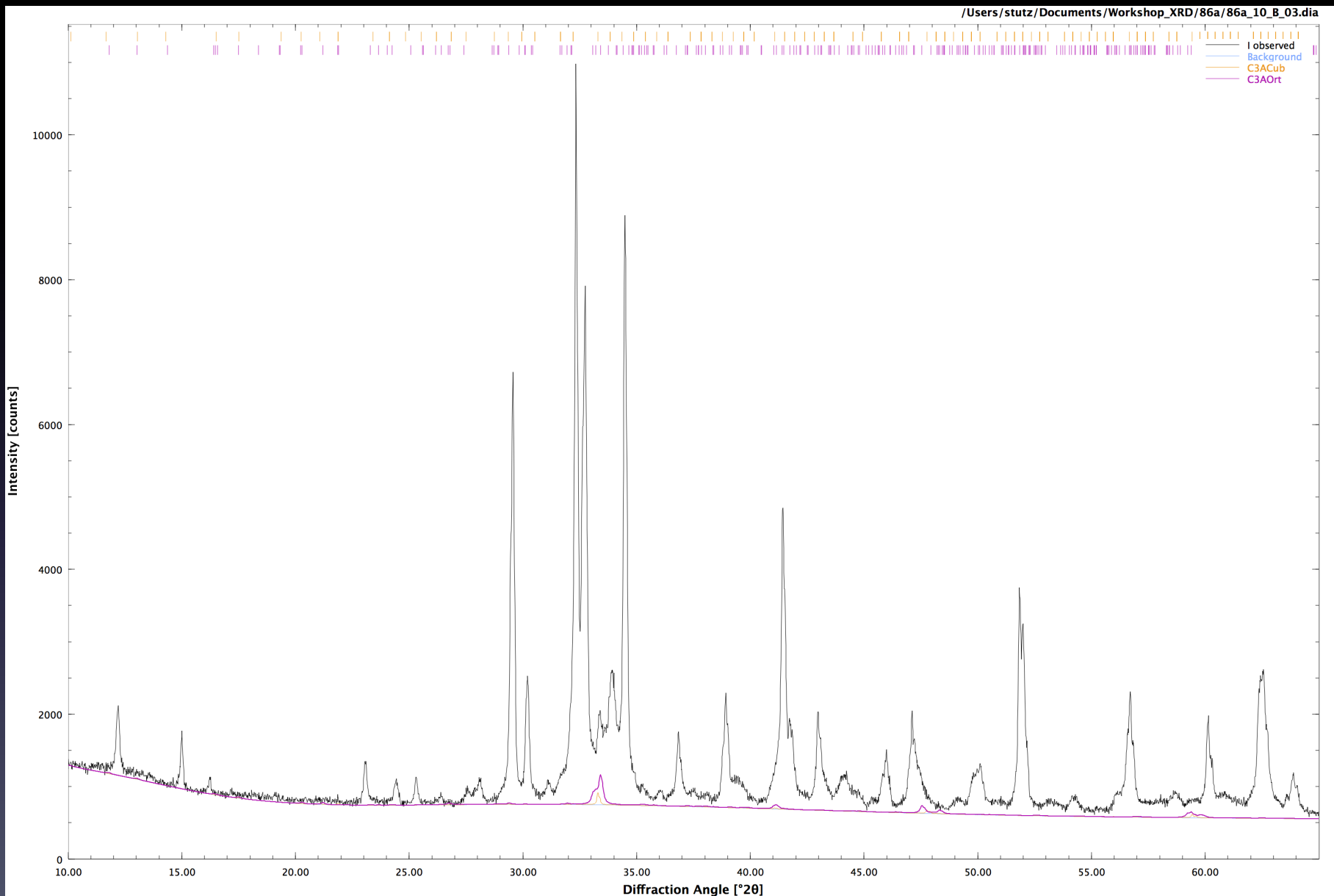

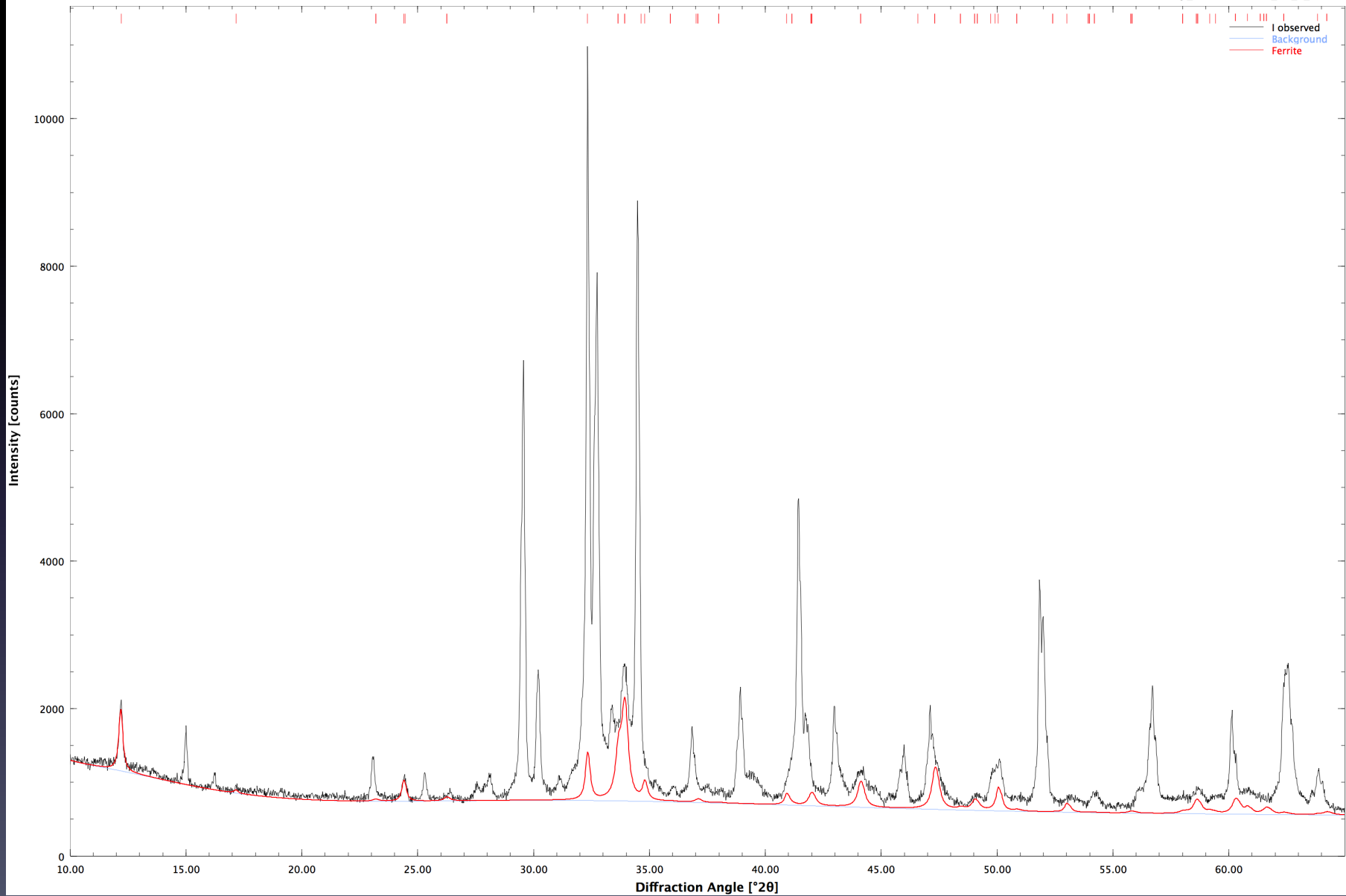/Users/stutz/Documents/Workshop_XRD/86a/86a_10_B_03.dia
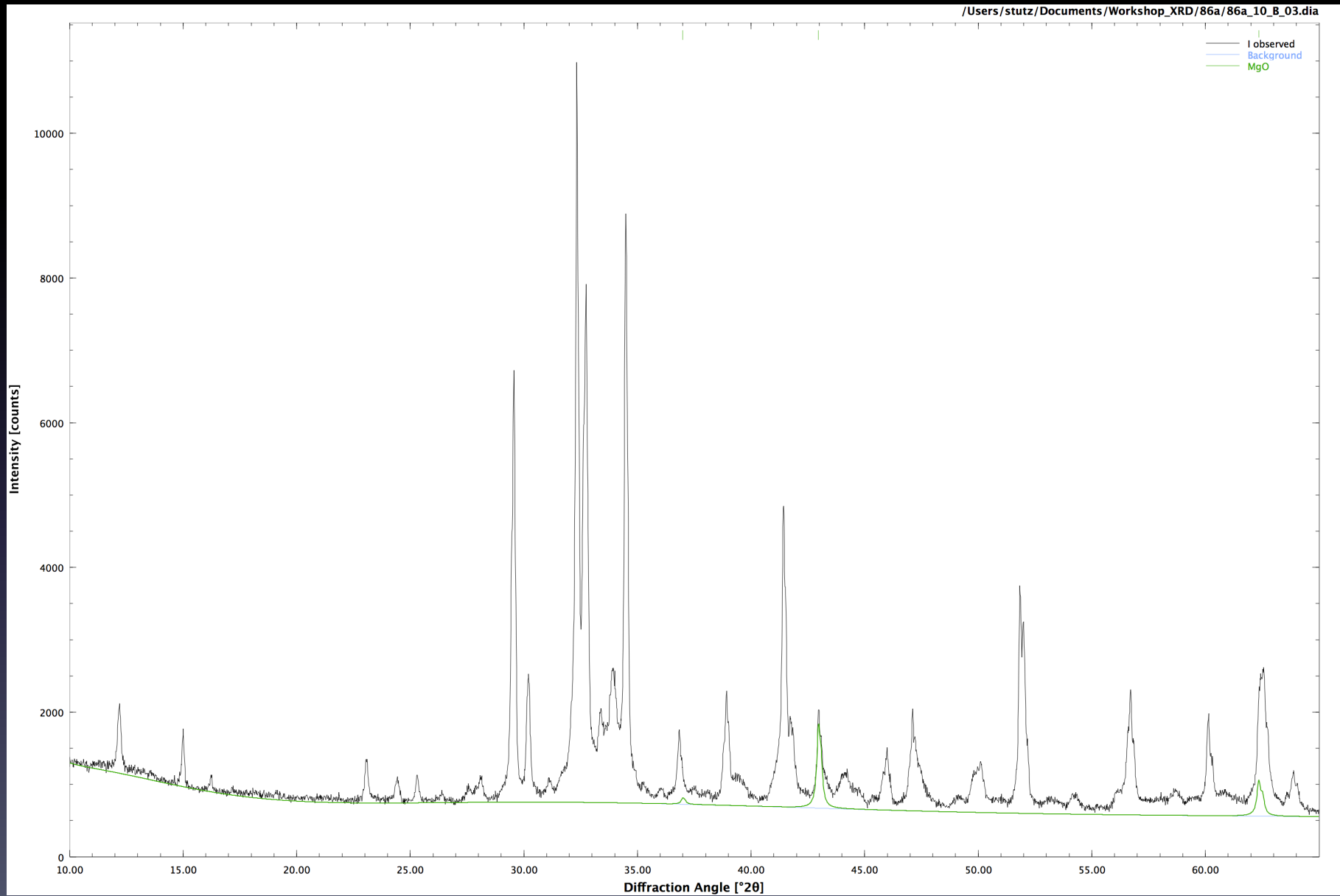
Aluminate: Cub., Ort.

/Users/stutz/Documents/Workshop_XRD/86a/86a_10_B_03.dia

Ferrite

Periclase

Recalculation of Selective Extraction Data

- provides an extra estimate based upon a concentrated residue of the selective extraction

	BULK	KOSH	SAM	IR
C3S	54.5	48.9		
b-C2S	21.6	18.1		
a-C2S	--	0.9		
C4AF	10.1		10.3	(43)
C3Ac	5.0		4.2	(17.5)
Arc.	0.4		0.1	(0.4)
Lang.	1.3		1.3	(5.4)
Peric.	3.2	3.5	3.7	(15.4)
Anh.	0.4		1.2	(5.0)
Bass.	2.8		4.1	(17.1)
Gyp.	0.1		0.2	(0.8)
Qtz.	0.1	0.2	0.1	(0.4)
Dolo.	0.8		1.0	(4.2)

142bulk.RAW:1

Dolomite   0.83 %
Bassanite   2.84 %
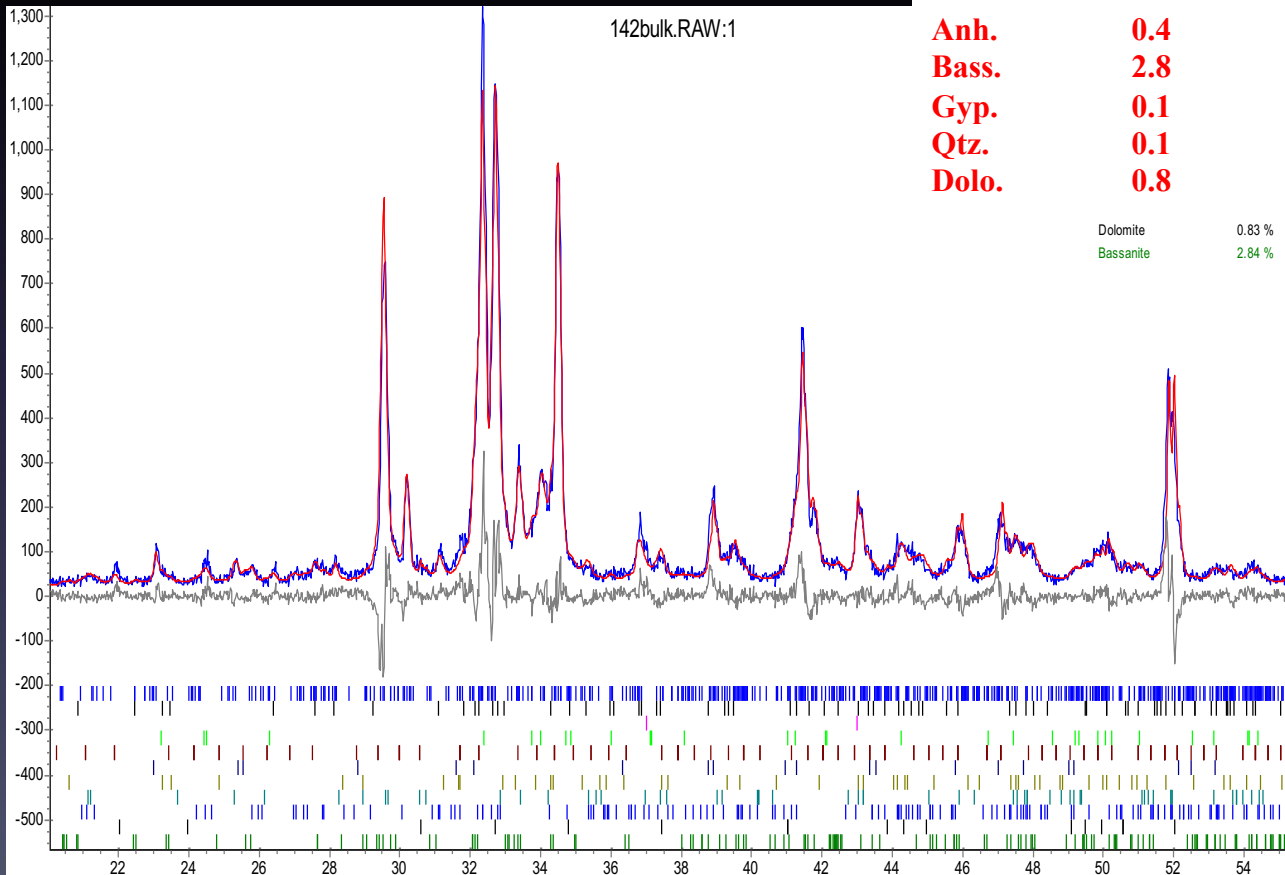
Practicum 3: SRM2686a

Start with phase identifications using the selective extraction patterns in the IMAGES folder
  Examine images SRM2686a_KOSH_d&I_1.png and SRM2686a_SAMd&I_1.png
  and their corresponding .txt files

With the knowledge that you are working with a portland cement clinker, look for key diffraction peaks for phases you might encounter in that material

Prepare a list of potential phases

Starting with the powder diffraction files found in the Bulk folder, read one of the KOSH or SAM patterns into profex, load the appropriate instrument file from the Device folder (D8_6Div_4SS.sav), load the appropriate phase files from the CementStructures folder and initiate the refinement. Transfer the results to the spreadsheet

Repeat for each of the two or three replicates for the SAM and KOSH

Proceed to the Bulk data files (86a_10_B_0*.raw) and repeat