Rietveld quantitative analysis and amorphous content quantitative analysis of six goethite samples

The present study is included in the paper "Noise of collapsing minerals: predictability of the compressional failure in Goethite mines" by Salje et al., accepted for publication on the American Mineralogist.

All data were collected in Bragg-Brentano geometry on our D8 Bruker diffractometer equipped with a primary Ge monochromator for Cu K $_1$ and a Sol-X solid state detector. The solid state detector filters out Fe fluorescence radiation, so that Fe bearing samples can be analyzed with a Cu X-ray tube. Collections conditions were: 6-60° in 2 , 0.03 step size, 30 seconds/step, divergence slits 0.2 mm, receiving slit 0.2 mm, sample spinner on. Rietveld refinements were performed with software Topas 4.1 (Coelho, 2007).

Crystal structures of all phases were retrieved from either the Crystallographic Open Database or from the ICSD: goethite (Hazemann et al., Materials Science Forum, V79, pp821-826, 1991); magnetite (Bragg, Nature (London), V95, pp561, 1915); clinochrysotile (Whittaker, Acta Crystallographica, V9, pp855-862, 1956); talc (Rayner & Brown, Clays and Clay Minerals, V21, pp103-114, 1973); quartz (Levien et al., American Mineralogist, V65, pp920-930, 1980); taramite (Oberti et al., American Mineralogist, V92, pp1428-1435); orthopyroxene (Chatterjee et al., Physical Review Series 3B - Condensed, V79, pp115103-1-115103-8, 2009). March-Dollase model for preferred orientation was applied on the following crystal planes: (1 1 0) and (1 1 1) for goethite; (1 0 0) and (1 1 1) for magnetite; (1 0 0) for cliniochrysotile; (0 0 1) for talc; (1 0 1) for quartz; (0 1 0) and (1 2 0) for taramite; (2 1 0) and (6 1 0) for orthopyroxene. No structural parameter was refined. A shifted Chebyshev function with ten parameters was used to fit the background. Peak shapes of all phases were modelled using Pseudo-Voigt functions. Table 1 reports weight percentages of phases; the reported e.s.d. have no bearing on the accuracy or otherwise of the quantification itself, being merely related to the mathematical fit of the model (Madsen & Scarlett 2008). Rietveld quantitative analysis is known to be unreliable in the presence of phases with strong preferred orientation such as talc and chrysotile. Thus the Rietveld refinements were repeated with and without correction for preferred orientations for some or for all phases as a test: while the goethite fractions changes by no more than 10% of the reported values, the quantification trends are preserved, so that YL17m as an example is always the sample with the largest content of goethite. Table 1 reports weight percentages of phases for all samples as obtained from the Rietveld refinements.

The amorphous content of the sampes was estimated with the internal standard method (Madsen & Scarlett 2008). Real amorphous fraction (W_i) in the sample can be calculated directly from:

$W_i = [1 / (1 - W_s)] \cdot [1 - (W_s / W_{s,c})]$, 1.18

where W_s is the experimental weight fraction of internal standard (corundum), while $W_{s,c}$ is the calculated weight fraction of internal standard from the refinement. Accuracy of the obtained figures with this method can't be estimated. Sample YL8m was mixed with three different quantities of internal standard (10%wt, 15%wt and 25%wt) in order to check the consistency of the method in the studied system when varying the internal standard content. Table 1 reports weight percentages of phases for this analysis as obtained from the Rietveld refinements.

W_s was 0.15 in our case. $W_{s,c}$ happens to be 0.27-0.30. This gives an amorphous content of 54 to 58%. The only exception is sample HZ54.8m for which $W_{s,c}$ is 0.21, i.e. an amorphous content of 34.6%. Table 2 reports weight percentages of phases for all samples as obtained from the Rietveld refinements.

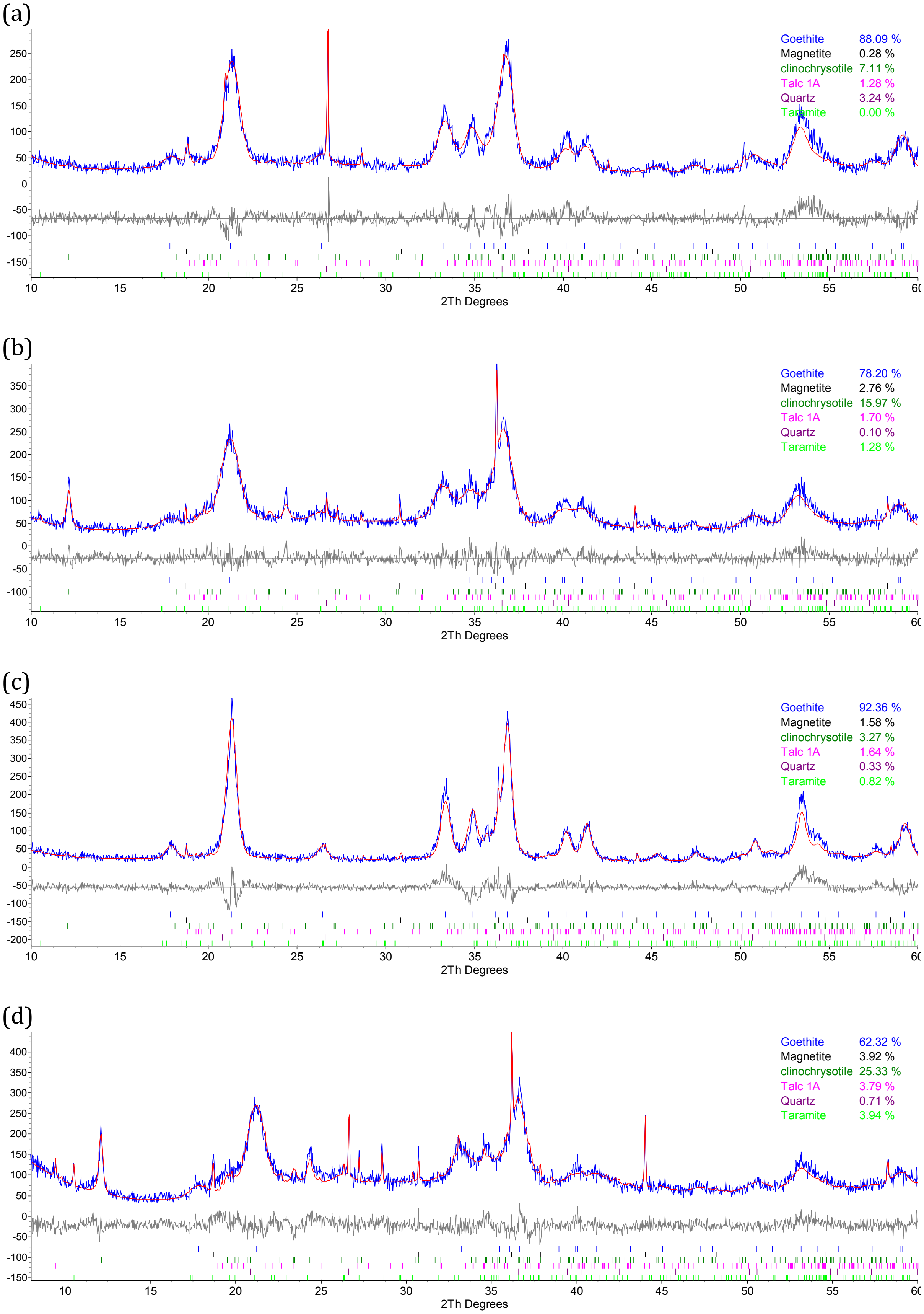
Table 1: Mineralogical composition (in wt. %) of the analyzed samples as obtained from the Rietveld refinements and relative goodness of fit; the e.s.d. relate to the mathematical fit and do not represent error in precision or accuracy. Talc, quartz, and taramite fractions are not reported as they were found to be always smaller than 5 % wt.

Sample	goethite	magnetite	clinochrys.	orthopyroxene	gof
YL25m	88.1%±3.8%	<5%	7.1±1.4%	not included	1.342
BW39m	78.2%±1.4%	<5%	16.0±1.2%	not included	1.185
YL8m	92.3%±1.1%	<5%	<5%	not included	1.410
BW39m(second)	62.3%±1.0%	<5%	25,3±1.0%	not included	1.198
HZ54.8m	63.6%±1.9%	5.2±0.4%	16.1±1.3%	11.1±0.8%	1.257
YL17m	96.2%±9.9%	<5%	<5%	not included	1.362

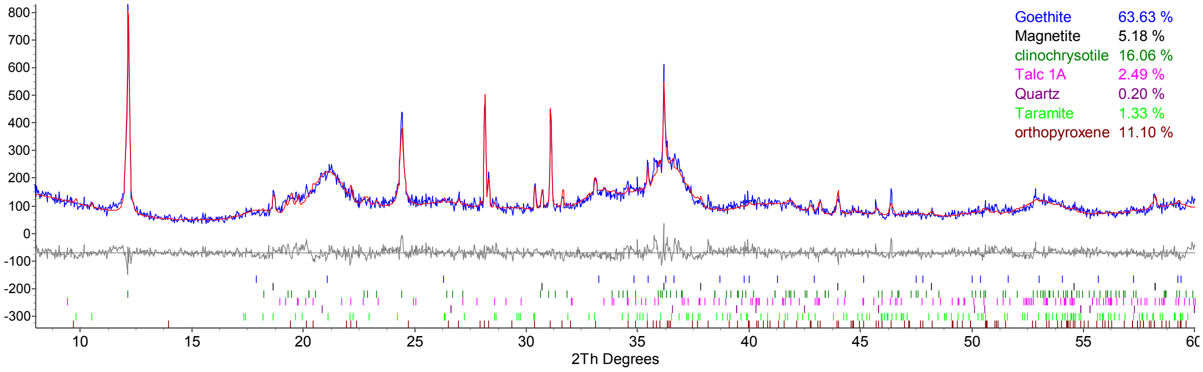
Table 2: Apparent corundum content (in wt. %) as as obtained from the Rietveld refinements and calculated amorphous content for all analyzed samples; the e.s.d. relate to the mathematical fit and do not represent error in precision or accuracy.

Sample	corundum	amorphous content
YL25m	27.5±1.1%	53.7%
BW39m	29.5±4.8%	58.1%
YL8m	28.6±0.9%	56.1%
BW39m(second)	28.4±2.2%	55.7%
HZ54.8m	21.2±1.8%	34.6%
YL17m	27.8±1.1%	54.4%

Figure 1: Experimental (blue), calculated (red) and difference (grey) curves for all Rietveld refinements (samples without internal standard): (a) YL25m(0,71); (b) BW39m; (c) YL8m; (d) BW39m(second); (e) HZ 54.8; (f) YL17m.



(e)


Goethite 63.63 %
Magnetite 5.18 %
clinochrysotile 16.06 %
Talc 1A 2.49 %
Quartz 0.20 %
Taramite 1.33 %
orthopyroxene 11.10 %
800
700
600
500
400
300
200
100
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-100
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-300
10
15
20
25
30
35
40
45
50
55
60
2Th Degrees

(f)

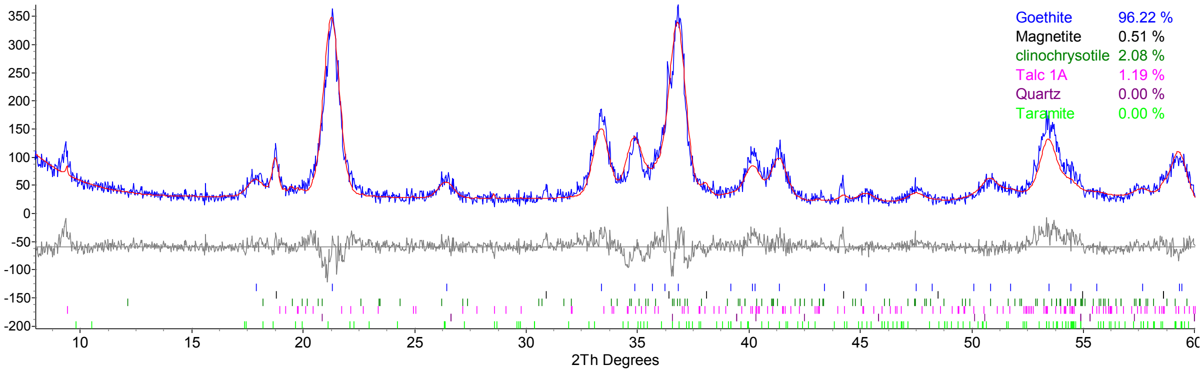
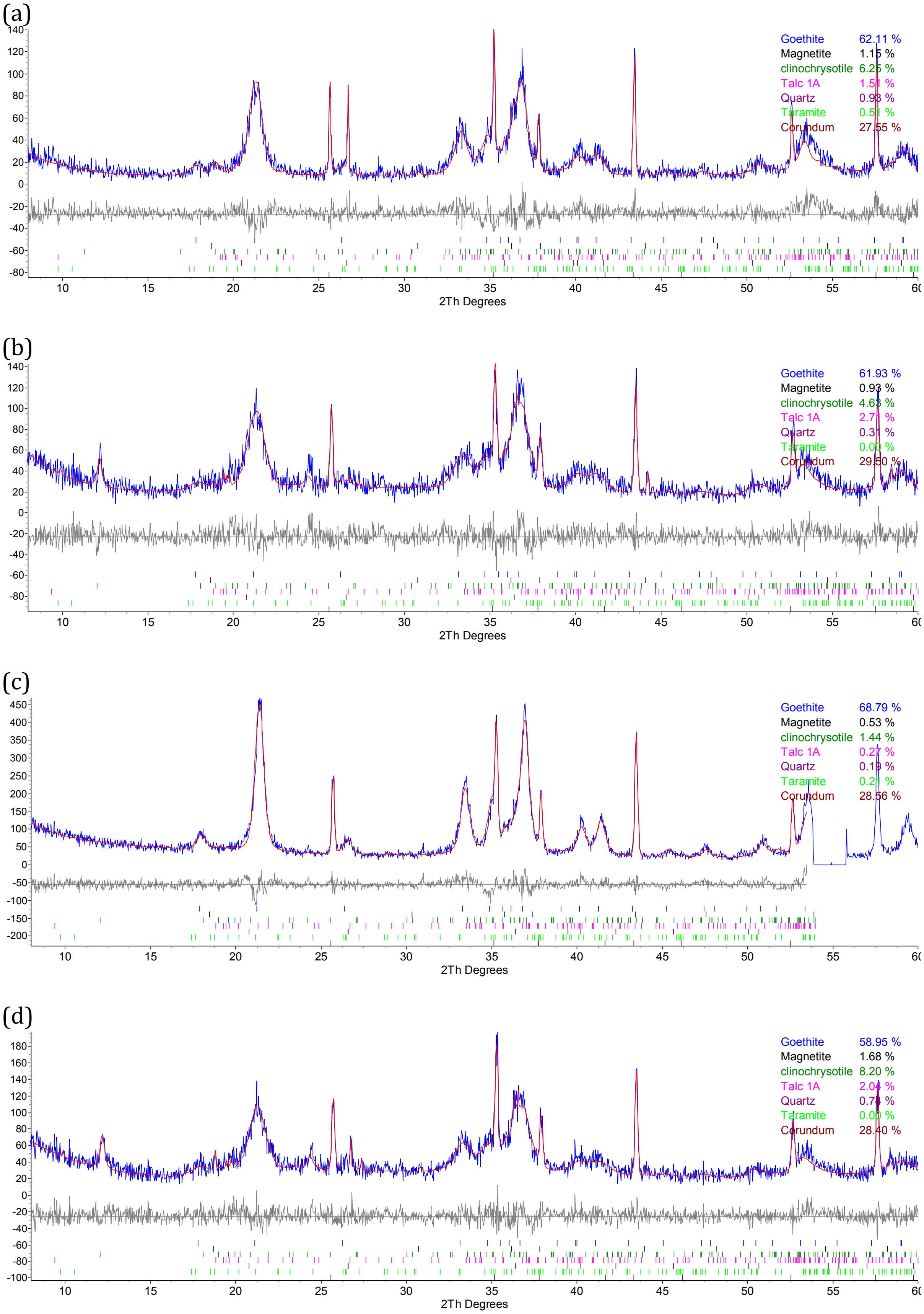
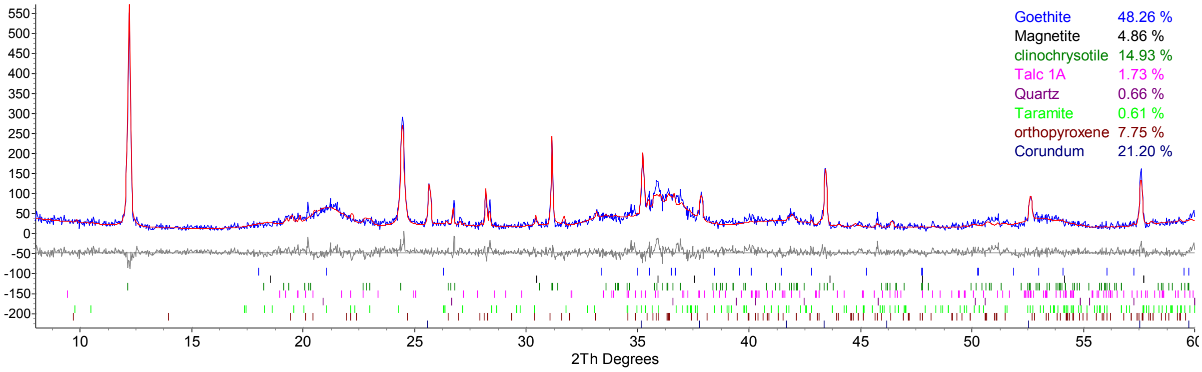

Goethite 96.22 %
Magnetite 0.51 %
clinochrysotile 2.08 %
Talc 1A 1.19 %
Quartz 0.00 %
Taramite 0.00 %
350
300
250
200
150
100
50
0
-50
-100
-150
-200
10
15
20
25
30
35
40
45
50
55
60
2Th Degrees

Figure 2: Experimental (blue), calculated (red) and difference (grey) curves for all Rietveld refinements (samples with internal standard): (a) YL25m; (b) BW39m; (c) YL8m; (d) BW39m(second); (e) HZ 54.8; (f) YL17m.



(e)


550
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450
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350
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250
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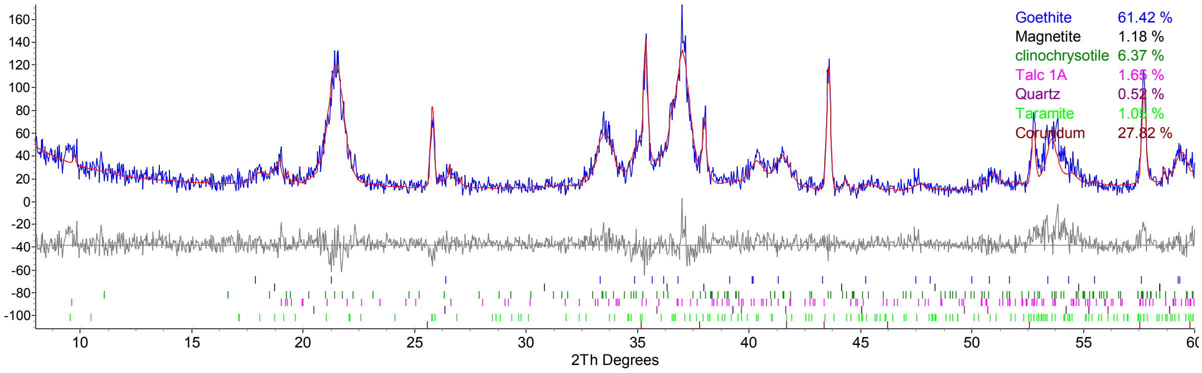
100
50
0
-50
-100
-150
-200
10
15
20
25
30
35
40
45
50
55
60
2Th Degrees
Goethite 48.26 %
Magnetite 4.86 %
clinochrysotile 14.93 %
Talc 1A 1.73 %
Quartz 0.66 %
Taramite 0.61 %
orthopyroxene 7.75 %
Corundum 21.20 %

(f)


160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
10
15
20
25
30
35
40
45
50
55
60
2Th Degrees
Goethite 61.42 %
Magnetite 1.18 %
clinochrysotile 6.37 %
Talc 1A 1.65 %
Quartz 0.52 %
Taramite 1.06 %
Corundum 27.82 %

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