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CHARACTERISATION AND SOURCE APPORTIONMENT OF AIR-FALL DUSTS, WHYALLA

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Executive Summary

Optical microscopy, quantitative X-ray diffraction and multi-element analysis were used to characterise dust samples collected from 10 locations within and around the pellet plant and air-fall dust samples from Hummock Hill, Walls Street and the Croquet Club over the period December 2003-March 2004. Optical estimation of the hematite (Fe_2O_3) content of the air-fall samples revealed values of up to 75% at Hummock Hill, up to 50% at Walls Street and up to 60% at the Croquet Club. Approximately 70% of the Fe_2O_3 in the air-fall dusts from all locations was $<30\mu\text{m}$ in size.

Quantitative XRD analysis revealed hematite constituted 30-65% of the air-fall dusts from Hummock Hill, 18-45% at Walls St. and 10-54% at Croquet Club. These air-fall dusts contained 39-76% Fe at Hummock Hill, 25-54% at Walls Street and 17-62% at Croquet Club. The background component was dominated by quartz, with lesser amounts of calcite, clay, gypsum, mica and halite (sea salt).

Source apportionment based on physical characteristics of the air-fall dusts identified raw materials (screening plant), post-drying and post-grinding areas as the main sources of fugitive Fe_2O_3 . The results of the source apportionment showed raw materials accounted for 17-50%, drying areas accounted for 24-60% and post-grinding areas accounted for 7-33% of the apportioned Fe respectively. The limited number of pellet plant source dusts and the similarity in characteristics between adjacent processes limited the confidence to which particular source areas could be unequivocally associated with air-fall dusts.

The air-fall samples were representative of a particular set of meteorological and emission conditions. However, the analysis revealed that appreciable amounts of fugitive hematite reach the surrounding environment. The announcement of a \$10 million program to move screening and crushing operations from the pellet plant to the mine site should result in appreciable reductions in the amount of fugitive hematite and goethite reaching the surrounding environment, as screening and crushing operations have been identified as major sources of this material.

PART 1. DUST CHARACTERISATION

Introduction

The objective of this work was to characterise the air-fall material depositing at three locations around Whyalla using a number of analytical methods. In conjunction with this, samples of dusts from the pellet plant were also examined. The information on the dusts, such as particle size, shape and colour were used to develop a source apportionment model to account for the observed air-fall mineralogy. The information from the source

apportionment may be used with high volume sampler data to better understand the source(s) of Fe dust reaching the community and to assist Onesteel to develop cost effective and appropriate methods of dust reduction.

This is the first of two reports; the second report covers the detailed chemical and mineralogical analysis of TSP and PM₁₀ high volume filters to determine the impact of fugitive dusts on air quality.

Samples and Methods

Pellet plant and air-fall dusts were analysed by optical microscopy, quantitative X-ray diffraction (QXRD) and X-ray fluorescence (XRF) in order to characterise their size distribution, mineralogy and composition. Mineralogical determination was performed on 10 pellet plant dust samples and 15 air-fall dusts collected from Hummock Hill (5), Walls Street (5) and Croquet Club (5). The air-fall dust samples were collected on 1m² stainless steel trays suspended 2m above the ground in the high volume sampler cages over the period December 2003-March 2004. Sampling episodes were of 12-19 days duration. The resultant dusts were collected from the trays following an agreed methodology. Visual estimation of grain size, mineralogy and physical characteristics of the dusts was conducted using Wild binocular microscope (400X magn.). The results of the visual estimation were $\pm 10\%$.

Quantitative X-ray diffraction (XRD) and X-ray fluorescence (XRF) analysis of pellet plant and air-fall dusts were performed by CSIRO Land and Water (Adelaide). XRD patterns were obtained using CoK α radiation, variable divergence slit and graphite monochromator. The diffraction patterns were recorded in steps of 0.05° 2-theta with a 3.0 second counting time per step. Quantitative analysis was performed using the commercial package SIROQUANT. The accuracy of this method was $\pm 1\%$.

X-ray fluorescence analysis was conducted on the pellet plant and air-fall dusts provided data on major and trace element concentrations. The major elements analysed by this method were Si, Al, Mg, Fe, Ca, Na, K, P, Ti, Mn and S, whilst the trace elements were Zn, Cu, Sr, Zr, Ni, Rb, Ba, V, Cr, Ia, Ce, Pb, Y, Co, Ga, U, Th, As, Sn and Cl. The method for Fe oxide analysis was developed specifically by CSIRO Soils over 10 years of work for Hammersley Iron. The samples were fused at 1050°C to produce borosilicate pellets which were then analysed using CoK α radiation. The results were normalized to 100% and reported as wt% oxide for major elements and parts per million (ppm) for trace elements. The normalised results enabled comparison between locations and samples.

RESULTS

1) Pellet Plant Dusts

1a) Microscopy

Hematite, quartz, goethite, calcite, coke breeze, magnetite and mill scale were the main phases identified by microscopic examination of pellet plant dusts, which ranged between ~2 μ m-2mm in size. The largest proportion of particles <10 μ m in size were associated with drying, post grinding and conveyor spillage (“black hole”) areas. The percentage of Fe₂O₃, particle size range and the approximate percent of dust < 5 μ m and <10 μ m are shown in Table 1.

TABLE 1. Microscopic Assessment of Pellet Plant Dusts

| Sample Location | %Fe ₂ O ₃ ^a | Size (μ m) | % <5 μ m | % <10 μ m ^b | % fract. ^c |
|------------------------------------|--|-----------------|--------------|----------------------------|-----------------------|
| 1) No.1 screening plant | 95 | 5-50 | ~1 | 10 | 5 |
| 2) Reclaims-storage shed | 80 | 2-40 | 5 | 40 | 10 |
| 3) Pre-drying #2744 conveyor | 70 | 2-50 | 10 | 30 | 40 |
| 4) Grinding Mill #4 feed in | 70 | 2-40 | 10 | 50 | 30 |
| 5) Post-grinding mill | 75 | 2-20 | 30 | 60 | 70 |
| 6) Induration multi-cyclone valve | 70 | 10-2000 | 0 | 0 | 0 |
| 7) Post induration | 95 | 5-1200 | ~1 | 2 | 0 |
| 8) Rotary Kiln-exit | 85 | 5-100 | 5 | 10 | 10 |
| 9) No. 3 screening plant | 95 | 5-70 | ~1 | 10 | 5 |
| 10) Conveyor spillage “black hole” | 80 | 2-30 | 20 | 60 | 10 |

a. visual estimate \pm 10%

b. includes <5 μ m fraction

c. % mechanically fractured grains

The physical characteristics of the pellet plant dusts exhibited a number of differences and similarities. Samples of raw material (ex-mine, samples 1 and 9) consisted almost entirely of blocky Fe₂O₃ grains ~5-70 μ m in size. The grain size of the Fe₂O₃ decreased and the proportion of grains exhibiting fresh surfaces from mechanical fracturing increased as material underwent processing prior to induration. Fugitive dusts collected from the drying (conveyor #2744), post grinding (conveyor #3310) and conveyor spillage in the “black hole” areas contained the largest proportion of material <10 μ m in size (~70-80%). Dust from the post-grinding area also exhibited the greatest amount of mechanical fracturing (~70%).

Fractured material was also identified in dusts from #2744 conveyor (40%) and pre-grinding (20%) areas. Minor amounts were identified in all samples except dusts from multi cyclone dust valve and from adjacent to the induration kiln cooler stack. Dusts from the induration process (samples 6, 7 and 8) consisted of coarse (5-2000 μ m), blocky material with abundant rounded/spherical particles in a massive matrix, the texture and colour being significantly different from other areas of the pellet plant. The induration dusts also contained minor amounts of magnetite/maghemite, which were readily extracted using a hand magnet.

1b) Quantitative XRD

The results of the quantitative XRD of pellet plant dusts (Table 2) revealed a relatively simple mineralogy. Hematite (Fe₂O₃) was identified as the main phase, constituting 52-89% of samples. Other phases identified included goethite (2-18%), kaolin (1-19%), calcite (1-17%) and dolomite (1-12%). Quartz was identified as a trace component in the samples, where it constituted ~1%. Magnetite (Fe₃O₄) and augite (Ca (Fe,Mg)Si₂O₆) were restricted to post-induration dusts, where they constituted 2% and 3-7% respectively. The ideal composition of phases identified by XRD are given in Appendix 1.

Table 2. Quantitative XRD Results of Pellet Plant Dusts

| Location | Hem. | Goeth | Qtz | Kaolin | Halite | Magnet | Calcite | Dolo. | Talc | Augite |
|------------------------------|------|-------|-----|--------|--------|--------|---------|-------|------|--------|
| 1).No.1 Screening plant | 69 | 14 | 1 | 14 | 0 | 0 | 0 | 0 | 2 | 0 |
| 2). Reclaims shed | 68 | 12 | 1 | 17 | <1 | 0 | 0 | 1 | 2 | 0 |
| 3). Spillage #2744 conveyor | 52 | 6 | 1 | 8 | 0 | 0 | 17 | 12 | 0 | 0 |
| 4). #4 feed in-pre grinding | 64 | 10 | 1 | 19 | 0 | 0 | 1 | 5 | 1 | <1 |
| 5). Post grinding | 73 | 8 | 1 | 6 | 0 | 0 | 2 | 10 | 0 | <1 |
| 6). Induration cyclone valve | 78 | 9 | 1 | 1 | 0 | 0 | 2 | 8 | 0 | <1 |
| 7). Post induration | 83 | 2 | <1 | <1 | 0 | 2 | 0 | <1 | 0 | 7 |
| 8). Exit end-induration kiln | 89 | 0 | 1 | 4 | 0 | <1 | 0 | 2 | 0 | 3 |
| 9). No.3 screening plant | 61 | 18 | 1 | 13 | 0 | 0 | 0 | 0 | 8 | 0 |
| 10). Spillage "black hole" | 71 | 9 | 1 | 14 | 0 | 0 | <1 | 3 | 1 | 0 |

Abbreviations: Hematite (hem), goethite (goeth), quartz (qtz), magnetite (magnet), dolomite (dolo)

Goethite was identified in all pellet plant dusts except those collected from the exit end of the rotary kiln. Goethite entered the system with the raw materials, identified in screening plant dusts at amounts of 14% and 18% (samples 1 and 9). During the induration process (at ~1200°C) the H₂O in the goethite is removed according to: 2FeO₂H = Fe₂O₃ + H₂O. The presence of calcite and dolomite in the samples represented addition as fluxes.

1c) Major Element Chemistry

As expected, the main element in the pellet plant samples was Fe, which ranged between 73.71-89.81% (ave. 85.20%). The other main constituents of the dusts were Si (2.61-7.74%), Al (0.88-4.84%), Ca (0.06-14.55%) and Mg (0.40-3.05%). The results are shown in Table 4.

Table 4. Major Element Chemistry of Pellet Plant Dusts

| Element | d.l. % | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|--------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| SiO ₂ | 0.35 | 5.53 | 6.55 | 4.50 | 7.74 | 2.97 | 2.61 | 3.33 | 6.64 | 4.20 | 6.87 |
| Al ₂ O ₃ | 0.20 | 3.69 | 4.73 | 2.64 | 5.45 | 2.45 | 0.88 | 1.86 | 3.70 | 2.75 | 4.84 |
| MgO | 0.10 | 0.40 | 0.62 | 3.05 | 1.42 | 2.13 | 1.69 | 1.72 | 0.60 | 1.22 | 1.33 |
| Fe ₂ O ₃ | 0.12 | 88.26 | 85.87 | 73.67 | 81.12 | 87.06 | 89.81 | 87.89 | 87.23 | 88.04 | 83.03 |
| CaO | 0.10 | 0.06 | 0.46 | 14.55 | 2.23 | 3.71 | 3.77 | 4.02 | 0.05 | 2.32 | 2.07 |
| Na ₂ O | 0.08 | 0.26 | 0.29 | 0.35 | 0.27 | 0.26 | 0.25 | 0.24 | 0.23 | 0.28 | 0.27 |
| K ₂ O | 0.05 | 0.04 | 0.05 | 0.05 | 0.07 | 0.05 | 0.04 | 0.03 | 0.03 | 0.03 | 0.07 |
| TiO ₂ | 0.03 | 0.44 | 0.42 | 0.28 | 0.70 | 0.24 | 0.09 | 0.20 | 0.44 | 0.37 | 0.49 |
| P ₂ O ₅ | 0.03 | 0.18 | 0.20 | 0.16 | 0.21 | 0.17 | 0.14 | 0.15 | 0.20 | 0.15 | 0.20 |
| MnO | 0.01 | 0.36 | 0.40 | 0.29 | 0.33 | 0.56 | 0.38 | 0.41 | 0.49 | 0.31 | 0.40 |
| SO ₃ | 0.02 | 0.13 | 0.15 | 0.21 | 0.18 | 0.11 | 0.10 | 0.05 | 0.15 | 0.13 | 0.19 |
| Cl | 0.002 | 0.084 | 0.111 | 0.058 | 0.106 | 0.044 | 0.074 | 0.002 | 0.104 | 0.072 | 0.097 |
| Sum | | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

The other elements characterised in the samples (Na, K, Ti, P, Mn and S) were present at concentrations < 1%. Chlorine was also present at low levels in the pellet plant dusts, attaining a maximum concentration of 0.11%. The low levels in the dusts also enabled the contribution of sea salt (halite) to be more easily determined in the air-fall dusts, as pellet plant dusts contributed virtually no Cl to these samples.

2) AIR-FALL SAMPLES

General

The mineralogy of the air-fall dusts reflected the combination of several variables, including meteorological conditions, emission rates from individual source areas, distance from the source, and retention at the receptor. The main difference in the air-fall dusts was the relative amounts of Fe₂O₃ and SiO₂. Dusts from Hummock Hill contained a greater proportion of Fe₂O₃ than samples from Walls Street or Croquet Club, due to proximity to the pellet plant boundary. The Fe₂O₃ in the air-fall samples exhibited a range of sizes, with material 10-30µm being most common.

Quartz (SiO₂) was the most abundant crustal component of the air-fall dusts. The size and morphology of the quartz was quite consistent, ranging between 5-100µm in size. Rare, larger grains to 500µm were also observed. The majority (>80%) of the quartz grains identified in the air-fall dusts were clear to pale orange in colour and exhibited rounded morphologies.

Minor phases identified in the dusts included calcite, magnetite, mica, coke and kish graphite. The presence of kish and coke in the air-fall dusts indicated that other processes unrelated to the pellet plant (ie: coke ovens, blast furnace) also contributed to air-fall material. Kish graphite was readily identified by its larger size (50-500µm) and hexagonal flaky morphology, whilst coke was identifiable due to its grey colour and large pore size. Organic matter (plant matter, insect carcasses) was also identified in the dusts, with Croquet Club > Walls Street > Hummock Hill.

2a). Hummock Hill

2a(i) Microscopy

Air-fall dusts from Hummock Hill were generally red-brown in colour with mineralogy dominated by Fe₂O₃, which constituted ~60-75% of total sample. The exception was the sample collected between 22/1-3/2, which was brown-pink due to the larger amount of crustal material (60% SiO₂) and less Fe₂O₃ (20%) in the dust. The results of the optical assessment of the dusts are shown in Table 5.

The grain size of the air-fall Fe₂O₃ was relatively constant, with ~70% being 10-30µm in size. A large proportion of the Fe₂O₃ particles also exhibited freshly exposed surfaces produced from mechanical fracturing. The dusts also contained rare Fe₂O₃ aggregates and quartz particles ~500µm in size. The amount of Fe₂O₃ less than 5µm in size ranged between 10-15%. The exception was the sample collected between 22/1-3/2/04, which contained ~1-2% of fine Fe₂O₃.

Table 5. Hummock Hill Air-Fall Dusts: Optical Assessment

| Date | %Fe ₂ O ₃ | Size (µm) | % <5µm | %<10µm | % fract. | Other ^d |
|---------------------|---------------------------------|-----------|--------|--------|----------|-------------------------------|
| 23/12-8/1/04 | 70 | 2-30 | 10 | 50 | 60 | Qtz, cc, mica |
| 8/1-22/1/04 | 60 | 2-20 | 10 | 30 | 60 | Qtz, coke, kish, organic, hal |
| 22/1-3/2/04 | 20 | 5-20 | 1-2 | 20 | 50 | Qtz, cc, hal |
| 13/2-23/2/04 | 60 | 2-20 | 10 | 60 | 30 | Qtz, mt, coke, kish |
| 23/2-11/3/04 | 75 | 2-50 | 10-15 | 30 | 30 | Qtz, mt, cc, kish |

d. **qtz** (quartz), **cc** (calcite), **hal** (halite), **mt** (magnetite), **organic** (grass, flower fragments, insect carcasses, pollen), **kish** (graphite carbon)

This sample was dominated by crustal/background material (SiO₂, CaCO₃ and NaCl), which constituted 50%, 10% and 10% respectively of the sample, whilst Fe₂O₃ content was ~20%. SiO₂ ranged in size between 5-400µm, with a majority being <50µm. The SiO₂ was dominated by rounded, pale orange-clear grains, features characteristic of extensive weathering and transportation. Halite (sea salt) occurred as clear, cubic crystals 20-100µm in size.

2a(ii) Quantitative XRD

The QXRD analysis identified 13 minerals in the air-fall dusts, with the samples dominated by hematite, quartz, goethite, halite, kaolin and calcite (Table 6). Minor components included dolomite, albite, orthoclase, gypsum, magnetite, talc and mica. These minor minerals accounted for <15% of the overall mineralogy. The Fe₂O₃ accounted for 30-65% of the samples, whilst SiO₂ accounted for 7-25%.

Table 6. Quantitative XRD Results for Hummock Hill Air-fall Dusts

| Hummock Hill | Hem | Goet | Qtz | Kaol | Hal | Mt | Cc | Dol | Talc | Alb | Or | Gyp | Mica |
|--------------------|-----|------|-----|------|-----|----|----|-----|------|-----|----|-----|------|
| HH-1: 23/12-8/1/04 | 65 | 8 | 7 | 9 | 1 | 1 | 1 | 2 | 2 | 1 | <1 | 1 | 1 |
| HH-2: 8/1-22/1/04 | 51 | 5 | 12 | 6 | 7 | 1 | 4 | 4 | <1 | 2 | 1 | 1 | 5 |
| HH-3: 22/1-3/2/04 | 30 | 2 | 25 | 5 | 7 | 1 | 10 | 4 | 2 | 3 | 2 | 2 | 6 |
| HH-4: 13/2-23/2/04 | 55 | 6 | 11 | 9 | <1 | 1 | 2 | 3 | 4 | 2 | 1 | <1 | 5 |
| HH-5: 23/2-11/3/04 | 51 | 5 | 11 | 8 | 4 | 1 | 6 | 4 | <1 | 2 | <1 | 2 | 5 |

Apart from SiO₂, mica and calcite were the next most commonly identified crustal minerals, present at 1-6% and 1-10% respectively.

2a(iii) Major Element Chemistry

The air-fall dusts deposited at Hummock Hill contained appreciable concentrations of Fe, which ranged between 38.79-75.50%. The other main element identified in the air-fall dusts was SiO₂, which ranged between 12.55-31.62% (Table 7). Other elements identified in the dusts were Al (4.87-7.76%), Mg (1.46-2.54%), Ca (2.29-8.75%), Na (0.48-3.69%), K (0.38-1.25%) and Cl (0.15-3.60%). The concentrations of Na, K and Cl in samples HH-2, 3 and 5 were greater than found in the pellet plant dusts.

The elevated Cl content was due to the presence of halite (NaCl). The concentrations of Ti, P, Mn and S were similar to pellet plant dusts, with all <0.60%.

Table 7. Hummock Hill Air-fall Dusts: Major Element Chemistry

| Major Elements | d.l. % | HH-1 | HH-2 | HH-3 | HH-4 | HH-5 |
|--------------------------------|--------|--------|--------|--------|--------|--------|
| SiO ₂ | 0.35 | 19.61 | 19.54 | 31.62 | 12.55 | 19.06 |
| Al ₂ O ₃ | 0.20 | 7.71 | 5.99 | 7.76 | 4.87 | 6.02 |
| MgO | 0.10 | 1.46 | 2.28 | 2.54 | 1.55 | 2.18 |
| Fe ₂ O ₃ | 0.12 | 65.31 | 57.79 | 38.79 | 75.50 | 61.12 |
| CaO | 0.10 | 3.05 | 4.76 | 8.75 | 2.29 | 6.05 |
| Na ₂ O | 0.08 | 0.48 | 3.30 | 3.69 | 0.67 | 1.79 |
| K ₂ O | 0.05 | 0.52 | 0.76 | 1.25 | 0.38 | 0.67 |
| TiO ₂ | 0.03 | 0.52 | 0.45 | 0.58 | 0.51 | 0.48 |
| P ₂ O ₅ | 0.03 | 0.22 | 0.22 | 0.24 | 0.23 | 0.23 |
| MnO | 0.01 | 0.40 | 0.41 | 0.29 | 0.41 | 0.40 |
| SO ₃ | 0.02 | 0.15 | 0.51 | 0.51 | 0.27 | 0.41 |
| Cl | 0.002 | 0.15 | 3.60 | 3.55 | 0.47 | 1.09 |
| Sum | | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

3a). Walls Street**3a(i) Microscopy**

The air-fall samples from Walls Street ranged in colour from brown-red to grey-brown, reflecting the varying proportions of Fe₂O₃ and background material in the dust. The samples were generally coarser grained than the corresponding samples from Hummock Hill and Croquet Club. The results of the optical assessment are shown in Table 8. The elevated Cl content was due to the presence of halite (NaCl). The concentrations of Ti, P, Mn and S were similar to pellet plant dusts, with all <0.60%.

The background component (SiO₂) constituted ~50% of the sample, and ranged in size between 5-300µm. Most of the SiO₂ was rounded, ~5-50µm in size and exhibited Fe-staining/coating derived from natural weathering and transportation processes. The Fe staining/coating imparted a pale orange colour to the SiO₂. The samples from Walls Street also contained a greater amount of kish, magnetite and organic matter than samples from Hummock Hill.

Table 8. Walls Street Air-Fall Dusts: Optical Assessment

| Date | % Fe ₂ O ₃ | Size | % <5µm | % <10µm | % fract. | Other |
|--------------------|----------------------------------|------|--------|---------|----------|-------------------------------|
| WS-1: 23/12-8/1/04 | 30 | 2-50 | 1 | 30 | 50 | Qtz, mt, organic |
| WS-2: 8/1-22/1/04 | 15 | 2-50 | 1 | 20 | 60 | Qtz, hal, coke, kish, organic |
| WS-3: 22/1-3/2/04 | 20 | 5-40 | 1 | 30 | 50 | Qtz, hal, organic |
| WS-4: 13/2-23/2/04 | 50 | 2-50 | 5 | 30 | 30 | Qtz, mt, kish, organic |
| WS-5: 23/2-11/3/04 | 40 | 2-40 | 5 | 30 | 50 | Qtz, mt, kish, organic, cc |

Magnetite (1-3%) identified in the samples occurred as shiny black spherical/oblate particles from ~5-100µm in size, identical to observed in post-induration dusts. The sample collected between 22/1-3/2/04 was notably different from all others, containing less Fe₂O₃, more SiO₂ and NaCl. The Fe₂O₃ constituted approximately 20% of the sample, whilst NaCl constituted ~10-20% of the sample and organic matter (grass, insect carcasses) ~20% of the sample.

3a(ii) Quantitative XRD

The XRD results (Table 9) showed the air-fall dusts contained less hematite (18-45%), increased quartz (14-27%) and halite (1-28%) compared to Hummock Hill. The amount of goethite and kaolin were approximately the same as observed at Hummock Hill. The input from background minerals albite, orthoclase, mica and gypsum was also larger than found at Hummock Hill. As well as having the same minerals identified in Hummock Hill dusts, all the air-fall samples from Walls street also contained gehlenite (Ca₂Al(Si,Al)₂O₇), a slag mineral identified only at this location.

Table 9. Quantitative XRD Results for Walls Street Air-fall Dusts

| Walls Street | Hem | Goet | Qtz | Kaol | Hal | Mt | Cc | Dol | Talc | Alb | Or | Gyp | Mica | Gehl |
|--------------|-----|------|-----|------|-----|----|----|-----|------|-----|----|-----|------|------|
| 23/12-8/1/04 | 43 | 6 | 14 | 8 | 6 | 1 | 1 | 3 | 4 | 3 | 1 | 2 | 7 | 2 |
| 8/1-22/1/04 | 20 | 3 | 19 | 4 | 28 | 2 | 4 | 1 | 0 | 3 | 3 | 2 | 5 | 2 |
| 22/1-3/2/04 | 18 | 2 | 27 | 5 | 12 | 1 | 6 | 3 | 0 | 7 | 4 | 3 | 7 | 4 |
| 13/2-23/2/04 | 45 | 5 | 18 | 8 | 1 | 1 | 1 | 4 | 2 | 4 | 4 | 0 | 6 | 2 |
| 23/2-11/3/04 | 26 | 4 | 21 | 9 | 6 | 1 | 10 | 2 | 3 | 5 | 2 | 0 | 9 | 1 |

The origin of this pyrometallurgical mineral cannot be traced to the pellet plant. However, its presence in the air-fall dusts indicates that material originating from other areas of the steelworks may be mobilised off-site and into the surrounding environment.

3a(iii) Major Element Chemistry

In comparison to Hummock Hill, the air-fall dusts at Walls Street (Table 10) contained appreciable, though lesser concentrations of Fe, which ranged between 24.65-53.57%. The increased contribution from crustal material was reflected by increased concentrations of Si, Al, Mg, Ca, Na and K. The appreciably higher amounts of Na and Cl present in the samples WS-2 and WS-3 corresponded to 28% and 12% salt whilst the increased K content reflected the increased mica content of the dusts.

Table 10. Walls Street Air-Fall Dusts: Major Element Chemistry

| Major Elements | d.l. % | WS-1 | WS-2 | WS-3 | WS-4 | WS-5 |
|------------------------------------|---------------|-------------|-------------|-------------|-------------|-------------|
| SiO₂ | 0.35 | 30.67 | 25.06 | 38.70 | 29.08 | 37.35 |
| Al₂O₃ | 0.20 | 7.49 | 6.36 | 8.73 | 7.90 | 10.44 |
| MgO | 0.10 | 2.23 | 3.61 | 2.67 | 1.84 | 2.64 |
| Fe₂O₃ | 0.12 | 53.57 | 26.88 | 24.65 | 52.51 | 32.77 |
| CaO | 0.10 | 3.50 | 8.30 | 10.19 | 3.77 | 8.62 |
| Na₂O | 0.08 | 2.44 | 12.66 | 6.12 | 1.03 | 2.57 |
| K₂O | 0.05 | 0.96 | 1.19 | 1.53 | 1.03 | 1.53 |
| TiO₂ | 0.03 | 0.59 | 0.46 | 0.59 | 0.67 | 0.66 |
| P₂O₅ | 0.03 | 0.29 | 0.25 | 0.30 | 0.23 | 0.29 |
| MnO | 0.01 | 0.36 | 0.45 | 0.34 | 0.42 | 0.40 |
| SO₃ | 0.02 | 0.46 | 0.87 | 0.68 | 0.26 | 0.57 |
| Cl | 0.002 | 2.13 | 12.85 | 4.92 | 0.49 | 1.99 |
| Sum | | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

4a). Croquet Club

4a(i) Microscopy

The air-fall samples from the Croquet Club varied in colour from red-brown to grey-brown, with Fe₂O₃ constituting ~15% to 60% of the total air-fall sample. The Fe₂O₃ in the air-fall dusts ranged between 2-50µm in size, and were similar to dusts collected at Walls Street. The results of the optical assessment are shown in Table 11.

The increased contribution from crustal material was reflected by increased concentrations of Si, Al, Mg, Ca, Na and K. The appreciably higher amounts of Na and Cl present in the samples WS-2 and WS-3 corresponded to 28% and 12% salt whilst the increased K content reflected the increased mica content of the dusts.

Table 11. Croquet Club Air-Fall Dusts: Optical Assessment

| Date | % Fe ₂ O ₃ | Size | % <5µm | % <10µm | % fract. | Other |
|--------------|----------------------------------|-------|--------|---------|----------|------------------------------------|
| 23/12-8/1/04 | 60 | 2-40 | 20 | 40 | 50 | Qtz, coke, cc, kish, organic, mica |
| 8/1-22/1/04 | 35 | 5-30 | 1 | 50 | 50 | Qtz, coke, organic |
| 22/1-3/2/04 | 15 | 10-50 | 0 | 2 | 20 | Qtz, organic, hal, cc |
| 13/2-23/2/04 | 50 | 2-30 | 10 | 60 | 50 | Qtz, mt, kish, organic |
| 23/2-11/3/04 | 40 | 2-50 | 10 | 40 | 50 | Qtz, hal, mt, kish, organic, cc |

The sample collected between 22/1-3/2/04 contained the least Fe₂O₃ (15%), similar to the samples from Hummock Hill and Walls Street. The sample was dominated by crustal material (SiO₂). This material constituted 30-50% of the total air-fall dust and ranged between 2-150µm, with most particles between 5-50µm in size. The air-fall samples from Croquet Club were found to contain the largest amount of organic matter. This was particularly noticeable for the samples collected between 8/1-22/1/04 and 22/1-3/2/04. The organic component of these samples was 30% and 20% respectively, with the majority of the material being derived from the trees in the immediate vicinity.

4a(ii) Quantitative XRD

The quantitative mineralogy of the Croquet Club air-fall dusts (Table 12) showed a much wider range in the amount of hematite and quartz than observed at Hummock Hill or Walls Street. The hematite content ranged between 10-54%, whilst quartz content ranged between 12-43%. The amounts of goethite, kaolin and crustal minerals were similar to that observed at Walls Street. The dust CC-3 (22/1-3/2/03) contained appreciably less hematite and goethite and more quartz, calcite and halite than the other samples from this site.

Table 12. Quantitative XRD Results for Croquet Club Air-fall Dusts

| Croquet Club | Hem | Goet | Qtz | Kaol | Hal | Mt | Cc | Dol | Talc | Alb | Or | Gyp | Mica |
|---------------------------|-----|------|-----|------|-----|----|----|-----|------|-----|----|-----|------|
| CC-1: 23/12-8/1/04 | 54 | 8 | 12 | 8 | 2 | 2 | <1 | 2 | 3 | 2 | 1 | <1 | 5 |
| CC-2: 8/1-22/1/04 | 41 | 5 | 19 | 9 | 4 | 2 | 3 | 2 | 2 | 3 | 1 | 2 | 6 |
| CC-3: 22/1-3/2/04 | 10 | 1 | 43 | 5 | 12 | 1 | 9 | <1 | <1 | 6 | 3 | 2 | 7 |
| CC-4: 13/2-23/2/04 | 47 | 6 | 14 | 10 | 4 | 1 | 2 | 1 | 2 | 2 | 1 | 3 | 6 |
| CC-5: 23/2-11/3/04 | 32 | 4 | 17 | 9 | 12 | 1 | 8 | 1 | 2 | 3 | 2 | 1 | 8 |

The amount of mica identified in the dusts was approximately the same as Walls Street, whilst the contribution of crustal minerals and sea salt were 36-88% and 2-12% respectively.

4a(iii) Major Element Chemistry

The Fe concentrations in air-fall dusts ranged between 17.11-62.11%, much greater than observed at Hummock Hill or Walls Street. The amount of Si in the dusts varied between 20.25-38.32%, whilst the amount of Ca in the dusts (2.38-8.25%) was slightly lower than found at Hummock Hill or Walls Street.

The concentrations of Al and Mg were similar to those at Hummock Hill and Walls Street. Na was present in all samples at concentrations between 1.71-8.97%, whilst the Cl content of the dusts ranged between 1.24-7.94%. This corresponded to 4-12% NaCl identified by XRD.

Table 13. Croquet Club Air-Fall Dusts: Major Element Chemistry

| Major Elements | d.l.% | CC-1 | CC-2 | CC-3 | CC-4 | CC-5 |
|------------------------------------|--------------|-------------|-------------|-------------|-------------|-------------|
| SiO₂ | 0.35 | 20.25 | 24.66 | 38.32 | 24.03 | 30.58 |
| Al₂O₃ | 0.20 | 6.99 | 6.47 | 8.14 | 7.98 | 8.94 |
| MgO | 0.10 | 1.84 | 2.98 | 3.88 | 2.70 | 2.97 |
| Fe₂O₃ | 0.12 | 62.11 | 48.53 | 17.11 | 52.81 | 35.48 |
| CaO | 0.10 | 2.38 | 5.45 | 8.25 | 3.62 | 7.50 |
| Na₂O | 0.08 | 1.71 | 3.82 | 8.97 | 2.31 | 5.02 |
| K₂O | 0.05 | 0.76 | 1.90 | 4.30 | 1.21 | 1.51 |
| TiO₂ | 0.03 | 0.58 | 0.53 | 0.58 | 0.57 | 0.58 |
| P₂O₅ | 0.03 | 0.27 | 0.51 | 1.03 | 0.32 | 0.27 |
| MnO | 0.01 | 0.37 | 0.49 | 0.24 | 0.40 | 0.36 |
| SO₃ | 0.02 | 0.53 | 0.53 | 0.62 | 0.78 | 0.72 |
| Cl | 0.002 | 1.24 | 3.59 | 7.94 | 2.54 | 5.01 |
| Sum | | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

PART 2 ~ SOURCE APPORTIONMENT

The source apportionment method used to assess the contribution of different areas of the pellet plant to air-fall dusts was based on a methodology developed in Port Pirie to relate indoor air-fall dusts to individual processes within the smelter. The use of optical microscopy provided important information on particle size, morphology and colour not available from chemical or XRD analysis. The result is a *qualitative* estimate based on the similarities between the particle size, morphology and degree of fracturing between pellet plant source samples and the air-fall dusts. A number of caveats to this method were;

- Estimates of individual source contributions to air-fall samples were $\pm 10\%$
- Limited number of pellet plant source dusts (10) used in apportionment
- Similarity between particle size and morphology of adjacent processes limited accuracy of apportionment
- Apportionment estimates provided no information on individual emission events
- Other sources of Fe_2O_3 dust, eg: roofs and horizontal surfaces, roads, material handling facilities and re-entrained dust may also contribute to the air-fall material
- The similarity in source dust chemistry precluded use of statistical approaches such as Principal Component Analysis (PCA)

Two sampled areas of the pellet plant were considered to make relatively minor contribution to fugitive material. These were the reclaims shed and induration kiln. The minor contribution from the reclaims shed was due to the material being enclosed whilst the induration-related material was due large particle size (10-2000 μm).

The main features identified from the characterisation of pellet plant dusts were;

- The main sources of $<5\mu\text{m}$ material were post-drying, post-grinding and “black hole” areas (samples 4, 5 and 10)
- Mechanically fractured material was a major constituent of dusts from the post-grinding area (sample 5)
- Coarser (20-70 μm) non-fractured Fe_2O_3 associated mainly with screening plant dust (sample 1)
- Black, shiny spherical material was characteristic of post-induration dusts (samples 6, 7 and 8)

Using these criteria, the following source apportionment results for the air-fall dusts are given in Table 14.

Table 14. Source Apportionment for Hummock Hill, Walls Street and Croquet Club Air-fall Samples.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | Total Fe% |
|-----------------------|----|---|----|----|----|---|---|---|----|-----------|
| Hummock Hill-1 | 20 | 2 | 7 | 10 | 20 | 0 | 1 | 0 | 10 | 70 |
| Hummock Hill-2 | 20 | 0 | 5 | 5 | 15 | 0 | 0 | 0 | 15 | 60 |
| Hummock Hill-3 | 5 | 0 | 2 | 2 | 5 | 0 | 1 | 0 | 5 | 20 |
| Hummock Hill-4 | 20 | 1 | 2 | 2 | 20 | 2 | 2 | 0 | 10 | 60 |
| Hummock Hill-5 | 20 | 2 | 10 | 10 | 20 | 0 | 3 | 0 | 10 | 75 |

| | | | | | | | | | | |
|-----------------------|----|---|---|---|----|---|---|---|----|-----------|
| Walls Street-1 | 10 | 0 | 5 | 2 | 5 | 1 | 0 | 0 | 7 | 30 |
| Walls Street-2 | 5 | 0 | 2 | 2 | 2 | 0 | 1 | 0 | 3 | 15 |
| Walls Street-3 | 10 | 0 | 0 | 5 | 2 | 0 | 1 | 0 | 2 | 20 |
| Walls Street-4 | 20 | 0 | 2 | 5 | 10 | 1 | 2 | 0 | 10 | 50 |
| Walls Street-5 | 10 | 1 | 2 | 5 | 10 | 0 | 2 | 0 | 10 | 40 |

| | | | | | | | | | | |
|-----------------------|----|---|---|----|----|---|---|---|----|-----------|
| Croquet Club-1 | 10 | 0 | 5 | 10 | 20 | 2 | 2 | 1 | 10 | 60 |
| Croquet Club-2 | 15 | 0 | 2 | 10 | 2 | 0 | 1 | 0 | 5 | 35 |
| Croquet Club-3 | 5 | 0 | 2 | 5 | 1 | 0 | 0 | 0 | 2 | 15 |
| Croquet Club-4 | 20 | 0 | 5 | 5 | 10 | 0 | 0 | 0 | 10 | 50 |
| Croquet Club-5 | 20 | 0 | 2 | 2 | 10 | 0 | 1 | 0 | 5 | 40 |

The results of the source apportionment indicated four areas of the pellet plant were most likely to be the main sources of fugitive dust. These were screening plant, post-drying, post-grinding and the “black hole” areas. A minor contribution (1-3%) was also apportioned to post-induration areas based on the identification of magnetic, spherical material identical to dusts associated with post-induration areas.

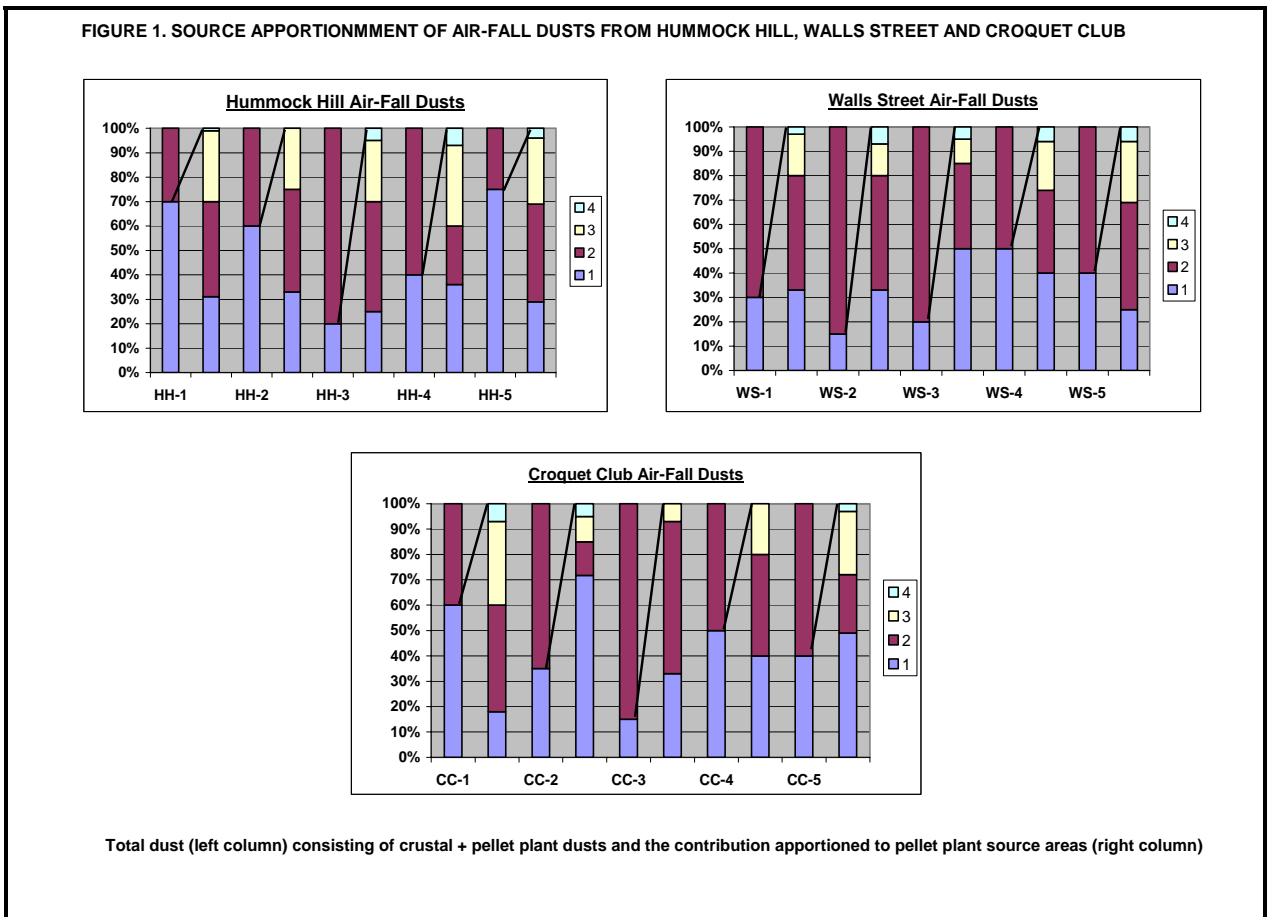
Identification of individual pellet plant source areas was made difficult because of the overlapping characteristics of dusts from adjacent operations. This was particularly so for dusts from the post-drying, post-grinding and “black hole” areas, each of which contained differing amounts of <5µm, <10µm and mechanical fractured material (see Table 1). As a result of this similarity, dusts from the pre-drying, post-drying and “black hole” areas were combined as a single source.

Dusts associated with the No.3 screening plant and adjacent export stockpiles were not included as separate source areas because these sources are situated much further from the receptors. The characteristics of dusts from these locations were identical to material from No. 1 screening plant. As a result, these areas were not included in the source

apportionment. However, it does not mean these areas do not contribute to the total fugitive emissions from the pellet plant and environs. Consequently, the source apportionment results have been reduced to four main source areas. These consisted of:

- (1) screening plant/reclaims shed (samples 1 and 2)
- (2) pre-drying, post-drying and “black hole” (samples 3, 4 and 10)
- (3) post-grinding, (sample 5) and
- (4) post-induration areas (samples 6, 7 and 8)

A comparison of the apportionment results for each location using these four sources are shown in Figure 1.



The contributions apportioned to each source area differed between sampling locations and dates. At Hummock Hill the results of the source apportionment showed the contributions from these four source areas were: (1) 25-35%, (2) 23-45%, (3) 25-33% and (4) 0-7% respectively. By comparison, the results from Walls Street were 28-50%, 35-47%, 10-25% and 3-7% respectively, whilst at the Croquet Club, the results were 17-50%, 23-60%, 6-33% and 0-8% respectively.

The results of the source apportionment showed that raw materials/screening plant and operations associated with drying (including “black hole”) areas were responsible for >60% of the Fe₂O₃ present in all air-fall dusts. The post-grinding area, the major source of material <5µm in size, accounted for up to one-third of the air-fall dust in certain samples, particularly at Hummock Hill and Croquet Club.

Main Findings

Characterisation of air-fall dusts collected from Hummock Hill, Walls Street and Croquet Club using optical, chemical and XRD approaches revealed the following features;

- Optical assessment of the air-fall dust showed Fe₂O₃ accounted for 20-75% at Hummock Hill, 15-50% at Walls Street and 15-60% at Croquet Club
- Chemical analysis of the air-fall dusts showed Fe₂O₃ content ranged between 39-76% at Hummock Hill, 25-54% at Walls Street and 17-62% at Croquet Club
- Higher Fe₂O₃ content in air-fall dusts at Hummock Hill due to proximity of pellet plant
- The largest range of Fe₂O₃ (17-62%) was found at the Croquet Club site
- Chlorine content of the air-fall dusts varied appreciably, reflecting the contribution of sea salt to the overall mineralogy
- The mineralogy of dusts was relatively simple, the pellet plant component consisting of hematite and goethite and background/crustal component consisting of quartz, halite, mica and calcite
- The presence of kish (graphite) indicated contribution from other areas of the steelworks
- Air-fall dusts represented a limited number of samples, determined by meteorological conditions, particulate deposition rates and distance from pellet plant

The results from the source apportionment identified the following features;

- Limited number of source samples (10) were used in assessment of possible dust sources
- Dust <5µm in size derived mainly from dry grinding and “black hole” areas
- Overlapping of physical and chemical characteristics between adjacent operations, making unambiguous apportionment very difficult
- The main sources of air-fall dust were;
 - (No. 1 screening plant) which accounted for 17-50% (ave. 35%),
 - drying and “black hole” which accounted for 23-60% (ave. 41%),

- dry grinding area, which accounted for 6-33% (ave. 21%)
- post induration, which accounted for 0-8% (ave. 4%)

The announcement of a \$10 million program to relocate the screening and crushing operations from the current location at the pellet plant to the mine site should result in appreciable reductions in fugitive emissions, particularly of material 10-50µm in size.

The amount of air-fall dust <10µm in size and the associated amenity problem indicate attention should be focussed on reducing the amount of fugitive dust associated with drying, grinding and “black hole” areas of the pellet plant. This may include a review of handling and conveyor operations, housekeeping or other engineering solutions.

Acknowledgements

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APPENDIX 1: MINERALS IDENTIFIED BY XRD and OPTICAL MICROSCOPY: CHEMICAL COMPOSITION (IDEAL)

The quantitative XRD and microscopic analysis of pellet plant dusts identified 14 phases. Optical microscopy also identified two poorly crystalline/amorphous phases coke and kish graphite. The composition (ideal) of these phases is listed below.

| Phase | Chemistry (ideal) |
|-------------------|--|
| Hematite | Fe ₂ O ₃ |
| Goethite | FeO ₂ H |
| Quartz | SiO ₂ |
| Kaolin (clay) | Al ₄ Si ₄ O ₁₀ (OH) ₈ |
| Halite | NaCl |
| Magnetite | Fe ₃ O ₄ |
| Calcite/aragonite | CaCO ₃ |
| Dolomite | CaMg(CO ₃) ₂ |
| Augite | Ca(Fe,Mg)Si ₂ O ₆ |
| Albite | NaAlSi ₃ O ₈ |
| Talc | Mg ₃ Si ₄ O ₁₀ (OH) ₂ |
| Mica (white) | KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂ |
| Othoclase | KAlSi ₃ O ₈ |
| Gehlenite (slag) | Ca ₂ Al(Si,Al) ₂ O ₇ |

Optical Identification

Kish C (graphite)
Coke C

XRD PATTERNS for PELLET PLANT SOURCE DUSTS

1A: No 1 SCREENING PLANT
2A: RECLAIMS SHED
3A: SPILLAGE, #2744 CONVEYOR
4A: PRE-GRINDING, No. 4 FEED IN
5A: POST GRINDING
6A: INDURATION-MULTI CYCLONE DUST VALVE
7A: INDURATION-ADJACENT TO COOLING STACK
8A: INDURATION KILN-EXIT END
9A: No.3 SCREENING PLANT
10A: "BLACK HOLE" CONVEYOR SPILLAGE

XRD Patterns for Air-Fall Dust Samples from Hummock Hill, Walls Street and the Croquet Club

Hummock Hill

23/12/03 - 8/1/04
8/1/04 - 22/1/04
22/1/04 - 3/2/04
13/2/04 - 23/2/04
23/2/04 - 11/3/04

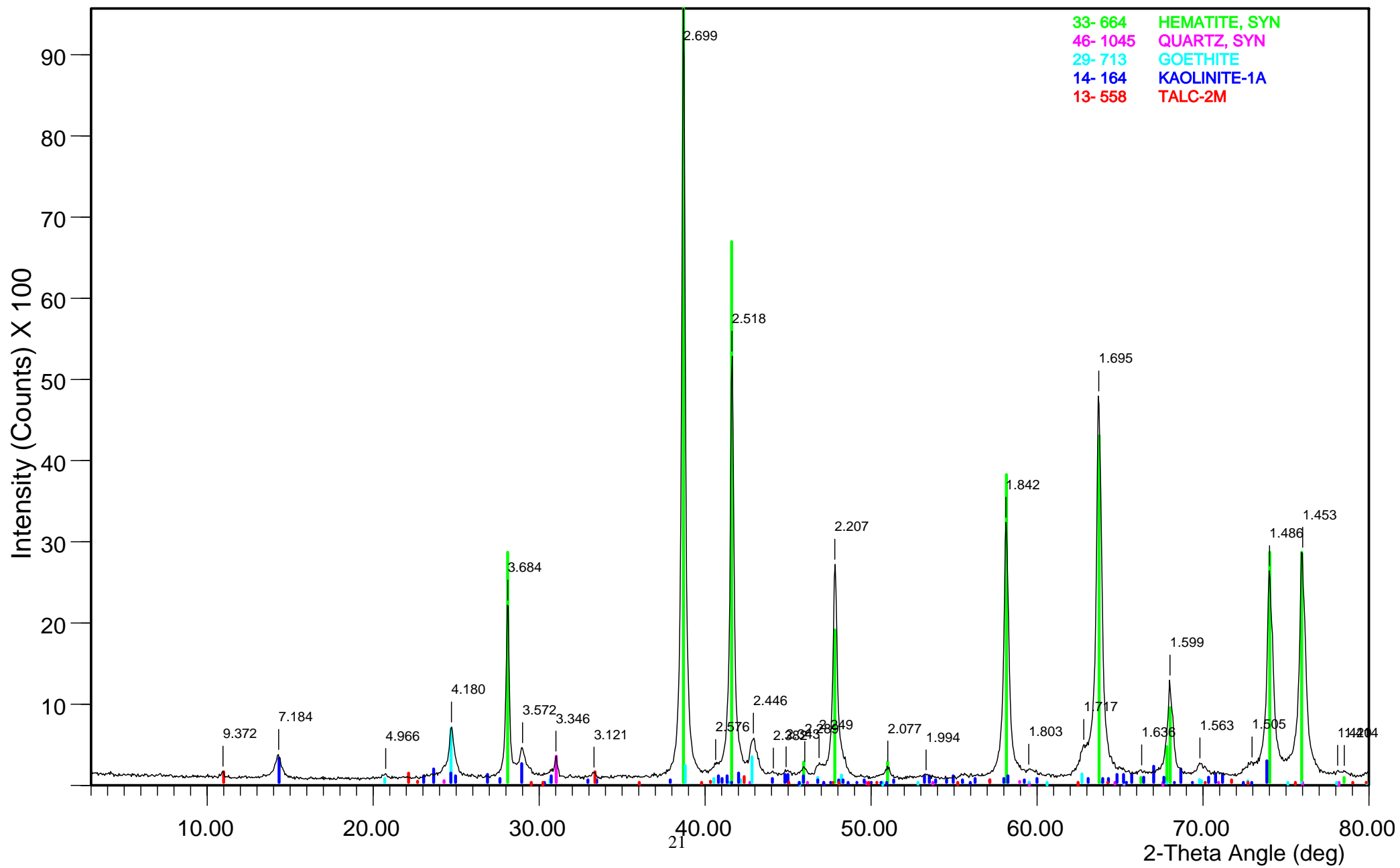
Walls Street

23/12/03 - 8/1/04
8/1/04 - 22/1/04
22/1/04 - 3/2/04
13/2/04 - 23/2/04
23/2/04 - 11/3/04

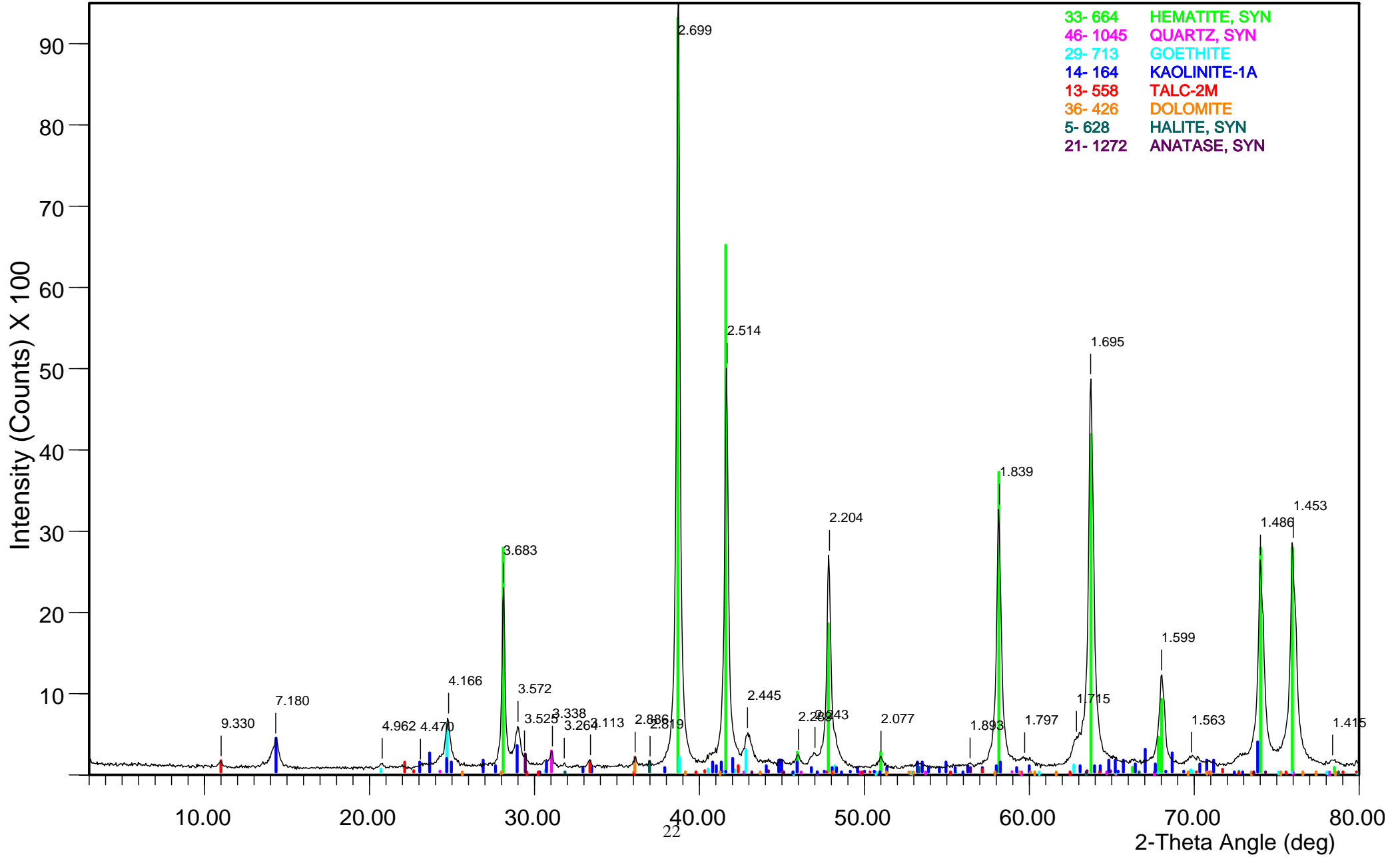
Croquet Club

23/12/03 - 8/1/04
8/1/04 - 22/1/04
22/1/04 - 3/2/04
13/2/04 - 23/2/04
23/2/04 - 11/3/04

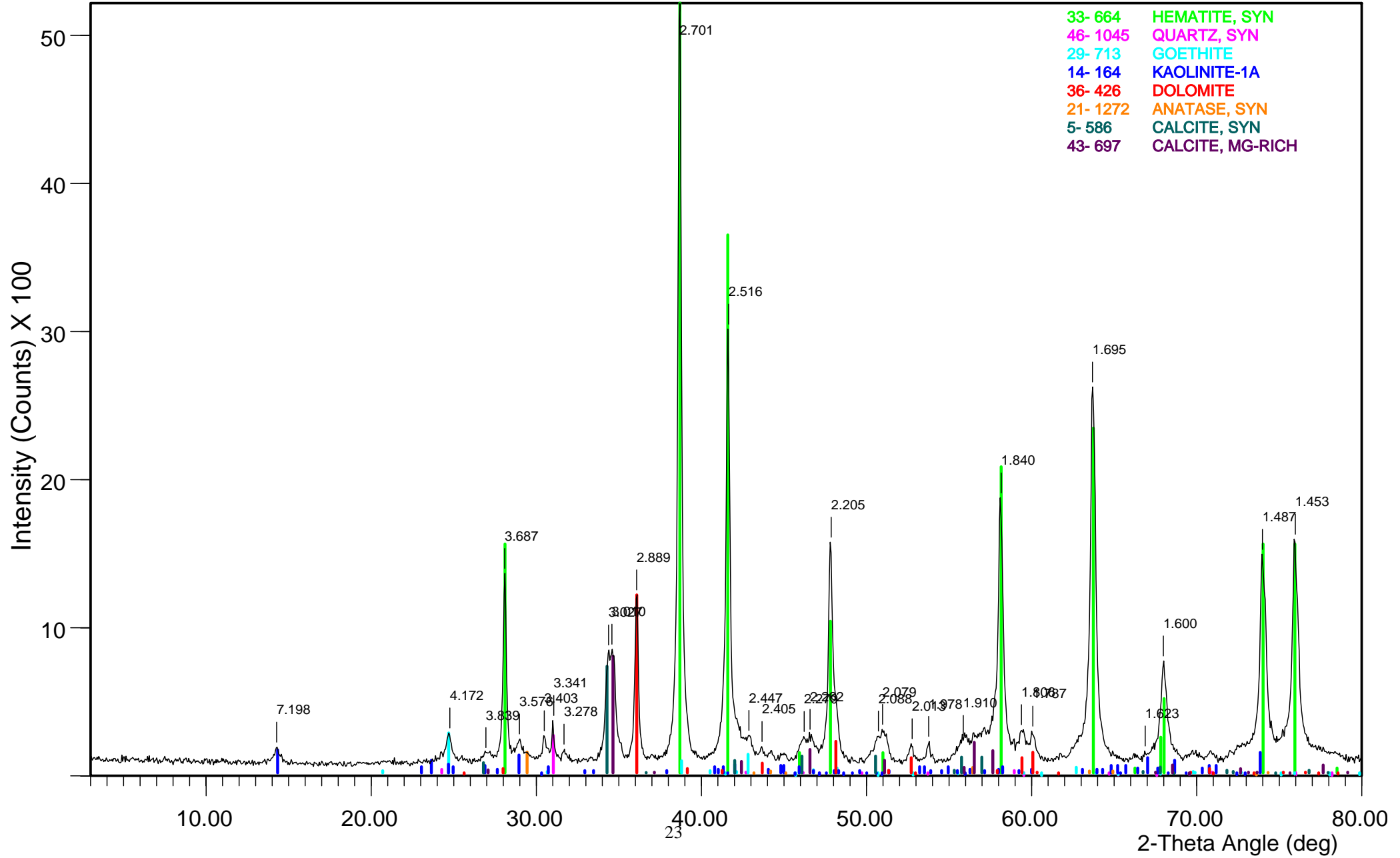
1A



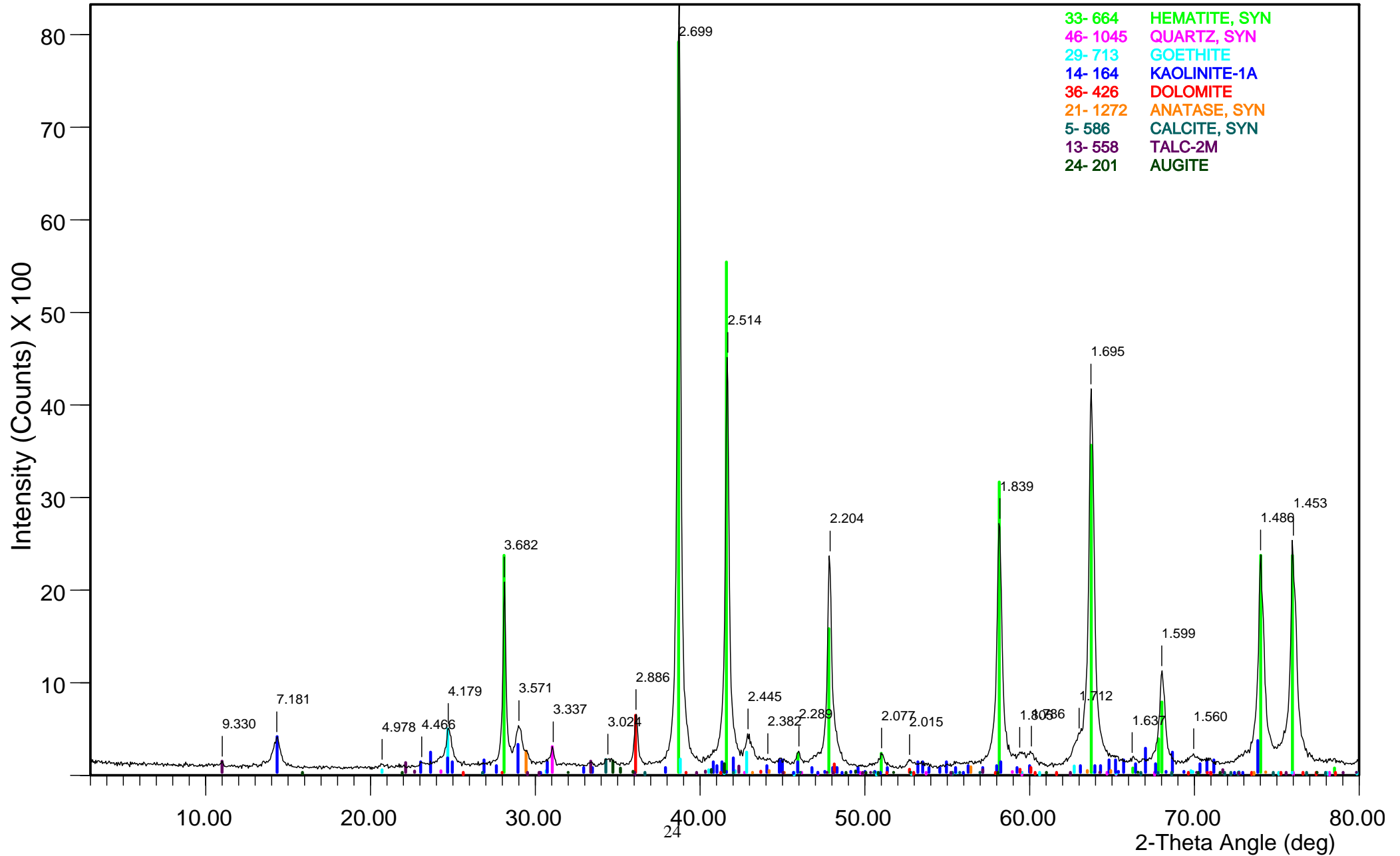
2A



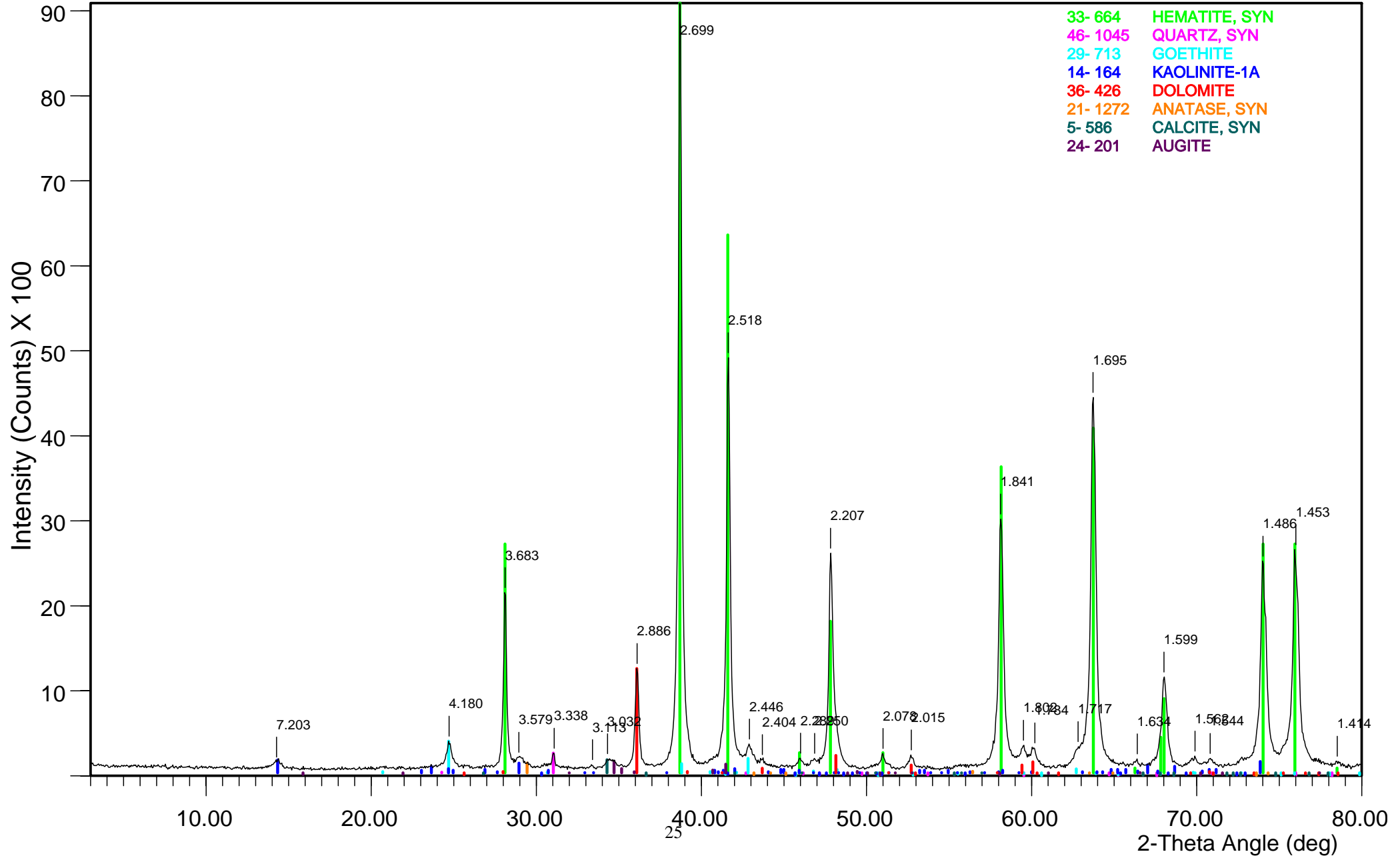
3A



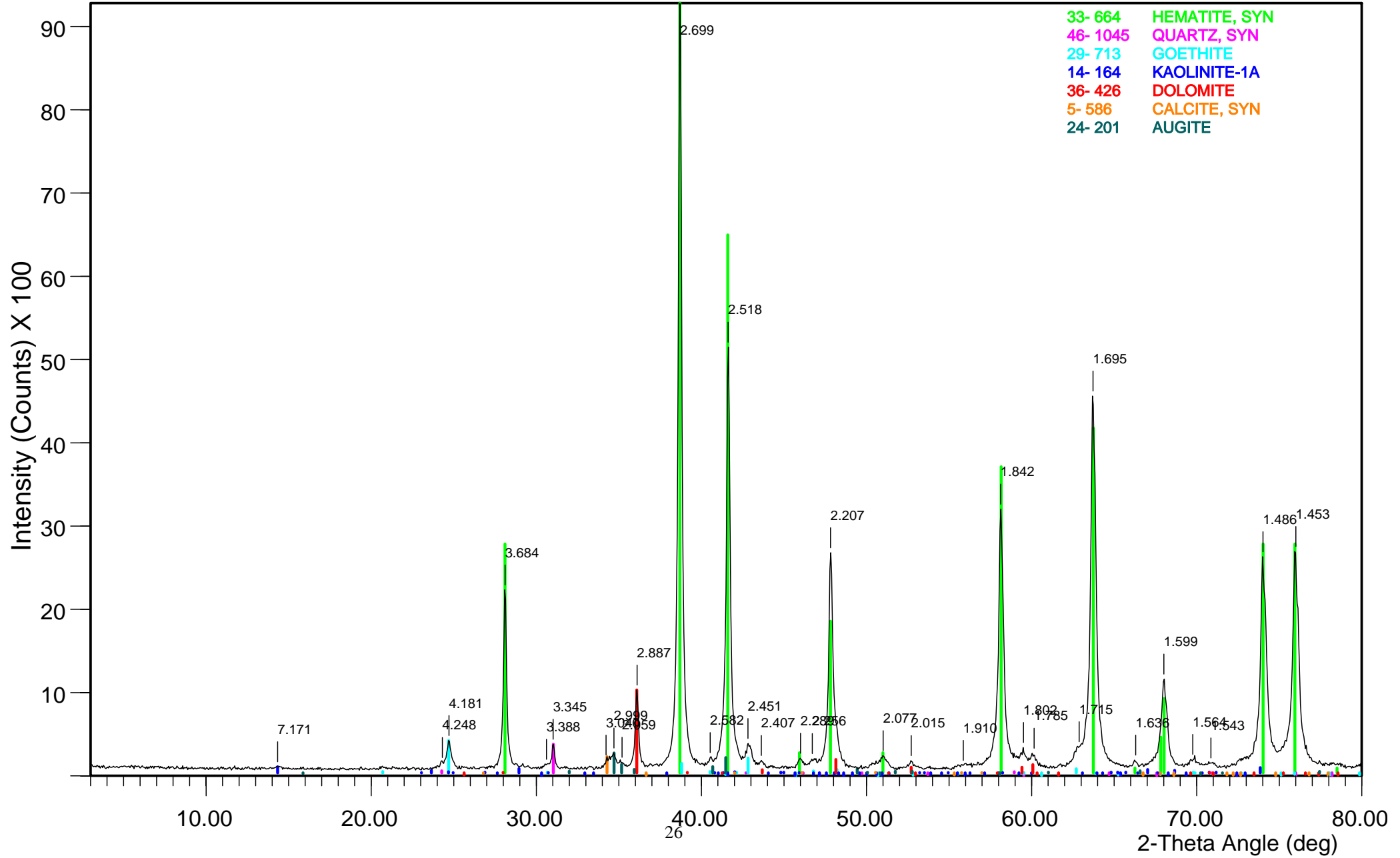
4A



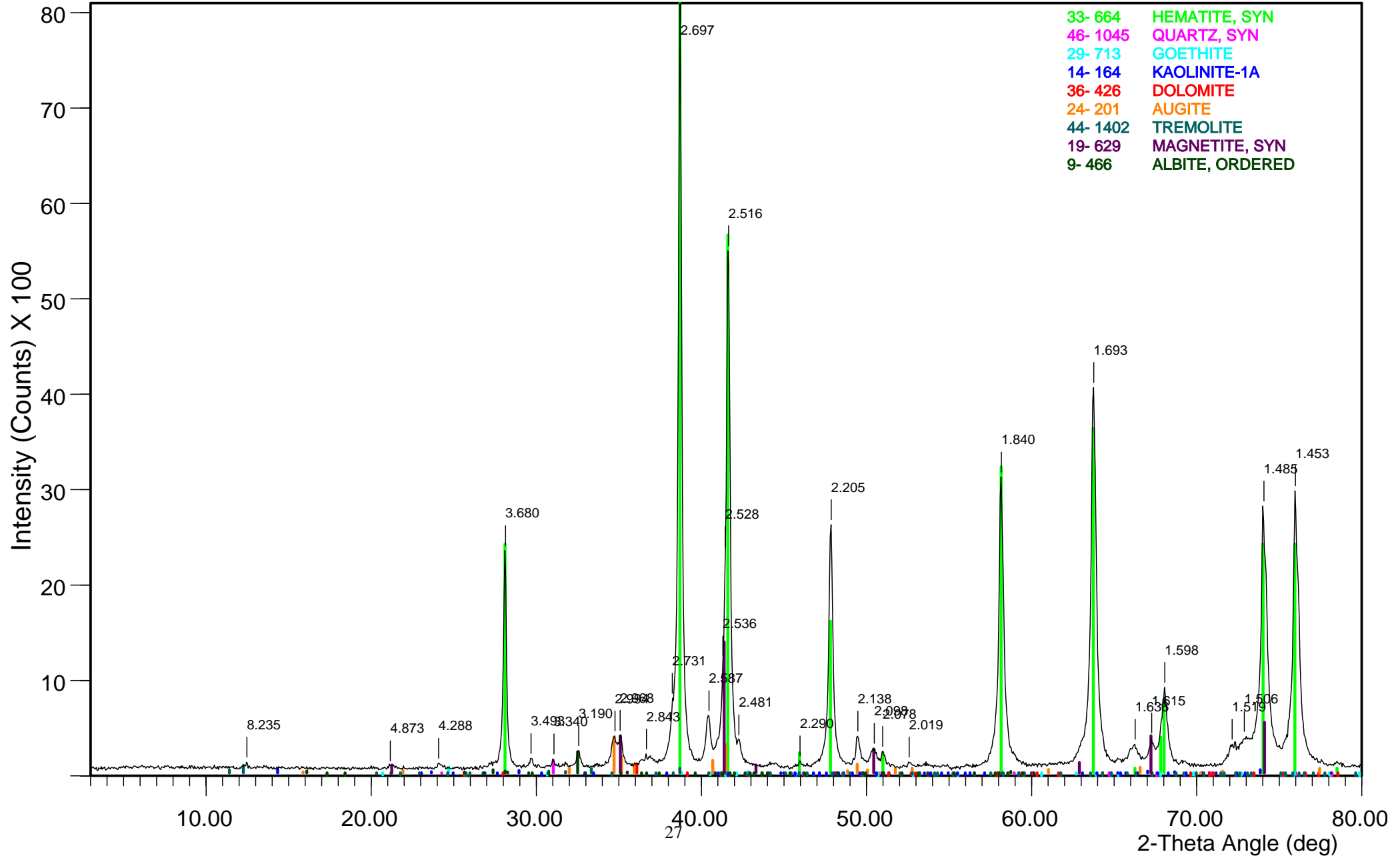
5A



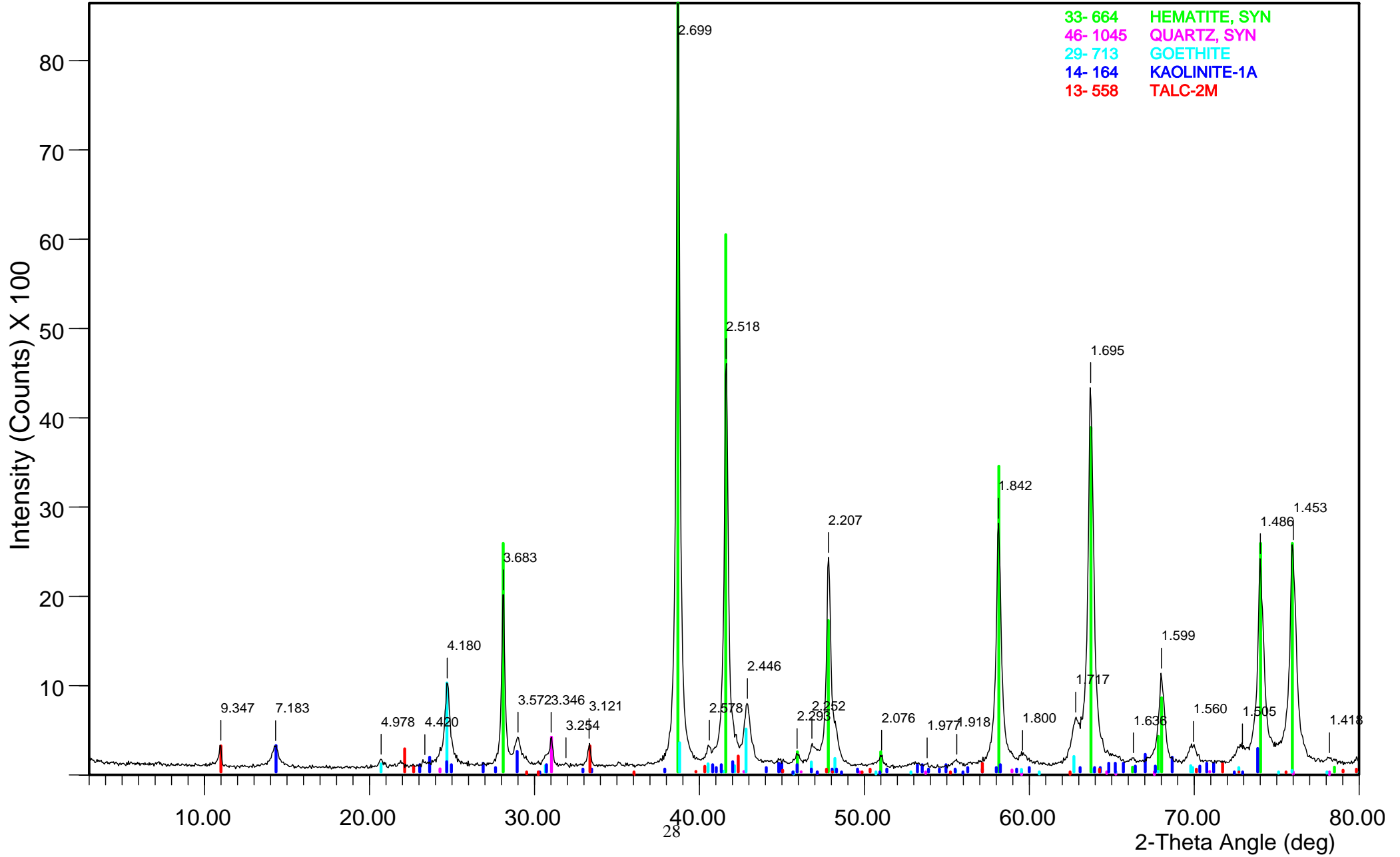
6A



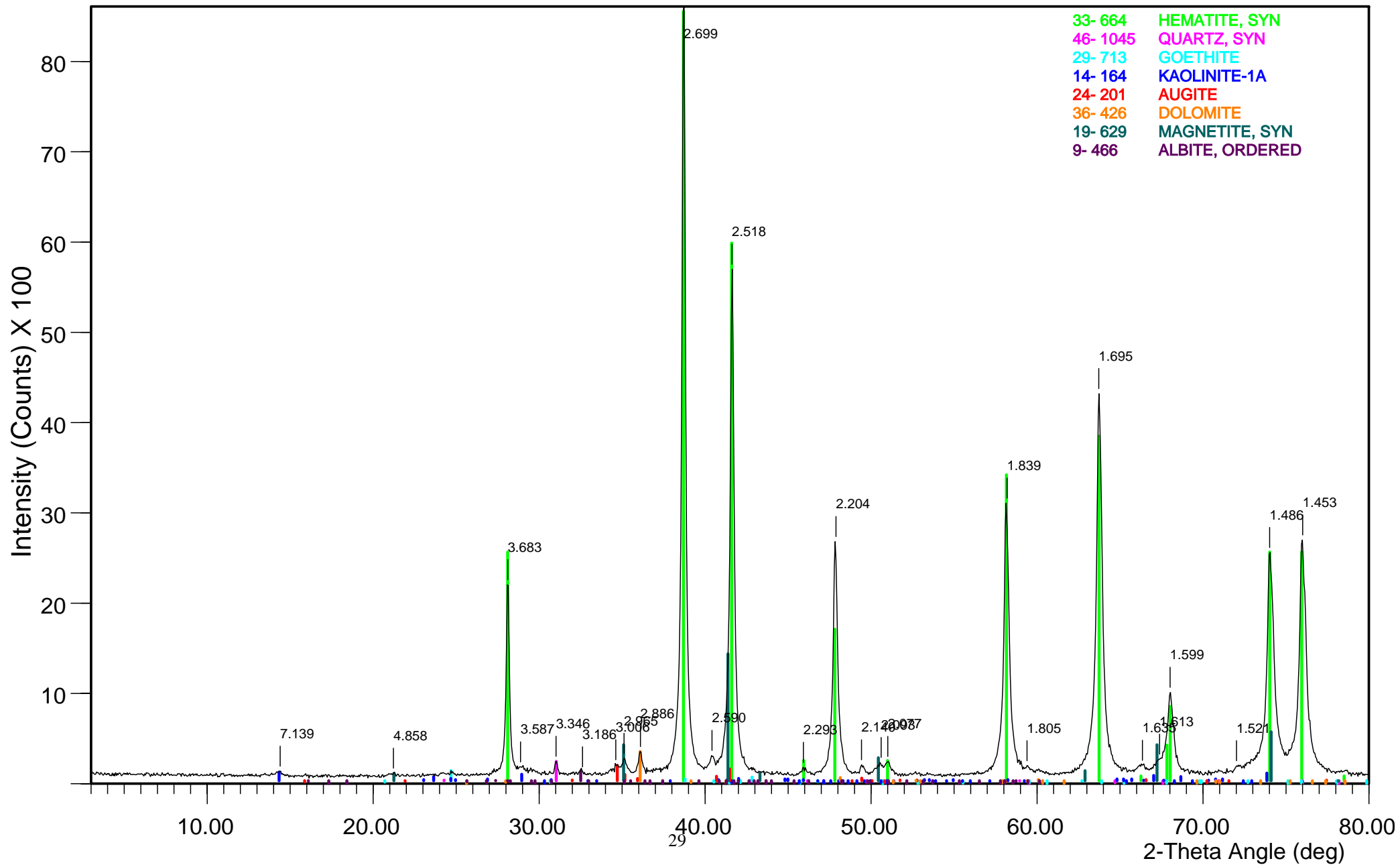
7A



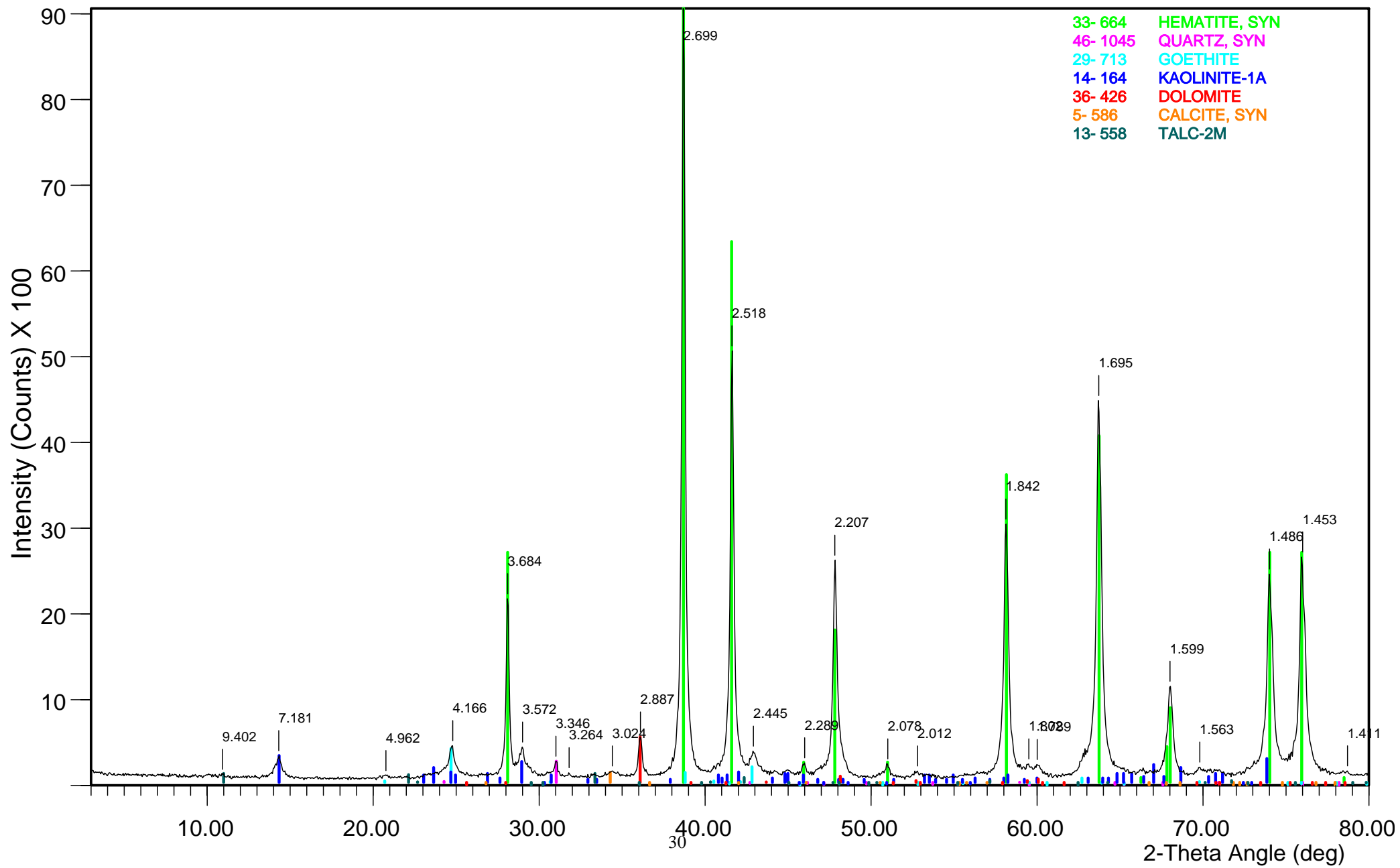
8A



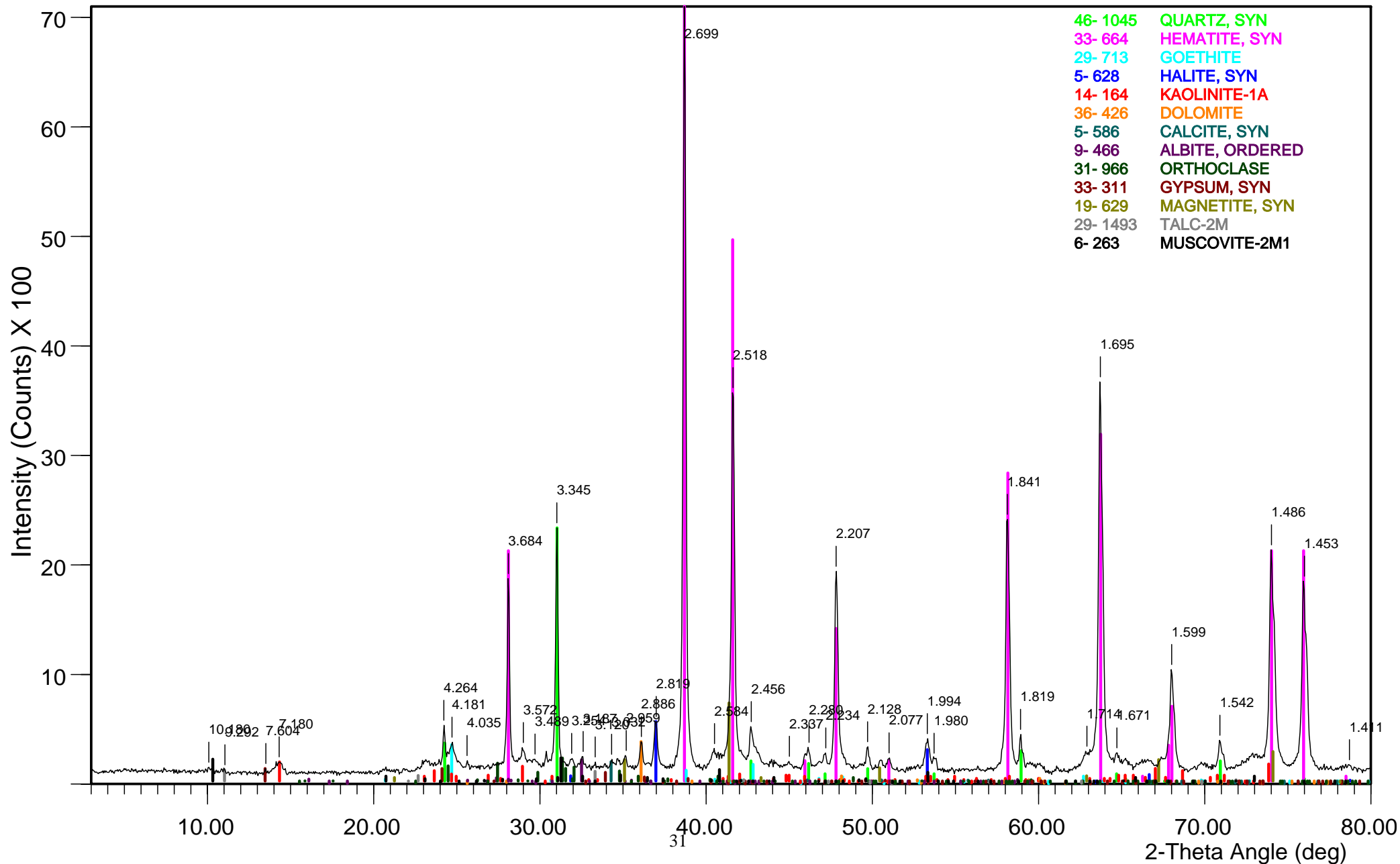
9A



10A

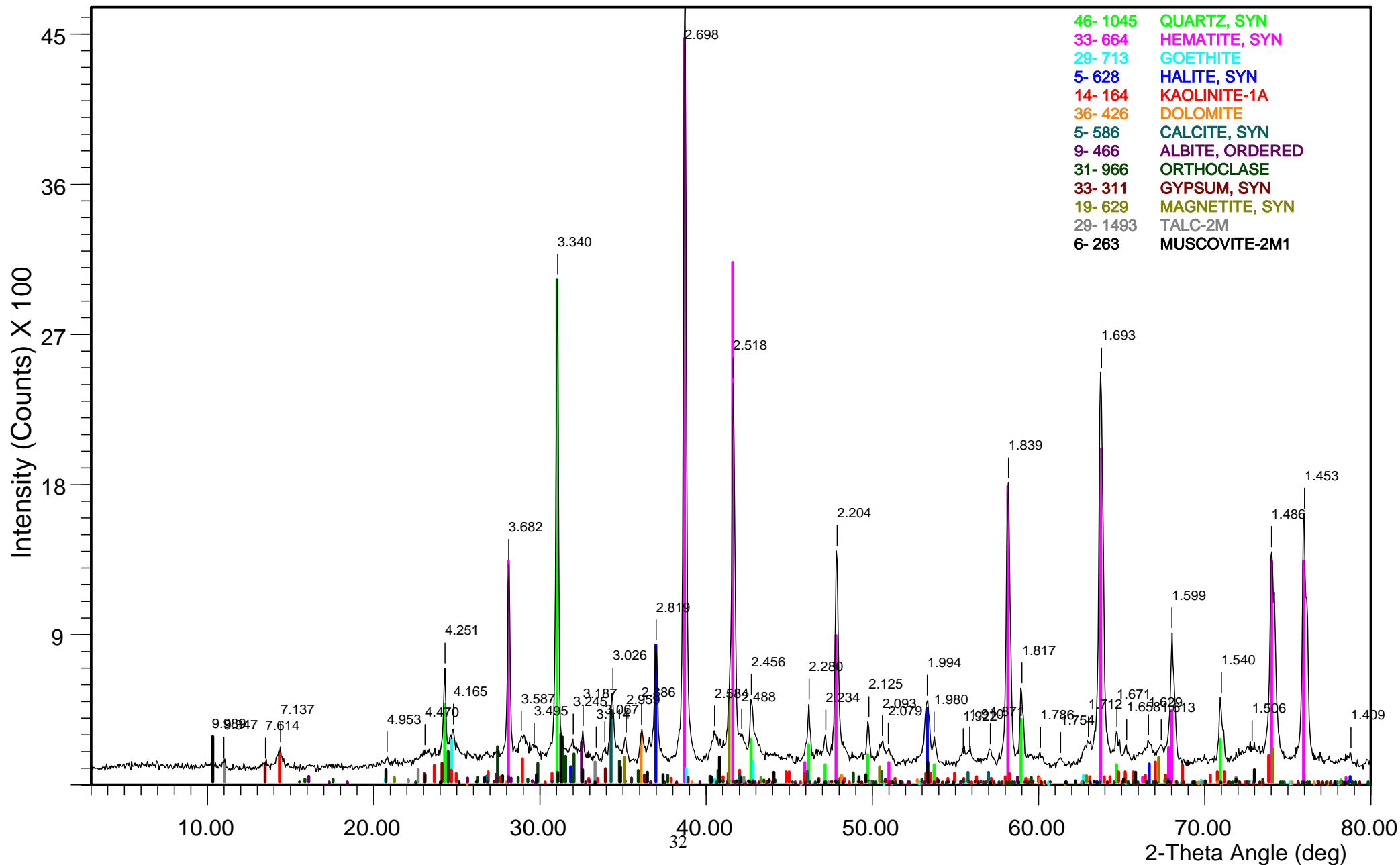


Croquet Club 23-12-03

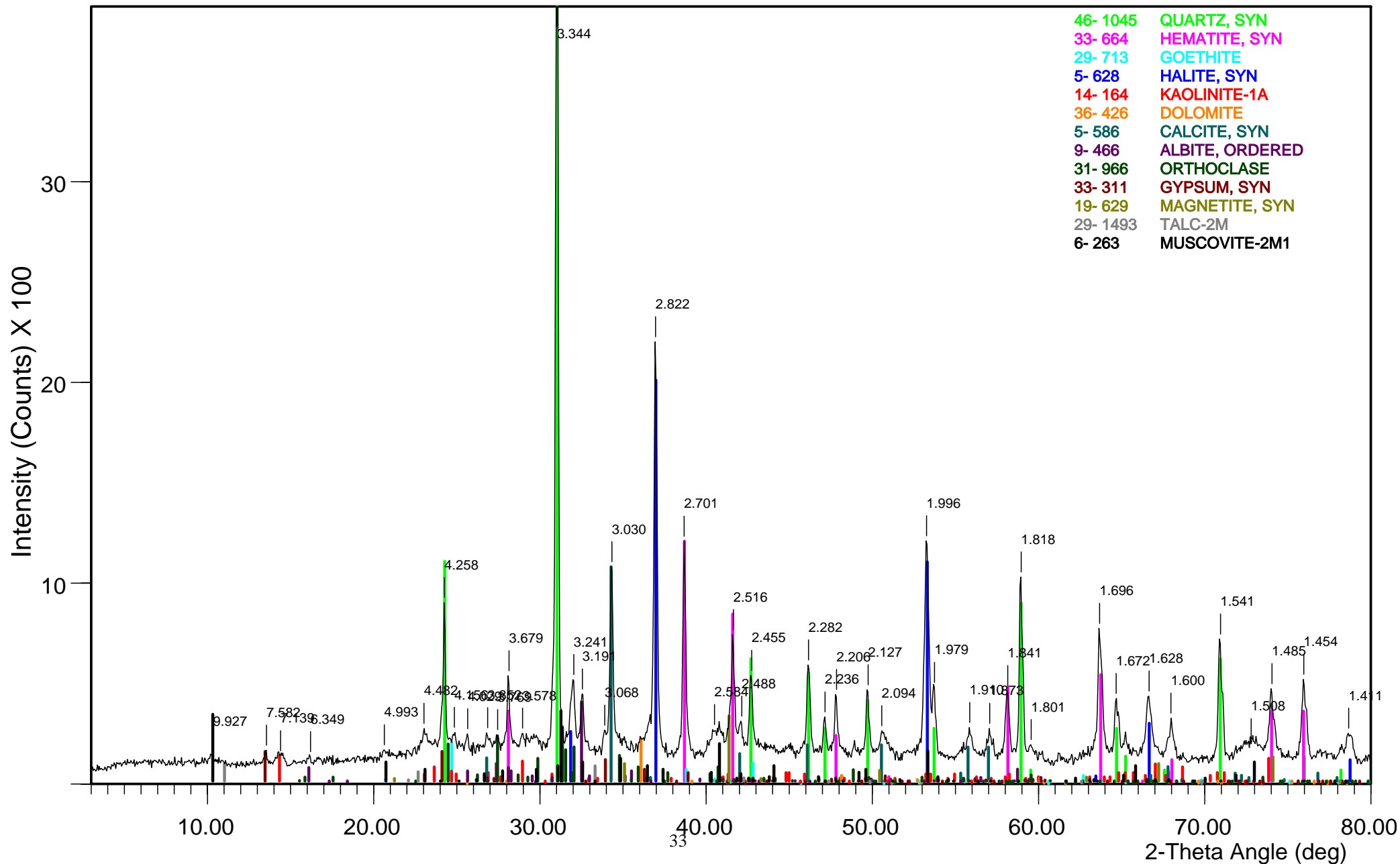


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Croquet Club 8-1-04

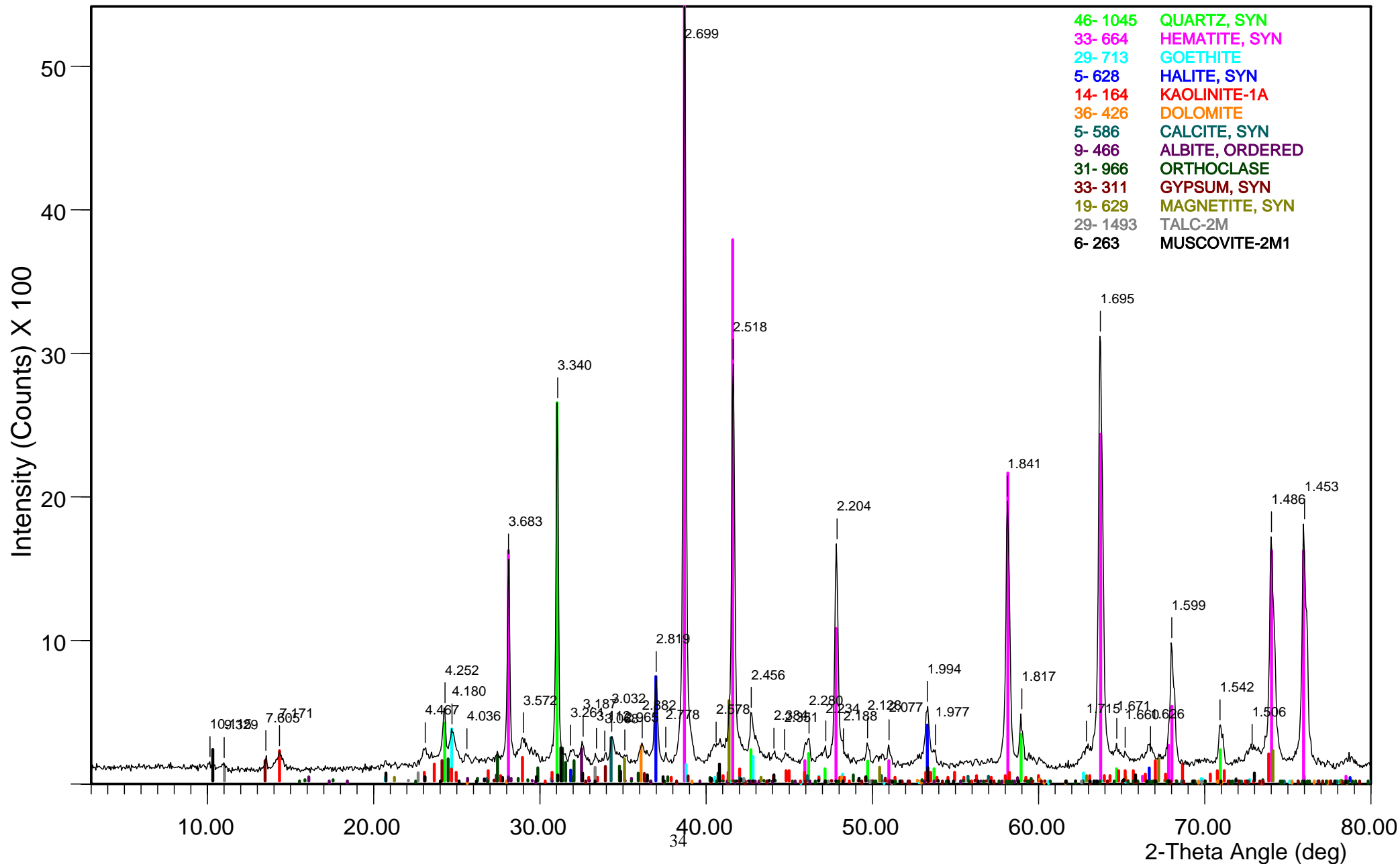


Croquet Club 22-1-04

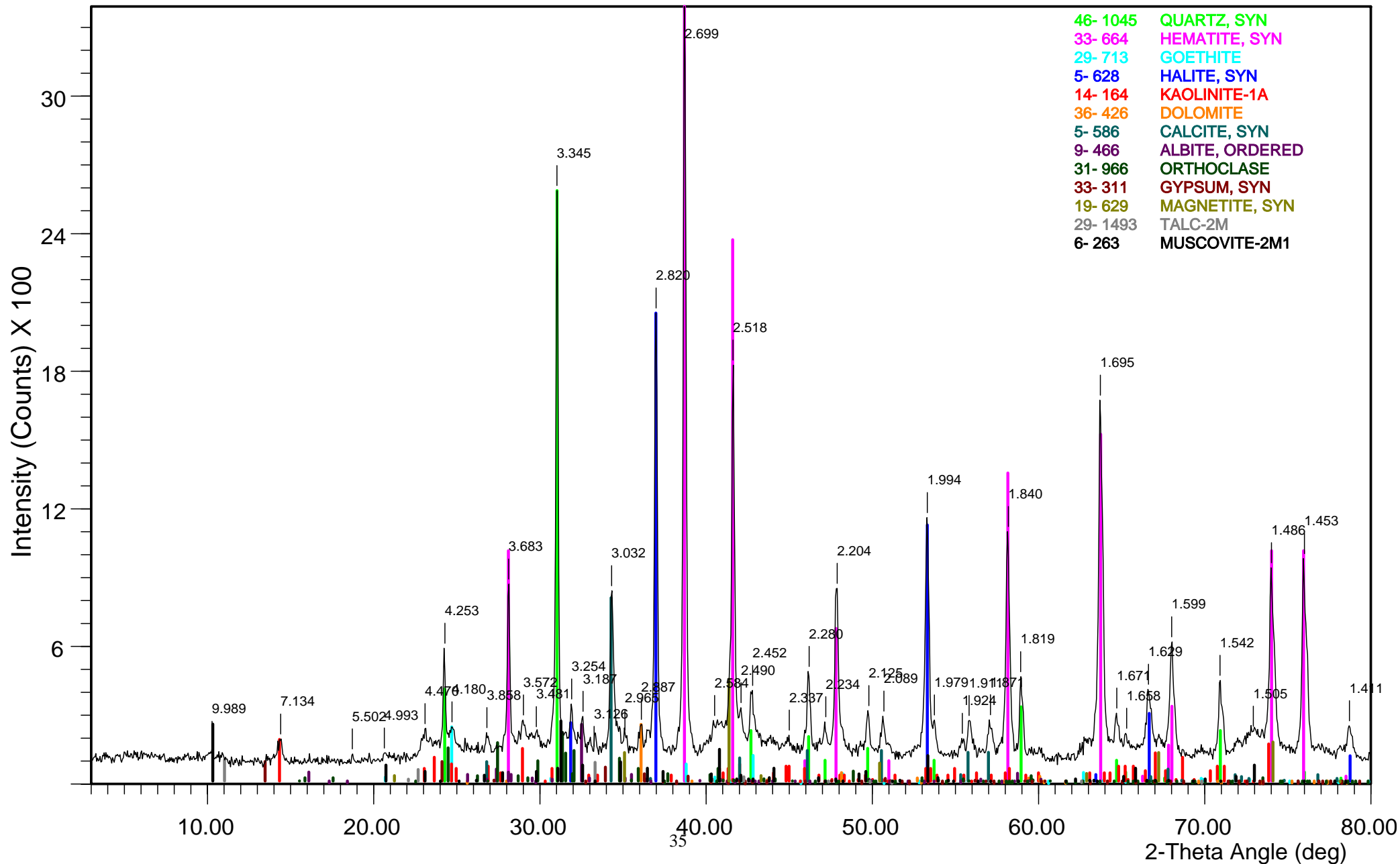


- 46- 1045 QUARTZ, SYN
- 33- 664 HEMATITE, SYN
- 29- 713 GOETHITE
- 5- 628 HALITE, SYN
- 14- 164 KAOLINITE-1A
- 36- 426 DOLOMITE
- 5- 586 CALCITE, SYN
- 9- 466 ALBITE, ORDERED
- 31- 966 ORTHOCLASE
- 33- 311 GYPSUM, SYN
- 19- 629 MAGNETITE, SYN
- 29- 1493 TALC-2M
- 6- 263 MUSCOVITE-2M1

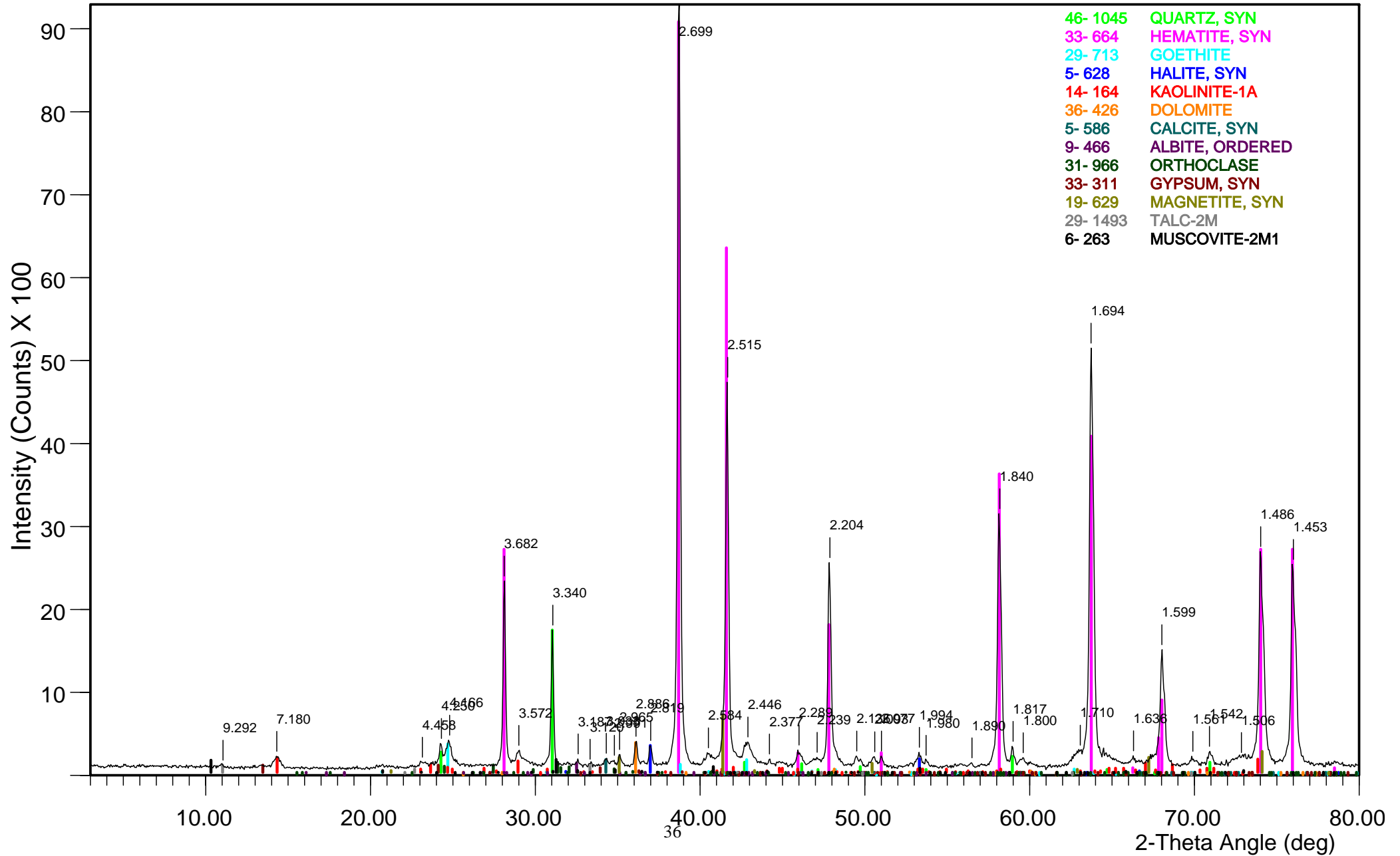
Croquet Club 13-2-04



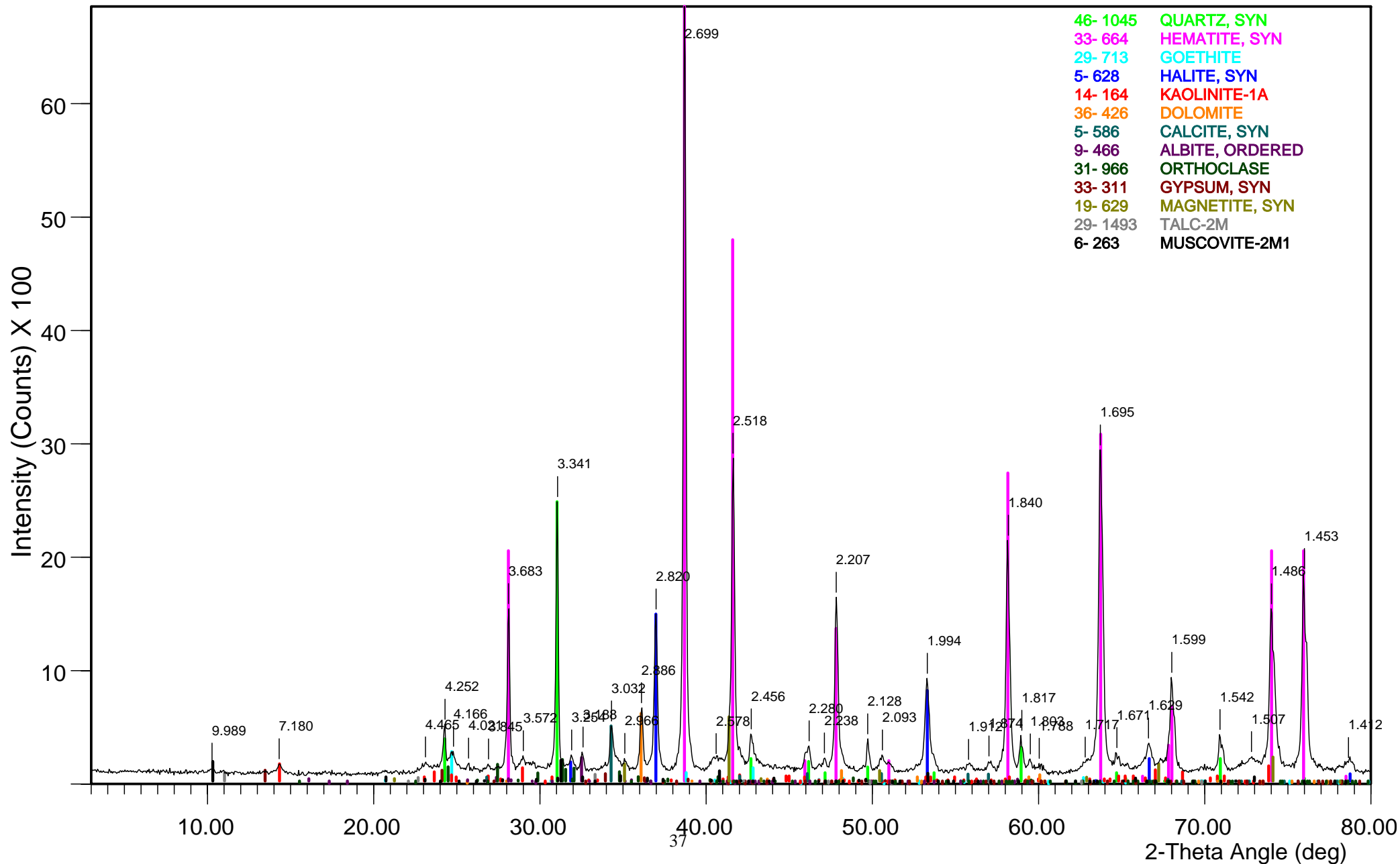
Croquet Club 23-2-04



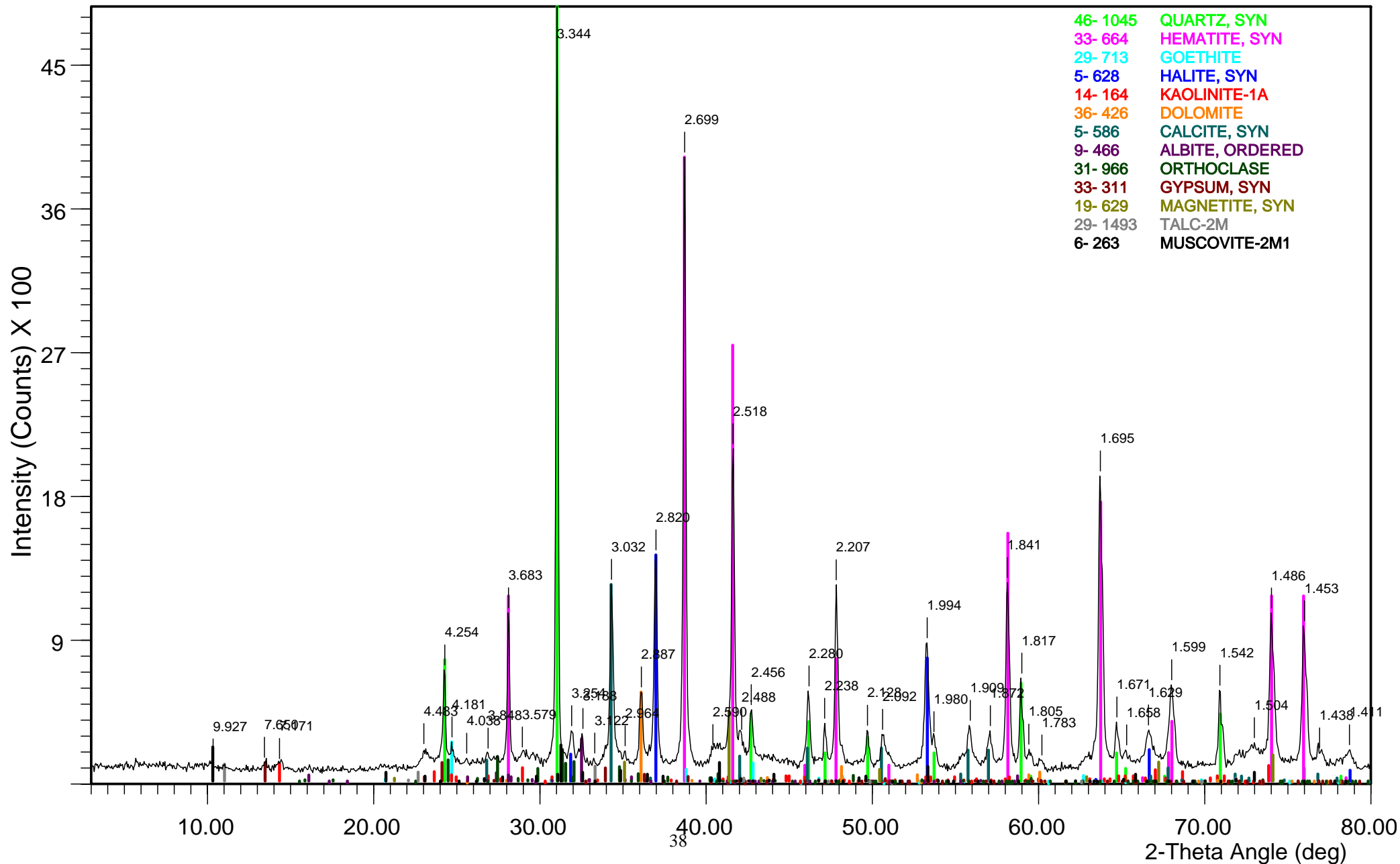
Hummock Hill 12-12-03



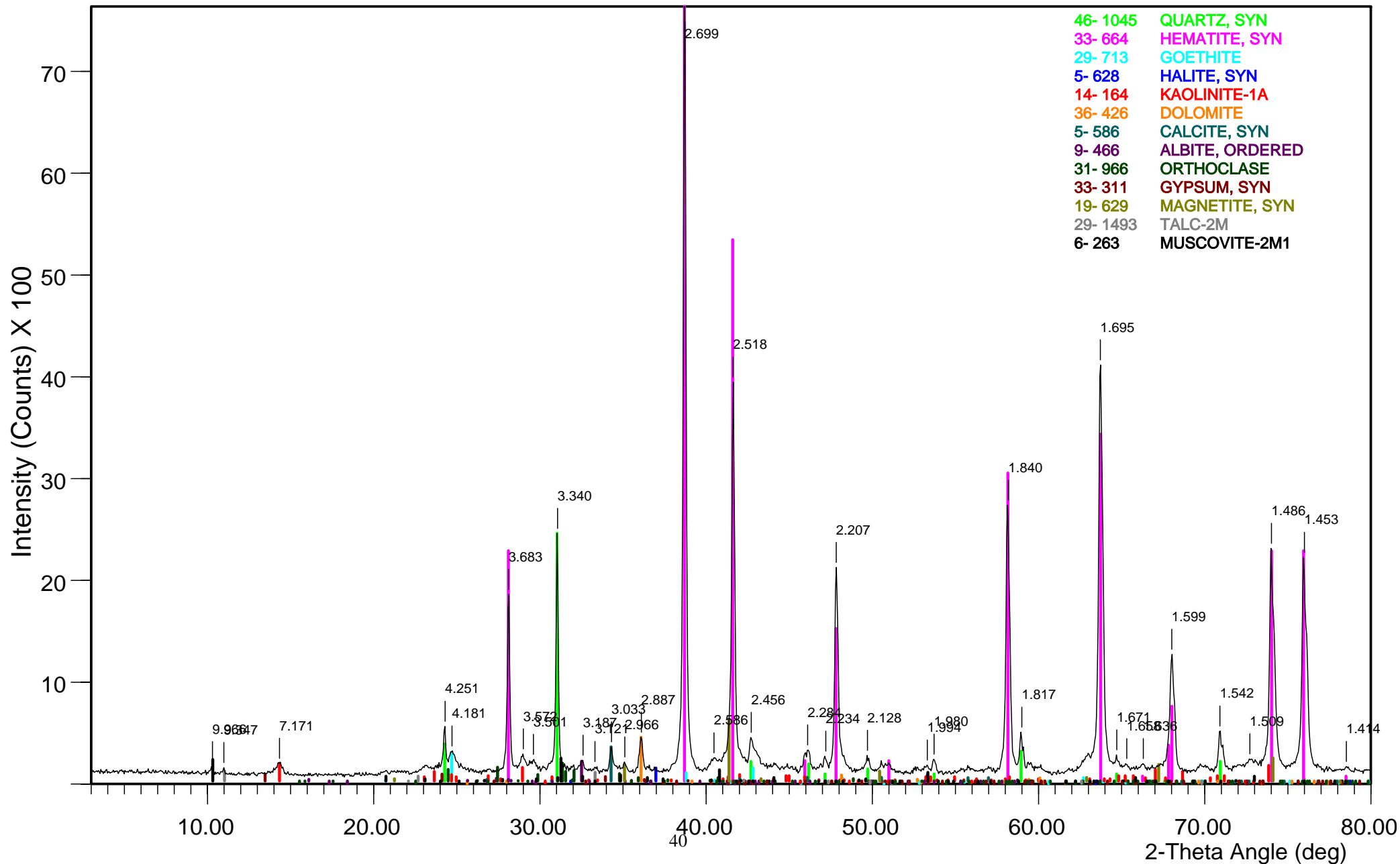
Hummock Hill 8-1-04



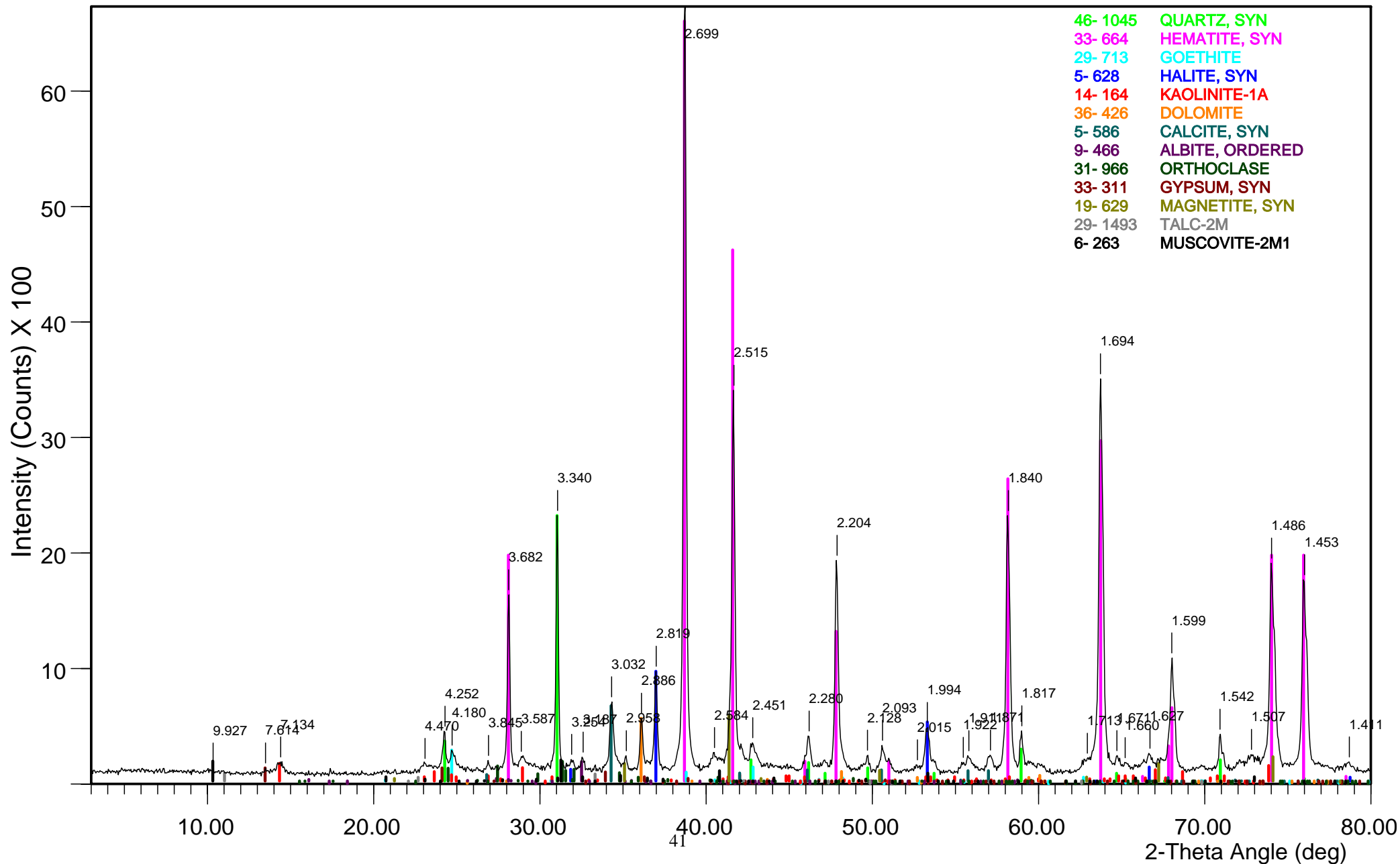
Hummock Hill 22-1-04



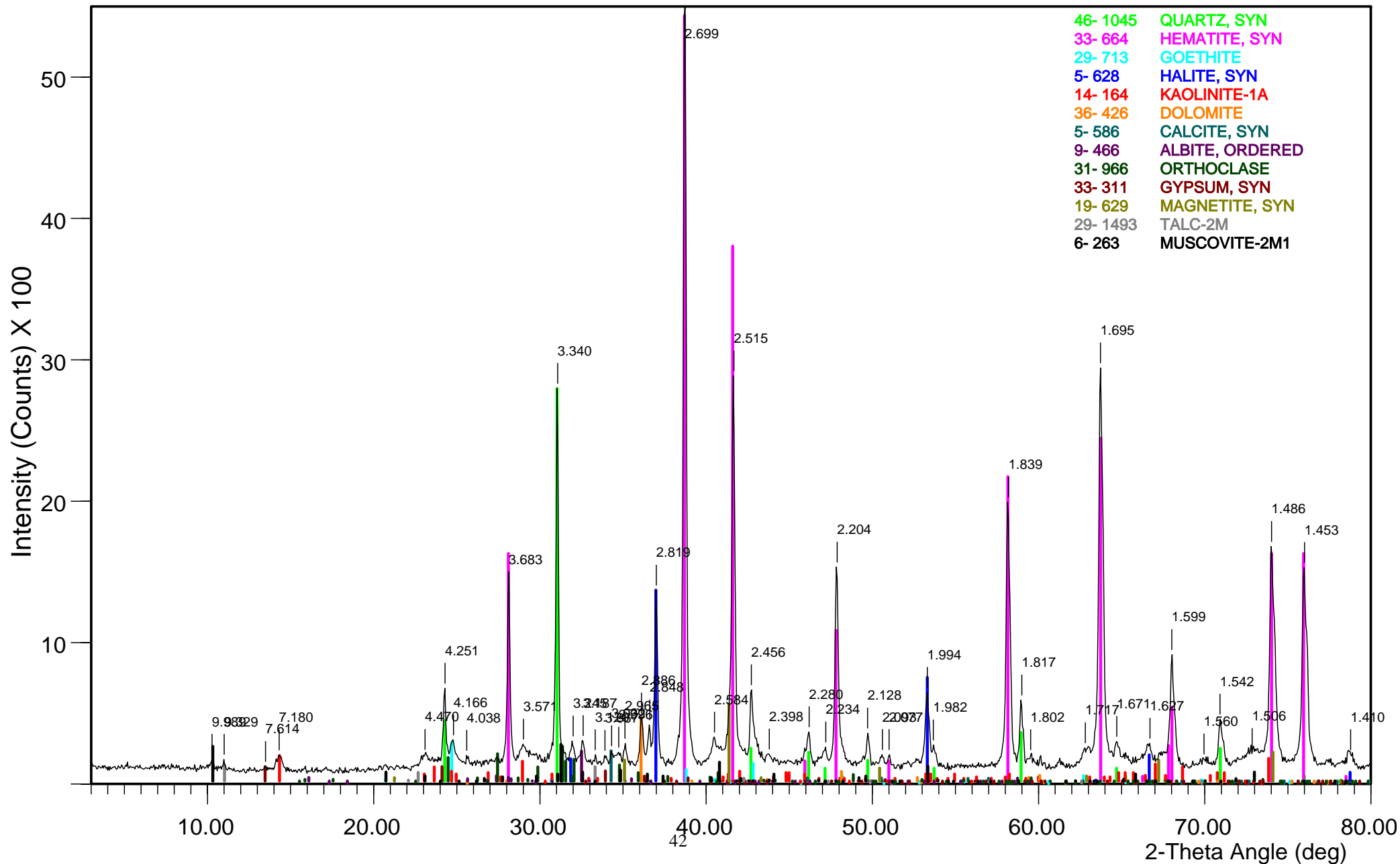
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Hummock Hill 23-2-04

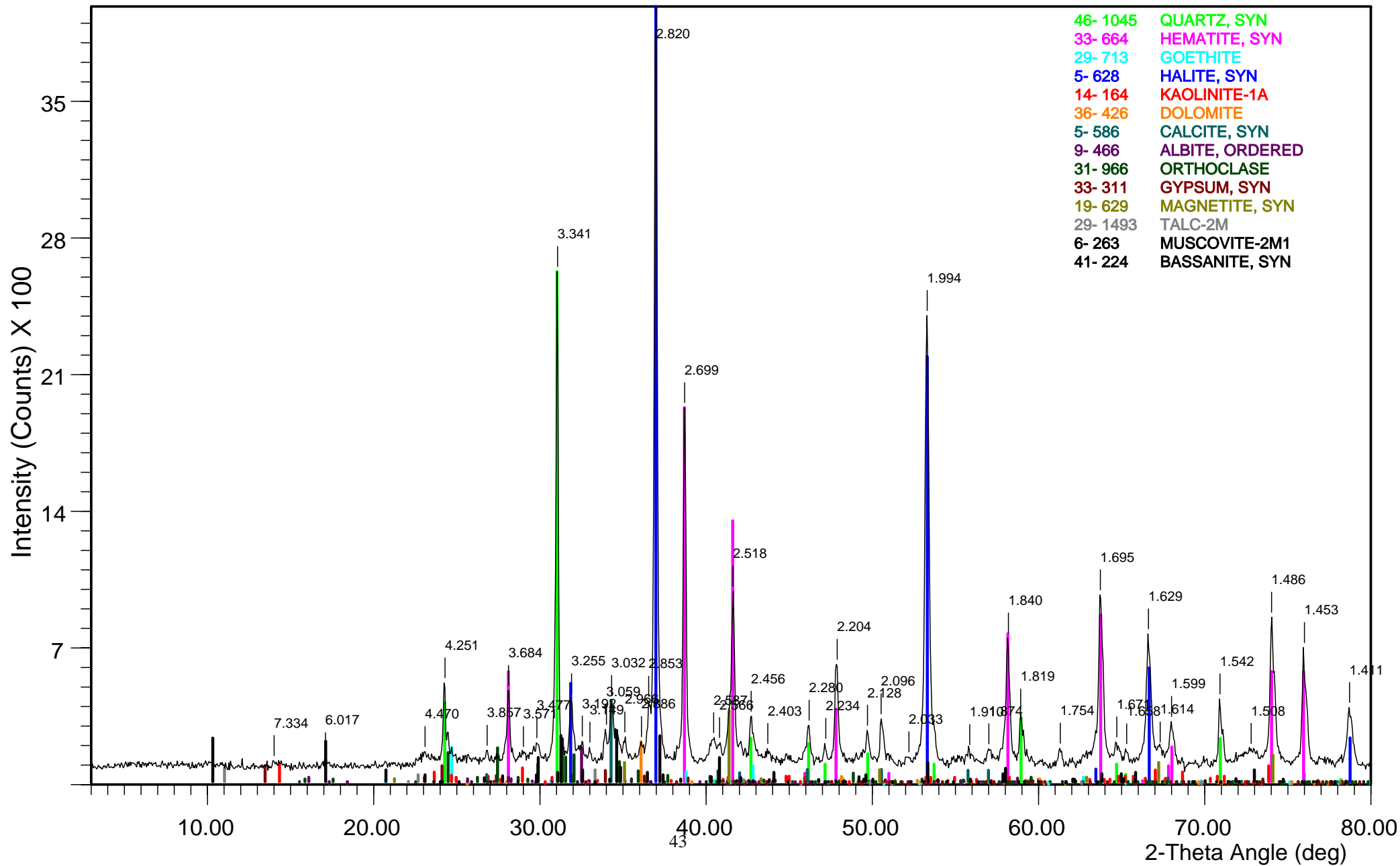


Wall Street 23-12-03



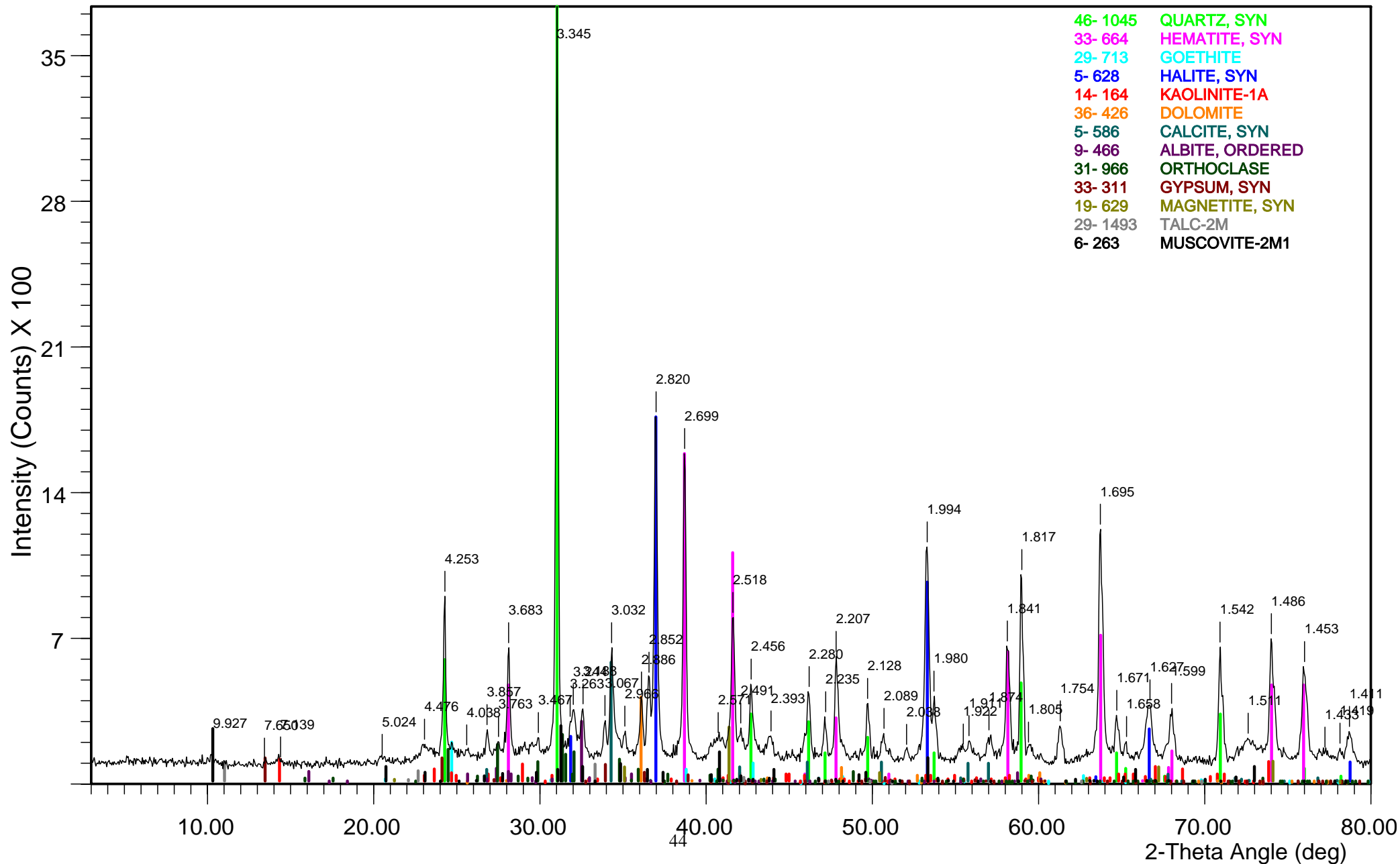
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Wall Street 8-1-04

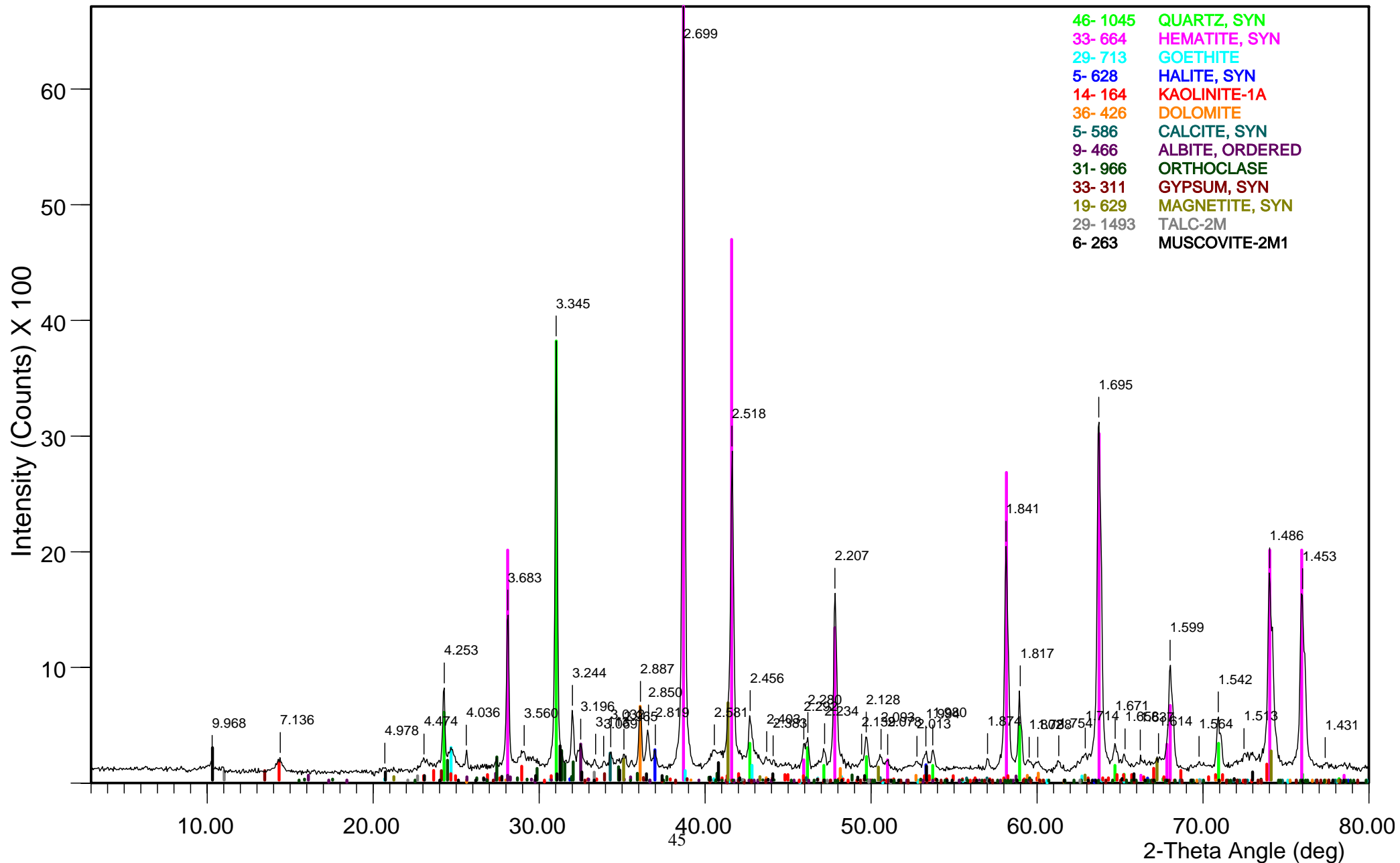


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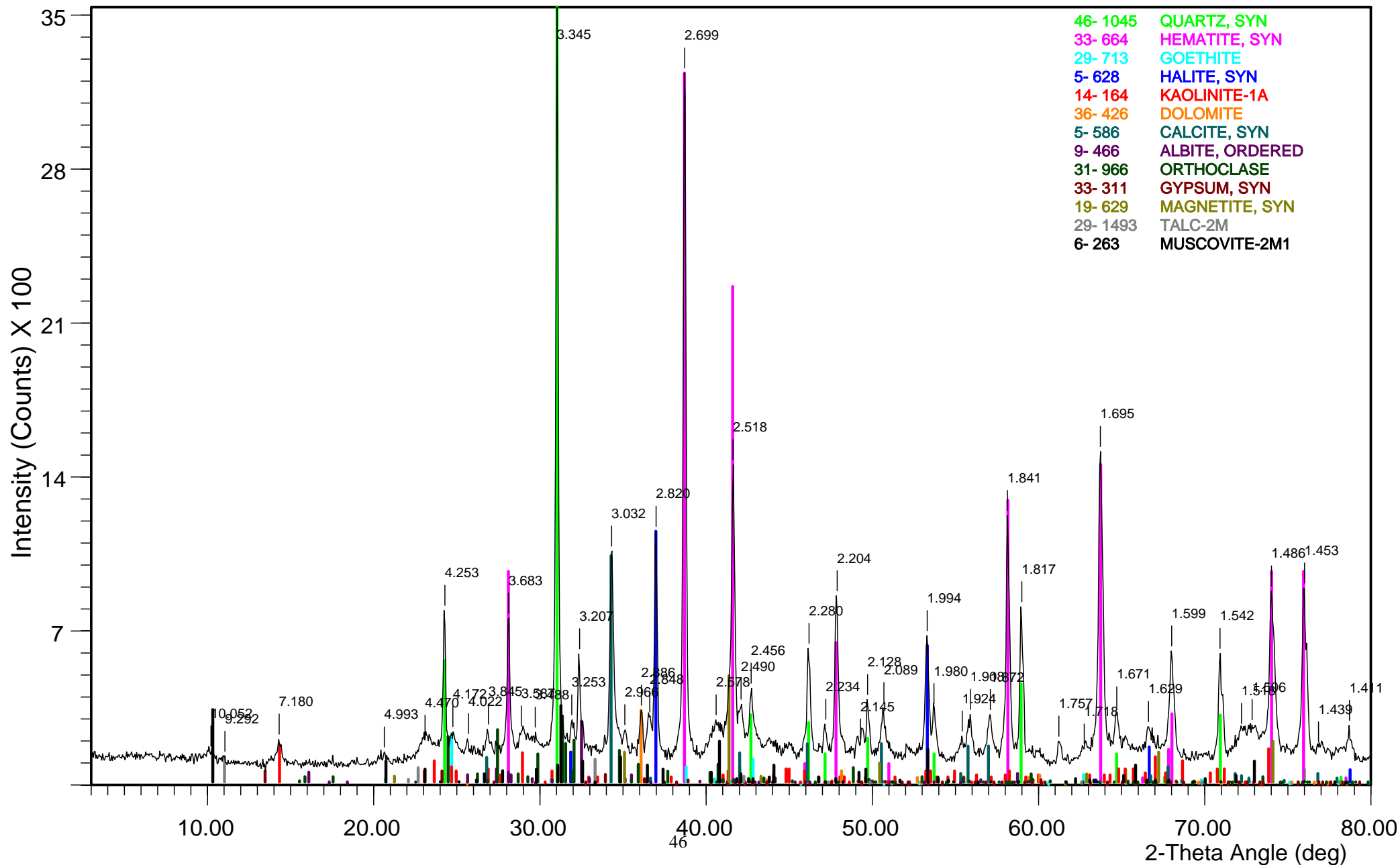
Wall Street 22-1-04



Wall Street 13-2-04



Wall Street 23-2-04



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