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Advanced XRD Analysis of Clay and Ultrafine Solids Separated from Oil Sands Ore

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Outline

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- Assessment of clay minerals separation
- Identification of smectite or smectite mixed layer clay in the <2um clay solids
- Mineralogy of the <0.2um ultrafine solids
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Previous Work and Objectives for Present Work

The presence of clays in oil sands ore has an adverse effect on bitumen recovery

In a previous study[1] by our group, higher clay contents were found in marine ore compared to estuarine ore, leading to poor bitumen recovery in batch extraction unit tests.

In this study, we perform the following

- **Repeat separation of <2μm clay solids from estuarine and marine ores**
- **Separation of <0.2um ultrafine solids from the <2um clay solids**
- **XRD analysis of the separated <2um clay and <0.2um ultrafine solids**

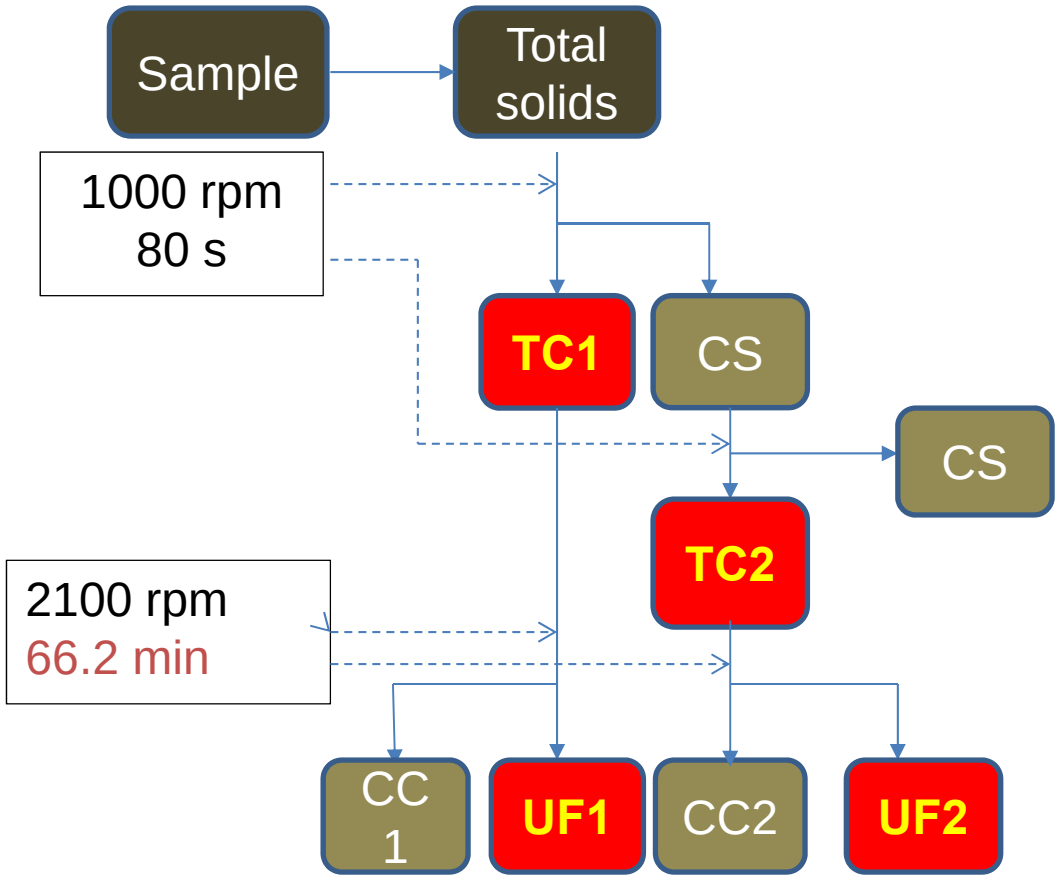
P. H. J. Mercier, B. Patarachao, J. Kung, D. M. Kingston, J. R. Woods, B. D. Sparks, L. S. Kotlyar, S. Ng, K. Moran, and T. McCracken (2008). X-ray diffraction (XRD)-derived processability markers for oil sands based on clay mineralogy and crystallite thickness distributions. Energy & Fuels, 22: 3174-3193.

Samples

Sample	Description	
E3	Esturine Ore	Oil sands ores
E7	Esturine Ore	
M13	Marine ore	
M18	Marine ore	
Imt-2	Illite	CMS source clays
Swy-2	Na Montmorillonite	
ISCz-1	Illite - Smectite mixed layer	

Separation of <2um Clay and <0.2um Ultrafine Solids

Centrifugation technique based on Stokes' law



Settled solids

Supernatant

CS= coarser solids, >2 μm
TC= total clays, <2 μm
CC= coarse clays (0.2–2 μm)
UF= ultrafines, <0.2 μm

- *<2um clay solids (TC1and TC2) were combined prior to XRD analysis*
- *<0.2um ultrafine solids were isolated only from marine ores (M13 and M18)*

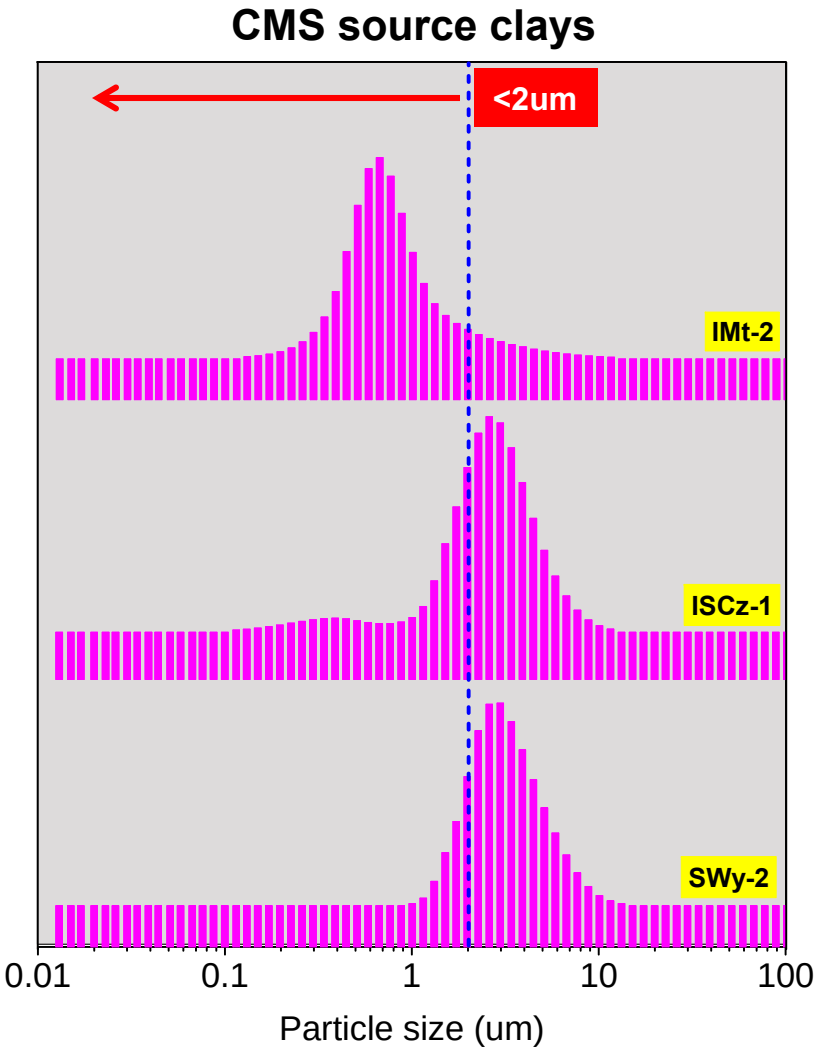
Clay and Ultrafine Content

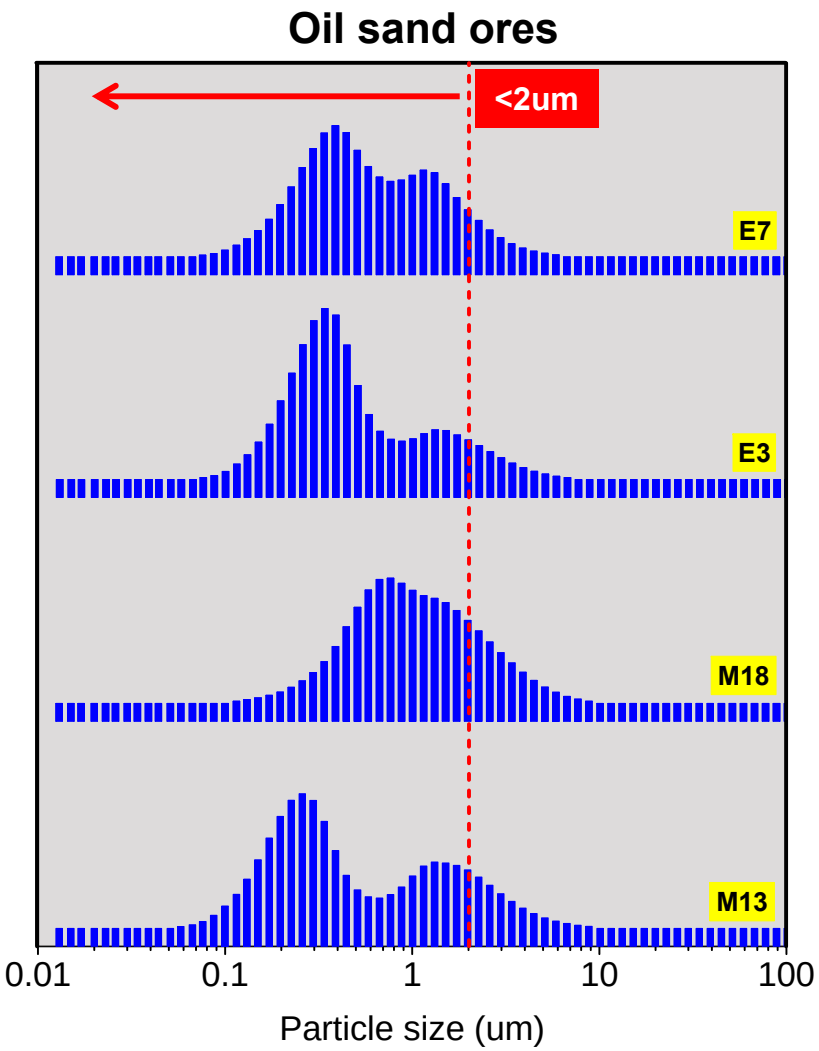
Clay Content (wt% of Oil sands ore)		
	Year 2008	Year 2016
M13	6.3	6.6
M18	5.2	5.3
E3	3.8	3.5
E7	1.3	2.4
Ultrafine Content (wt% of Oil sands ore)		
	Year 2008	**Year 2016**
M13	-	0.4
M18	-	0.7

These values agree within 0.3-1.1wt% with our previous work, thus showing excellent reproducibility in the quantitative separation technique.

Particle Size Distribution (<2um Clay solids)

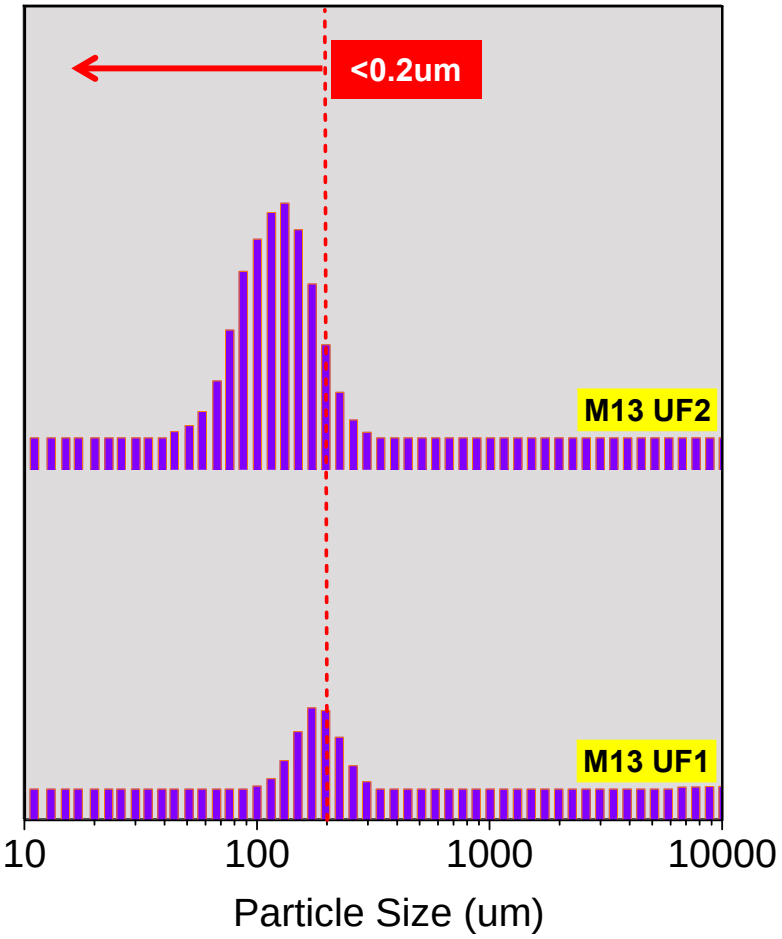
Laser scattering measurement

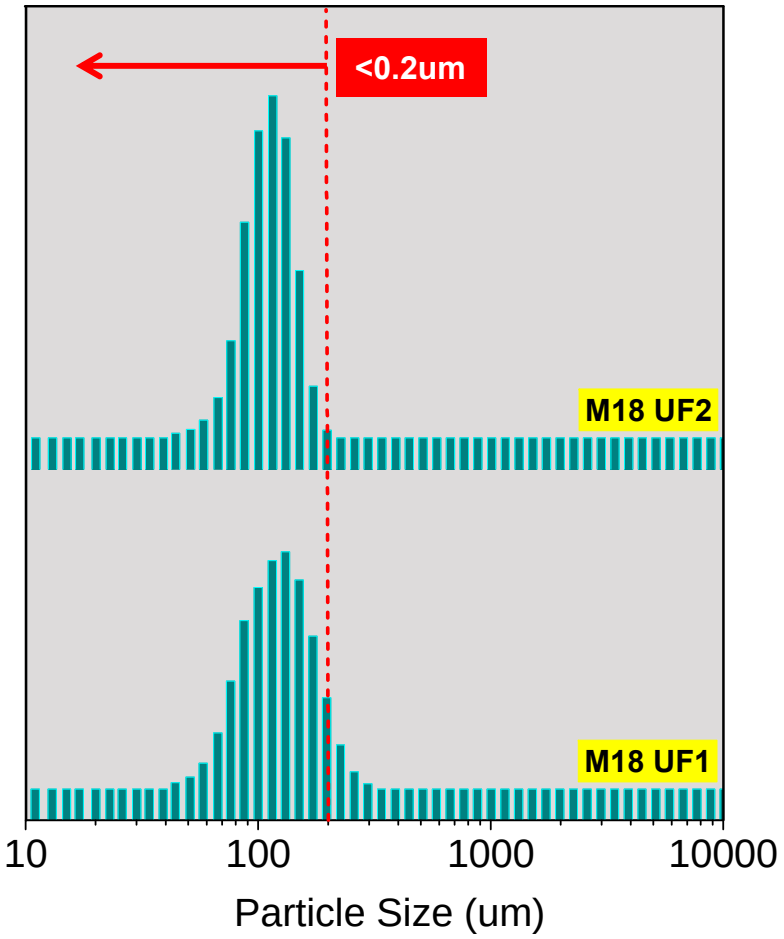




Particle Size Distribution (<0.2um Ultrafine solids)

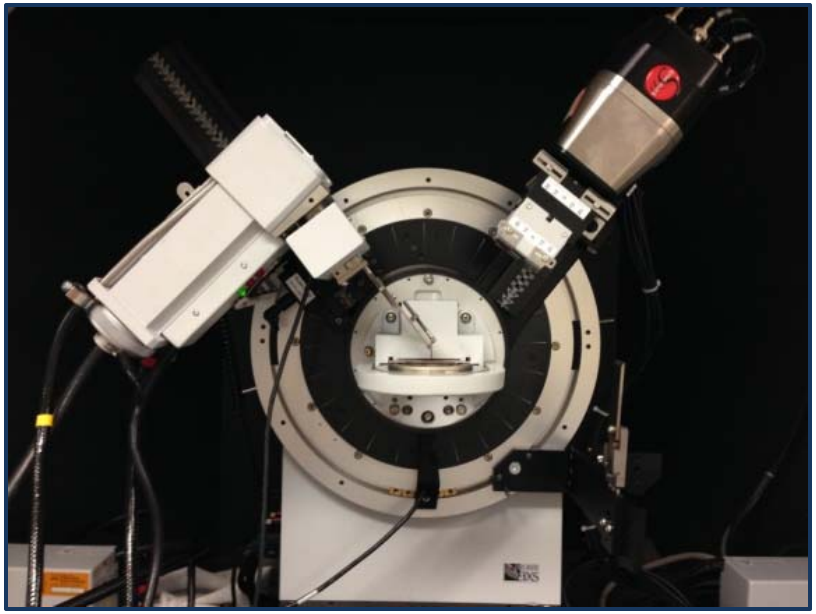
Laser scattering measurement





XRD Measurement

1-dimensional Powder X-ray Diffractometer

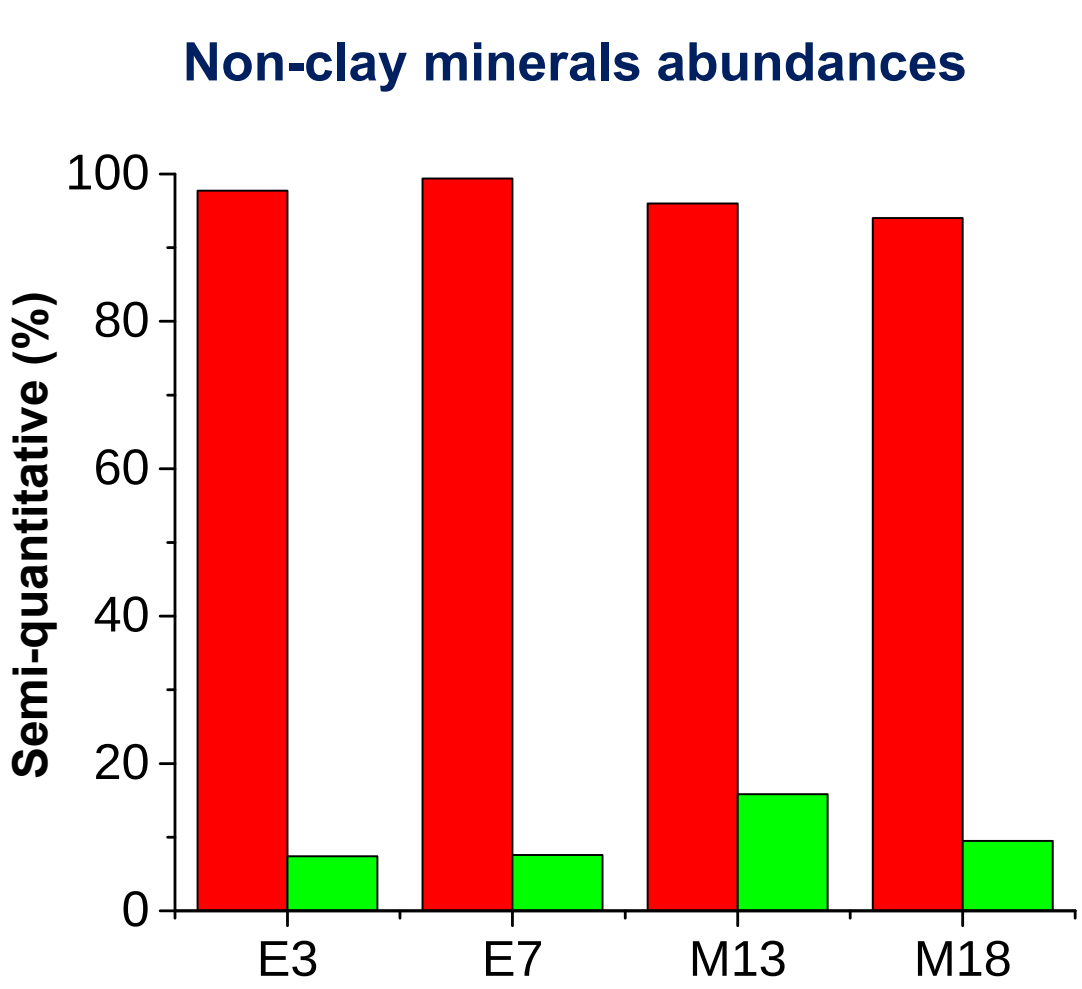


Bruker D8 Advance XRD set up in Bragg Brentano geometry (theta-theta), configured with a Cobalt (Co) X-ray tube and a Position Sensitive Detector (VÅNTEC-1)

Preparation of Random powder mount

Purpose: Bulk mineralogy analysis to confirm that clay minerals were successfully isolated.

Assessment of clay minerals separation



Semi-quantitative analysis

Quartz (SiO_2)

Calcite ($CaCO_3$)

Dolomite ($CaMg(CO_3)_2$

Gypsum ($CaSO_4$)

Rutile (TiO_2)

Anatase (TiO_2)

Pyrite (FeS_2)

Siderite ($FeCO_3$)

Sum of non-clay minerals

Preparation of Oriented Clay Slides

Purpose: To identify smectite or smectite mixed layer clay minerals in <2um clay solids

Ca Saturated suspension

Add $CaCl_2$ into 50mL clay suspension and stir to allow the salt to dissolve

Remove excess chlorides

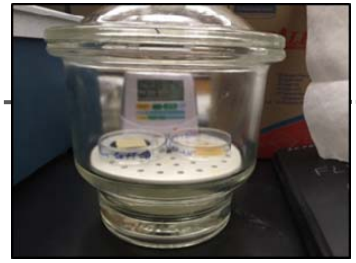
Filter the Ca-saturated clay suspension and wash away any excess chlorides

Oriented clay slide

Place the wet filter cake up side down on a glass slide. Peel off the filter paper

Pretreatment Procedures

Air dry at 54% Relative Humidity (RH)



super saturated solution of $MgNO_3$

Expand d-spacing (001) of smectite clay to ~15 Å

XRD

Ethylene Glycol Solvation

Further expand d-spacing (001) of smectite clay to ~17 Å

XRD

Heat Treatment at 375°C for 2hrs

Collapse d-spacing (001) of smectite/smectite-illite mixed layer clay to 10Å resembled pure illite structure

XRD

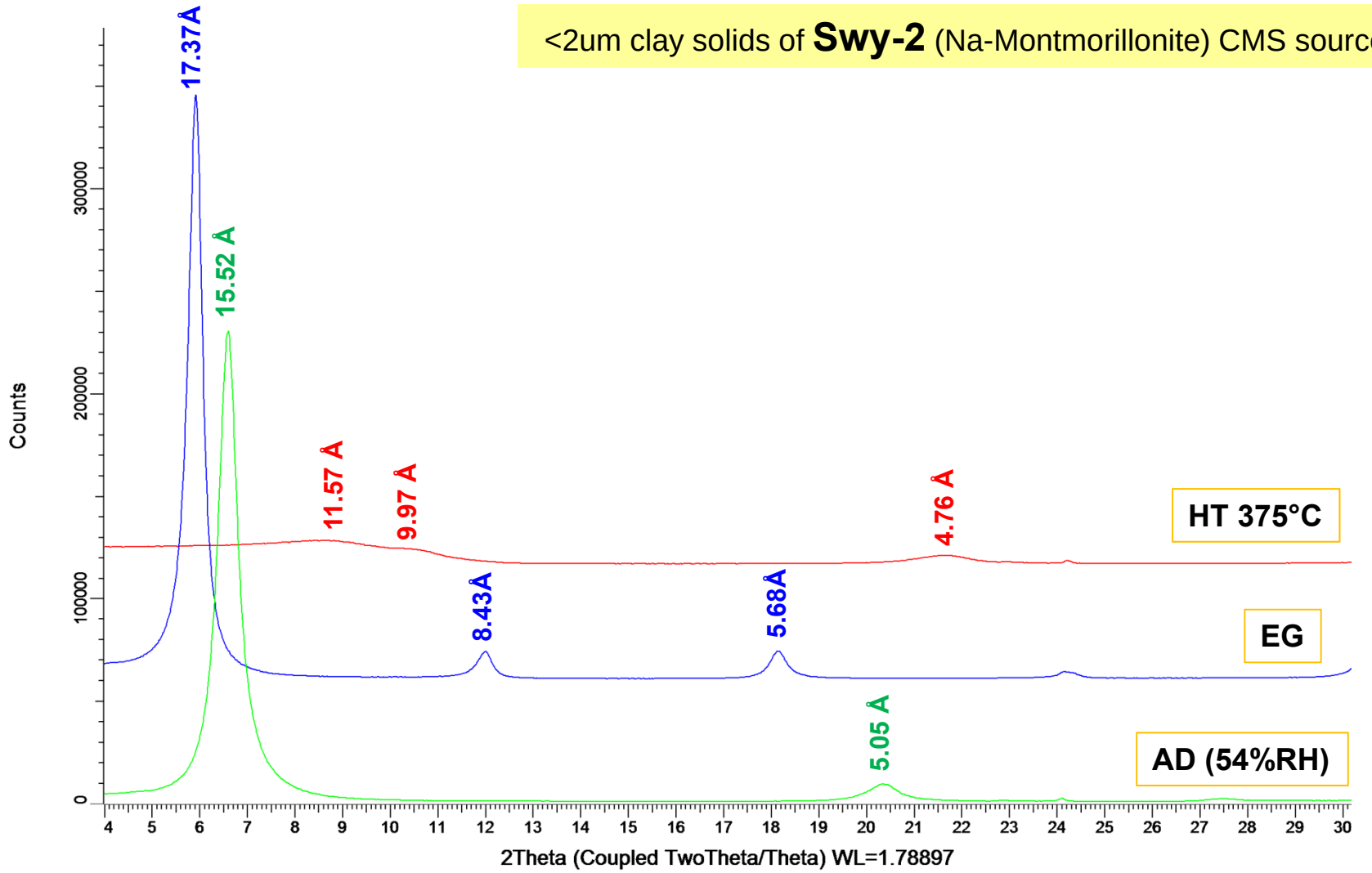
Heat Treatment at 550°C for 2hrs

Decompose structure of Kaolinite clay

XRD

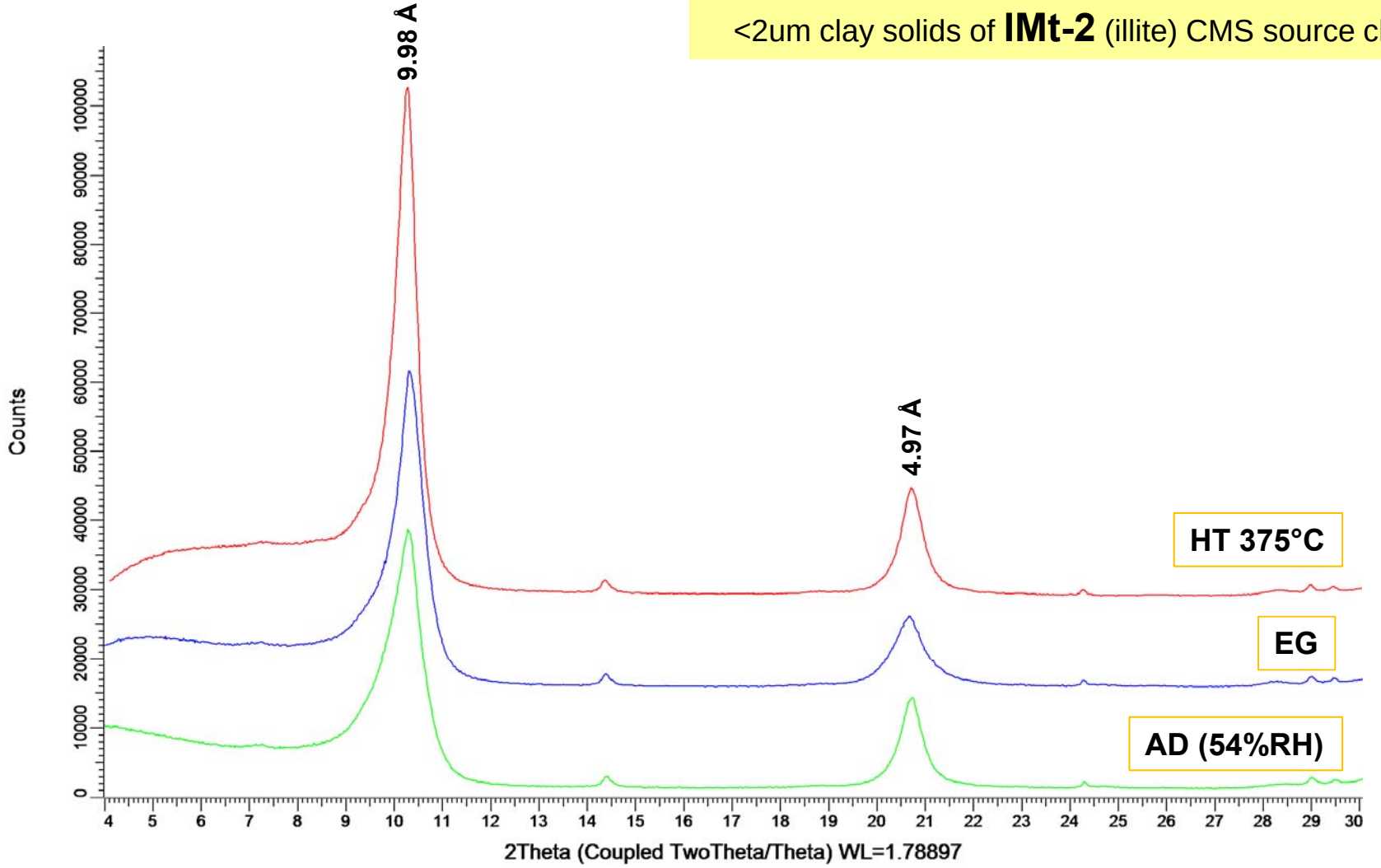
Identification of smectite/smectite mixed layer clay

<2um clay solids of **Swy-2** (Na-Montmorillonite) CMS source clay



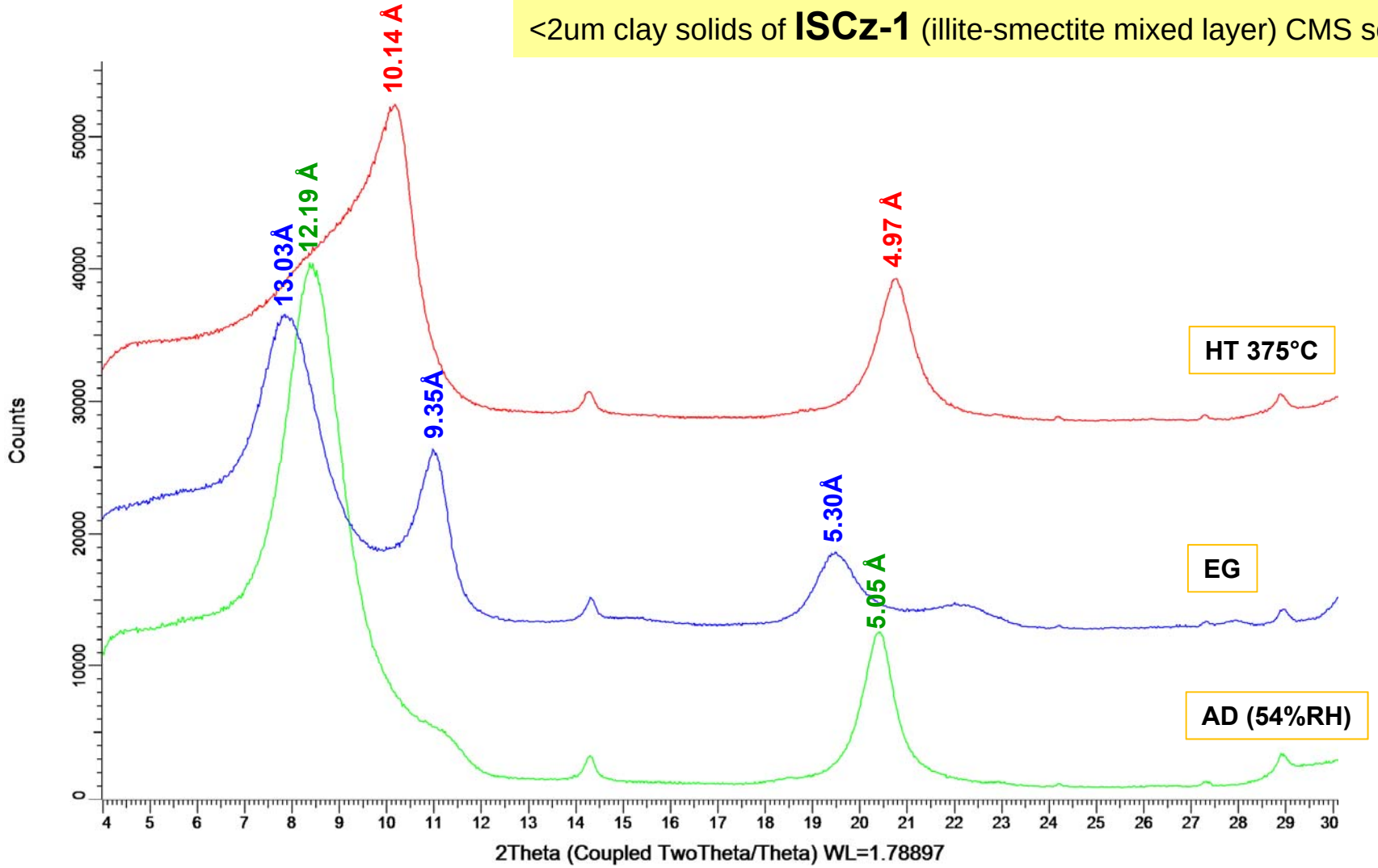
Identification of smectite/smectite mixed layer clay

<2um clay solids of **IMt-2** (illite) CMS source clay



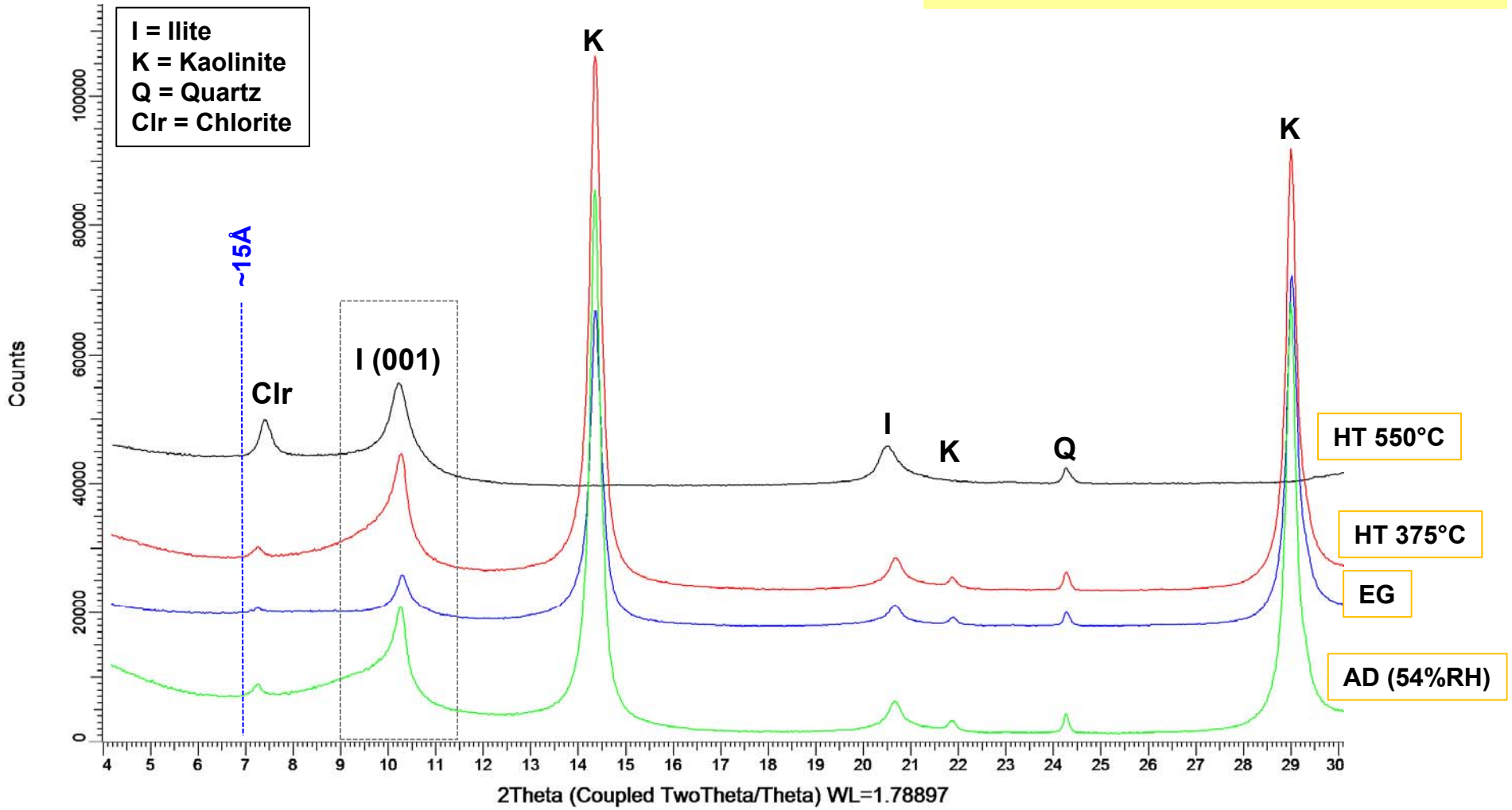
Identification of smectite/smectite mixed layer clay

<2um clay solids of **ISCz-1** (illite-smectite mixed layer) CMS source clay



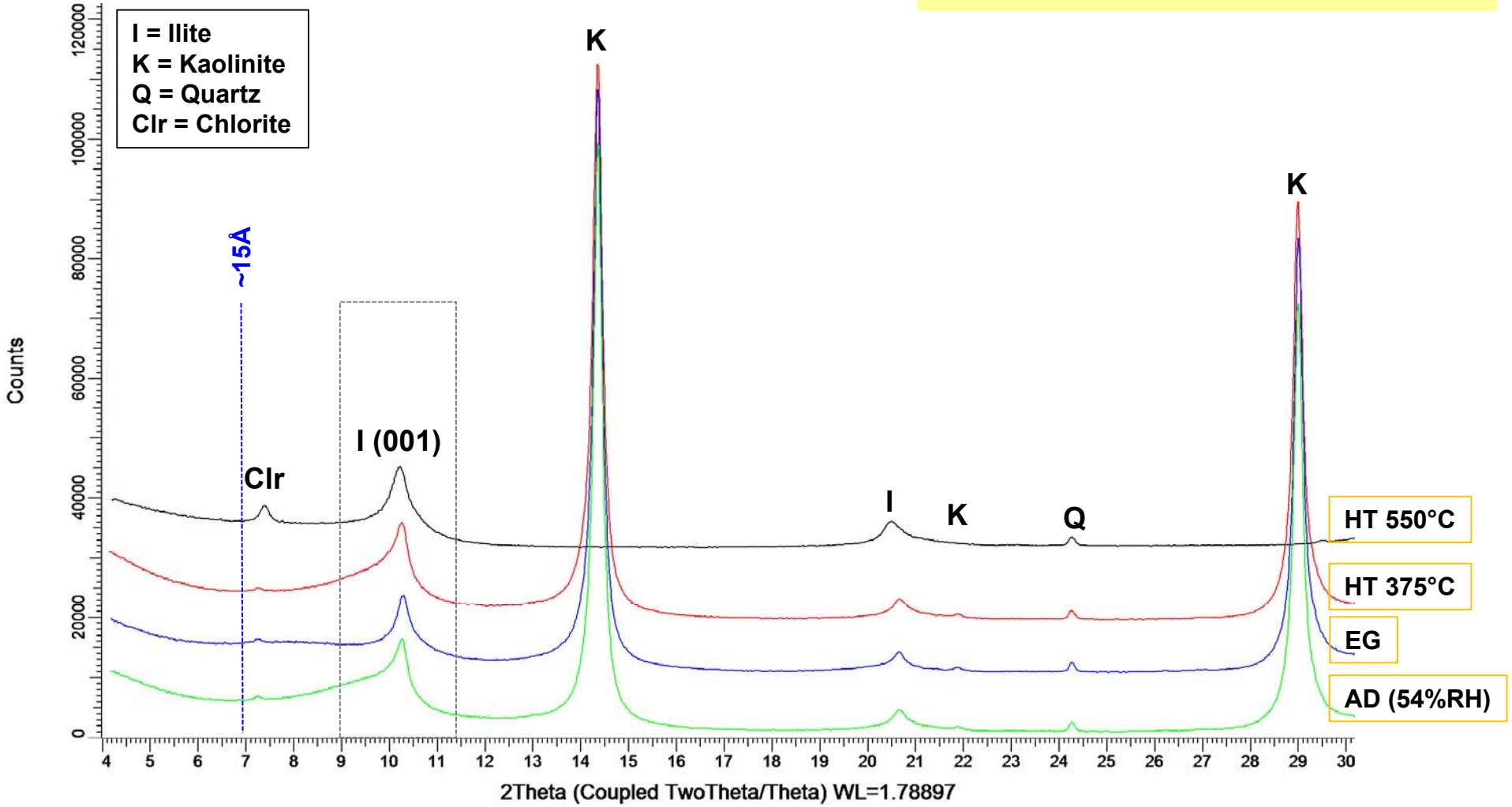
Identification of smectite/smectite mixed layer clay

<2um clay solids of **M13** (Marine ore)



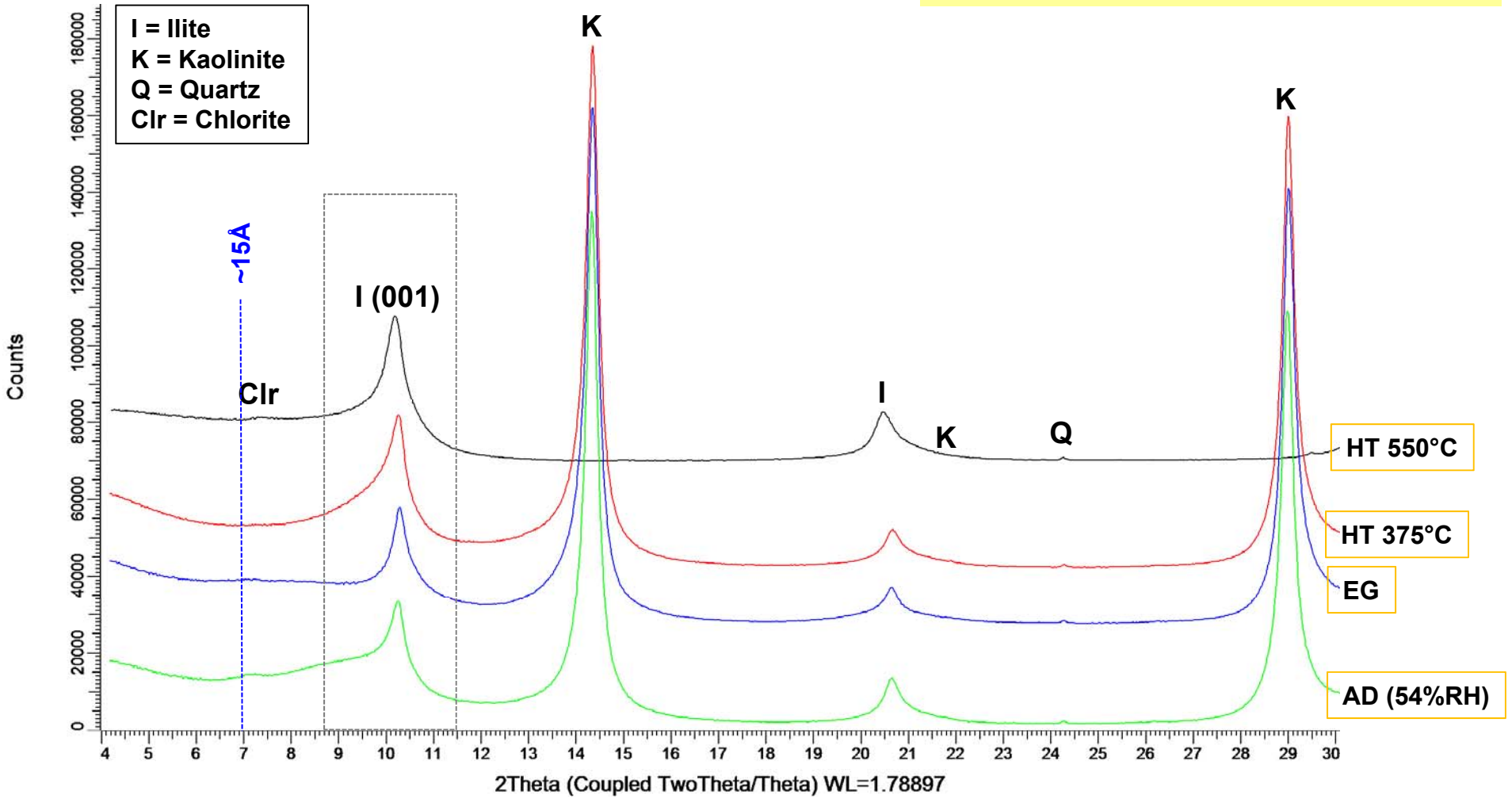
Identification of smectite/smectite mixed layer clay

<2um clay solids of **M18** (Marine ore)



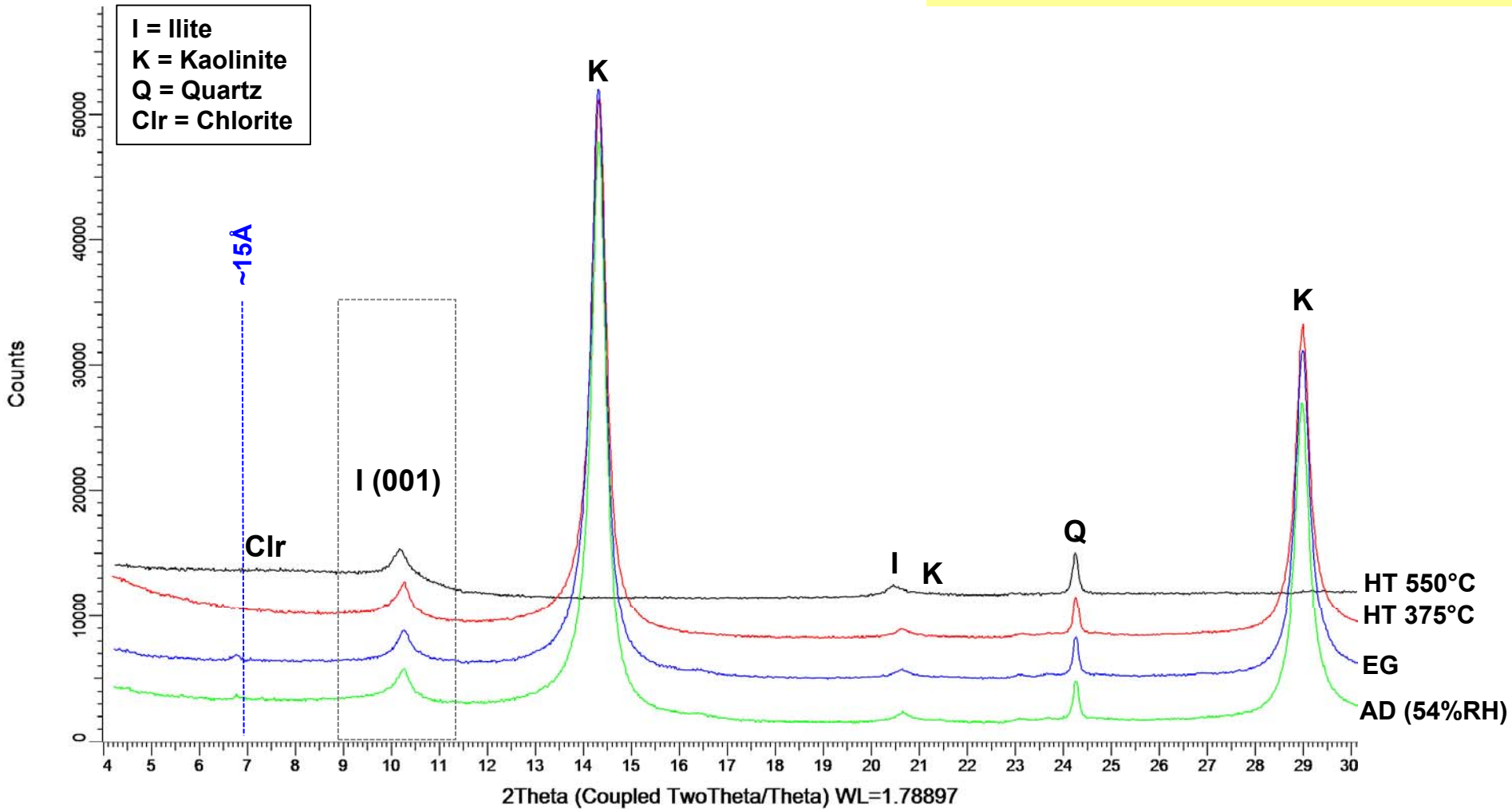
Identification of smectite/smectite mixed layer clay

<2um clay solids of **E3** (Estuarine ore)



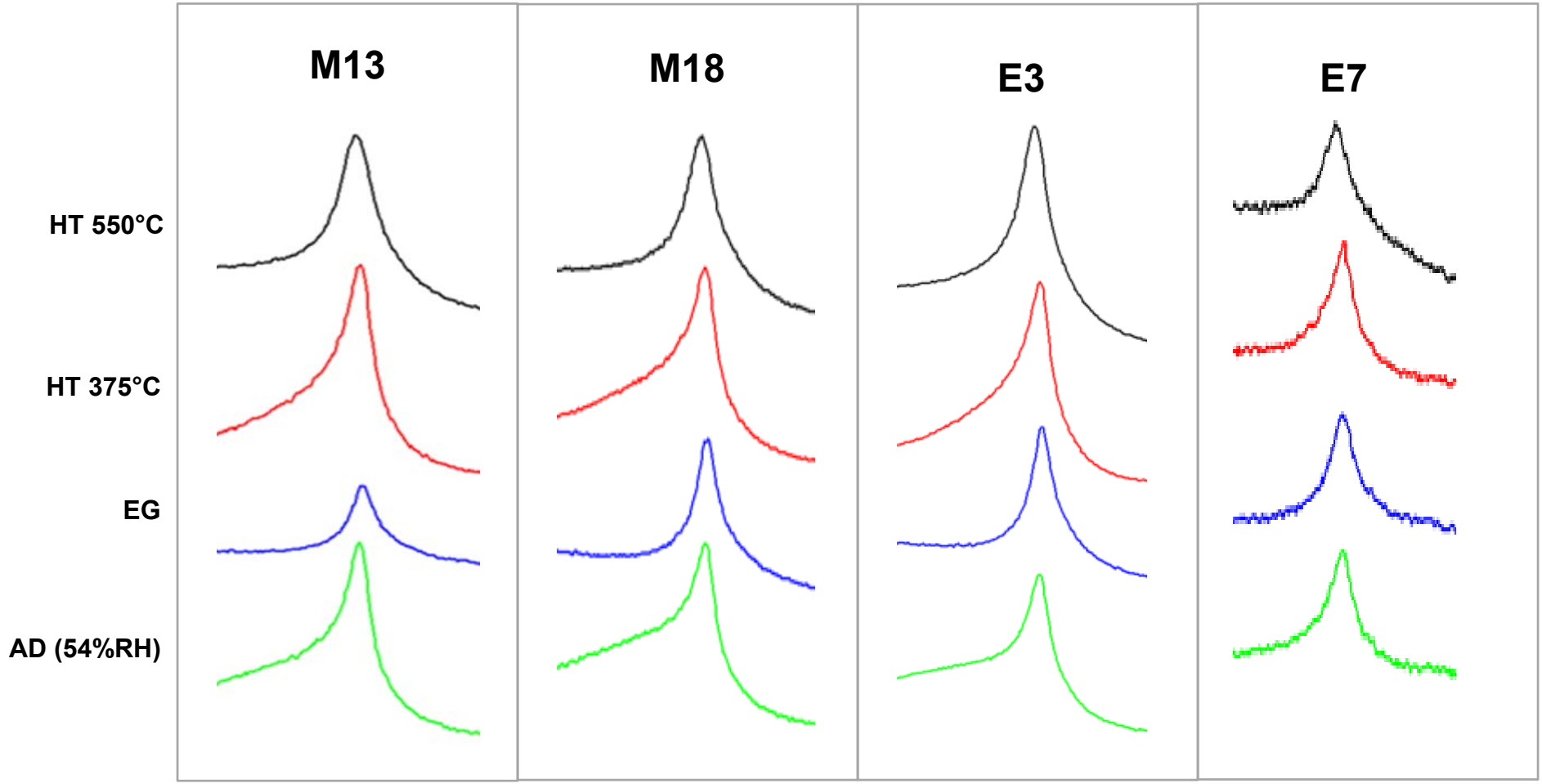
Identification of smectite/smectite mixed layer clay

<2um clay solids of **E7** (Estuarine ore)



Alteration of Illite 001 peak shape

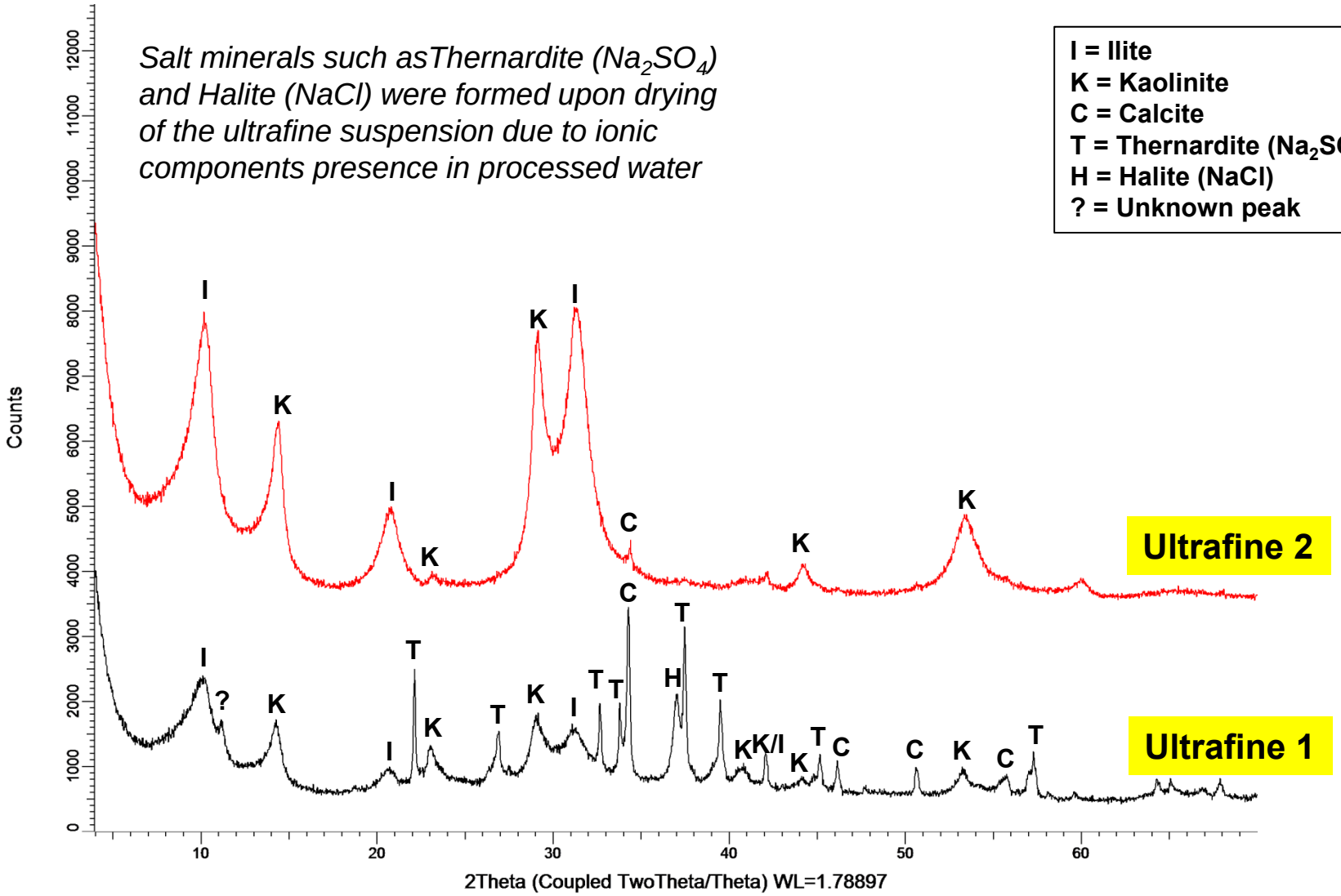
<2um clay solids of marine ores (M13 and M18) and estuarine ore (E3 and E7)



Mineralogy of <0.2um ultrafine solids (M18)

Salt minerals such asThernardite (Na_2SO_4) and Halite (NaCl) were formed upon drying of the ultrafine suspension due to ionic components presence in processed water

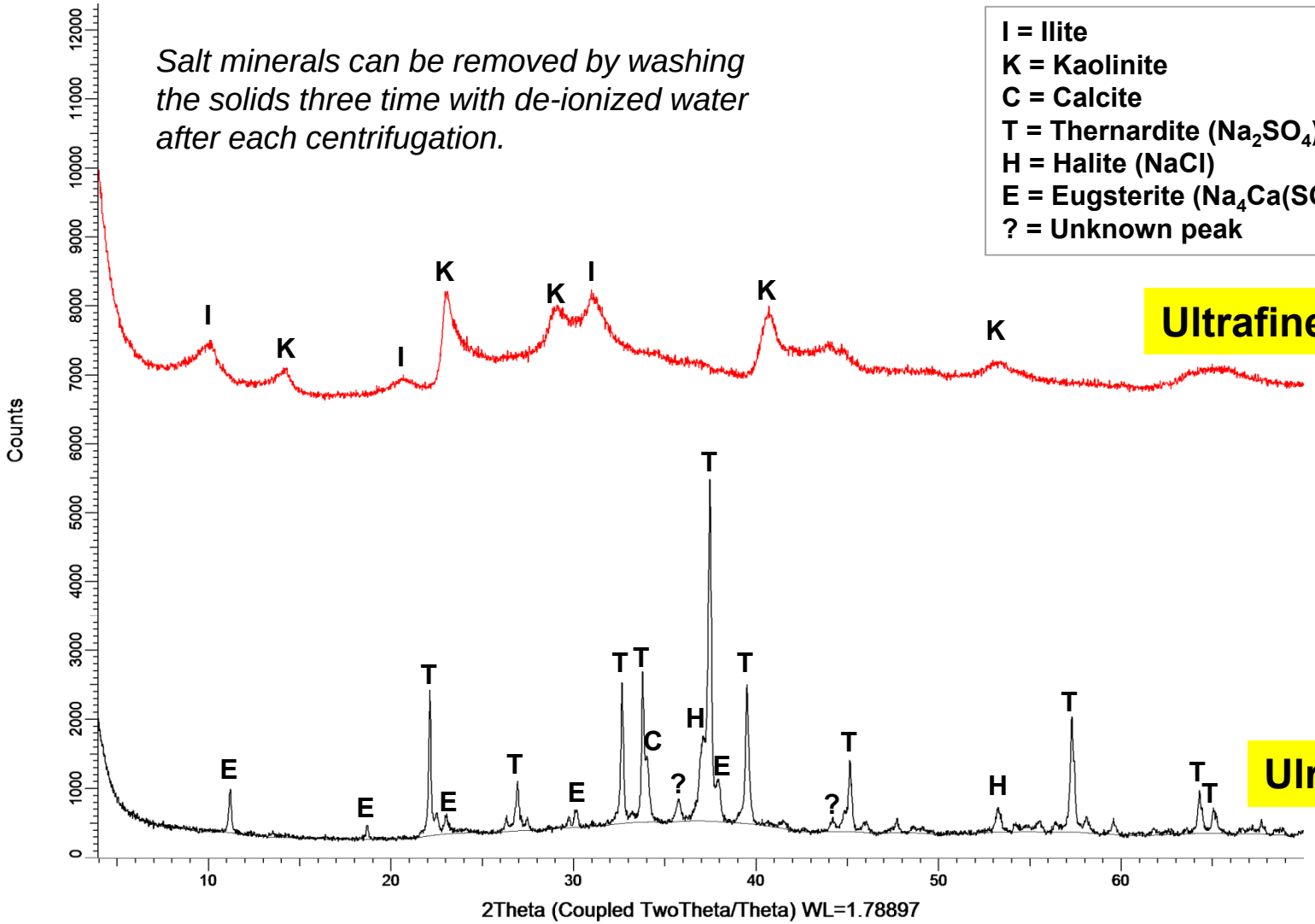
I = Ilite
K = Kaolinite
C = Calcite
T = Thernardite (Na_2SO_4)
H = Halite (NaCl)
? = Unknown peak



Mineralogy of <0.2um ultrafine solids (M13)

Salt minerals can be removed by washing the solids three time with de-ionized water after each centrifugation.

I = Ilite
K = Kaolinite
C = Calcite
T = Thernardite (Na_2SO_4)
H = Halite (NaCl)
E = Eugsterite ($Na_4Ca(SO_4)_3.2H_2O$
? = Unknown peak



Conclusions

- Clay (<2μm) and ultrafine solids (<0.2μm) were successfully isolated from selected oil sand ores using centrifugation technique based on Stokes' law.
- Based on comparison with three CMS source clays (IMt-2, Swy-2 and ISCz-1), no detectable amounts of smectite or mixed-layer clays is observed in the oil sand ores used in this study.
- The clay minerals found in these oil sands ores were mostly kaolinite and illite in all clay and ultrafine solids, and minor chlorite was found in significant quantity only in the clays from marine ores
- Ethylene glycol solvation altered the illite 001 peak shape, causing it to become sharper and more symmetric. The shape of this peak reversed back to its original shape after heat treatment at 375°C.
- The change in illite 001 peak shape is most noticeable in the clays from marine ores (M13 and M18) but very negligible in the clays from estuarine ores (E3 and E7)
- Significant amount of impurities (non-clay minerals and salts) were observed in Ultrafine-1 solids of M13 and M18, but not in the Ultrafine-2 solids.
- Compared to the clay size solids, there were no non-clay minerals (quartz, siderite, pyrite, etc.) as well as chlorite detected in the ultrafine solids from M13 and M18 ores.

Acknowledgements

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Questions, comments, discussion?

Thank you

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