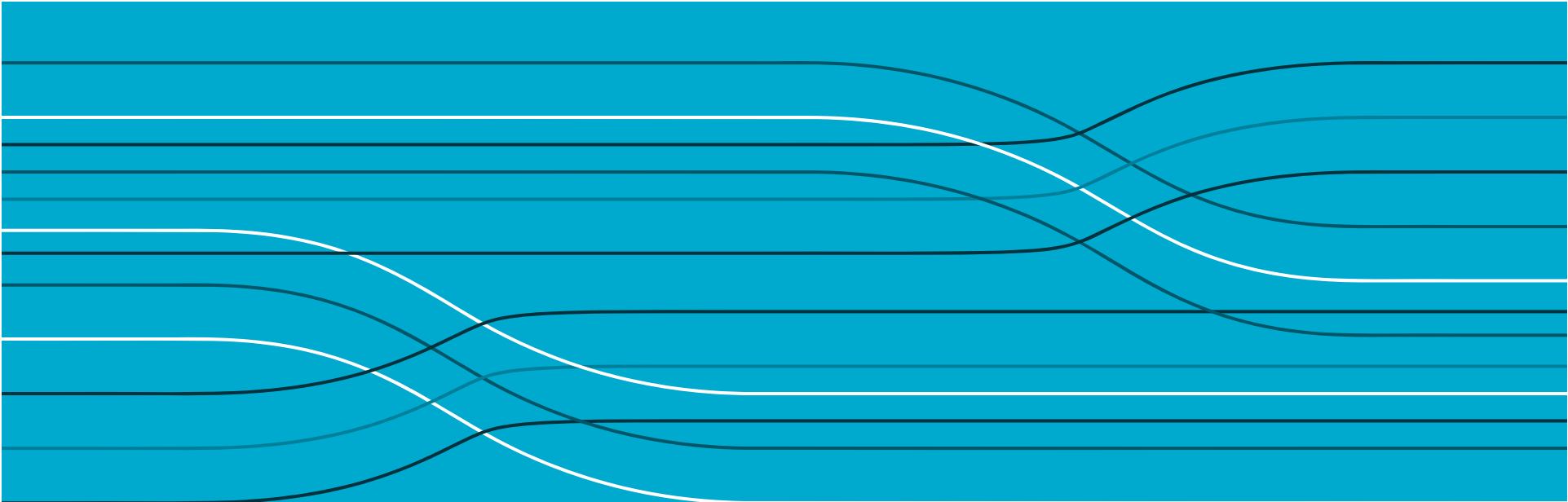




Characterisation of two Australian smectite clays for possible submission to the CMS Source Clays Repository

Mark Raven, Peter Self, Rodrigo Gomez-Camacho, Will Gates and Stephen Hillier

June 2017

LAND AND WATER
www.csiro.au



Background Information

- The Clay Minerals Society Source Clays Repository
 - In the early 1970's, the CMS identified a need for a source of homogeneous clay specimens available for comparison between researchers
 - Two series of materials proposed
 - Source Clays
 - Large stocks of reasonably homogeneous milled samples
 - Special Clays
 - Smaller stocks of usually inhomogeneous unmilled samples
 - Commenced in 1973 with 8 specimens available KGa-1, KGa-2, SWy-1, STx-1, SAz-1, SHCa-1, PFI-1 and Syn-1
 - Continually evolving with new clays added and replacement of old clays as they become depleted
 - Currently housed at Purdue University, Indiana. Cliff Johnston as Curator
 - Important source of funds for the CMS ~\$72k in 2016
 - New or replacement clays are always gratefully received

The Source Clays Repository

- Source Clays

- KGa-1b Kaolinite (low defect - Warren County Georgia USA) KGa-1b (125grams/unit)
- KGa-2 Kaolinite (high defect - Warren County Georgia USA) KGa-2 (125grams/unit)
- PF1-1 Palygorskite (attapulgitite - Gadsden County Florida USA) PF1-1 (125grams/unit)
- SHCa-1 Hectorite (contains calcite - San Bernardino County California USA) SHCa-1 (250/grams/unit)
- STx-1b Ca-montmorillonite (white - Gonzales County Texas USA - replaces STx-1) STx-1b (250grams/unit)
- SWy-3 Na-rich Montmorillonite, Crook County, Wyoming, USA (250grams/unit)
- SYn-1 Barasym SSM-100 (synthetic mica-montmorillonite - NL Industries) SYn-1 (250grams/unit)

- Special Clays

- CCa-2 Ripidolite (chlorite - Flagstaff Hill El Dorado County California USA) CCa-2 (50grams/unit)
- RAr-1 Rectorite (regular-mixed layer - Garland County Arkansas USA) RAr-1 (50grams/unit)
- SYnH-1 Optigel SH (Synthetic hectorite - Sud-Chemie Rheologicals - United Catalysts Inc.) SYnH-1 (50grams/unit)
- SYnL-1 Synthetic laponite (Southern Clay Products Inc.) SYnL-1 (50grams/unit)
- SCa-3 Montmorillonite (Otay - Otay San Diego County California USA) SCa-3 (50grams/unit)
- SAz-2 Ca-montmorillonite (Cheto - in natural chunk form - Apache County Arizona USA) SAz-2 (50grams/unit)
- IMt-2 Illite (Silver Hill Montana USA (Cambrian Shale) Char.by Hower et al. AmerMin.51 p825-854 1966) IMt (50grams/unit)
- ISCz-1 Illite-smectite mixedlayer (70/30 ordered) Slovakia ISCz-1 (50grams/unit)
- NAu-1 Nontronite (green color Al-enriched from Uley Mine - South Australia) NAu-1 (50grams/unit)
- NAu-2 Nontronite (brown color Al-poor contains tetrahedral Fe from Uley Mine - South Australia) NAu-2 (50grams/unit)
- NG-1 Nontronite (Hohen Hagen Germany - Nontronite cemented sand: 15-20% nontronite) NG-1 (10grams/unit)
- SepSp-1 Sepiolite (Valdemore Spain - Miocene age contains minor calcite) SepSp-1 (50grams/unit)
- SSBld-1 Beidellite (Idaho USA) SSBld-1 (50grams/unit)
- CAR-1 Cookeite (Arkansas USA - cookeite flakes scattered on surface of rock chips) CAR-1 (10grams/unit)

The Source Clays Repository

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- Special Clays

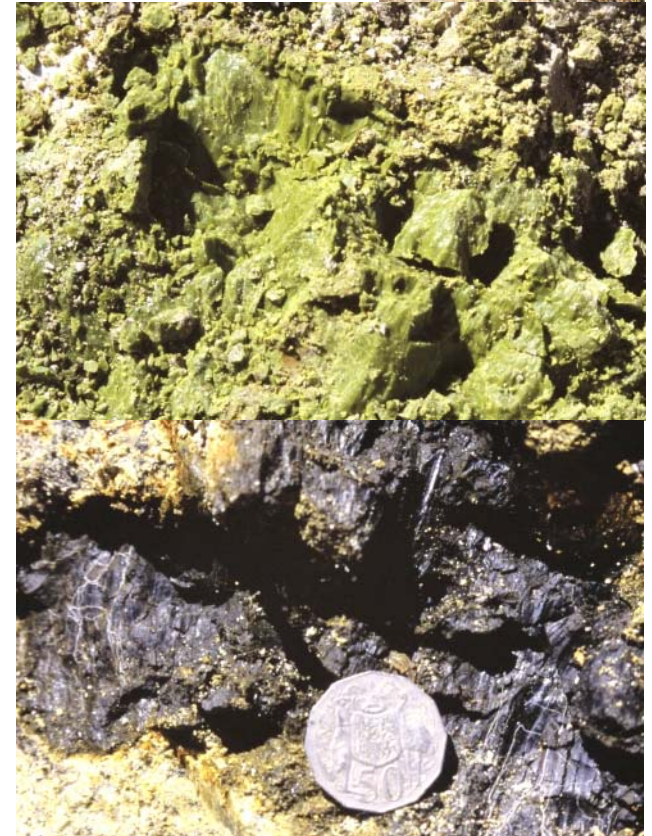
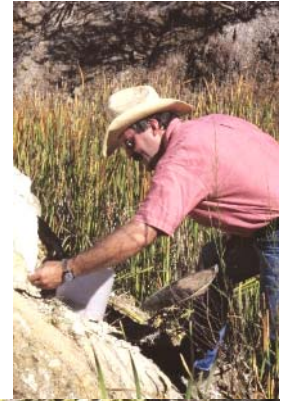
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Australian Clays



Uley Nontronite

- Uley graphite mine near Port Lincoln, southern Eyre Peninsula, South Australia
- NAu-1 - bright yellowish-green clay
- NAu-2 - earthy dark-brown clay
- 120 kg of each clay supplied to CMS
 - NAu-1 ~21 kg (17%) remains
 - NAu-2 ~46 kg (39%) remains
 - ~10-15 year supply remaining



Uley Graphite Mine circa 1996



Uley Graphite Mine circa 2012



The Source Clays Repository - Exhausted

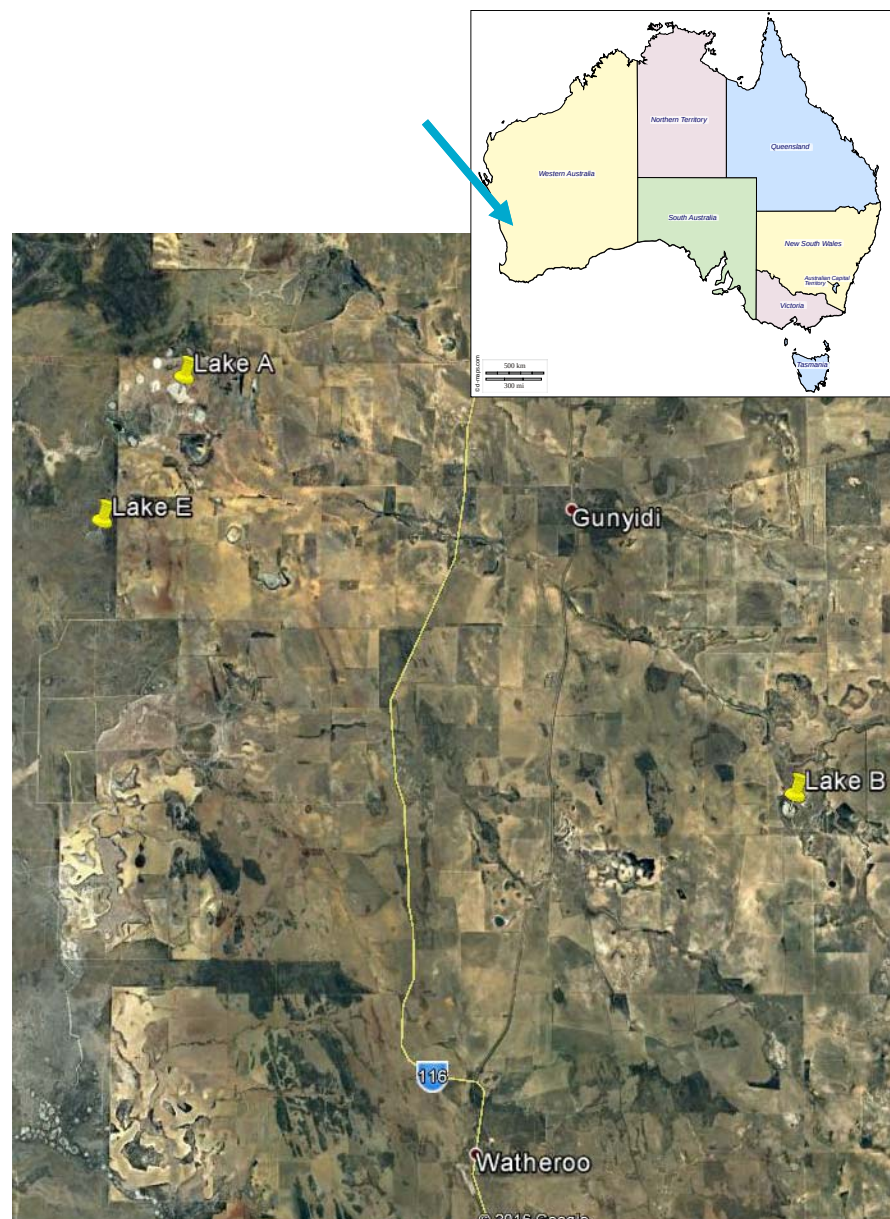
- IMt-1 Illite, Silver Hill, Mont.(Cambrian shale)
- SWa-1 Ferruginous Smectite, Grant County, Washington, USA
- VTx-1 Vermiculite ("Llano"), Llano, Texas, USA. A mixture of magnesite, phlogopite and vermiculite. The vermiculite can be separated with hand picking.
- IWi-1 Illite, Waukesha, Wisconsin, USA (Silurian)
- ISMt-1 Illite-smectite mixed layer (60/40 ordered), Mancos shale Cretaceous.
- CorWa-1 Corrensite, Pachwuk, WA. (Ohanapecoh form.). (Altered Eocene tuff, containing 25-50% corrensite; quartz and plagioclase impurities separable by wet sedimentation)
- SapCa-2 Saponite, Ballarat, CA. (contains up to 3%diopside, separable by wet sedimentation)
- SepNev-1 Sepiolite, Two Crows, Nevada (Clays & Clay Minerals, v.26, p.58-64, 1978)
- SBCa-1 Beidellite, California, USA
- SAz-1 Ca-rich Montmorillonite ("Cheto"), Apache County, Arizona, USA

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- SapAu-1 Saponite, Watheroo, WA, Australia (contains carbonates, gypsum, halite and some sepiolite)
- SepNev-1 Sepiolite, Two Crows, Nevada (Clays & Clay Minerals, v.26, p.58-64, 1978)
- SBCa-1 Beidellite, California, USA
- SAz-1 Ca-rich Montmorillonite ("Cheto"), Apache County, Arizona, USA
- ISAu-1 Illite-smectite mixed layer (10/90 random), Arumpo, NSW, Australia

Watheroo Saponite

- Location of Watheroo
 - 245 km North of Perth, Western Australia
- Deposits
 - Playa lakes and claypans A, B and E
- Formation
 - Reaction of Mg-rich water with colloidal silica and alumina and precipitation in a lacustrine environment during the Cainozoic
- Current uses
 - Soil improver, pet litter, agriculture, cosmetics, mining and engineering, food processing, fabrication, pollution management, containment and treatment
 - Inferred resource of ~350,000 t.

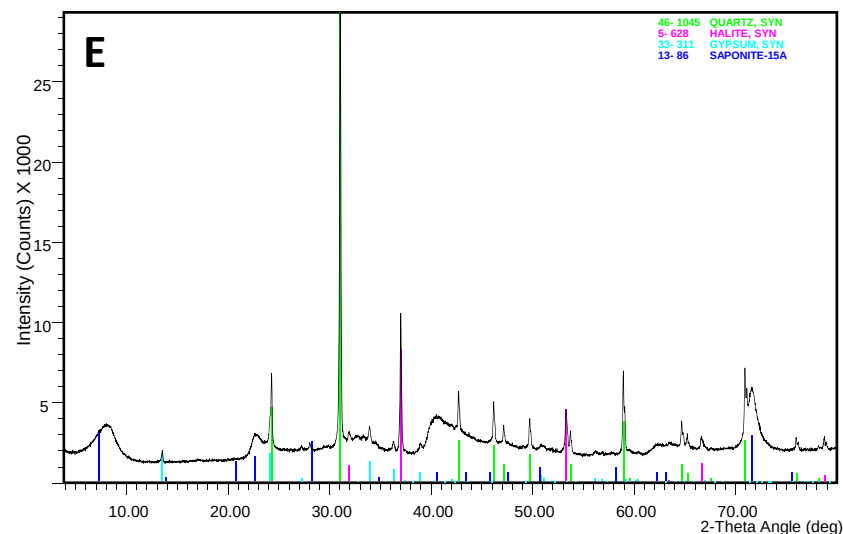
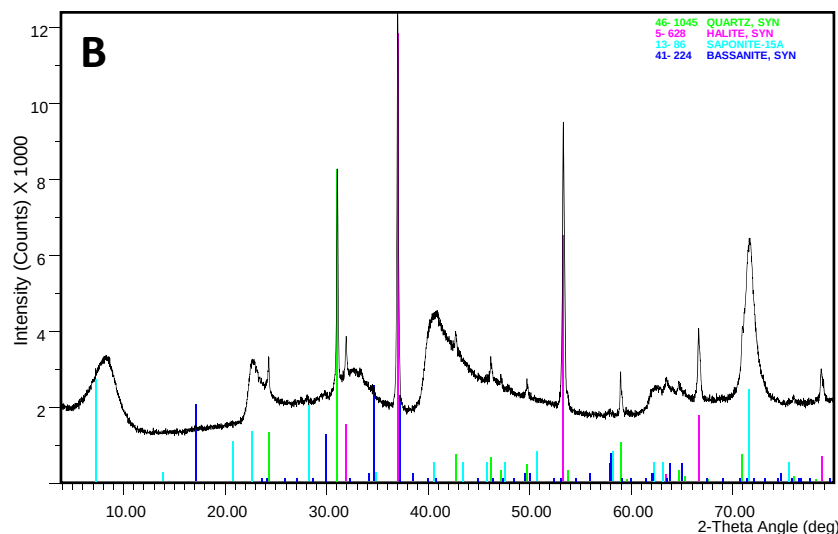
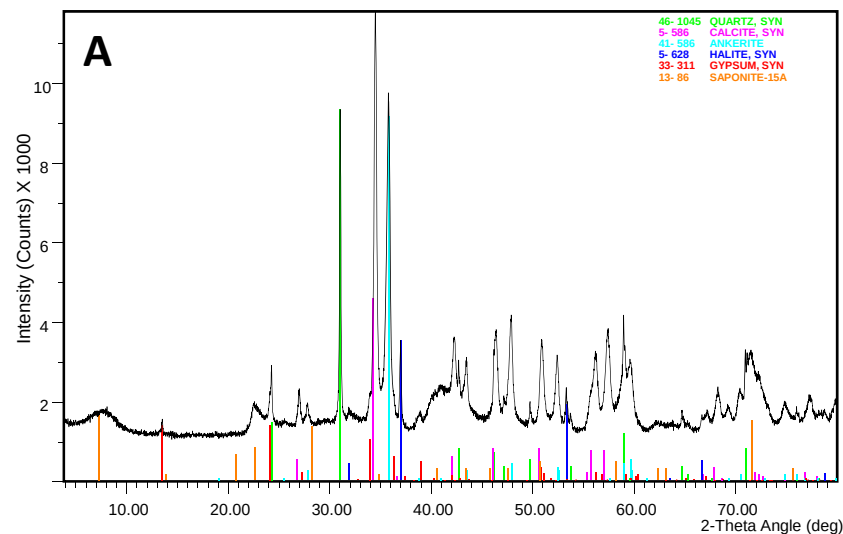


Watheroo Saponite



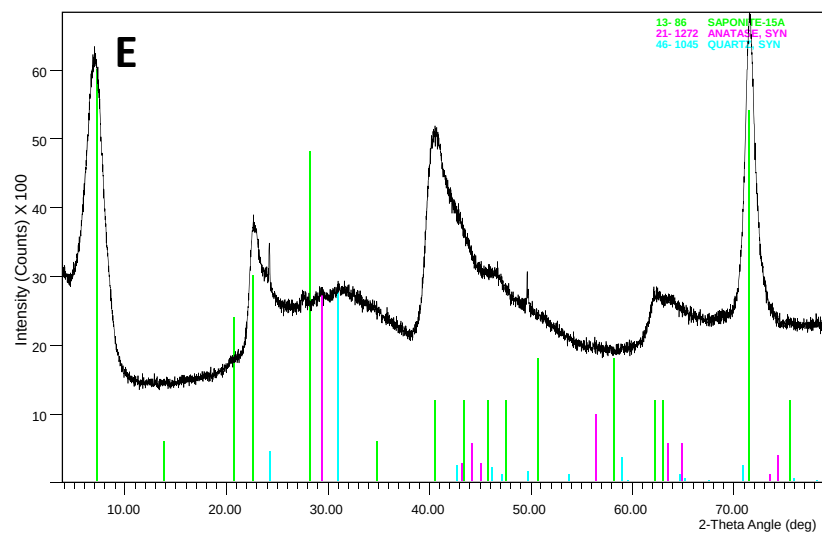
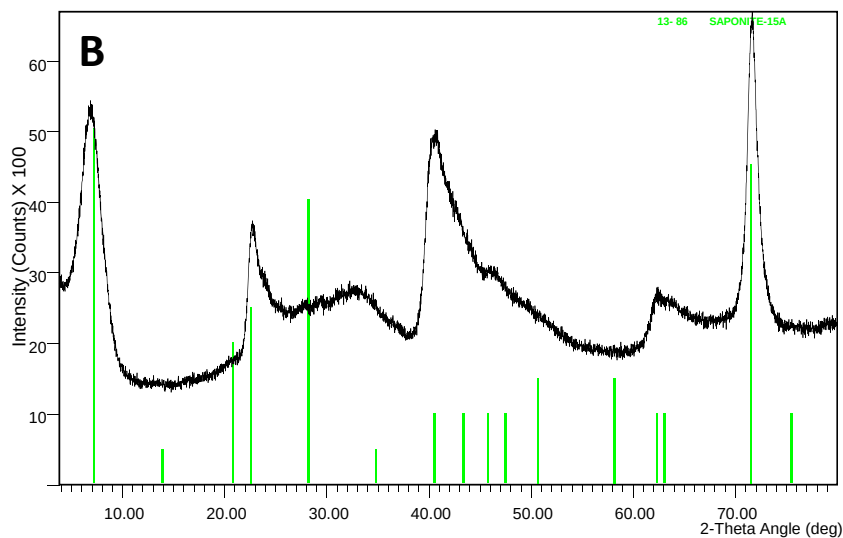
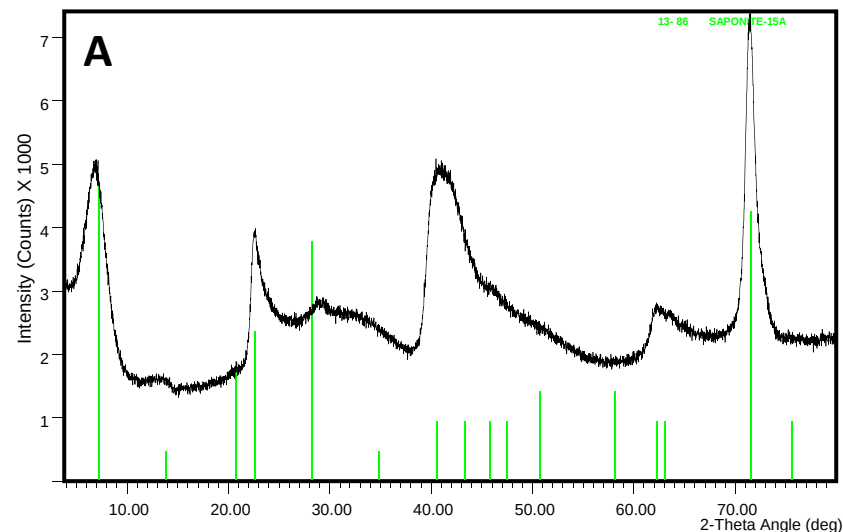
Watheroo Saponite - Bulk XRD

	Saponite A	Saponite B	Saponite E
Quartz	5	3	11
Calcite	21		
Dolomite	24		
Saponite	48	93	84
Gypsum	2	<1	2
Halite	1	4	2

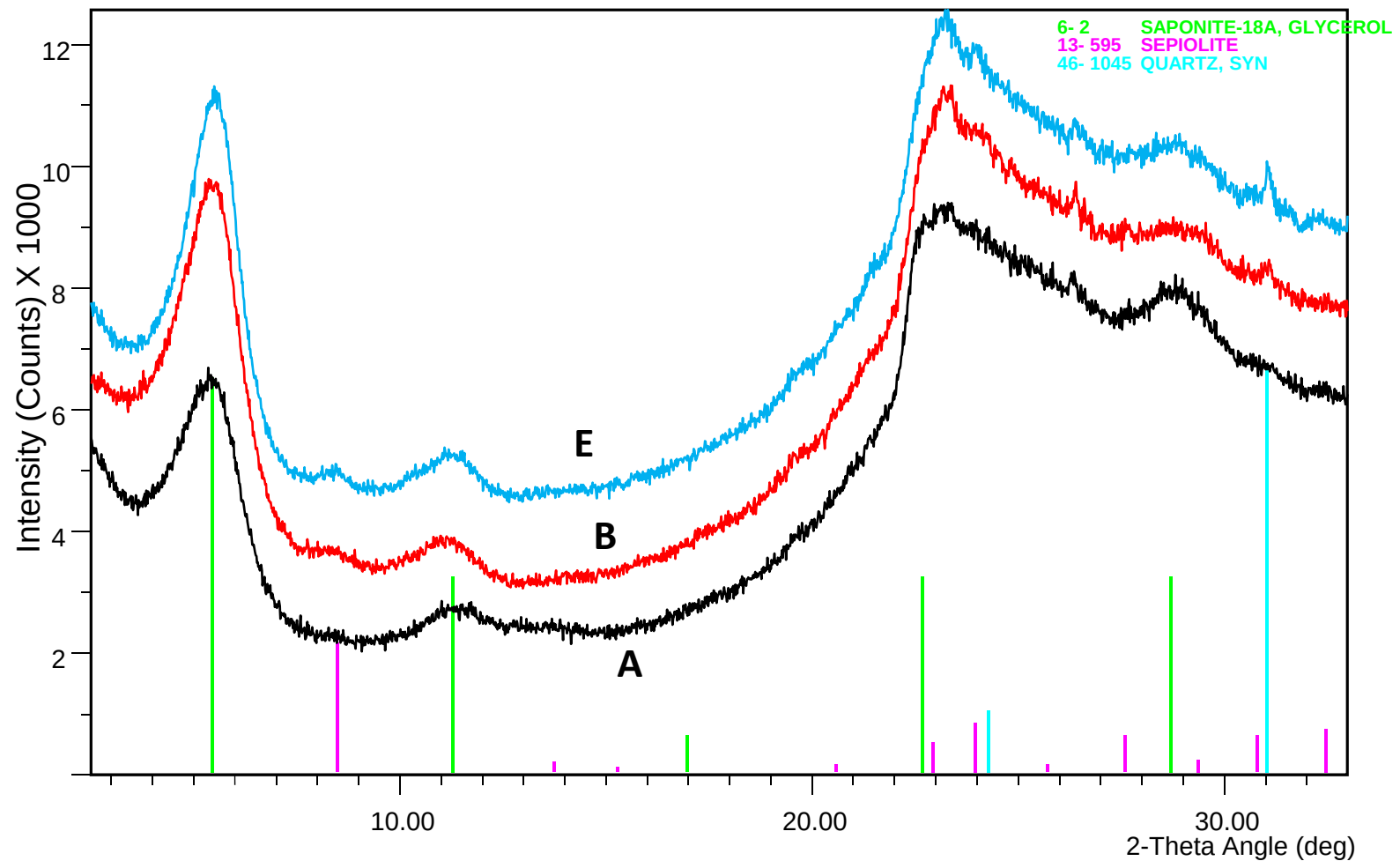


Watheroo Saponite - <0.2 μm fraction

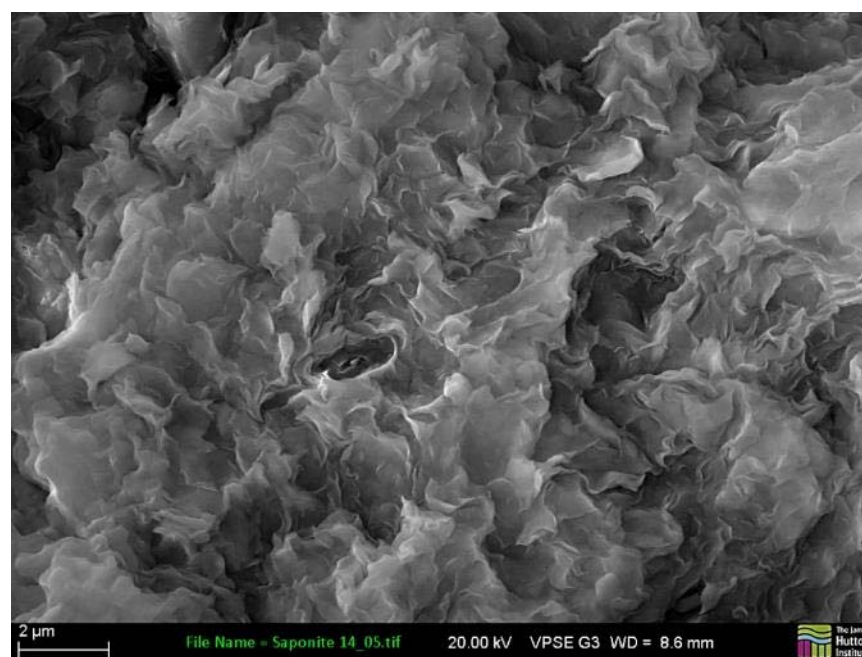
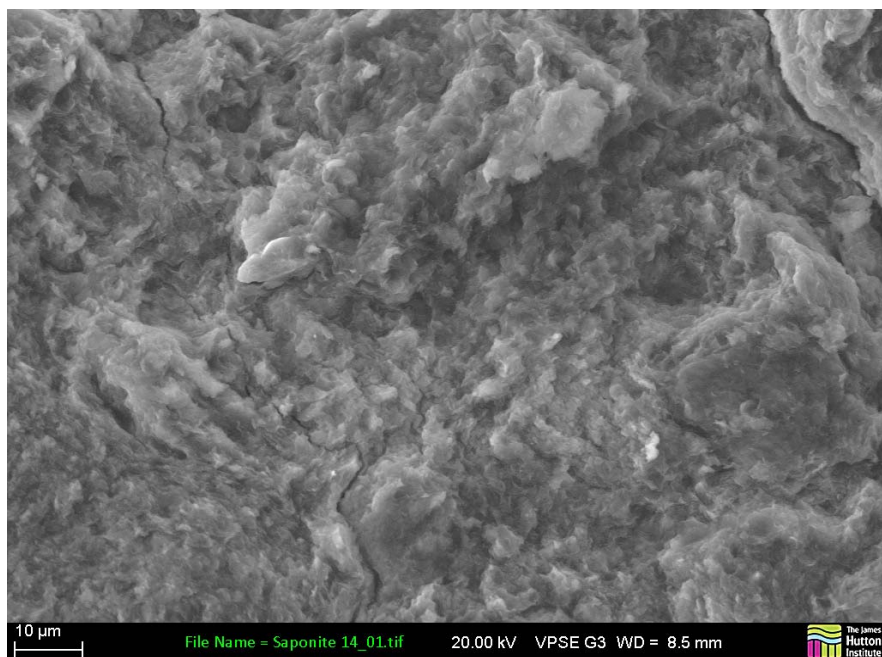
	Saponite A	Saponite B	Saponite E
<0.2 μm	41	81	77
Quartz			<1
Anatase			<1
Saponite	>99	>99	>99
Sepiolite		<1	<1



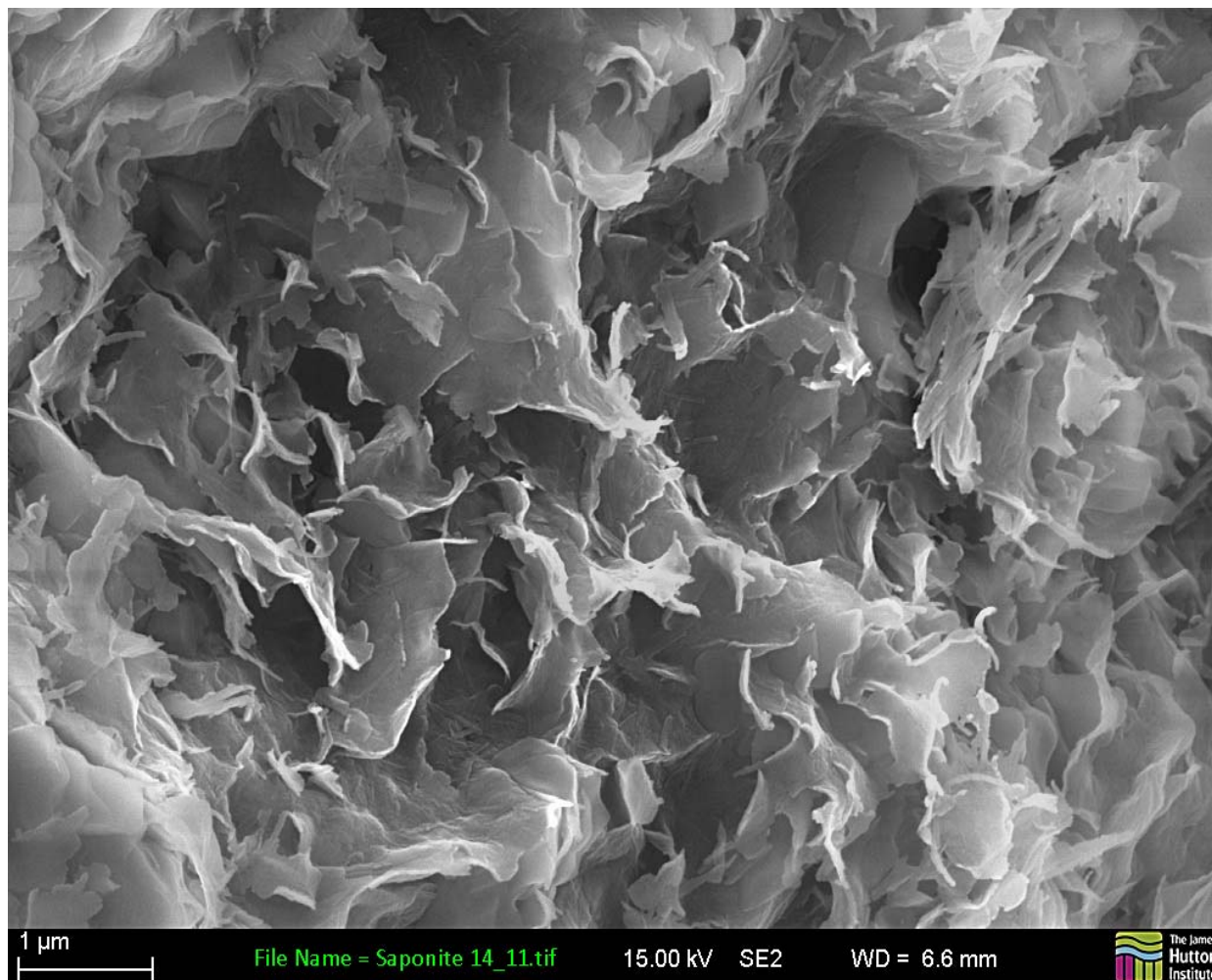
Watheroo Saponite - <0.2 μ m Oriented Mg saturated and glycerolated



Watheroo Saponite - SEM Saponite E



Watheroo Saponite - SEM Saponite E



Watheroo Saponite - Exchangeable cations

	Exchangeable Cations (pH 8.5)				Total	CEC (NH ₄)
	Ca	Mg	Na	K		
	cmol(+)/kg					
Saponite A	8.2	8.5	16	0.9	34	25
Saponite B	5.1	15	47	2.8	70	62
Saponite E	8.8	20	42	2.0	73	59

Watheroo Saponite - Bulk and <0.2 µm XRF

Bulk oven dried sample (105°C)

	Saponite A	Saponite B	Saponite E
SiO ₂	28.25	51.23	57.17
TiO ₂	0.19	0.30	0.40
Al ₂ O ₃	2.76	5.02	5.62
Fe ₂ O ₃	0.99	2.47	2.17
MnO	0.02	0.05	0.06
MgO	18.58	25.65	21.83
CaO	20.97	0.32	1.38
Na ₂ O	1.46	5.96	3.41
K ₂ O	0.16	0.42	0.40
P ₂ O ₅	0.05	0.06	0.05
SO ₃	1.10	0.59	2.11
Cl	11.2	6.5	2.1
Sum	75.73	98.52	96.75
LOI (XRF)	24.27	1.48	3.25

<0.2 µm fraction oven dried (105°C)

	Saponite A	Saponite B	Saponite E	SapCa-2
SiO ₂	51.84	55.10	54.62	51.26
TiO ₂	0.20	0.18	0.27	0.09
Al ₂ O ₃	5.90	5.50	6.68	4.42
Fe ₂ O ₃	1.95	2.38	2.43	1.14
MnO	0.04	0.05	0.07	0.03
MgO	29.29	26.17	25.50	23.54
CaO	1.94	2.14	2.28	1.25
Na ₂ O	0.07	0.12	0.08	1.14
K ₂ O	0.05	0.15	0.17	0.18
P ₂ O ₅	0.03	0.04	0.04	
SO ₃				
Cl				
Sum	91.31	91.82	92.14	93.13
LOI (XRF)	8.69	8.18	7.86	6.58

Post, J.L. (1984) Saponite from Near Ballarat, California. *Clay and Clay Miner.* 32(2):147-153

Watheroo Saponite - Structural Formula

	Saponite A	Saponite B	Saponite E
SiO ₂	51.84	55.10	54.62
TiO ₂	0.20	0.18	0.27
Al ₂ O ₃	5.90	5.50	6.68
Fe ₂ O ₃	1.95	2.38	2.43
MnO	0.04	0.05	0.07
MgO	29.29	26.17	25.50
CaO	1.94	2.14	2.28
Na ₂ O	0.07	0.12	0.08
K ₂ O	0.05	0.15	0.17
P ₂ O ₅	0.03	0.04	0.04
SO ₃	0.00	0.00	0.00
Cl	0.00	0.00	0.00
Sum	91.31	91.82	92.14
LOI (XRF)	8.69	8.18	7.86

	Saponite A	Saponite B	Saponite E	SapCa-2
Tetrahedral				
Si	3.52	3.70	3.66	3.77
Al	0.47	0.30	0.34	0.23
Total	4.00	4.00	4.00	4.00
Octahedral				
Al		0.14	0.19	0.16
Fe	0.11	0.13	0.14	0.06
Mg	2.96	2.62	2.55	2.58
Total	3.08	2.89	2.87	2.81
Interlayer				
Ca	0.14	0.15	0.16	0.10
Na	0.01	0.02	0.01	0.16
K	0.00	0.01	0.01	0.02
Total	0.16	0.18	0.19	0.27
Tetrahedral layer charge	-0.49	-0.30	-0.34	-0.23
Octahedral layer charge	0.19	-0.04	-0.01	-0.15
Interlayer cation charge	0.30	0.34	0.35	0.38

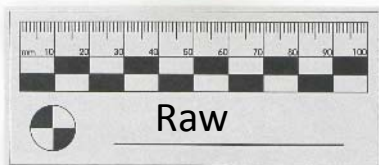
Post, J.L. (1984) Saponite from Near Ballarat, California. *Clay and Clay Miner.* 32(2):147-153

Arumpo Bentonite

- Location of Arumpo
 - 95 km NE of Mildura, NSW, Australia
- Deposits
 - ~10 km long by 5 km wide large flat-lying seams typically 5 m thick covered by 5-10 m of clay and sand overburden
- Formation
 - Weathered volcanic ash falls ~3 million years ago
- Current uses
 - Soil improver, pet litter, agriculture, cosmetics, mining and engineering, food processing, fabrication, pollution management, containment and treatment
- Inferred resource of >70 Mt

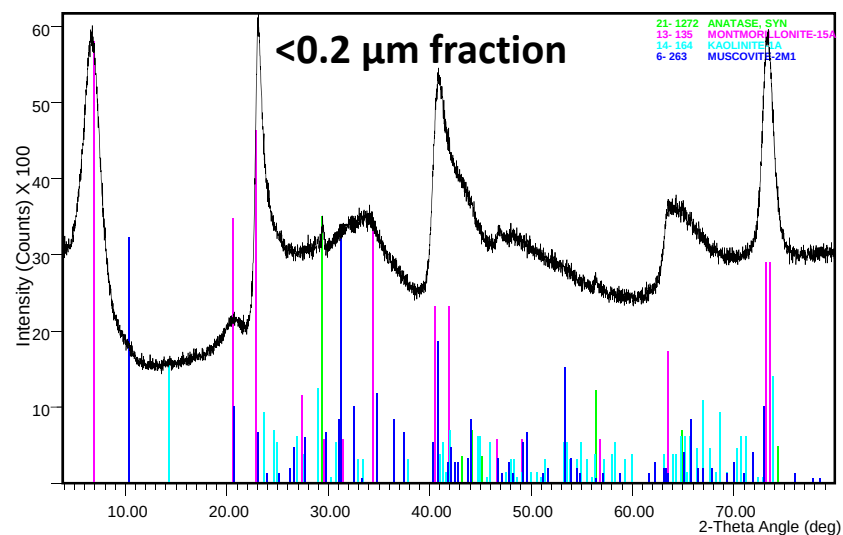
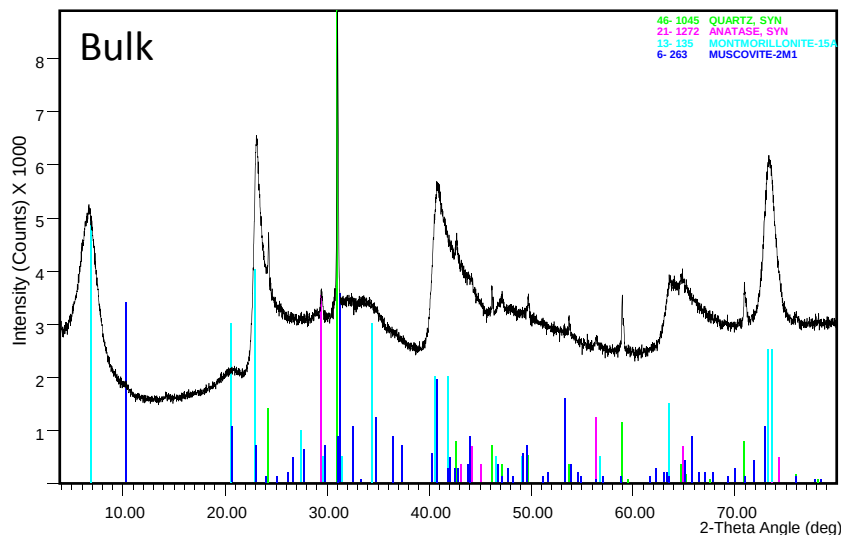


Arumpo Bentonite - Appearance

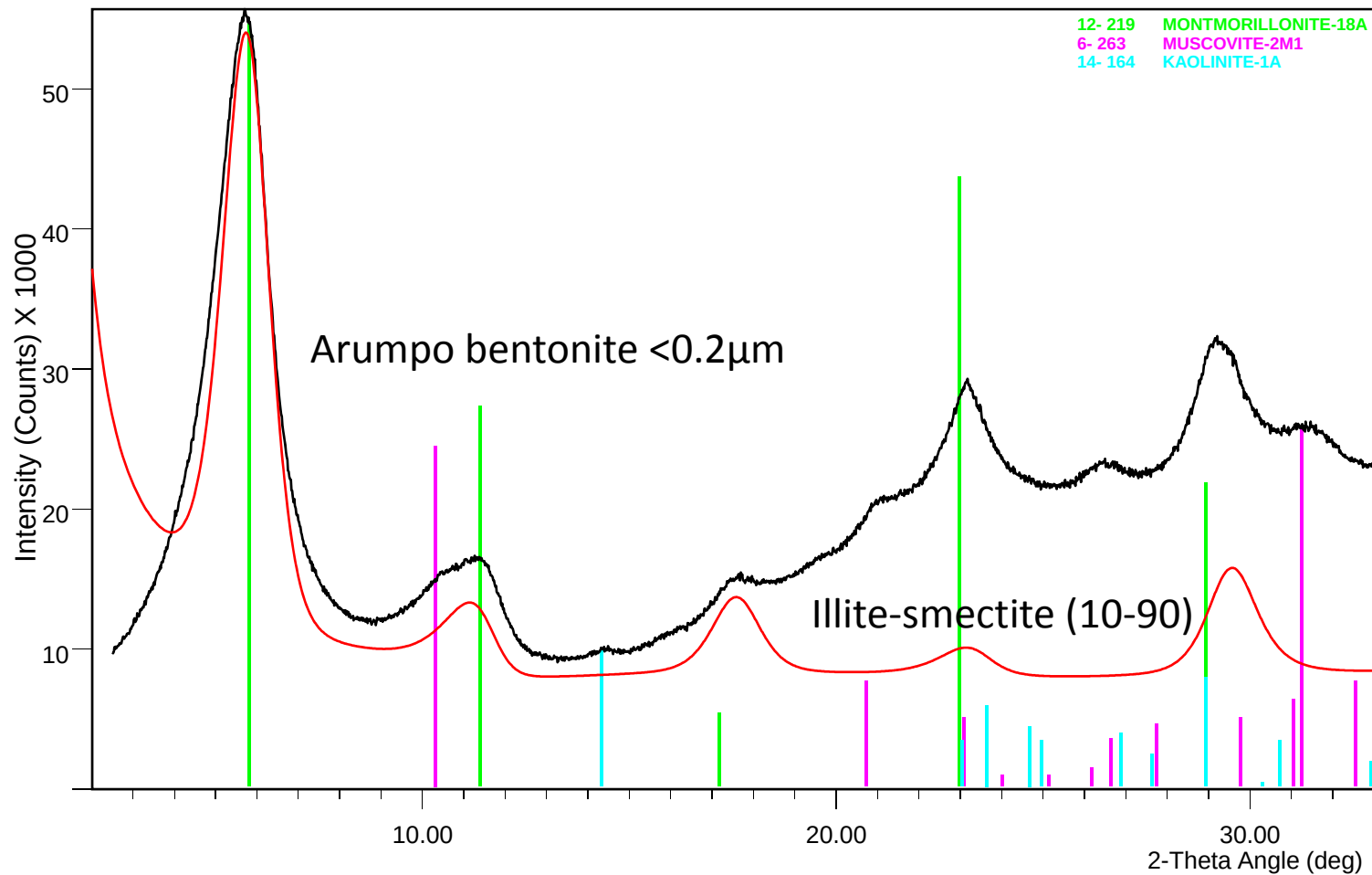


Arumpo Bentonite - Bulk and <0.2 μm XRD

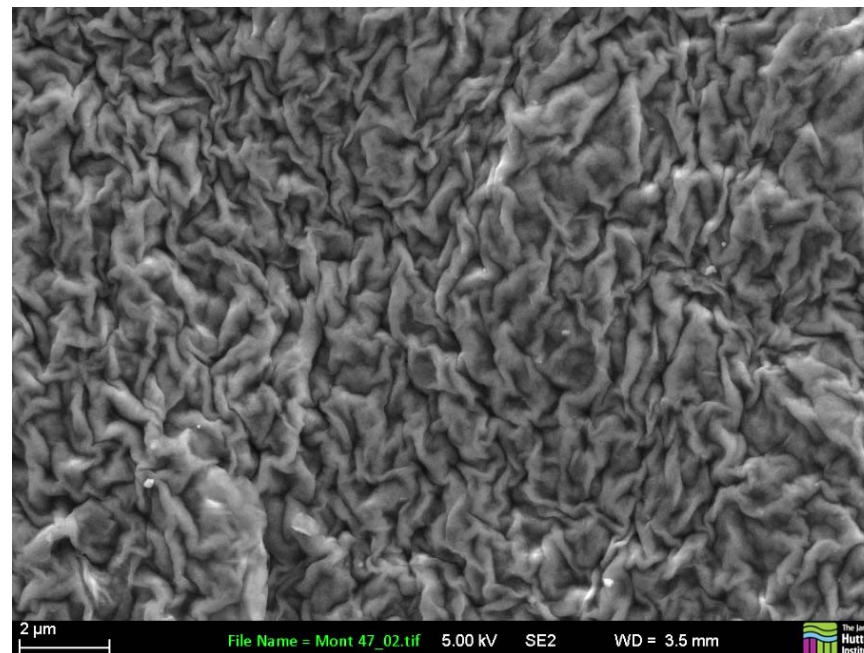
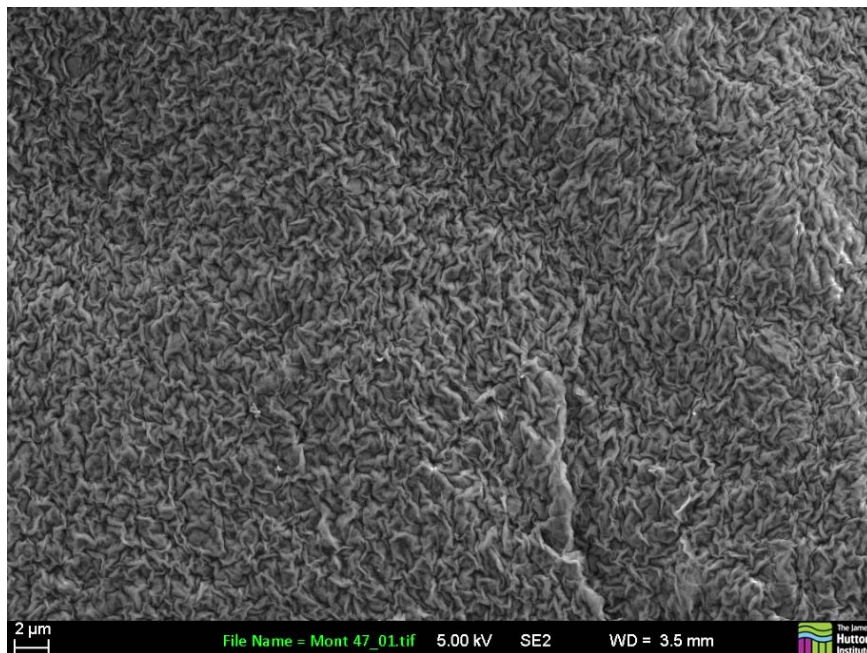
Client ID	Quartz	Montmorillonite	Kaolin	Anatase	Illite
Ultraben 150 Bulk	3	91	2	<1	4
Ultraben 150 <0.2 μm		97	<1	<1	2



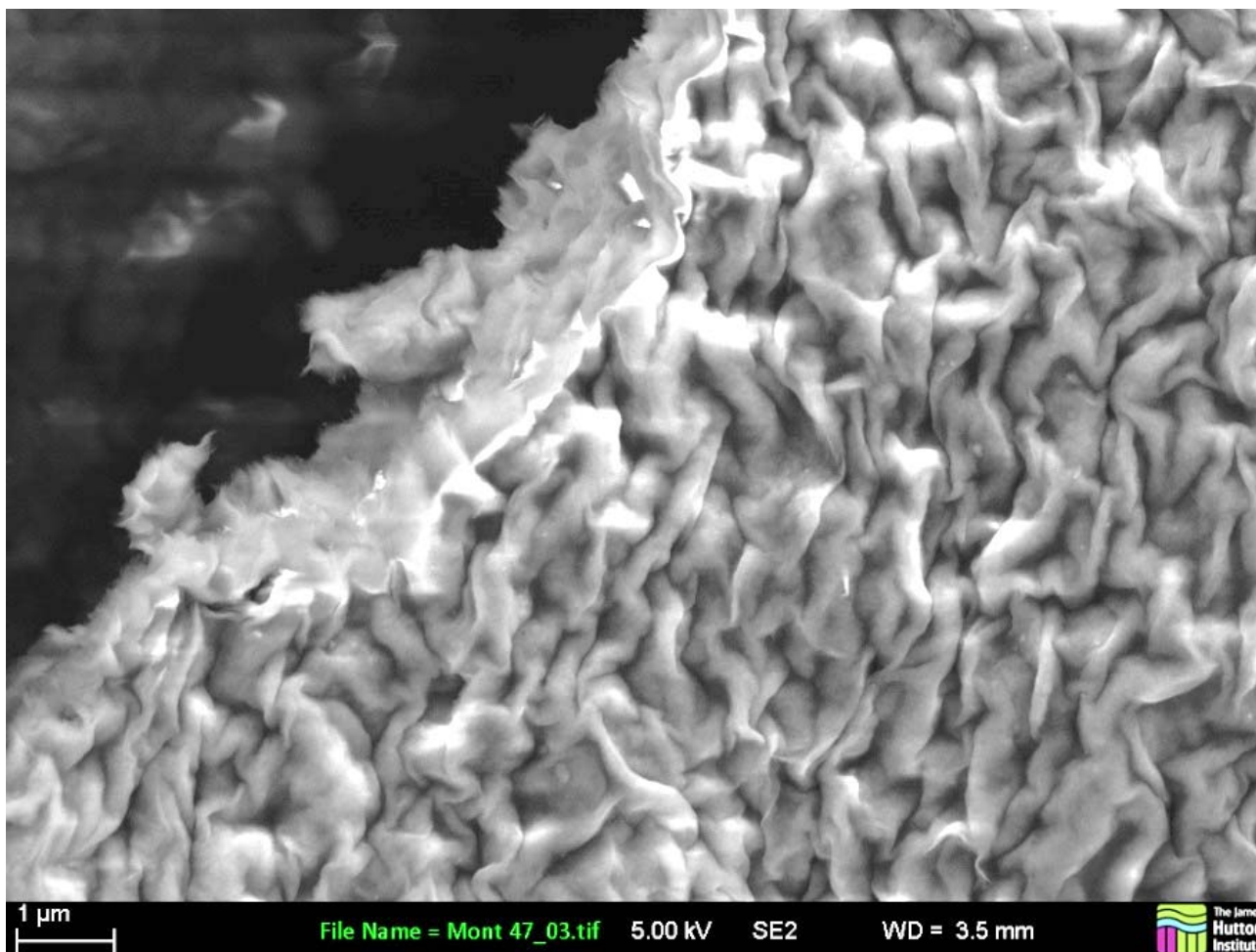
Arumpo Bentonite - <0.2 μ m Oriented Mg saturated and glycerolated



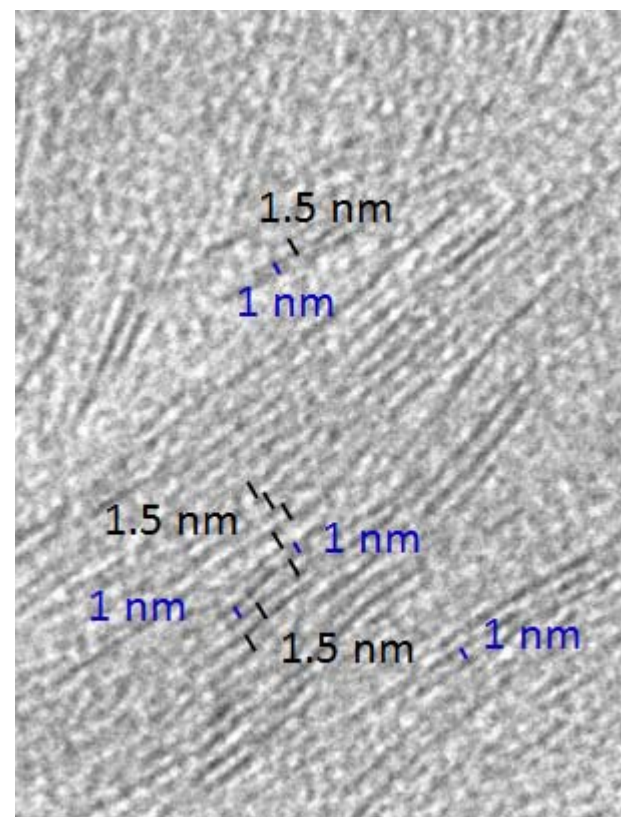
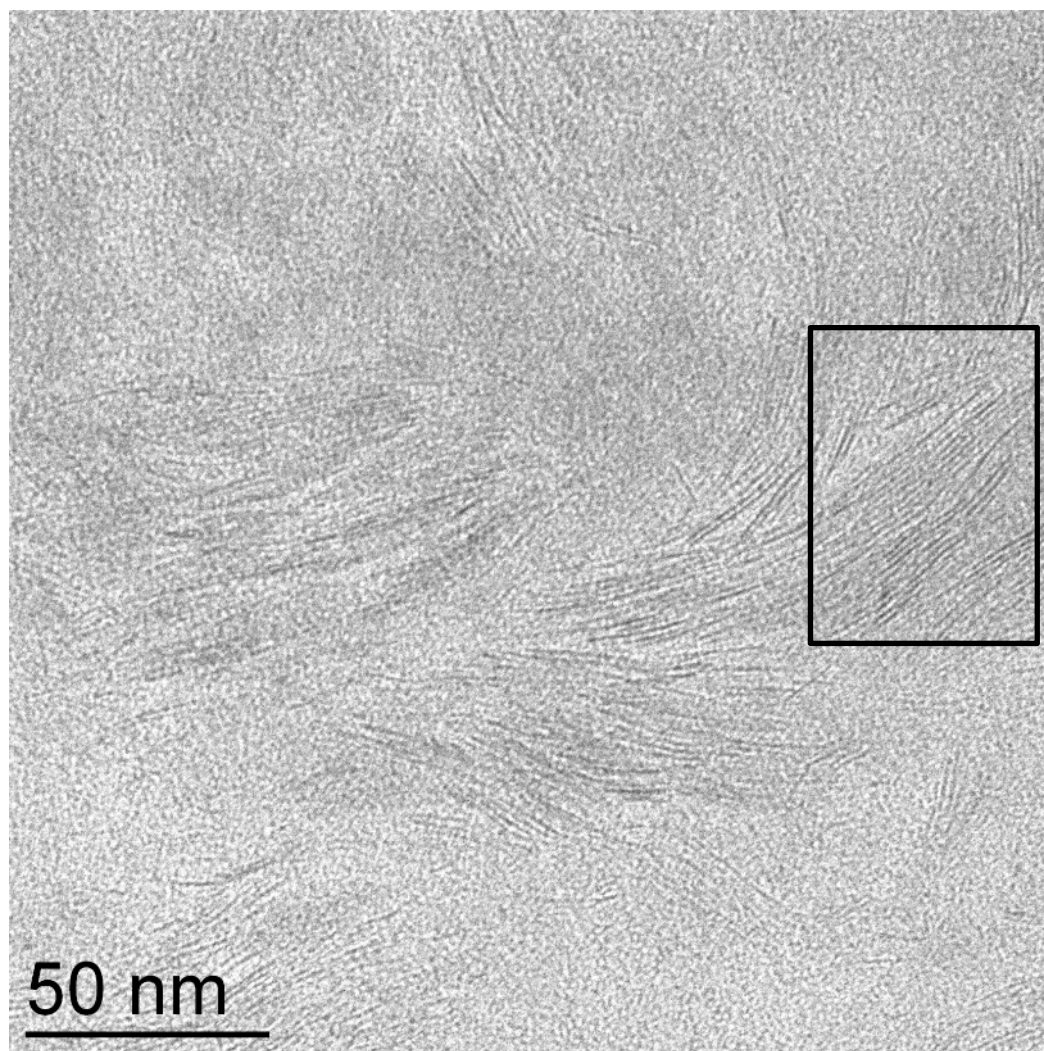
Arumpo Bentonite - SEM



Arumpo Bentonite - SEM

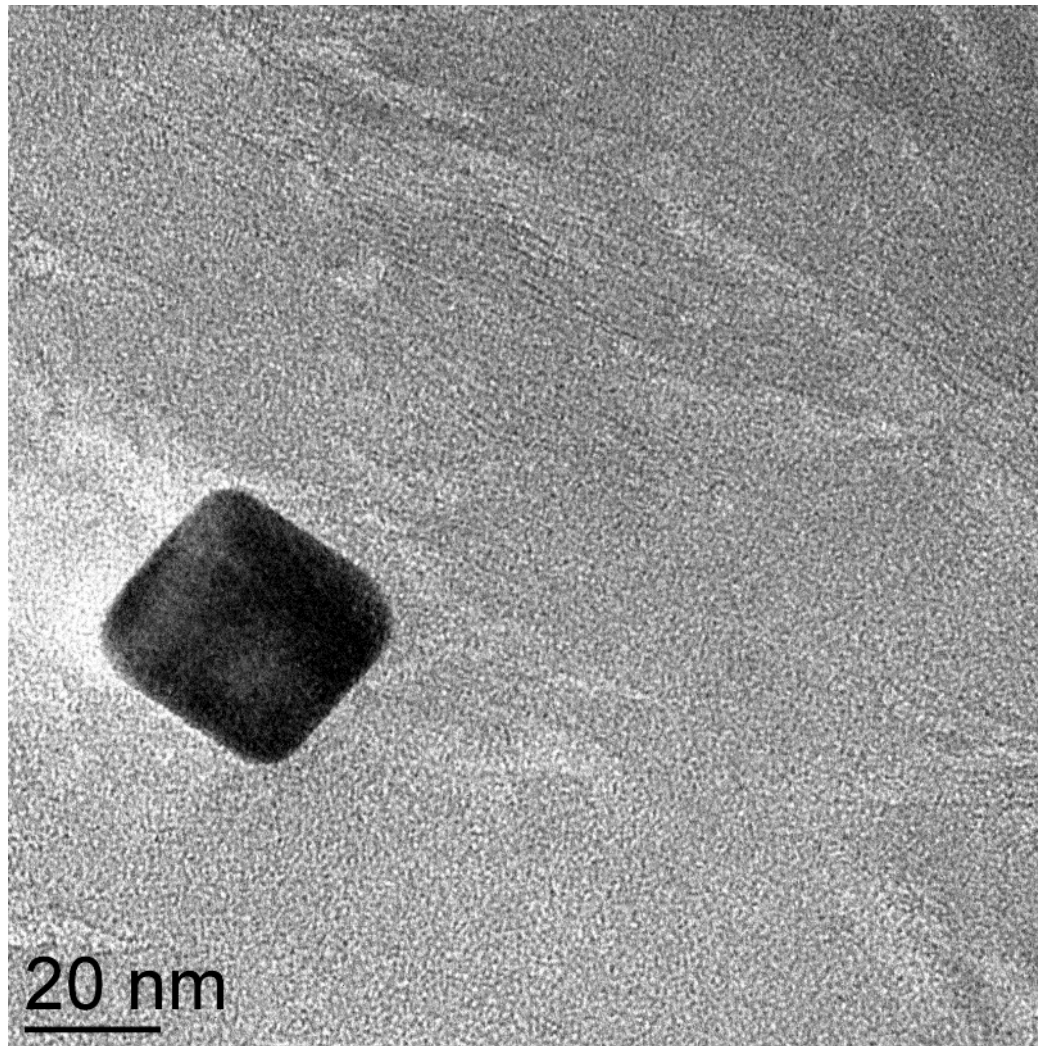


Arumpo Bentonite - TEM



Liu, Y. et al. (2017) Impact of acid leachates on the microtexture of bentonites used in geosynthetic clay liners

Arumpo Bentonite - TEM



Arumpo Bentonite - Exchangeable cations

	Exchangeable Cations (pH 8.5)					CEC
	Ca	Mg	Na	K	Total	(NH ₄)
	cmol(+)/kg					
Ultraben 150	0.7	36	46	3.0	86	78

Arumpo Bentonite - Structural Formula <0.2µm fraction

	0% Illite	5% Illite	All Illite
SiO ₂	59.29	59.83	60.05
TiO ₂	0.00	0.00	0.00
Al ₂ O ₃	21.73	21.63	21.24
Fe ₂ O ₃	5.02	5.12	5.22
MnO	0.01	0.01	0.01
MgO	3.49	3.52	3.53
CaO	2.32	2.44	2.60
Na ₂ O	0.10	0.11	0.10
K ₂ O	0.97	0.61	0.00
P ₂ O ₅	0.02	0.02	0.02
SO ₃	0.00	0.00	0.00
Cl	0.00	0.00	0.00
Sum	92.98	93.28	92.79
LOI (XRF)	7.02	6.72	7.21

	0% Illite	5% Illite	All Illite	SWy-2
Tetrahedral				
Si	7.62	7.65	7.69	7.76
Al	0.38	0.34	0.31	0.24
Total	8.00	8.00	8.00	8.00
Octahedral				
Al	2.92	2.91	2.90	3.04
Fe	0.48	0.50	0.50	0.41
Mg	0.67	0.66	0.67	0.55
Total	4.07	4.08	4.08	4.02
Interlayer				
Ca	0.32	0.33	0.36	0.16
Na	0.02	0.02	0.02	0.36
K	0.16	0.10		0.03
Total	0.51	0.46	0.38	0.55
Tetrahedral layer charge	-0.37	-0.35	-0.38	-0.24
Octahedral layer charge	-0.45	-0.44	-0.43	-0.47
Interlayer cation charge	0.83	0.79	0.73	0.71

Summary

- Two possible new clays for the Source Clays Repository:
 - Watheroo Bentonite saponite - SapAu-1
 - Arumpo Bentonite illite-smectite (10/90) - ISAu-1
- Many people have already analysed the Arumpo Bentonite clay
 - 15% used in the 2012 Reynolds Cup sample RC6-1
- Consider donating a clay(s) to the CMS Source Clays Repository
 - Satisfaction of knowing that you're helping the international clay community
 - Keeling, Raven and Gates (2000) *Clays and Clay Minerals* 48(5):537-548
156 citations

**XXII MEETING OF THE INTERNATIONAL
MINERALOGICAL ASSOCIATION**
13-17 AUGUST 2018 | MELBOURNE



<http://www.ima2018.com/>

Acknowledgements

- Tony Perkins and Alan Savage from Watheroo Bentonite
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Thank you

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