



***DRAGONITE™***

Halloysite Based: Halogen Free, Reinforcing  
Flame Retardant for Engineering Thermoplastics

BCC – Stamford CT, May 22<sup>nd</sup> 2012  
Dr. Chris DeArmitt - CTO

# Agenda

- Applied Minerals
- Halloysite structure & properties
- Enhancing plastics
- Case study: PET pallets
- Commercial aspects
- Conclusions

# Applied Minerals at a Glance

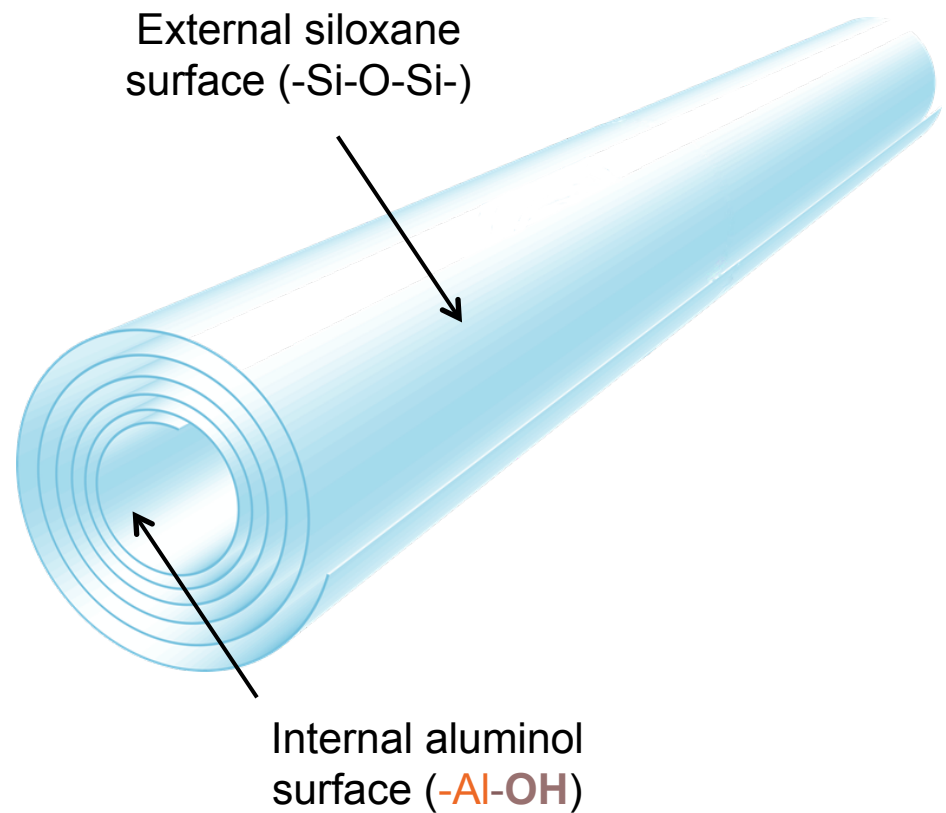
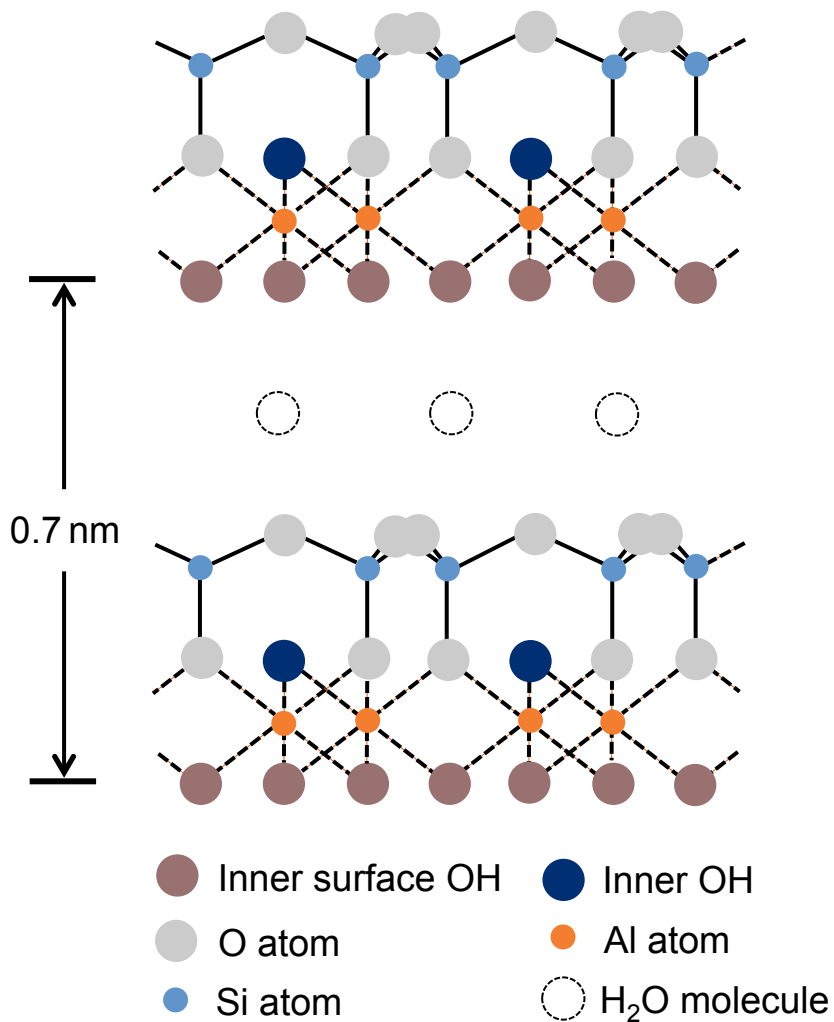
- US based publicly traded SEC reporting company.
- Owner and operator of the Dragon Mine Halloysite Clay Deposit in Utah USA
- Over 30 years of proven reserves
- Product grades marketed under the *Dragonite*™ trade name
- World renowned technical experts in geology, minerals characterization, plastics and materials
- Over \$ 7M invested to date in resource characterization and quantification
- Became commercial in 2010 with 30 000 tons annual capacity and expanding in 2012

# Technology Description - What is Halloysite?



- Halloysite is a natural aluminosilicate clay with a hollow tubular morphology
- Naturally exfoliated morphology means no need to chemically separate particles and makes for easy dispersion
- Halloysite nanotubes typically have diameter ~50nm with lengths ranging from 1 to 2 microns giving an aspect ratio of ~20
- Traditional uses include fine china, fillers in paints and paper, food extenders, catalysts and molecular sieves

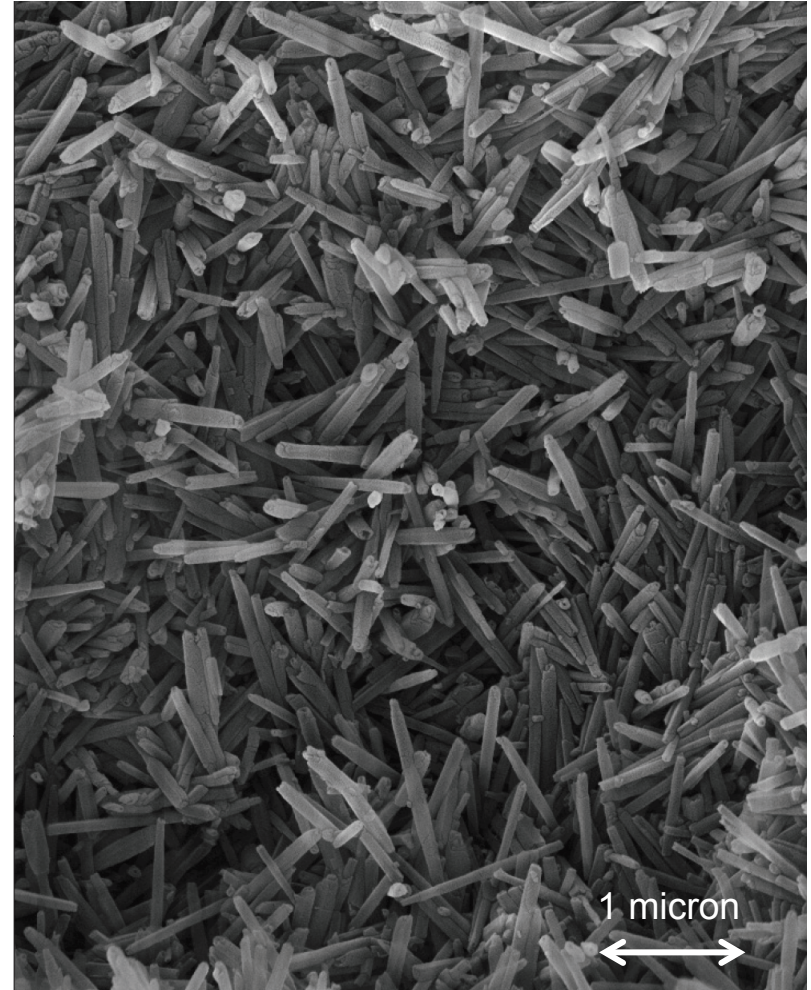
# Dragonite Chemistry





# Characterization and Quality Control

○ Length	0.2-2 $\mu\text{m}$
○ Outside Diameter	50-70 nm
○ Inside Diameter	15-45 nm
○ Aspect Ratio (L/D)	10-40
○ Particle Size ( $d_{100}$ ) < 5 $\mu\text{m}$	95-100%
○ Particle Size ( $d_{90}$ ) < 2 $\mu\text{m}$	80-98%
○ BHT Surface Area	65 $\text{m}^2\text{g}^{-1}$
○ True Specific Gravity	2.53 $\text{gcm}^{-3}$
○ Bulk Density	~16 lbs / $\text{ft}^3$
○ BHT Pore Volume	20%
○ Oil (linseed) Absorption	40 lbs / 100 lbs
○ Cation Exchange Capacity	11 meq / 100g



# Halloysite Property Overview

- Aluminosilicate mineral:  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$
- Molecular weight: 294.19
- CAS: 1332-58-7
- Density:  $2.54 \pm 0.03 \text{ gcm}^{-3}$
- Refractive index at room temperature: 1.534, dried at 100°C 1.548
- Specific heat capacity:  $0.92 \text{ kJkg}^{-1}\text{K}^{-1}$
- Thermal conductivity:  $0.092 \text{ WK}^{-1}\text{m}^{-1}$
- Thermal diffusivity:  $5.04 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$
- CTE:  $10.0 \pm 1.5$  perpendicular to the layer,  $6.0 \pm 2.0$  parallel
- Colorless and UV transparent
- pH in water 6.4-7.2
- Particle shape: 1-2 microns long, 50nm across, 15nm diameter hole
- Modulus ~130 GPa
- Surface area:  $65\text{-}120 \text{ m}^2\text{g}^{-1}$
- Dragonite™ purity: 95-100%



# Dragonite™ Intrinsic Properties and Applications

## High aspect ratio

- Reinforcement of plastics, elastomers, coatings etc.

## High surface area

- Catalysts, adsorbents, carrier, elastomers, immobilization, nucleation of crystal growth and foam cell formation

## Hollow

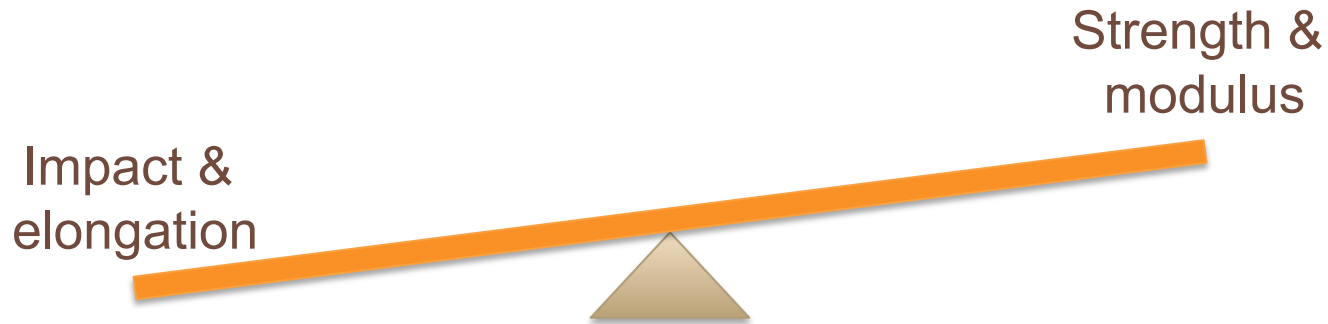
- Controlled release, thermal insulation, light-weighting, wicking, membranes, reverse osmosis

## Bound water

- Fire retardance, temperature indicator, foaming agent



# Property See-Saw



- Isotropic fillers retain impact but do not reinforce
- Reinforcing fillers ruin impact resistance and elongation to break
- Halloysite reinforces and retains or improves impact and elongation
- This is possible due to shape, surface area and easy dispersibility

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# The Challenge

Customer target is for a high-performance pallet:

- Flexural Modulus ~1000 kpsi
- Flexural Strength ~18000 psi
- Notched Izod Impact resistance ~1 J/cm<sup>2</sup>
- MFI 15 g/10 min due to existing mold
- Fire retardance to UL 2335
- Safe, non-migrating and halogen free FR requirement
- Starting point is Rynite 35% GF filled PET but unable to achieve mechanicals and UL 2335 with existing FR packages



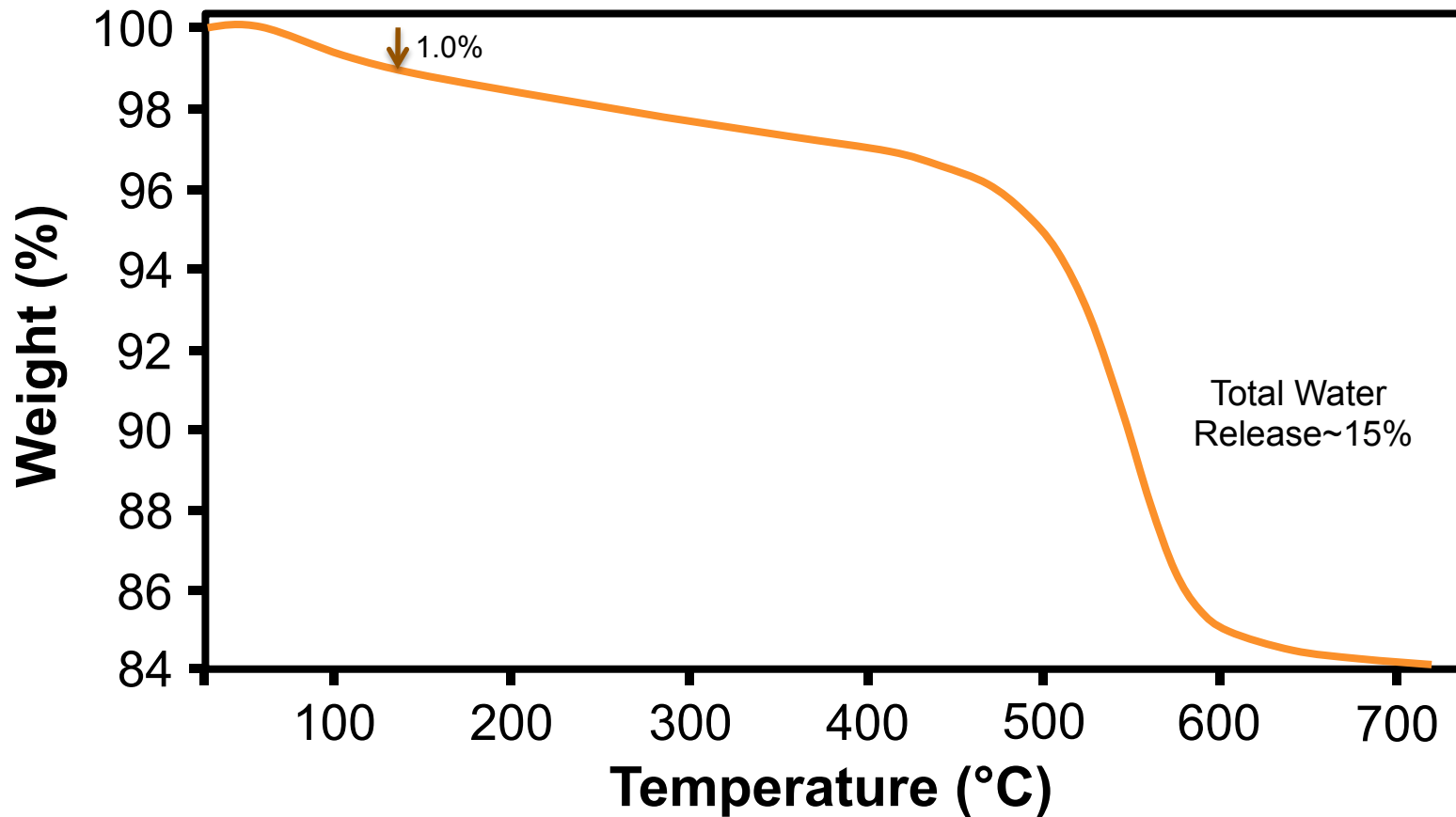
# Why Dragonite?

- Other solutions had failed to provide the answer
- Phosphorous-based systems plasticize
- Halogenated products not acceptable
- Mineral based FR like ATH and MDH not appropriate for PET
- Dragonite known to reinforce while retaining impact and providing FR
- Natural, safe, non-migrating, cost-effective and commercially available in quantity

# Experimental Plan

- Prepare a highly loaded Dragonite masterbatch in recycled PET copolymer that can be combined with commercial Rynite GF PET
- Pre-drying the Dragonite and good dispersion essential
- Selected Americhem due to their experience with hydrolytically unstable polymers, excellent dispersion ability and QC
- Dragonite has some reactivity so adding a surfactant or stabilizer can be beneficial
- In this case 2% RDP was chosen due to proven affinity to Dragonite and previously reported results (BCC 2011)
- The aim was to add the Dragonite masterbatch in the minimum amount needed to pass UL 2335

# Dragonite Thermal Stability by TGA





# Dragonite Solution

**35%GF Rynite Control- 7 g/10'**  
**65 Rynite/ 35 Americhem MB - 20 g/10'**  
**60 Rynite/ 40 Americhem MB - 24 g/10'**

	Ctrl	1	2	3
Rynite 35% CGF filled PC	100	80	65	60
<b>45% MB of HNT in Copolyester</b>	<b>0</b>	<b>20</b>	<b>35</b>	<b>40</b>
residue from ash test 750 C, 30 minute	34.3	36%	37.8	36.8
% Actual clay	0	9.9	16	18.6
% CGF	34.3	27.6	15.75	21
Color	black	black	black	black
Speific Gravity	1.58	1.595	1.585	1.598
Flex modulus, tangent, Kpsi	1577	1115	1085	1026
Flex modulus,1 %, kpsi	1510	1110	1066	1020
Flex Strength, psi	31112	19849	19417	17643
Break strain under flex	3.2	2.37	2.4	2.24
Tensile Strength, psi	16690	11538	12281	11056
% el @ yield	6.5	5	4.92	4.63
% El @ break	6.5	5	4.92	4.63
Notched Izod Impact, ft-lb/in	1.58	0.75	0.89	0.71
Unnotched izod ft-lb/in	13.4	8.1	9.2	7.2



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% Actual clay	0	9.9	16	18.6
% CGF	34.3	27.6	15.75	21
Density of char				1.485
UL vertical, 23x 10 sec S/E	X	X	X	X
Burning up to clamp	CB	CB	CB	CB
Flaming VB Drip	No	No	No	No
S/E < 30 seconds	No	No	No	No
Smoke	blk	blk	blk	blk
seconds to burn 5 cm (needs >180s)	135	150	165	229
burning rate horizontal,	0.344827586	0.333	0.3030	0.2183
Average weight of tensile bars	12.71	12.8	12.99	13.18



# PET FR Development

- Reinforcing, halogen free flame retardant
- Good mechanicals in combination with glass fiber
- High water release temperature  $> 400^{\circ}\text{C}$  means Dragonite is ideally suited to polymers processed at high temperature
- Char strength boosted with Dragonite™ plus glass fiber
- Synergistic fluxing effect



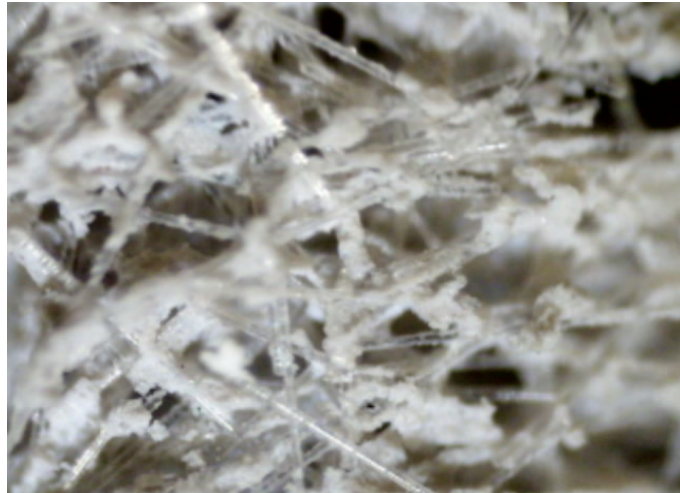
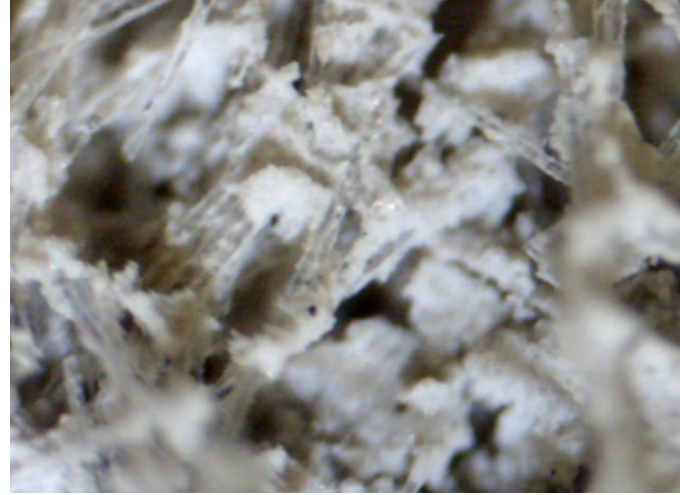
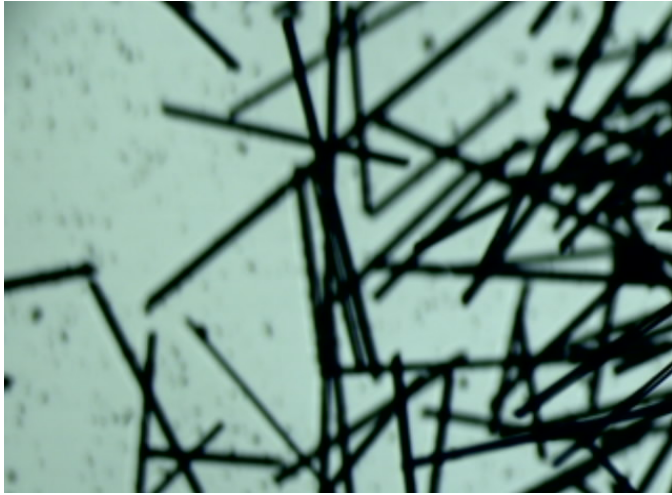
30% GF + 5% HNT

30% GF + 10% HNT

30% GF + 15% HNT



# Ceramification?



# Pallet Formulation Summary

- All mechanical targets met
- Dragonite is reinforcing so it was possible to replace a portion of the glass fiber and still have good strength and modulus
- Impact resistance was retained at an acceptable level
- By adding the Dragonite in recycled PET copolymer the flow was increased, essential for injection molding
- Fire retardance to UL 2335 certification anticipated (underway)
- Safe, non-migrating and halogen free FR requirement
- We continue to optimize this formulation while also extending this reinforcing FR masterbatch approach to PP, PA6 etc.



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# Commercial Status



- Dragon Mine Halloysite deposit characterized and proven in 2010
- Commercialization status:
  - Nucleation of HDPE and PP for better mechanicals and reduced cost in injection molded parts and extruded profiles
  - The only reinforcing and halogen-free mineral fire retardant for engineering plastics (recent Samsung press release)
  - Reinforces foams, improves productivity and helps surface appearance
  - Several new developments in the pipeline



# Availability

- Dragonite™ brand high-purity Halloysite is commercially available from Applied Minerals
- Dragonite™ is shipped directly from the Dragon Mine in Utah, USA
- Masterbatch concentrates are available as well as neat powder
- Supply is plentiful (>30 ktons) to support large-scale applications
- Samples are available to interested parties
- Technical support is also available

# Thank You For Your Time

## Q&A