Electronic Supplementary Material (ESI) for RSC Advances

Activation of serpentine for CO_2 mineralization by flux extraction of soluble magnesium salts using ammonium sulphate

James G. Highfield, Hui Qi Lim, Johan Fagerlund, Ron Zevenhoven

SUPPORTING INFORMATION

Table S1: Glossary of Compounds

Chemical name	Formula	Abbrev.	Mineral name	XRD (ICDD) reference pattern
Ammonium sulphate	$(NH_4)_2SO_4$	AS	Mascagnite	00-040-0660
Serpentinite (class)	$(Mg,Al)_3[(Si,Fe)_2O_5](OH)_4$	L	Lizardite	00-050-1625
Ammonium bisulphate	NH_4HSO_4	ABS	—	—
Sulphamic acid	NH_3SO_3	SA	—	—
Ammonium pyrosulphate	$(NH_4)_2 S_2O_7$	APS	—	—
Ammonium magnesium sulphate hydrate	$(NH_4)_2Mg(SO_4)_2{\bullet}6H_2O$	B	Boussingaultite	00-035-0771
Ammonium magnesium sulphate	$(NH_4)_2Mg_2(SO_4)_3$	E	Efremovite	00-042-1432
Magnesium sulphate heptahydrate	$MgSO_4{\bullet}7H_2O$	EP	Epsomite	01-072-0696
Magnesium oxide	MgO	—	Periclase	00-004-0829
Silica	SiO_2	—	EU-20	00-043-0745

Electronic Supplementary Material (ESI) for RSC Advances

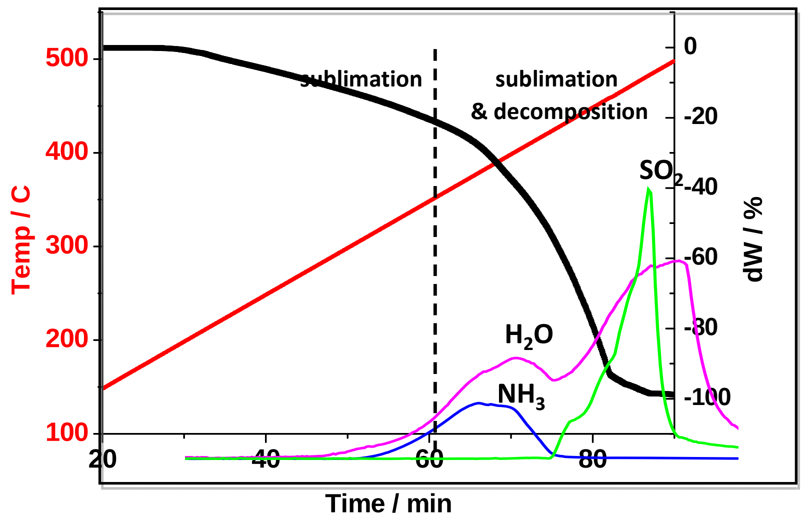

Fig. S2 TG-FTIR: Sulphamic acid in dry air flow ramped to 500 °C

T (°C)	dW (%)	Likely Process	FTIR (EGA)	Progressive reaction(s)
≤ 300	26	ABS (NH_4HSO_4) AS SA (NH_3SO_3)	NH_3, H_2O	A: $(NH_4)_2SO_4 \rightarrow NH_4HSO_4 + NH_3$ (dW = 12.9%) $(NH_4)_2SO_4 \rightarrow NH_3SO_3 + NH_3 + H_2O$ (dW = 26.5%) B: $NH_4HSO_4 \rightarrow NH_3SO_3 + H_2O$ (dW = 15.7%)
300 to 350	15.5 7.0	dry SA ABS H_2O H_2O APS	NH_3, H_2O	B: $2NH_4HSO_4 \rightarrow 2NH_3SO_3 + 2H_2O$ (dW = 15.7%) C: $(NH_4)_2S_2O_7 \leftrightarrow 2NH_3SO_3 + H_2O$ (dW = 8.7%) D: $2NH_4HSO_4 \leftrightarrow (NH_4)_2S_2O_7 + H_2O$ (dW = 7.8%)
> 350 400 450	~70 100	sublimation decomposition	SO_2, N_2O, H_2O	D: $2NH_3SO_3 \rightarrow 2SO_2 + 2NH_2OH$ E: $2NH_2OH \rightarrow N_2O$ (+ H_2O + $2H_2$?)

Fig. S3 Scheme of processes in ammonium sulphate thermolysis up to 450 °C in air.

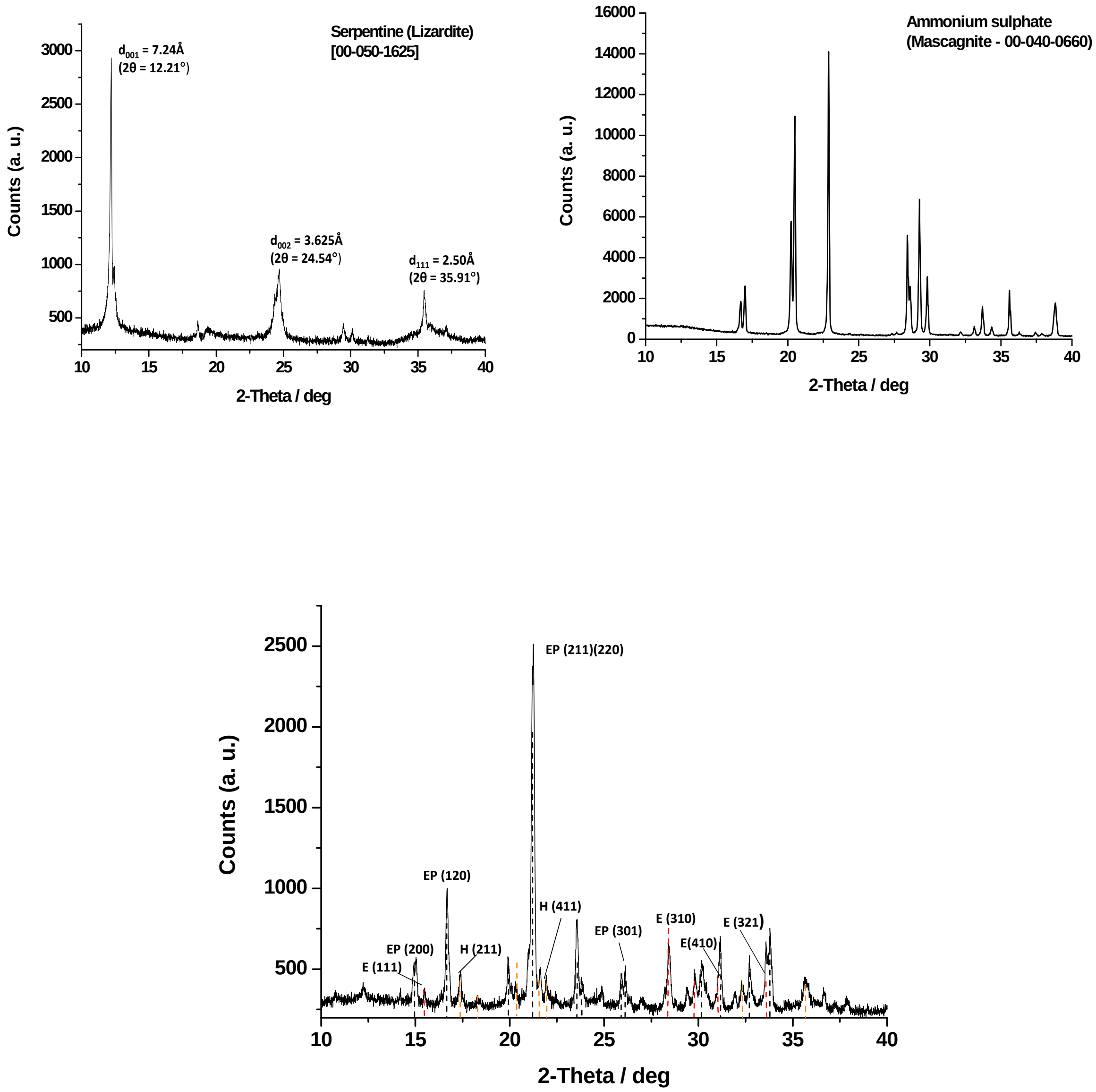

Fig S4 XRD patterns for reactants Lizardite, ammonium sulphate (Aldrich >99%), and the product from heating a 1/3 mol/mol mixture in dry air at 400 °C for 1 hour
[EP = Epsomite (black), E = Efremovite (red), H = Hexahydrite (orange)].

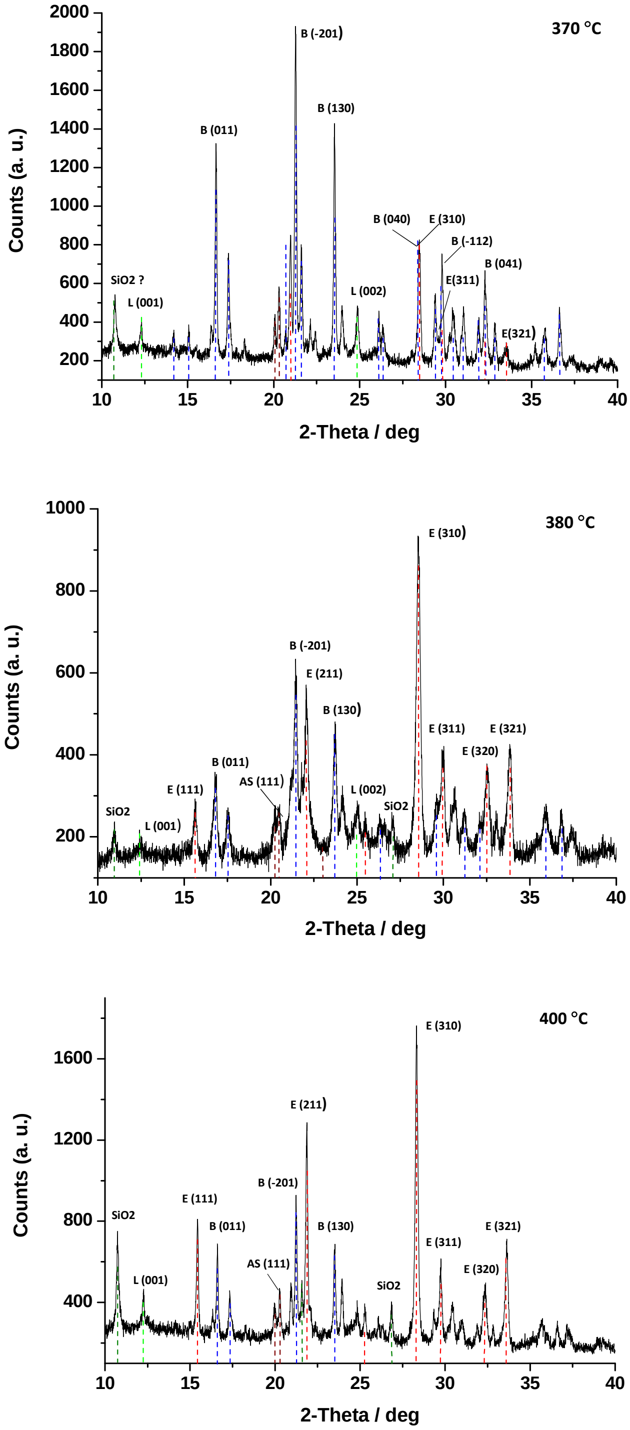

Fig S5 XRD of products from Lizardite/ammonium sulphate mixtures (1/4.5 mol/mol) held for 1 hour at 370, 380, and 400 °C [B = Boussingaultite (blue), E = Efremovite (red), L = Lizardite (green), AS = ammonium sulphate (brown)]

T (°C)	dW (%)	Product phase(s) (XRD)	FTIR (EGA)	Progressive reaction(s)
300	25	$(NH_4)_2Mg(SO_4)_2.6H_2O$ [*Boussingaltite*: #35-0771]	NH_3, H_2O	A: $2(NH_4)_2SO_4 + MgO \rightarrow (NH_4)_2Mg(SO_4)_2 + 2NH_3 + H_2O$
350	30	$(NH_4)_2Mg(SO_4)_2.6H_2O$ & $(NH_4)_2Mg_2(SO_4)_3$ [*Efremovite* #42-1432]	NH_3, H_2O	B: $(NH_4)_2Mg(SO_4)_2 + (NH_4)_2SO_4 + MgO \rightarrow (NH_4)_2Mg_2(SO_4)_3 + 2NH_3 + H_2O$
400	40	$(NH_4)_2Mg_2(SO_4)_3$ & $MgSO_4.7H_2O$ [*Epsomite* #1-072-0696]	NH_3, H_2O	C: $(NH_4)_2Mg_2(SO_4)_3 + MgO \rightarrow 3MgSO_4 + 2NH_3 + H_2O$
----	----	----------------	----------	$3(NH_4)_2SO_4 + 3MgO \rightarrow 3MgSO_4 + 6NH_3 + 3H_2O$
450 500	>55 >55	$MgSO_4.nH_2O$ (n =5-6)	NH_3, H_2O SO_2, N_2O	A+B+C: D: $2NH_3SO_3 \rightarrow 2SO_2 + 2NH_2OH$ E: $2NH_2OH \rightarrow N_2O$ (+ $H_2O + 2H_2$?)

Fig. S6 Formation and interconversion of ammonium/magnesium (Tutton salt) intermediates leading to hydrated $MgSO_4$ from Lizardite/ammonium sulphate at increasing temperature [reaction scheme based on MgO for simplicity].