Supplementary Information

for

Solid-State NMR Study of Various Mono- and Divalent Cation Forms of the Natural Zeolite Natrolite

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Figure Captions

Fig. S1 Powder XRD patterns of the hydrated form of various mono- and divalent cation-exchanged natrolite zeolites.

Fig. S2 TGA/DTA traces of the hydrated form of mono- and divalent cation-exchanged natrolite zeolites.

Fig. S3 Powder XRD patterns of the hydrated form of different mono- and divalent cation-exchanged natrolites measured during in situ heating under vacuum to a residual pressure of 5×10^{-3} Torr. The top traces denoted as RT(air) are the patterns measured at room temperature after temperature-programmed XRD experiments up to 800 °C followed by exposure to ambient air for 0.5 h. The asterisk denotes X-ray peaks from the Pt sample holder.

Fig. S4 Experimentally observed ^{29}Si MAS NMR chemical shifts of the dehydrated form of monovalent cation-exchanged NAT materials vs the shifts calculated using eq. 1 (see text). Si_2(3Al) and Si_1(2Al) species are designated by ■ and ●, respectively.

Fig. S5 ^{27}Al MQMAS NMR spectra of the hydrated form of various mono- and divalent cation-exchanged natrolite zeolites.

Fig. S6 Decomposition of the ^{27}Al MAS NMR spectra of dehydrated Na-NAT (left) and K-NAT (right) obtained at 300 (bottom) and 400 MHz (top) MAS NMR spectrometers.

Fig. S7 ^{27}Al MQMAS NMR spectra of the hydrated form of divalent cation-exchanged natrolites.

Fig. S8 Powder XRD patterns of hydrated Ca-NAT (left) and scolecite (right) before (bottom) and after (top) stirring twice in 2.0 KNO_3 solutions (1.0 g solid/100 mL solutions) at 80 °C for 6 h. The arrow denotes the most intense X-ray peak corresponding to the (220) reflection of hydrated K-NAT.

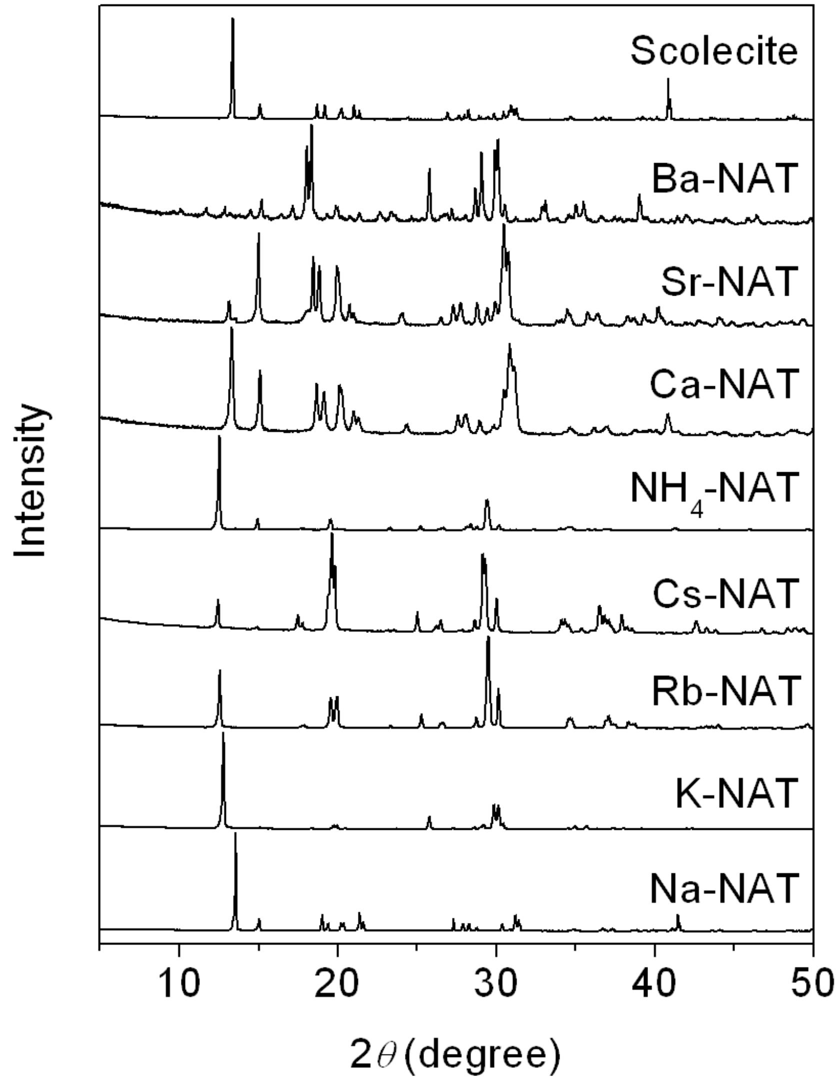

Scolecite
Ba-NAT
Sr-NAT
Ca-NAT
NH4-NAT
Cs-NAT
Rb-NAT
K-NAT
Na-NAT
Intensity
10
20
30
40
50
2θ (degree)

Fig. S1

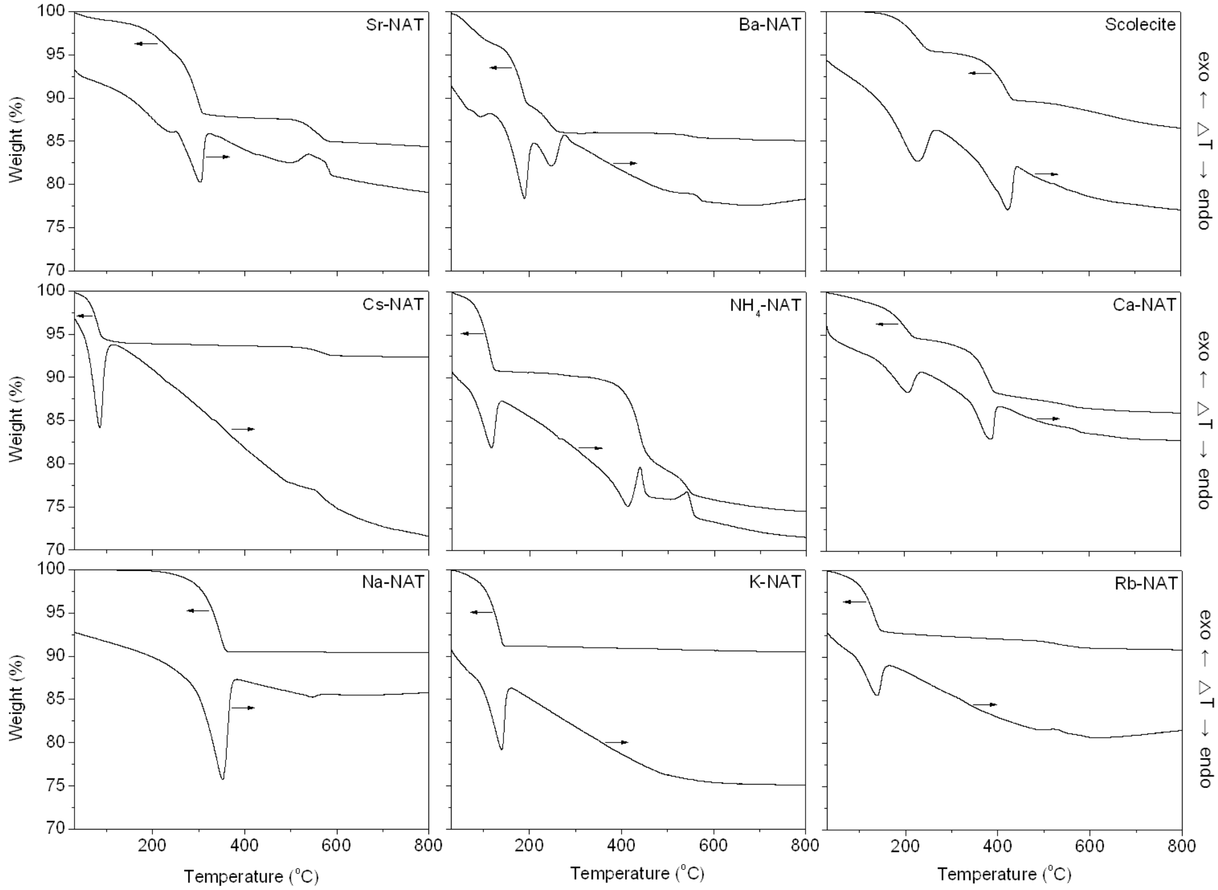

Sr-NAT
Ba-NAT
Scolecite
Cs-NAT
NH4-NAT
Ca-NAT
Na-NAT
K-NAT
Rb-NAT
Weight (%)
Temperature (°C)
exo ← ΔT → endo
100
95
90
85
80
75
70
200
400
600
800

Fig. S2

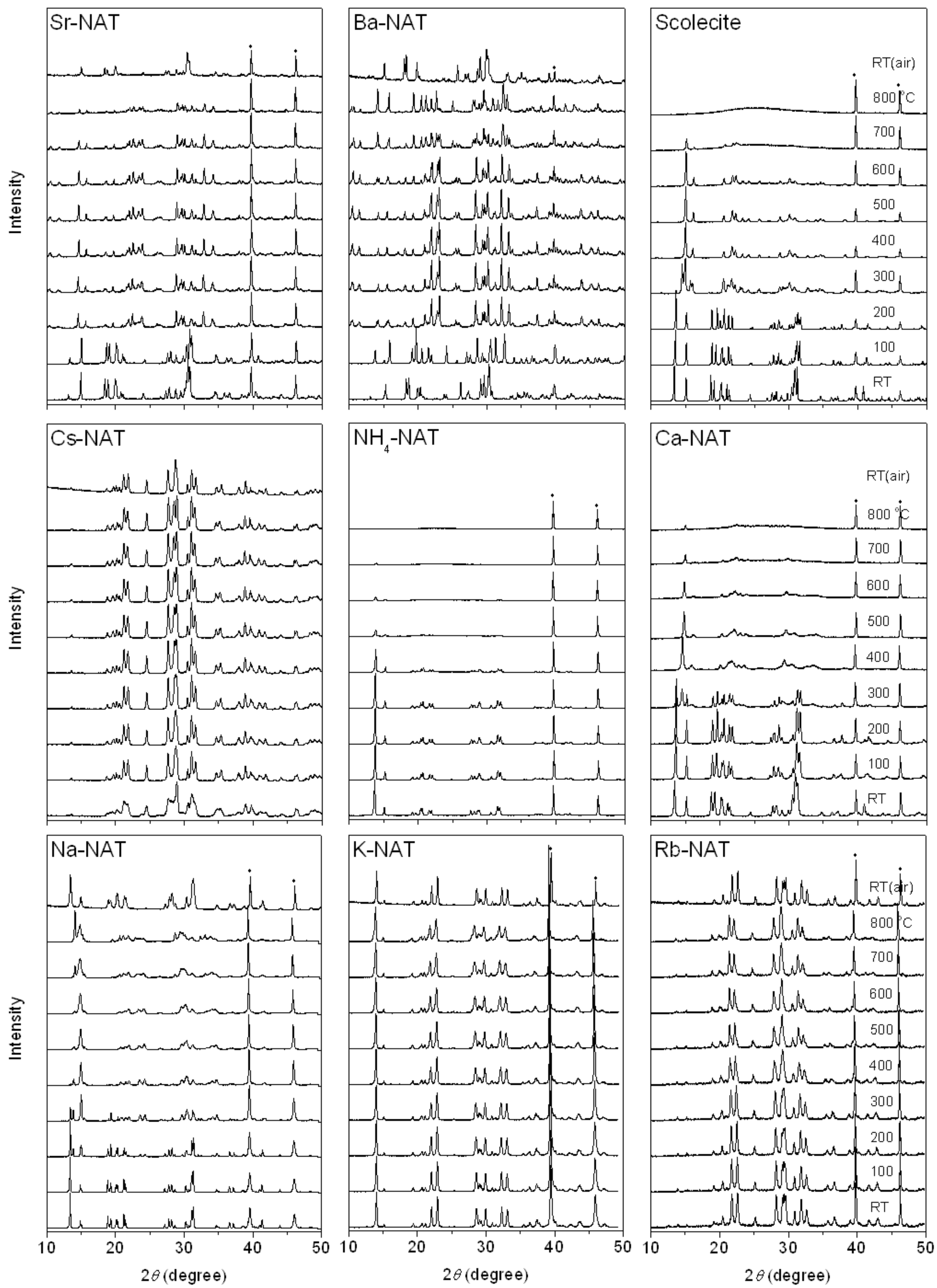

Sr-NAT
Ba-NAT
Scolecite
RT(air)
800 °C
700
600
500
400
300
200
100
RT
Cs-NAT
NH4-NAT
Ca-NAT
Na-NAT
K-NAT
Rb-NAT
Intensity
10
20
30
40
50
2θ (degree)

Fig. S3

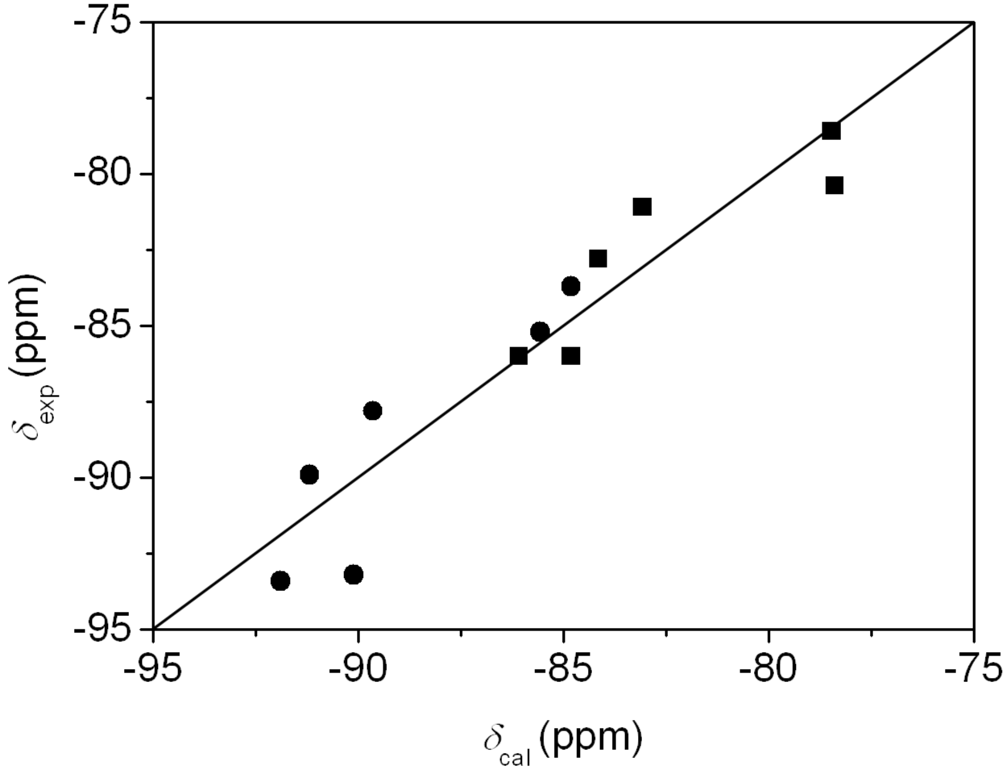


Fig. S4

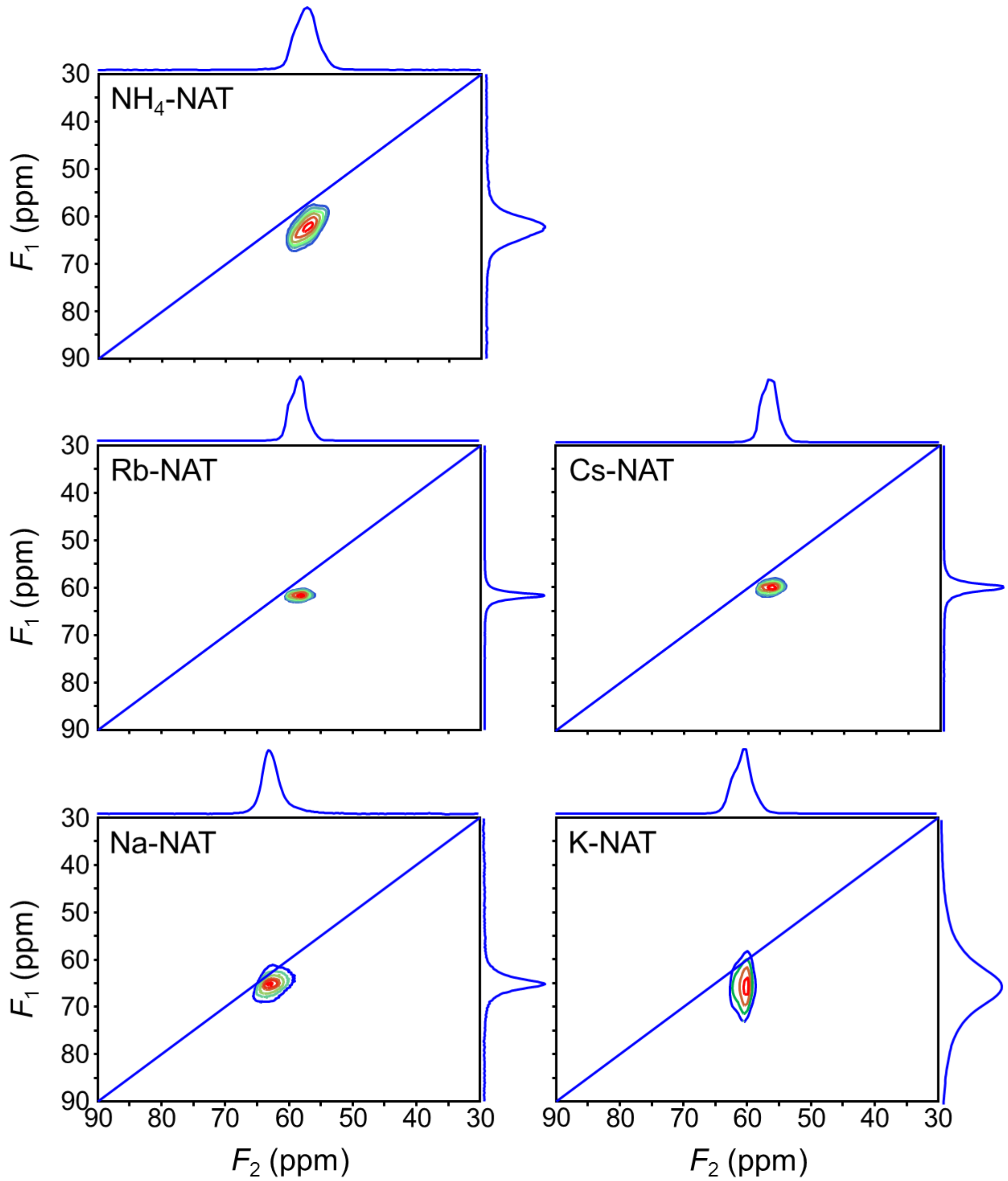
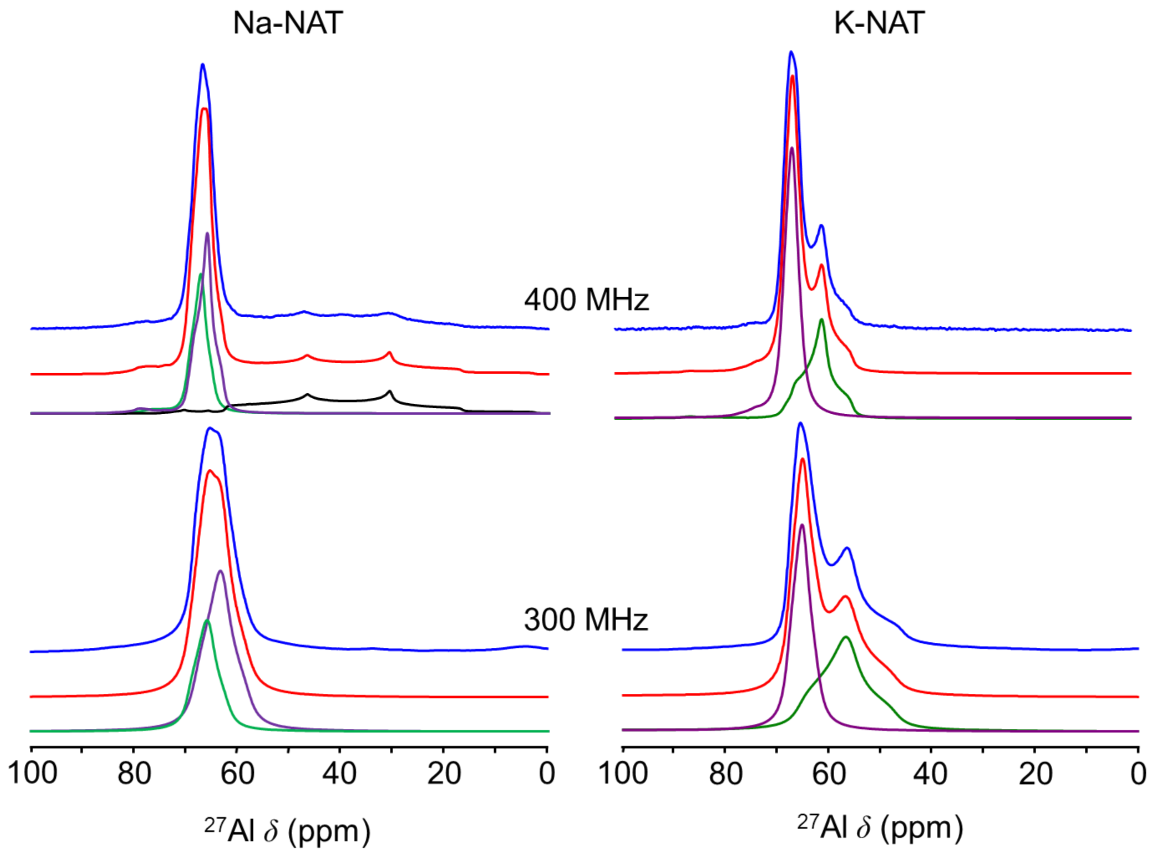


Fig. S5



Material	Structural unit	δ_{CS}, ppm (300 / 400 MHz)	C_Q, MHz	η
Na-NAT	$Al_1(4Si)$	68.4 / 68.9	2.0	0.9
	$Al_2(4Si)$	- / 65.1	6.7	0.4
	$Al_3(4Si)$	69.3 / 69.4	1.8	0.9
K-NAT	$Al_1(4Si)$	67.5 / 67.4	1.6	0.8
	$Al_2(4Si)$	65.7 / 65.3	2.8	1.0

Fig. S6

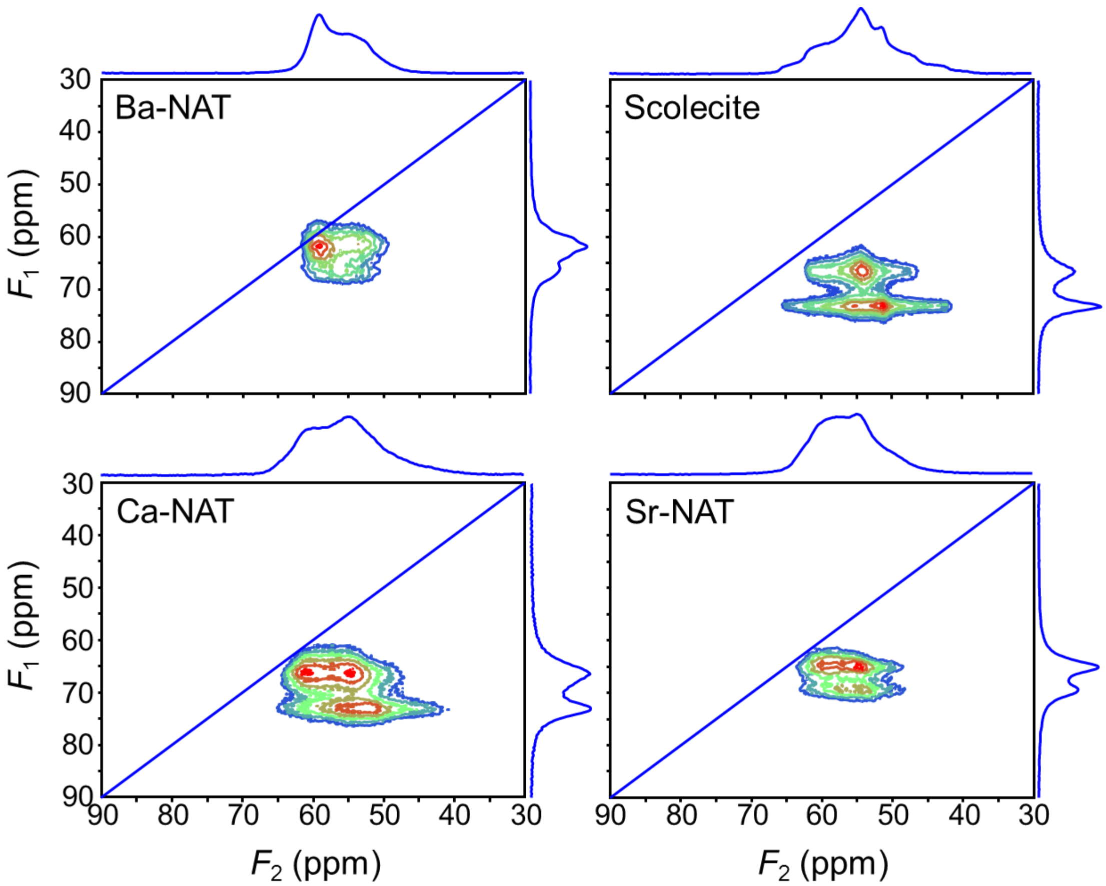


Fig. S7

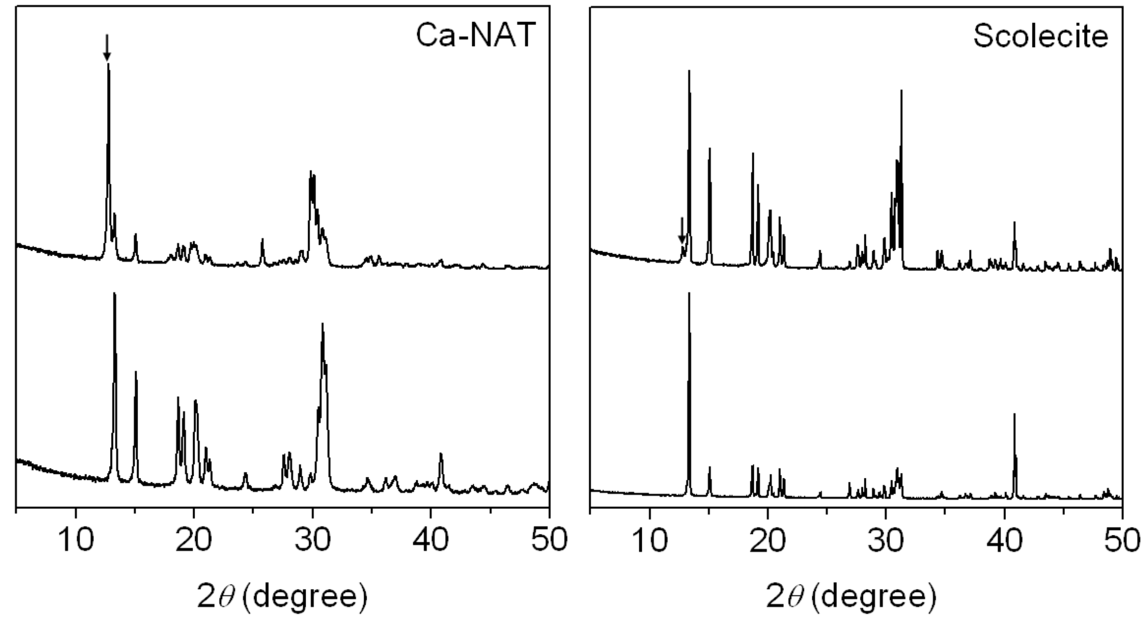


Fig. S8