UNIMORE
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA
Dipartimento di scienze Chimiche e Geologiche

Centro Interdipartimentale Grandi Strumenti
CINQUANTA

Alcune applicazioni dell'NMR in stato solido

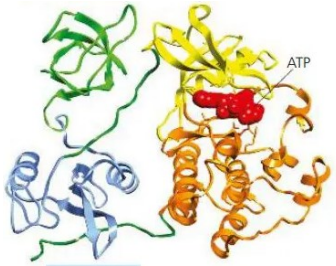
Adele Mucci

Cinquantennale CIGS - Modena, 8 novembre 2024

NMR in stato solido

Struttura e dinamica di solidi

- catalizzatori
- vetri
- minerali
- polimeri
- proteine



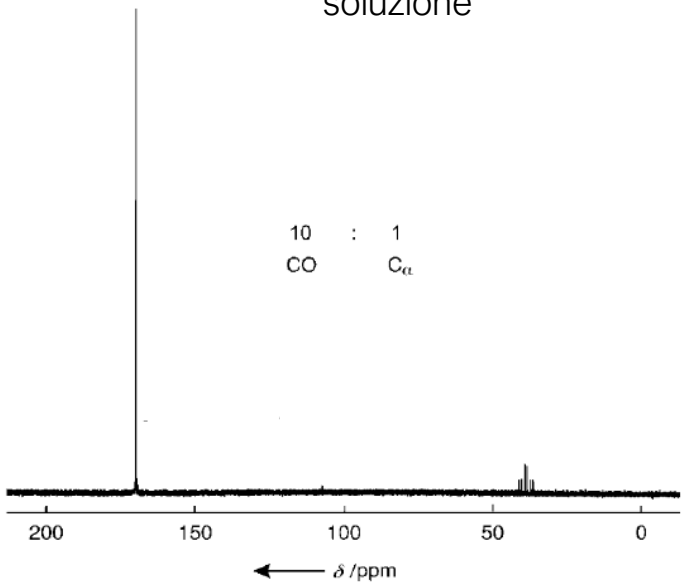
Spettri ^{13}C non disaccoppiato della glicina marcata ^{13}C al C-1

Angew. Chem. Int. Ed. **2002**, *41*, 3096 – 3129

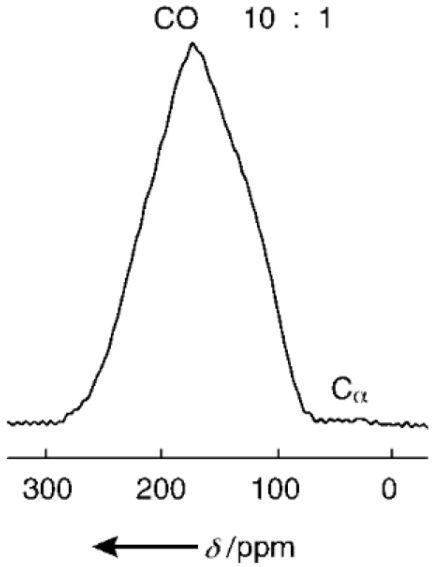
Solid-State NMR Spectroscopic Methods in Chemistry

David D. Laws, Hans-Marcus L. Bitter, and Alexej Jerschow*

soluzione



solido in polvere cristallina

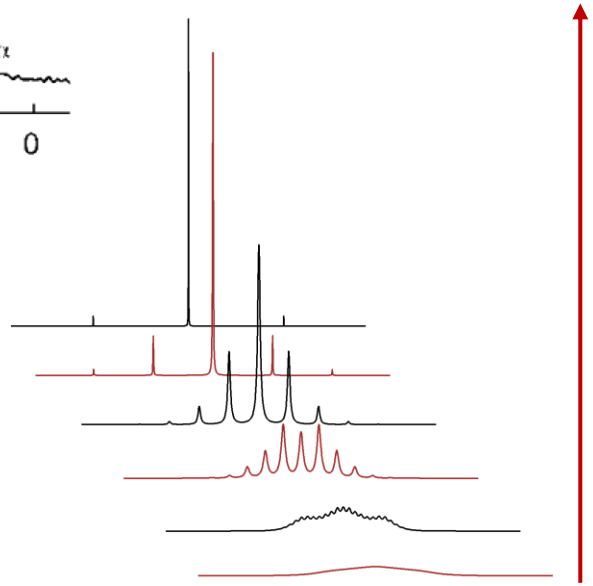


moto molecolare ridotto

Interazione dipolari tra spin (eteronucleari e omonucleari)

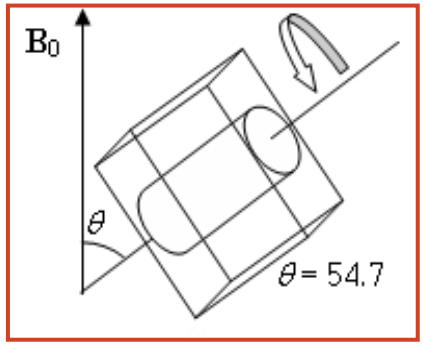
Anisotropia di chemical shift

Interazione quadrupolare (spin >1/2)



rotazione all'angolo magico

Rotore Φ_{out} 2.5 mm x ca. 1 cm

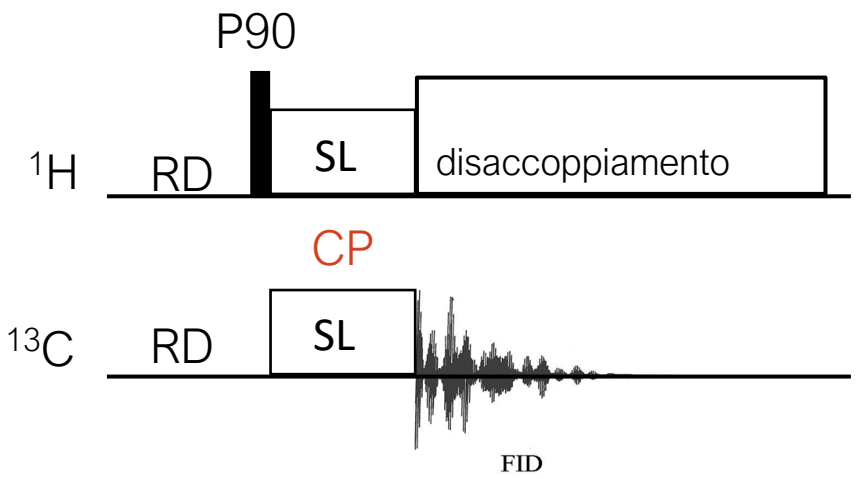


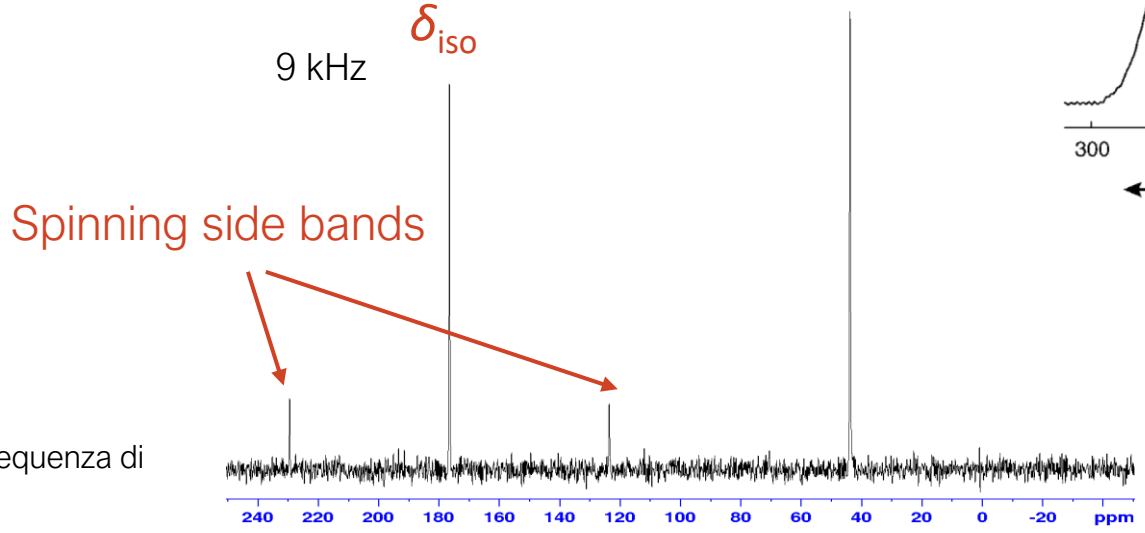
Azzera i termini ($3 \cos^2\theta - 1$)
se la velocità di rotazione è abbastanza elevata

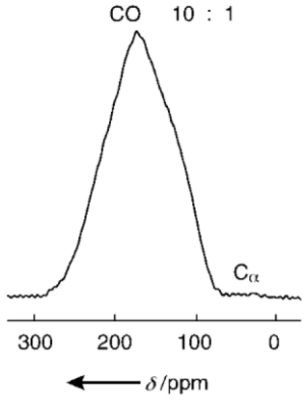
UNIMORE
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA
Dipartimento di scienze Chimiche e Geologiche

Centro Interdipartimentale Grandi Strumenti
CINQUANTA

Condizioni standard per ^{13}C NMR: cross polarizzazione = CP







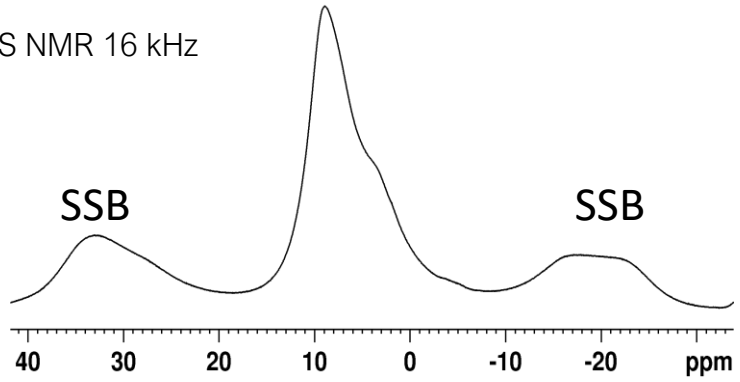
Spettro ^{13}C in alta risoluzione
(glicina non arricchita)

^1H e ^{13}C o X irradiati durante il tempo di contatto imponendo la stessa frequenza di nutazione (stesso P90)

In qualche ms si ha il trasferimento di polarizzazione da ^1H vicino a ^{13}C o X e aumento S/N.

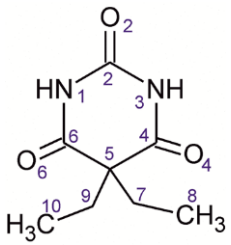
RD dipende da T_1 ^1H

^1H MAS NMR 16 kHz



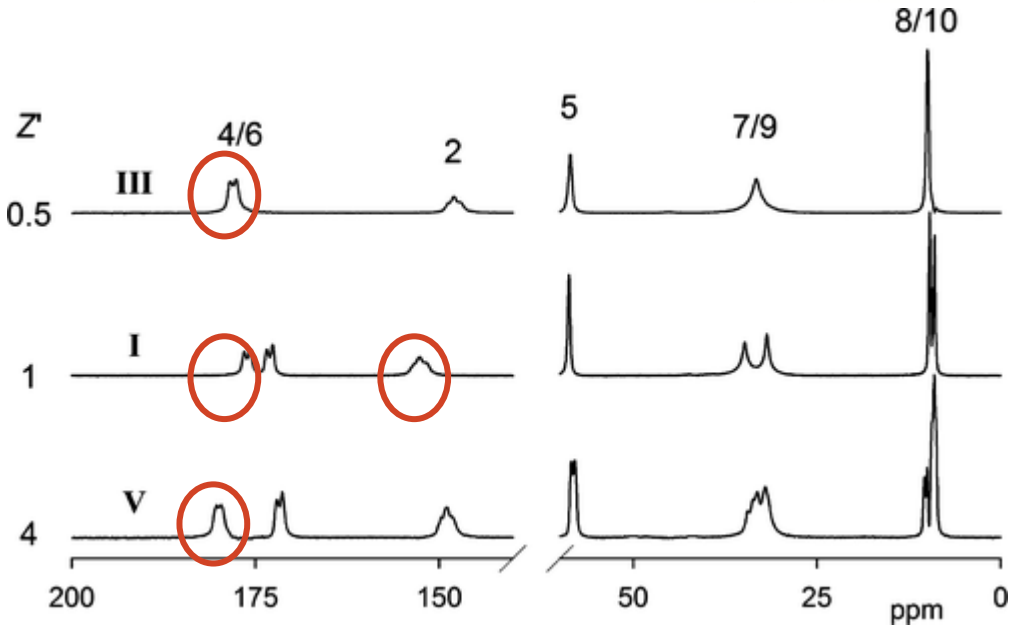
Campo farmaceutico

Distinzione fra polimorfi o solvati



Esempio: 3 dei 6 polimorfi del Barbital

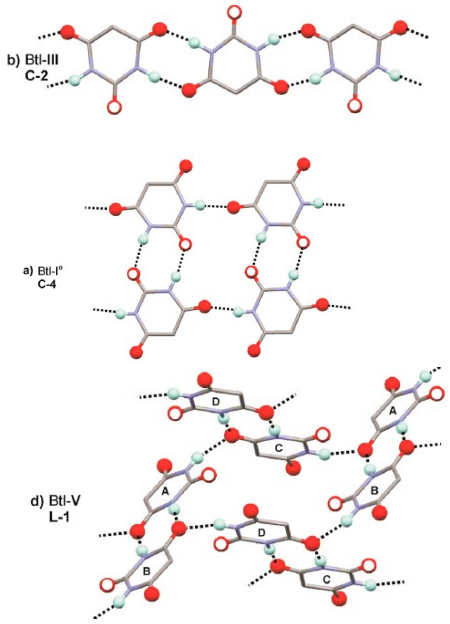
N. Zencirci et al. Mol. Pharmaceutics 2014, 11, 1, 338–350



unità asimmetrica: mezza molecola, con piano di simmetria

unità asimmetrica: una molecola, senza piano di simmetria

unità asimmetrica: quattro molecole



il legame a idrogeno sposta i segnali dei C=O a sx

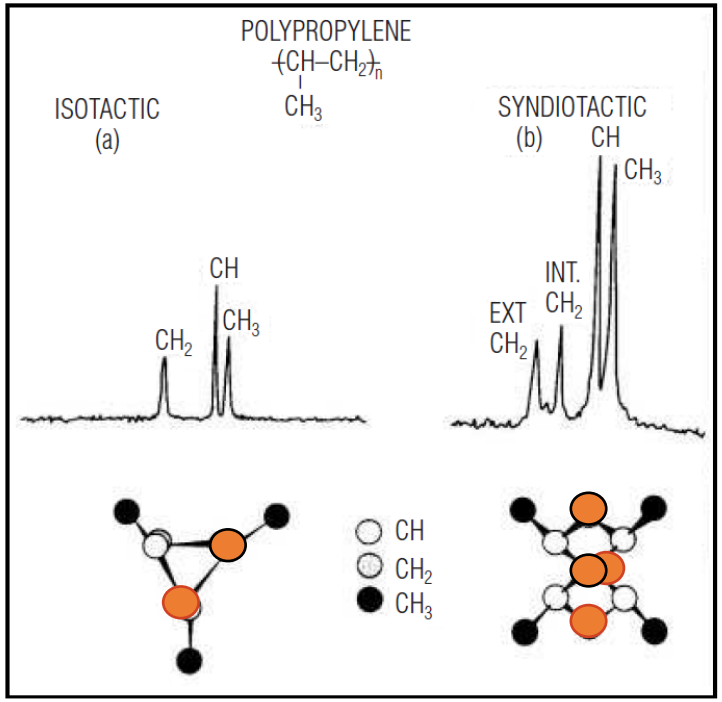
Studi di miscele (preparazioni)

Polimeri

Studio della tatticità in polimeri insolubili: ^{13}C CP NMR{^{1}H}

Conseguenza della diversa cfm:
gtgtgt per i-PP e ttggttgg per s-PP

A.E. Tonelli, Ann. Rep. NMR Spectr., 1997, 34, 185

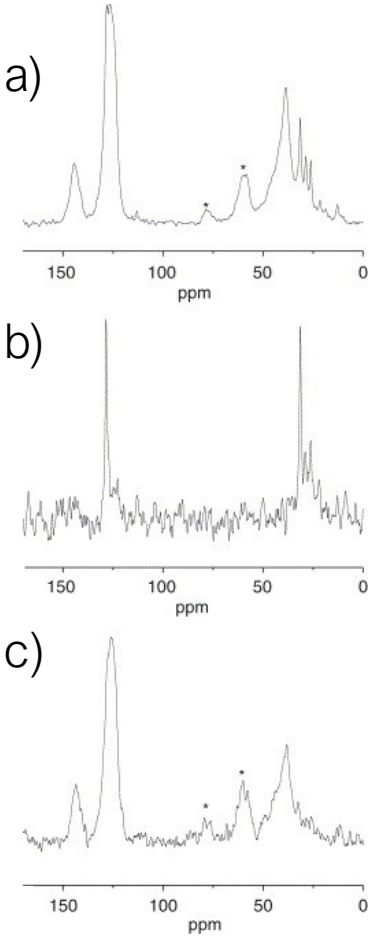


CH_2 sopra

CH_2 sotto

Differenze spettrali per i diversi impaccamenti

Polimeri cristallini: righe ^{13}C strette
Polimeri in fase vetrosa: righe ^{13}C larghe, distribuzione di δ
Polimeri gommosi: righe ^{13}C strette, media dei δ



Polimero a blocchi SBS

Differenze spettrali per le diverse fasi

a) spettro ^{13}C CP complessivo

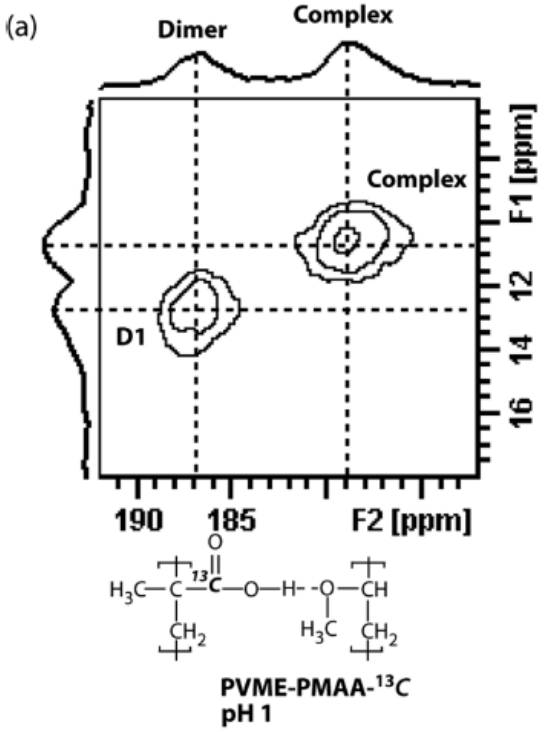
b) blocco butadienico, mobile (r.t. spin-lock 30 ms)

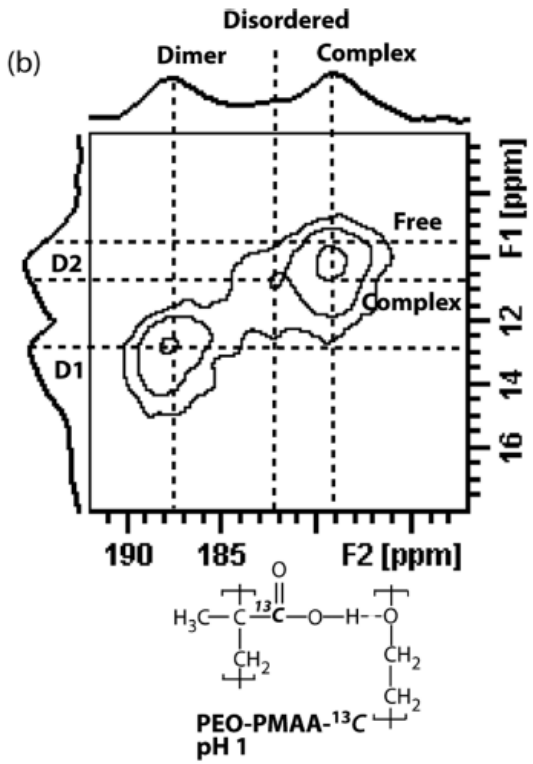
c) blocco stirenico, rigido (233 K, spin-lock 12 ms)

Ferrini et al. Solid State NMR 2005, 27, 215

Studi di dinamica molecolare (T_1 e $T_{1\rho}$)

Interazioni inter-catena in miscele di polimeri





^{1}H - ^{13}C HETCOR

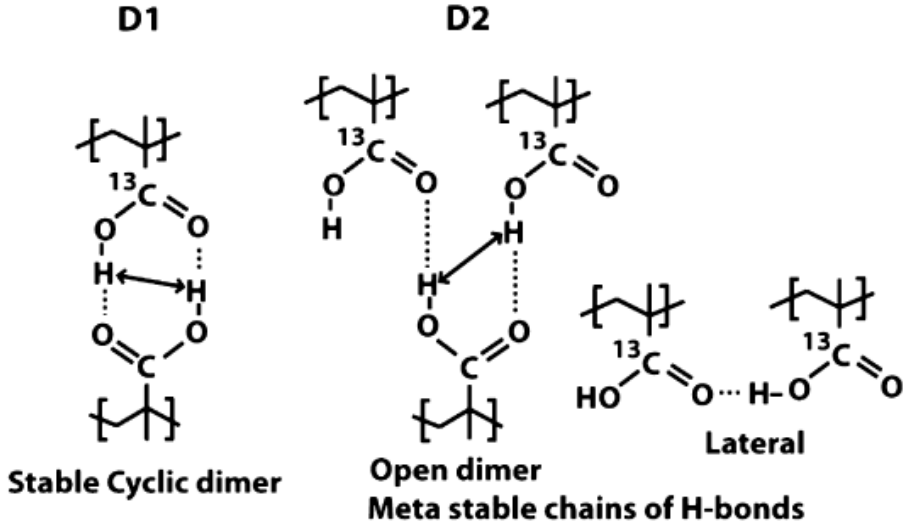
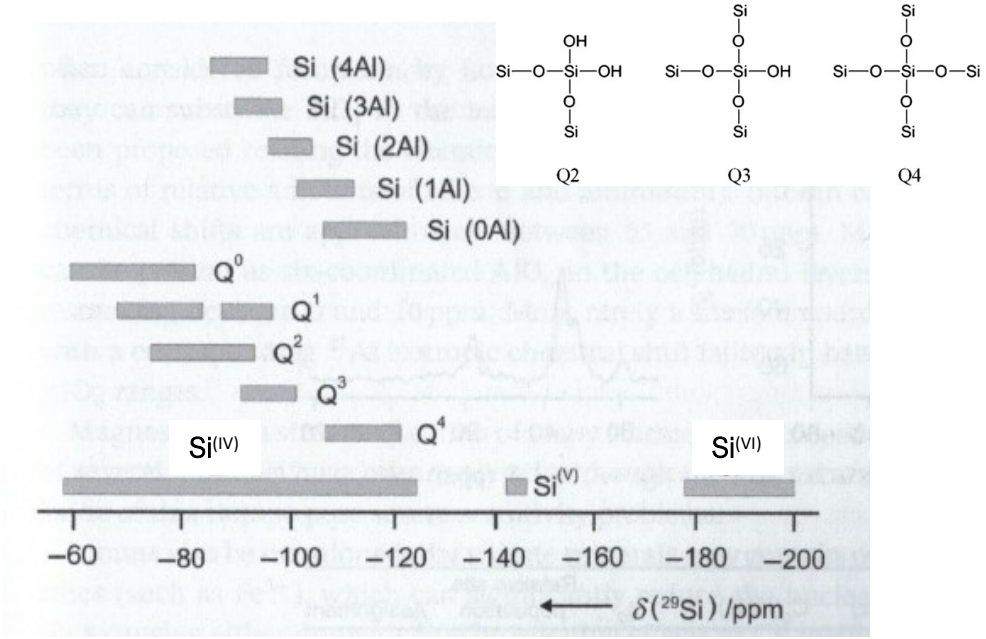


Figure 3. Possible hydrogen bonded structures within PMAA.[26–28]

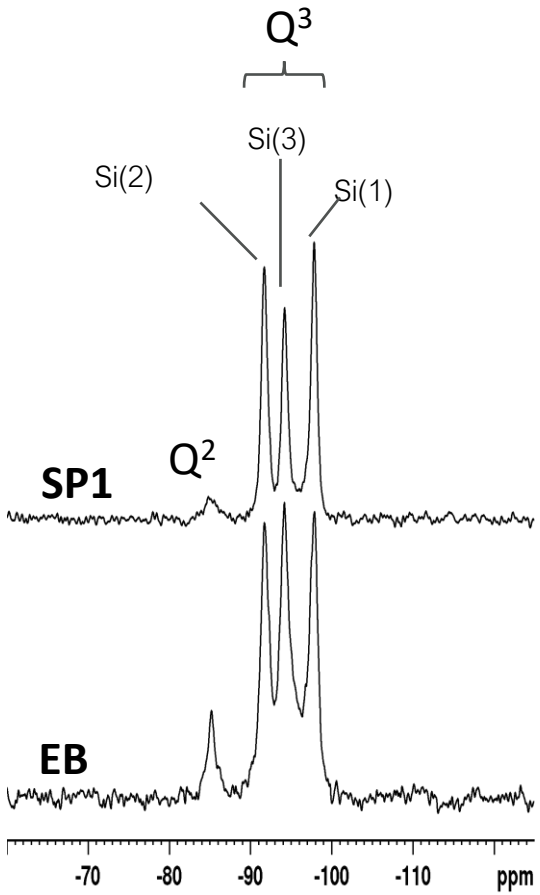
Fortier-McGill et al. Macromolecules 2012, 45, 6015−6026

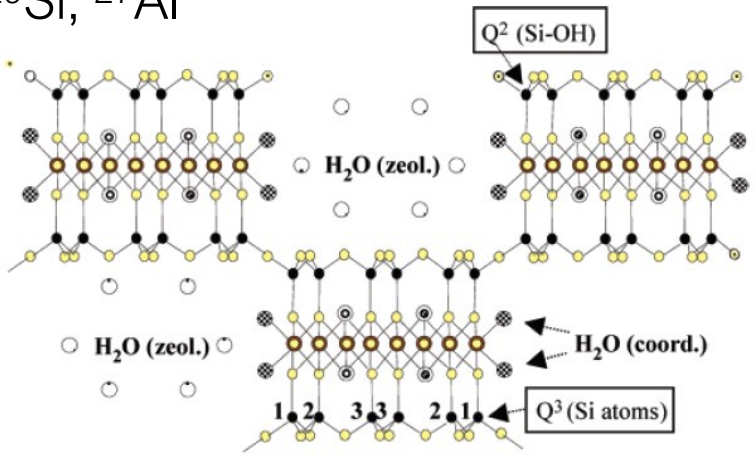
Minerali e vetri: silico alluminati e silicati → ^{29}Si, ^{27}Al



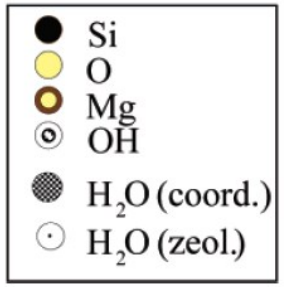
Sepiolite

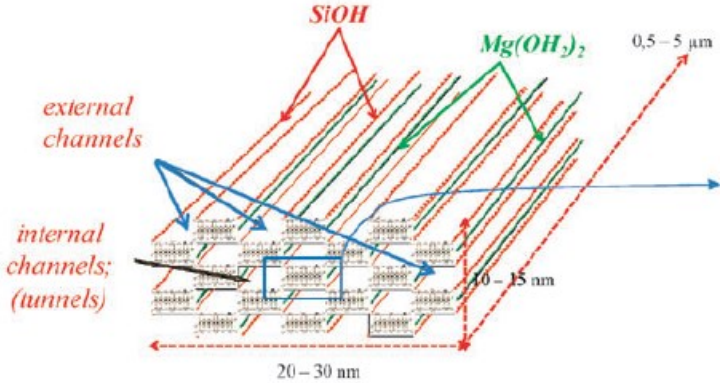
CP-MAS ^{29}Si NMR





Facey et al. J. Phys. Chem. B 2005, 109, 22359



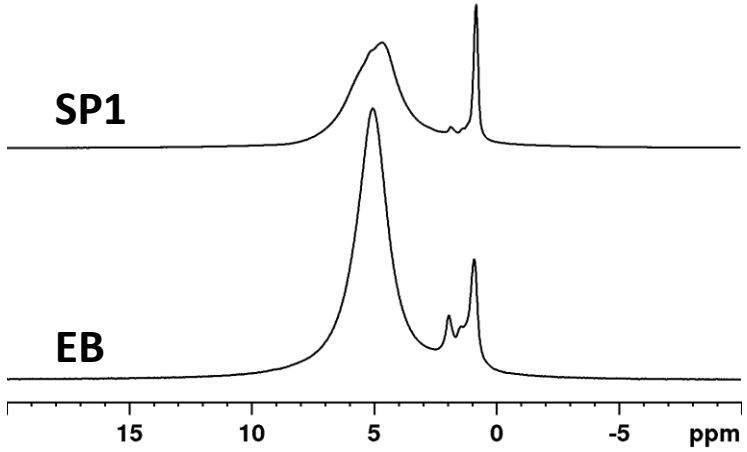


Castellini et al, Microporous Mesoporous Mater. 285 (2019) 150

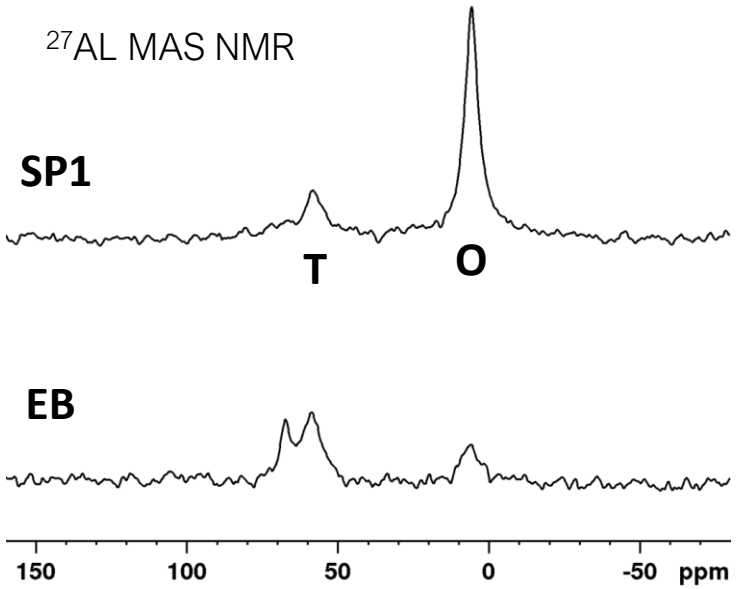
UNIMORE
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA
Dipartimento di scienze Chimiche e Geologiche

Centro Interdipartimentale Grandi Strumenti
CINQUANTA

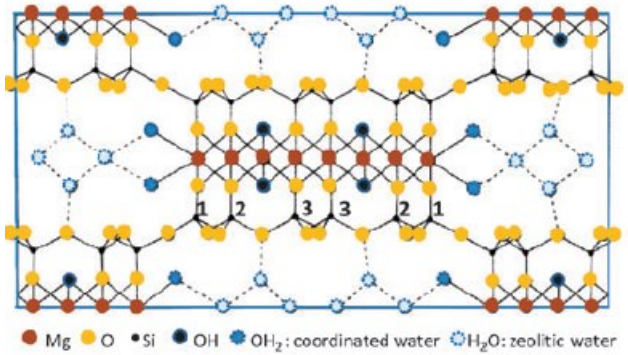
^{1}H MAS NMR 33 kHz

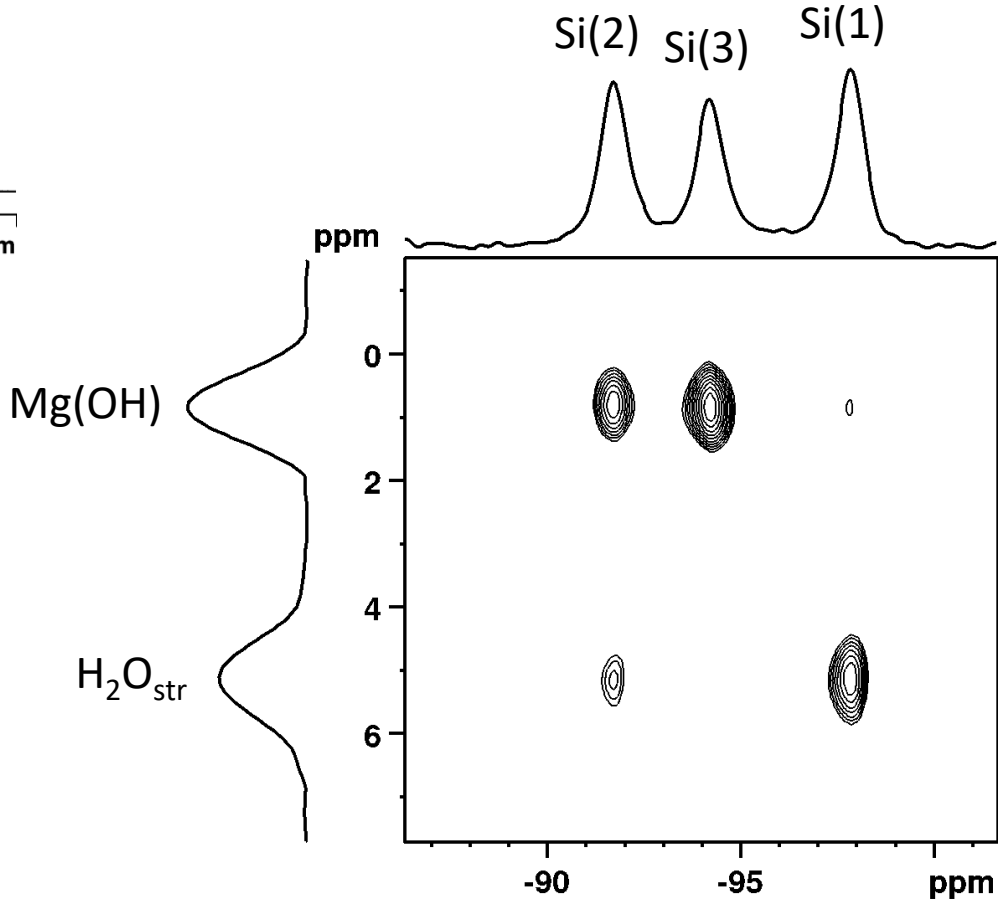


^{27}AL MAS NMR



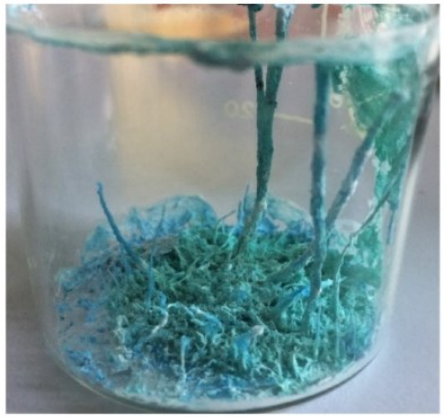
Raya et al. Phys. Chem. Chem. Phys., 2010, 12, 14508





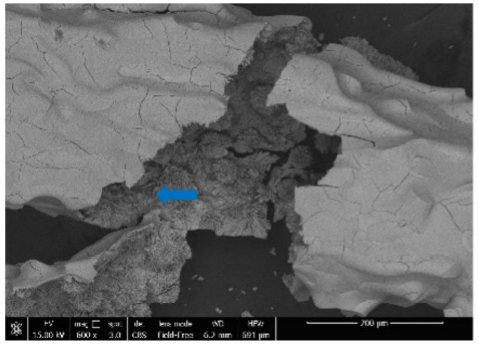
UNIMORE
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA
Dipartimento di scienze Chimiche e Geologiche

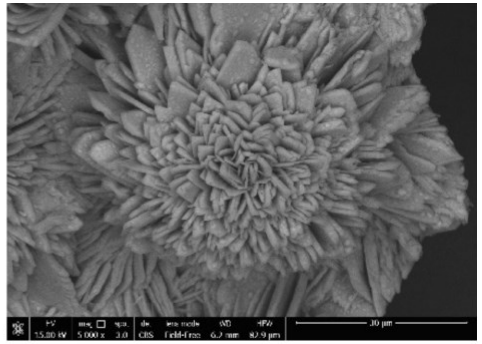
Centro Interdipartimentale Grandi Strumenti
CINQUANTA



Chemical garden

$Na_2Si_2O_5 + CuSO_4$

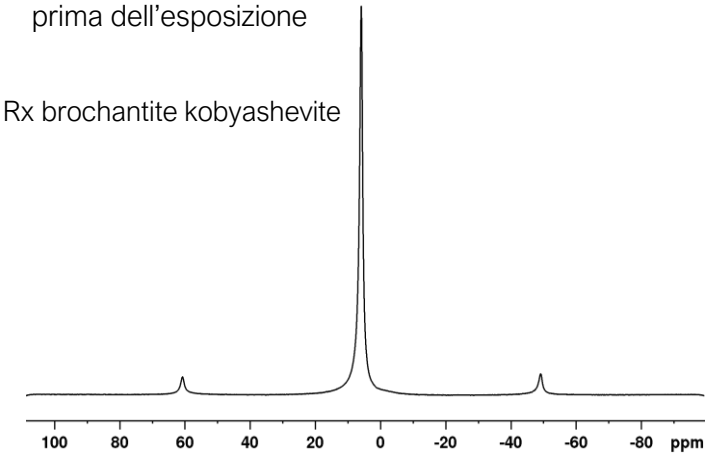




Castellini et al. ChemSystemsChem 2022, 4, e202100034

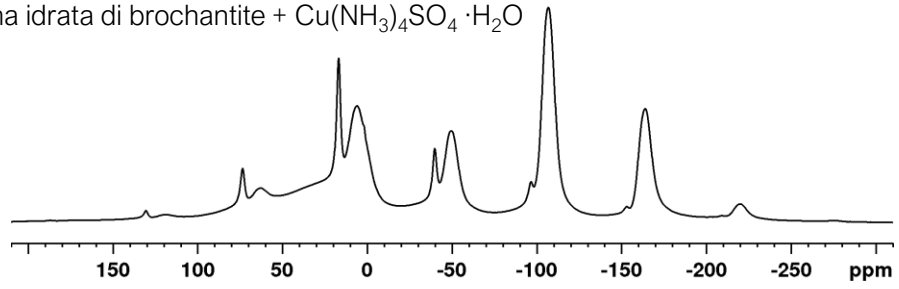
^{1}H MAS NMR $CGCuSO_4$ 33 kHz
prima dell'esposizione

Rx brochantite kobyashevite

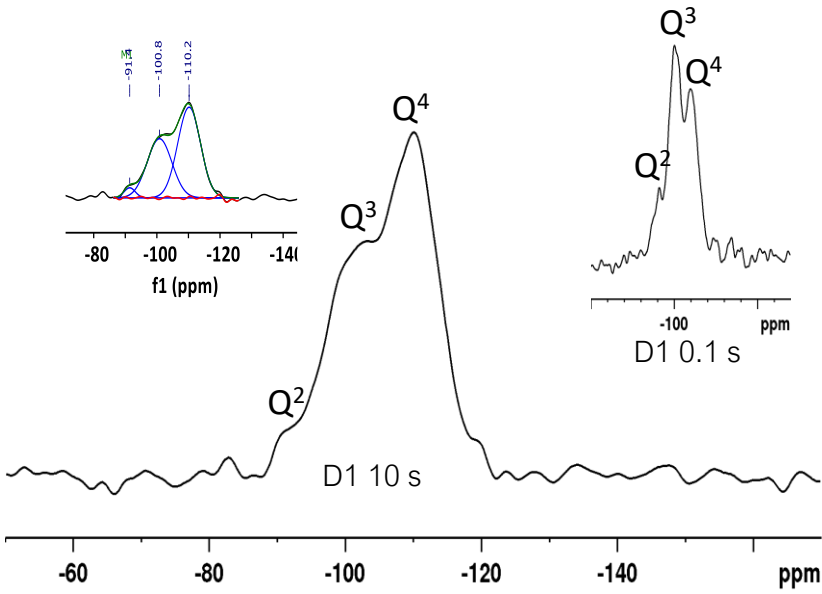


^{1}H MAS NMR $CGCuSO_4$ esposto a NH_3 33 kHz

Rx forma idrata di brochantite + $Cu(NH_3)_4SO_4 \cdot H_2O$



^{29}Si NMR MAS $CuSO_4$



UNIMORE
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA
Dipartimento di scienze Chimiche e Geologiche

Centro Interdipartimentale Grandi Strumenti
CINQUANTA

Solid-State NMR Spectroscopic Methods in Chemistry

David D. Laws, Hans-Marcus L. Bitter, and Alexej Jerschow*

Angew. Chem. Int. Ed. **2002**, *41*, 3096 – 3129