



Utiliser la capacité de mémoire en température et en pression du verre pour comprendre les événements géologiques : possibilités et limites

Dominique de Ligny

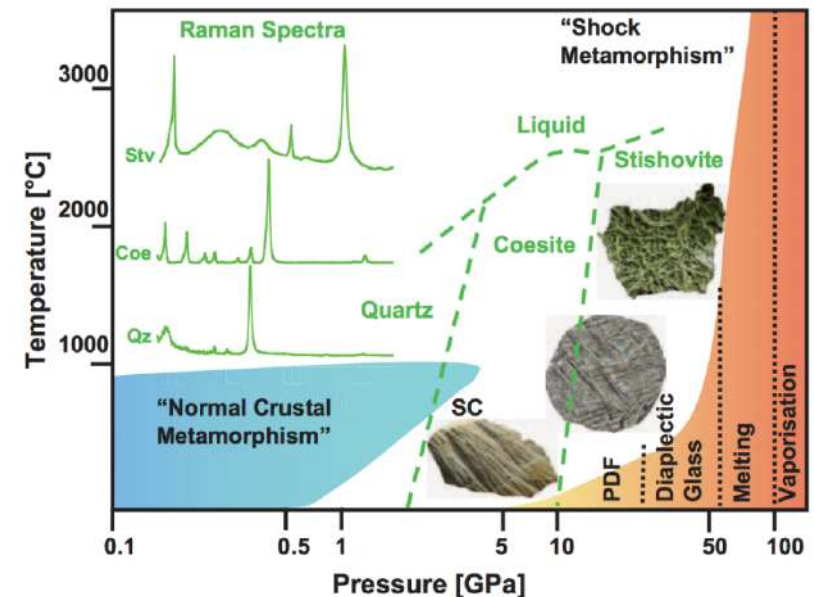
Universität Erlangen-Nürnberg, Lehrstuhl für Glas und Keramik, Erlangen, Germany

30. Mai 2022, Paris

Géologie



- Science historique
- Recherche d'indices pour comprendre les conditions Pression, Température, durée, temps
- Méthodes à l'équilibre
 - Champs de stabilité thermodynamique
 - Equilibre redox
- Méthodes cinétiques
 - Gradient de diffusion
 - Vitesse de croissance
- **Verres ont une mémoire spécifique**



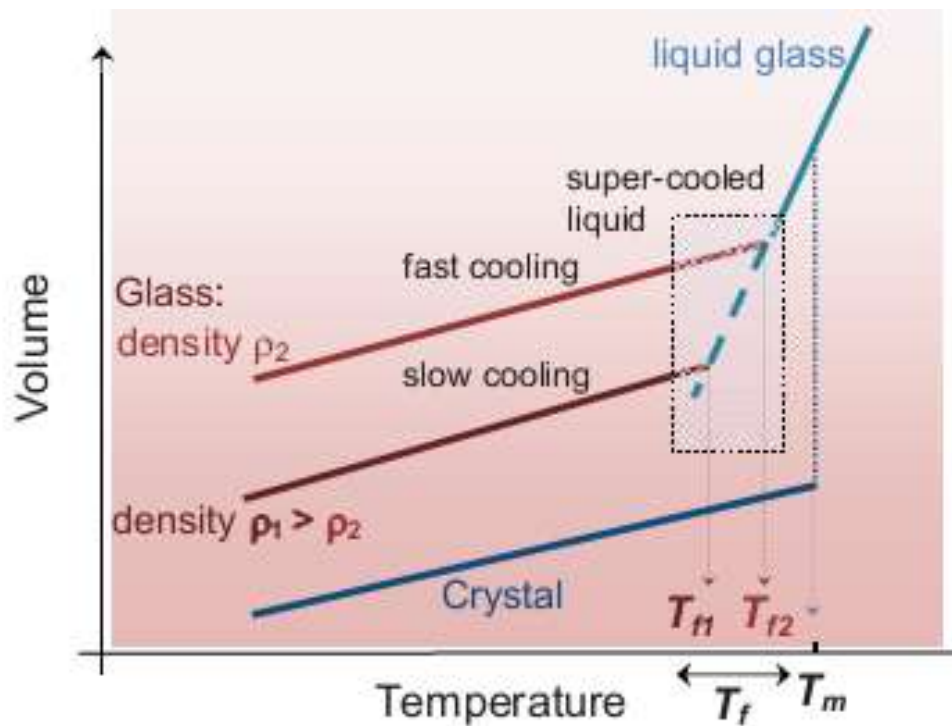
Cicconi & Newville 2019: Natural glasses. Springer Handbook of Glasses

Sommaire

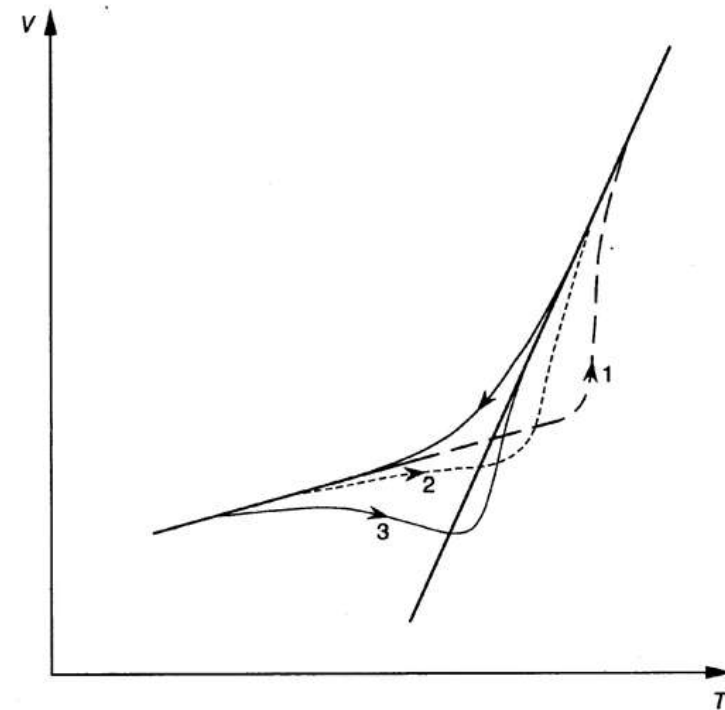
- D'où vient la mémoire du verre
- Comment peut on la lire
- Exemple venant de l'industrie
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 - Fulgurites
 - Obsidiennes



Effet de la température



Refroidissement à différentes vitesses

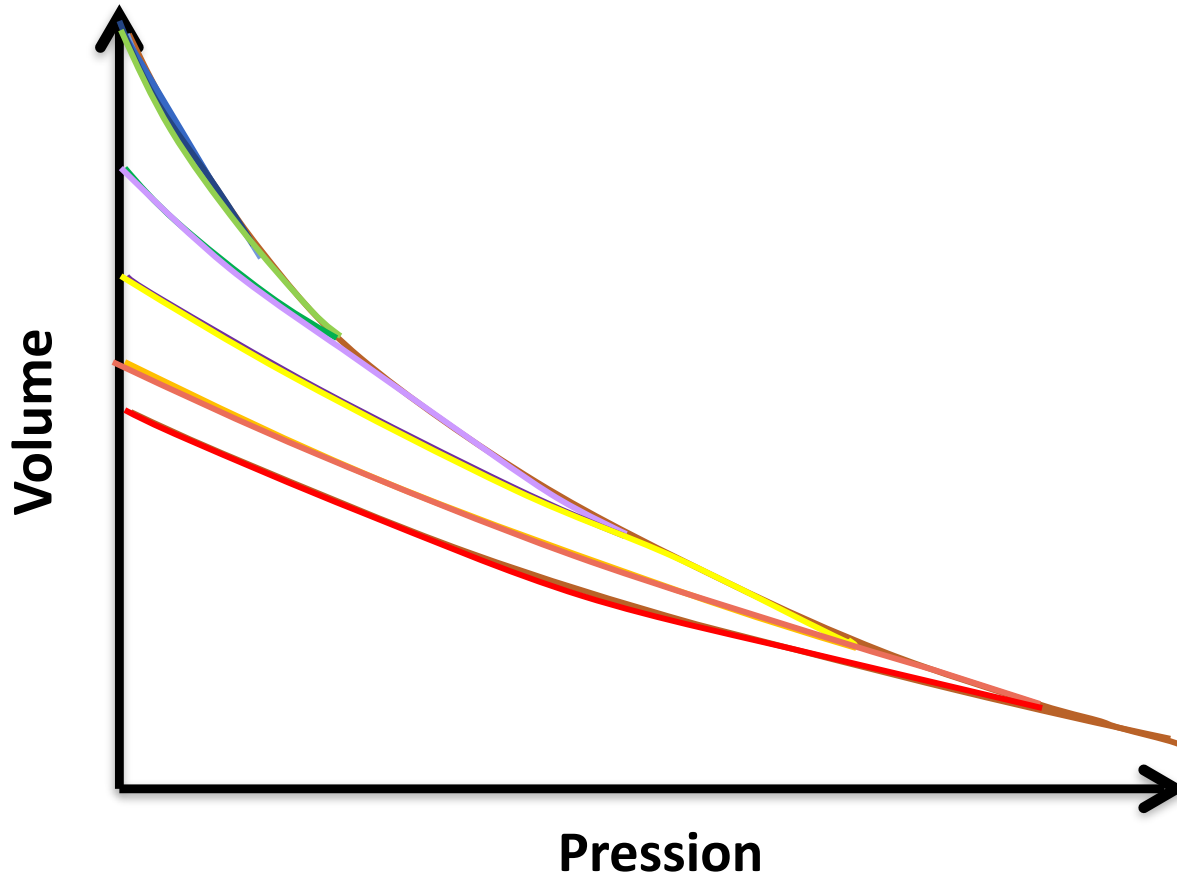


Chauffage à différentes vitesses

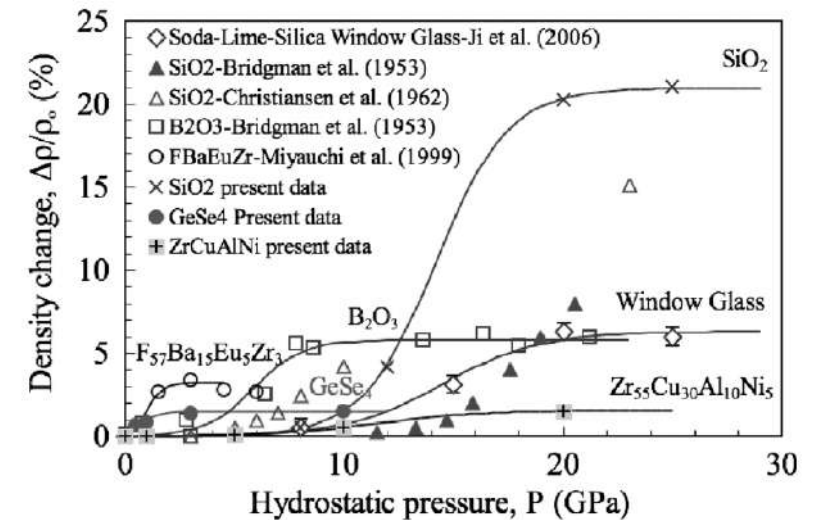
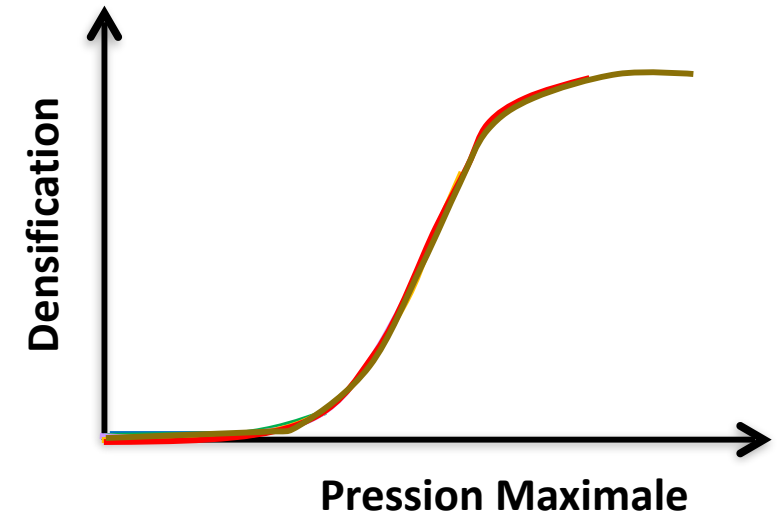
La vitesse de refroidissement dans la zone de transition vitreuse est enregistrée.

La température fictive représente la température de transition vitreuse pour une vitesse de refroidissement donnée.

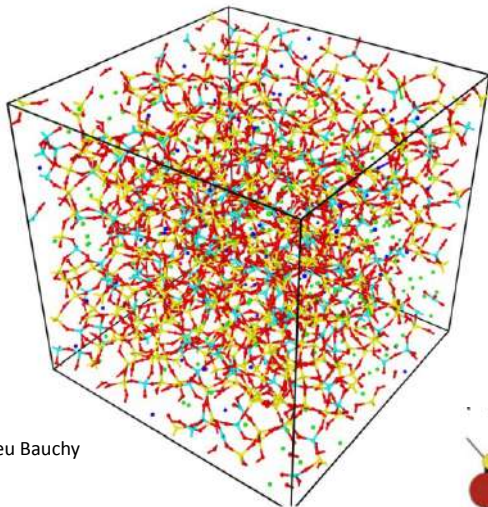
Effet de la pression



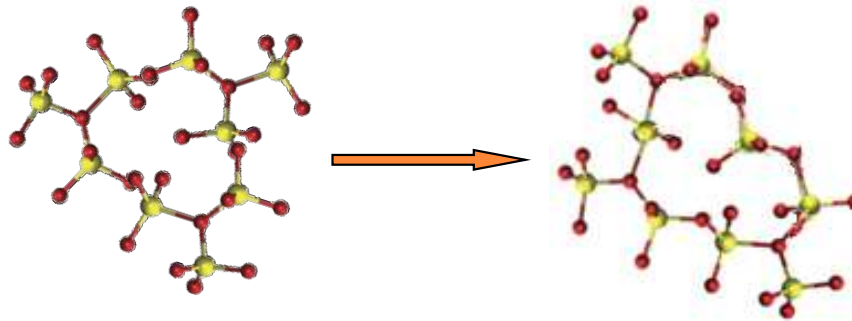
La pression maximale est enregistrée



Modifications atomiques liées aux changements de volume



Mathieu Bauchy

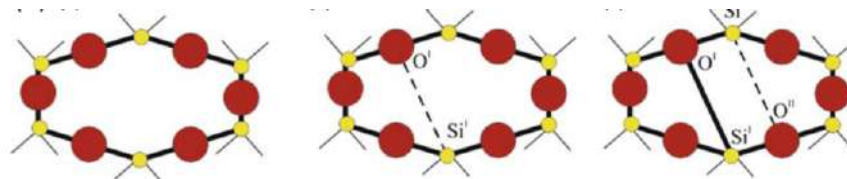


Changement d'angle entre tétraèdres

T_f P_{max}

Si-O-Si

+ -



Zeidler et al. 2014 PRL 113, 135501

Changement des tailles d'anneaux

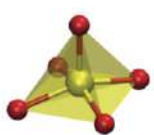
petit/gros

+/+ +/-

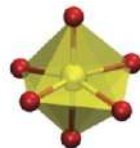
CN4



CN5



CN6



Modification de la coordination de l'oxygène des éléments formant le réseau Si, B, Al



Misawa et al. Science Advances 2017

provoque également une modification de l'angle et de la taille des anneaux.

CN

- +

Sommaire

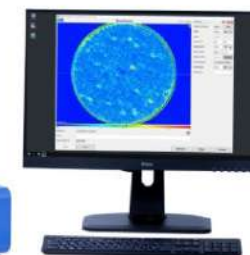
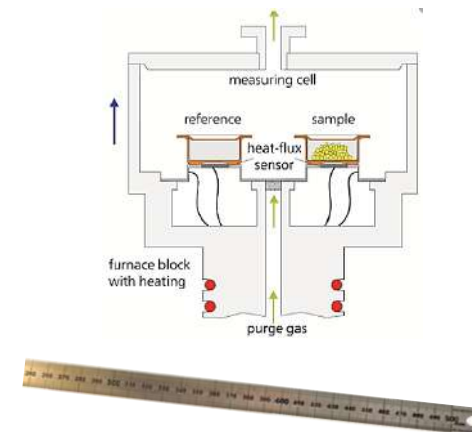
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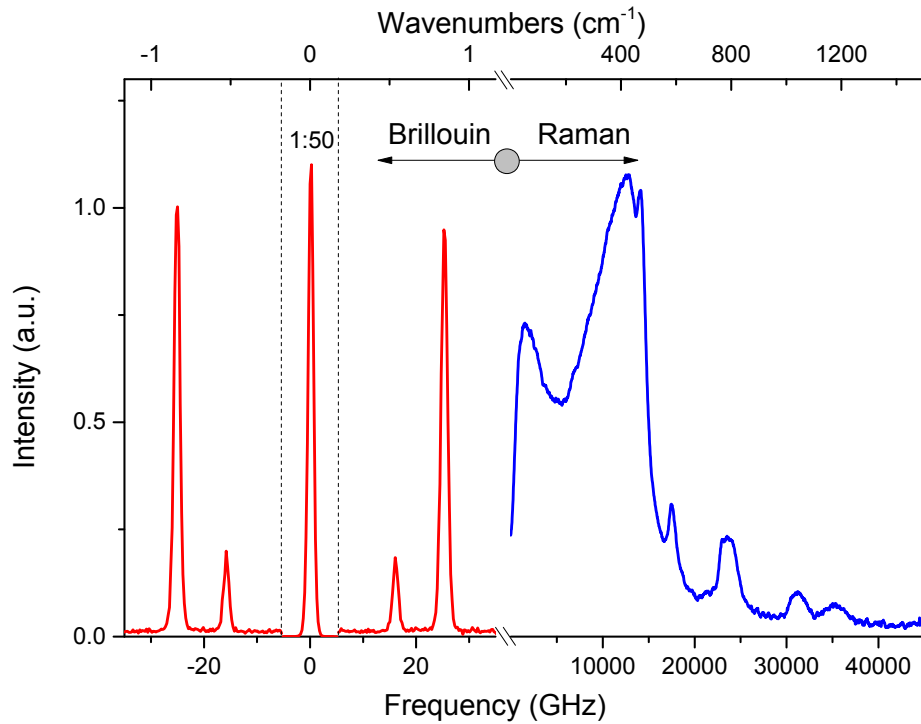
Lire la mémoire du verre

Différents instruments

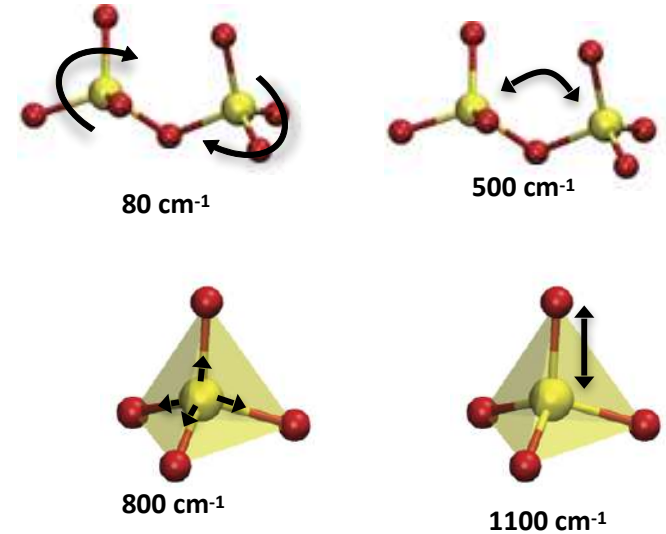
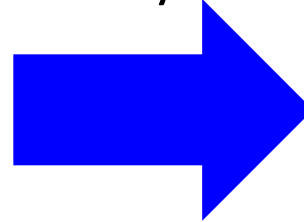
Method	Size observed	Form	Calibration
DSC Calorimétrie	mm	Poudre	pas
Volume	mm	Régulière	pas
Indice de réfraction	100 μm	Régulière	Coef. photoélastique
Densité	cm	Complexe	pas
Raman	1 μm	Complexe	Spécifique
Brillouin	1 μm	Complexe	Spécifique
Luminescence	1 μm	Complexe	Spécifique



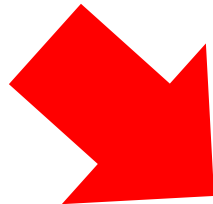
Spectroscopie vibrationnelle



Raman analysis



interpretation
du Brillouin



Vitesse du son

$$c = \frac{\lambda}{\sqrt{2}n} f^{90}$$

λ – longueur d'onde du laser
 n – indice de réfraction
 f^{90} – fréquence

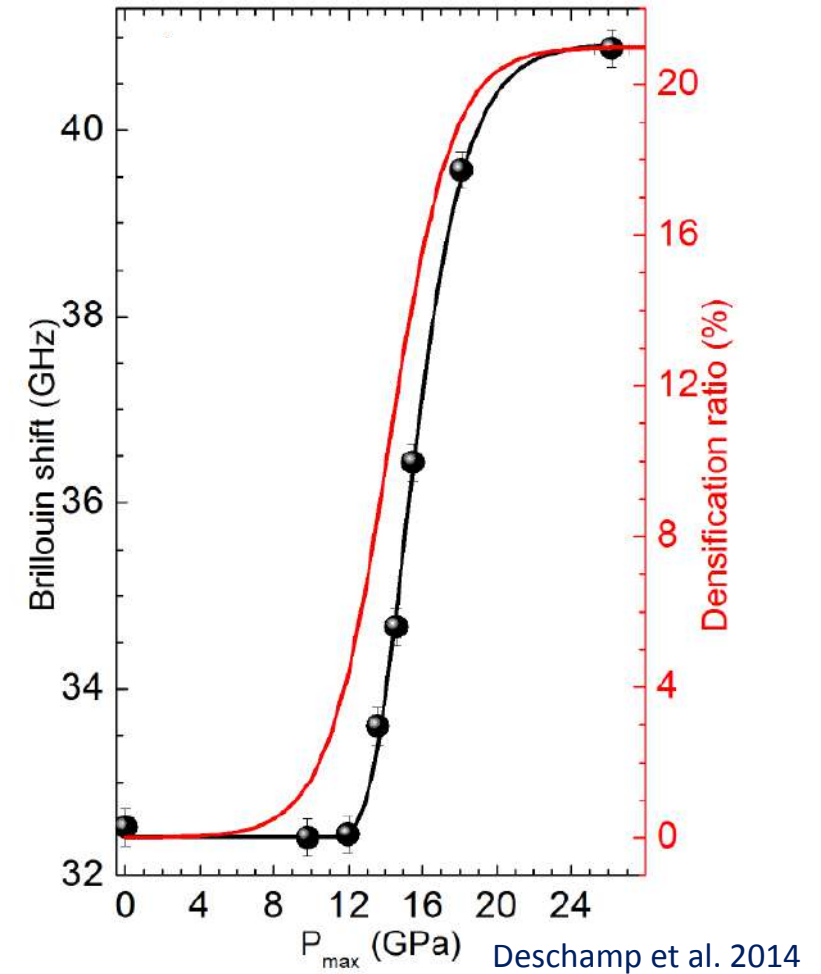
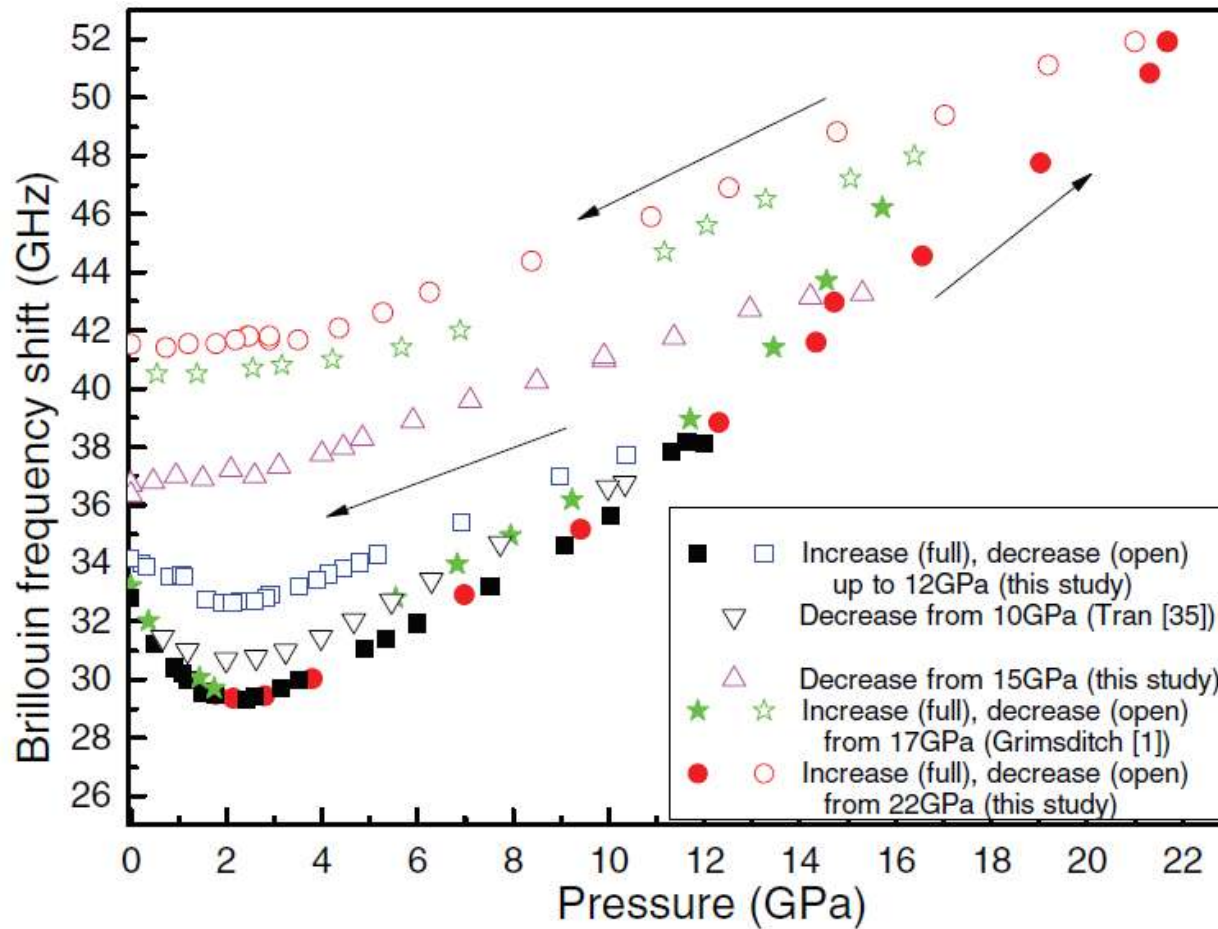
module de cisaillement

$$G = \rho c_t^2$$

module
d'imcompressibilité

$$K = \rho c_l^2 - \frac{4}{3}\mu$$

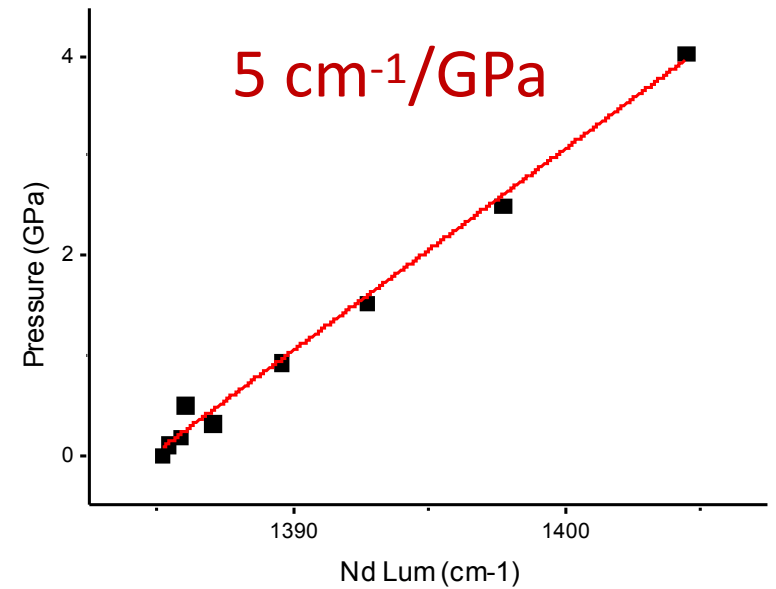
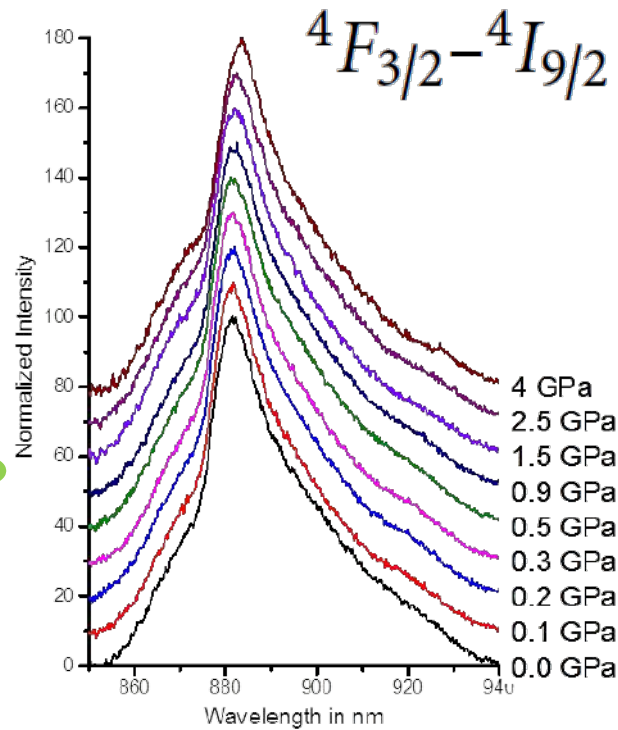
Spectroscopie Brillouin



Le signal Brillouin montre une évolution progressive avec une pression maximale. Pas tout à fait proportionnel à la compression.

Luminescence des Terres Rares

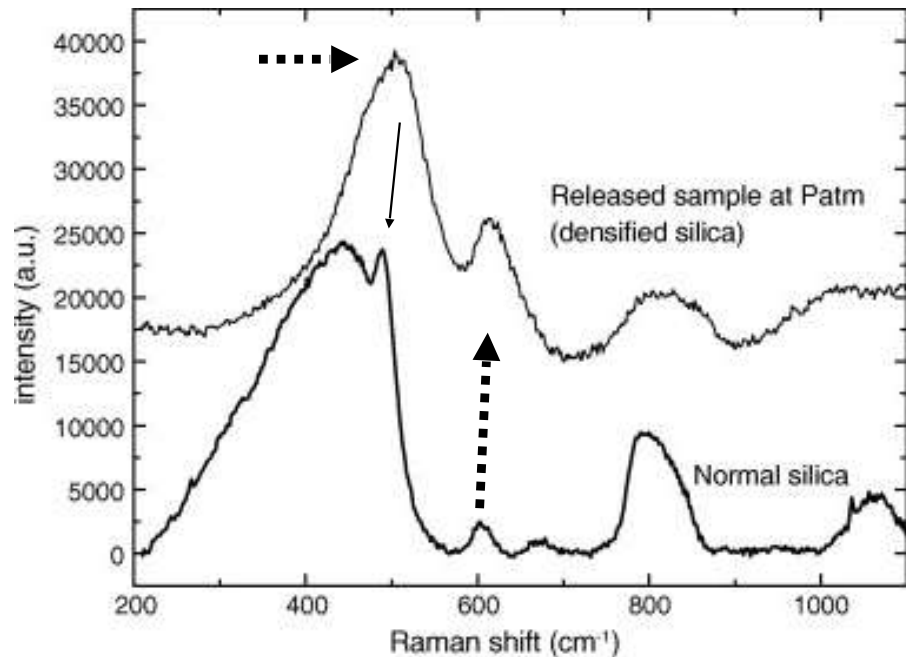
Periodic Table of the Elements



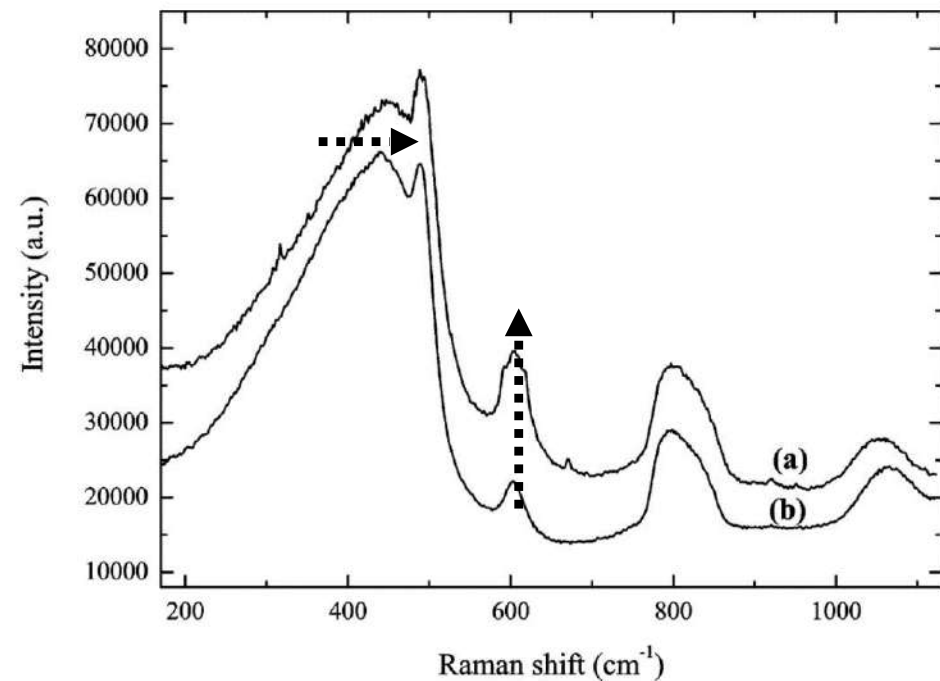
La luminescence est proportionnelle à la densité, soit par compression, soit par contrainte résiduelle.

Verre SiO₂ , que peut on espérer voir?

Haute Pression



Haute Température



Pression et Trempe rapides induisent une densification D1 très distincte si Trempe rapide

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Vitesse de refroidissement des fibres

ISG International Standard Glass

60.2 SiO₂ -16.0 B₂O₃ -12.6 Na₂O -3.8 Al₂O₃ - 5.7 CaO -1.7 ZrO₂

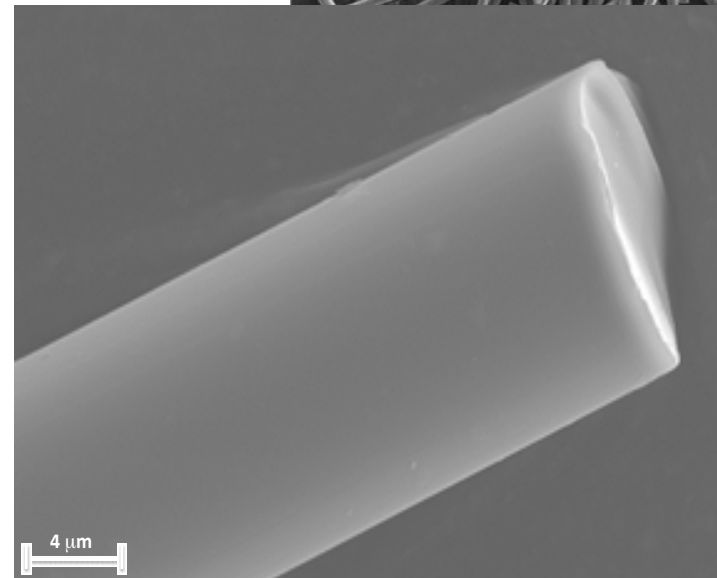
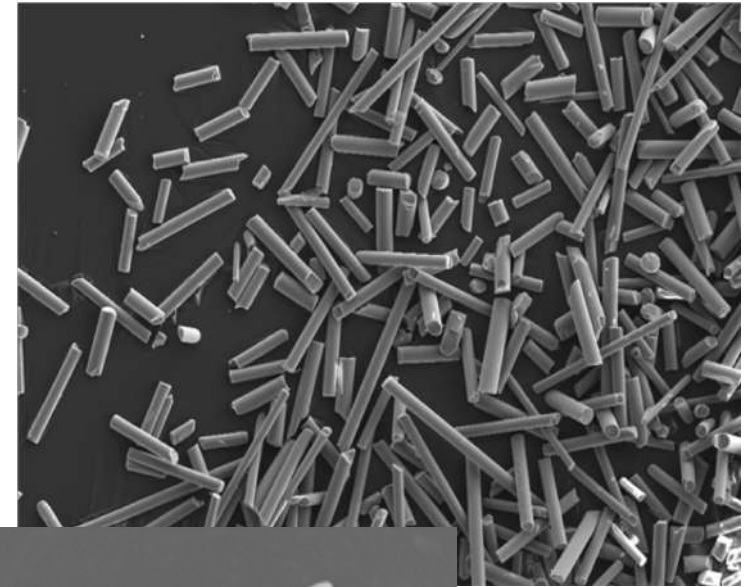
Analogie entre l'auto-irradiation et la température fictive élevée

Grands échantillons irradiés difficiles à produire

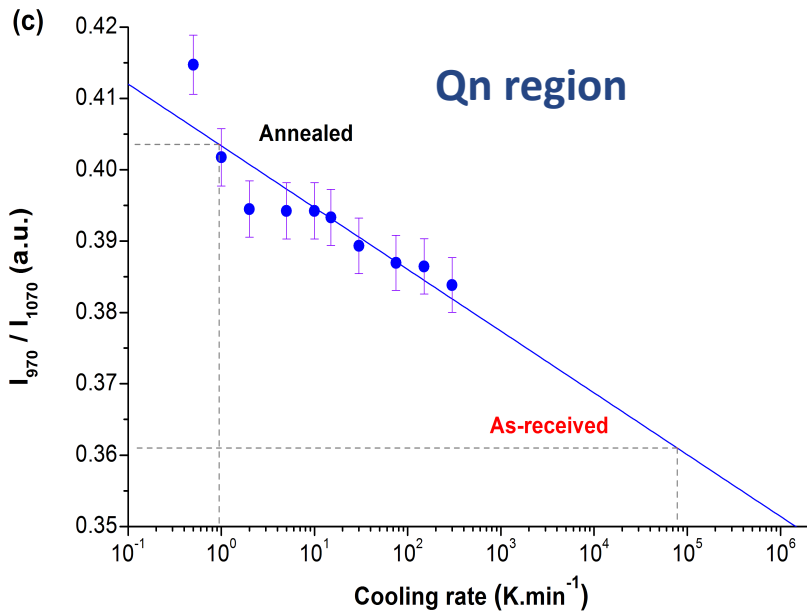
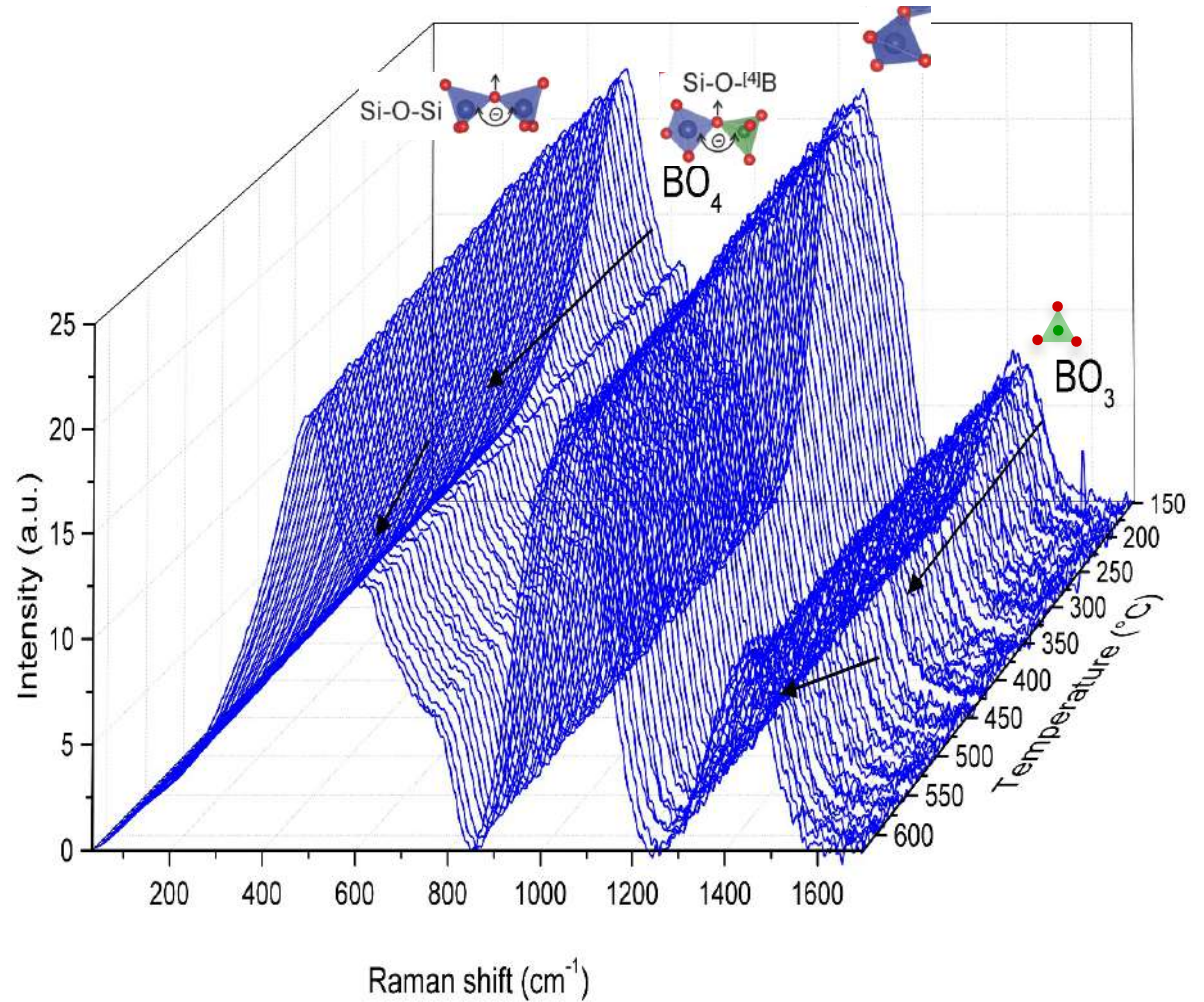
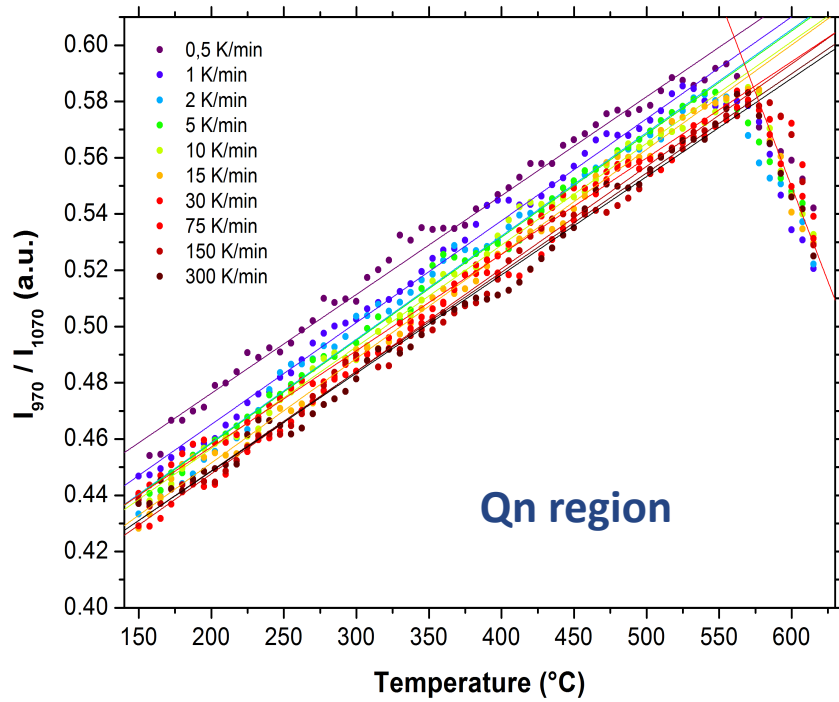
Les fibres sont un bon moyen d'obtenir des échantillons hypertrempés.

Quel est le taux de refroidissement ou la température fictive de la fibre ?

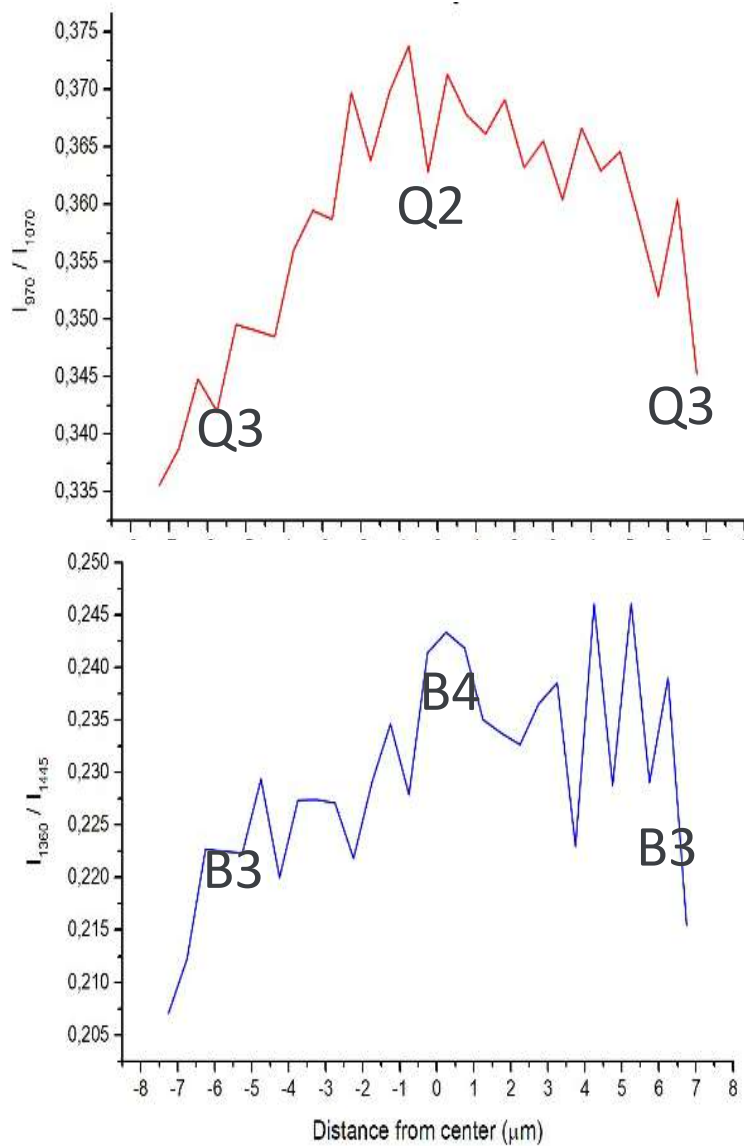
Ici, il est difficile d'effectuer une mesure DSC directe



Vitesse de refroidissement des fibres

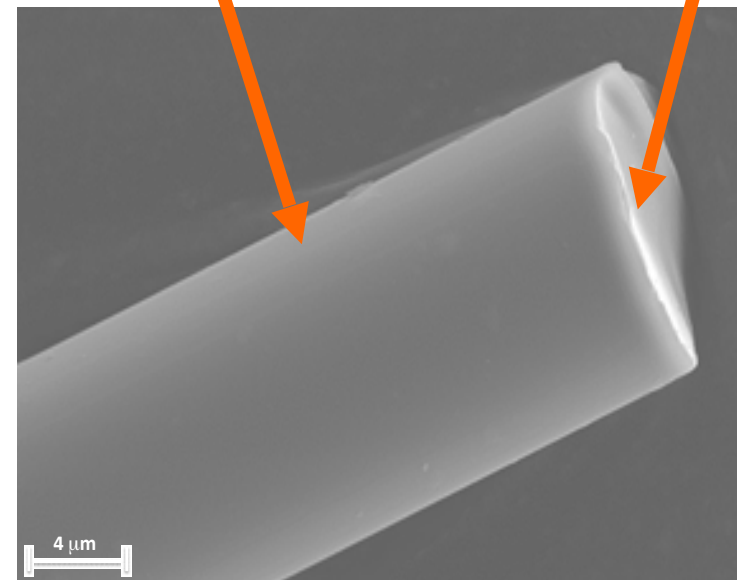


Vitesse de refroidissement des fibres



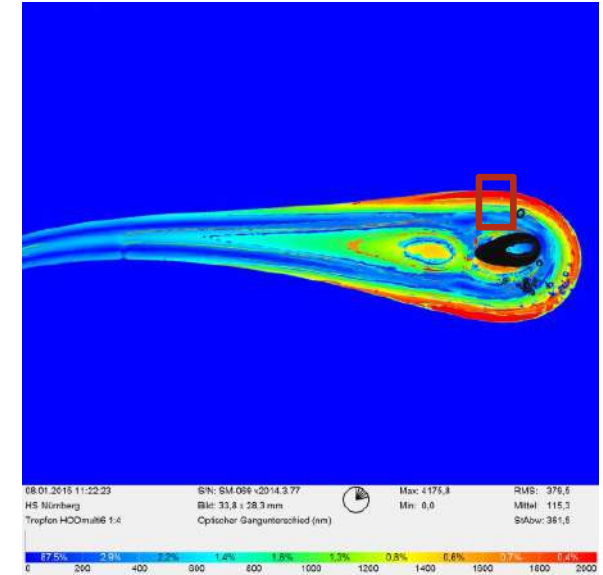
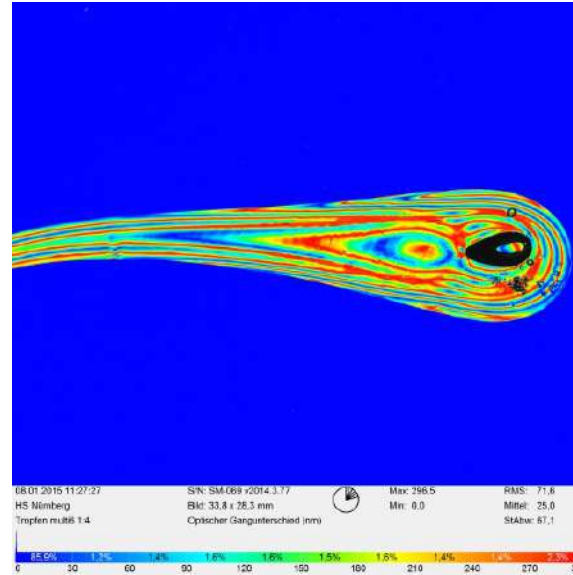
$\sim 10^6 \text{ K.min}^{-1}$

$\sim 5 \cdot 10^4 \text{ K.min}^{-1}$



Larmes bataviques

Mystery of Prince Rupert's Drop at 130,000 fps - Smarter Every Day 86
YouTube



Forme complexe

Approximation à un cylindre avec un coefficient photoélastique de 2.7 TPa⁻¹
500 Mpa pour les 2-3mm

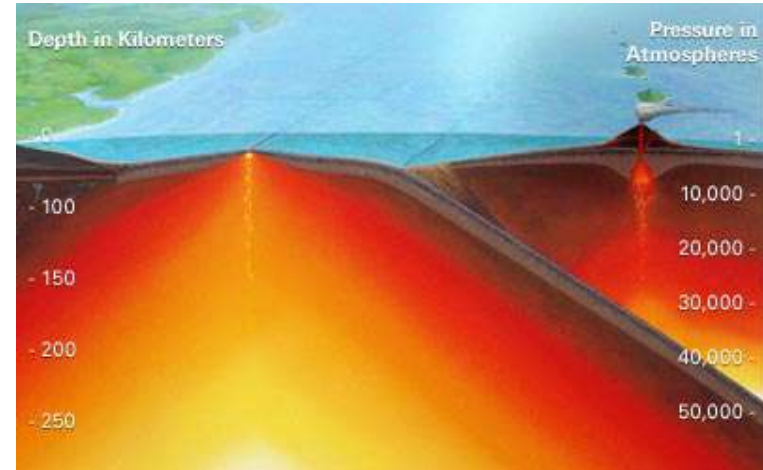
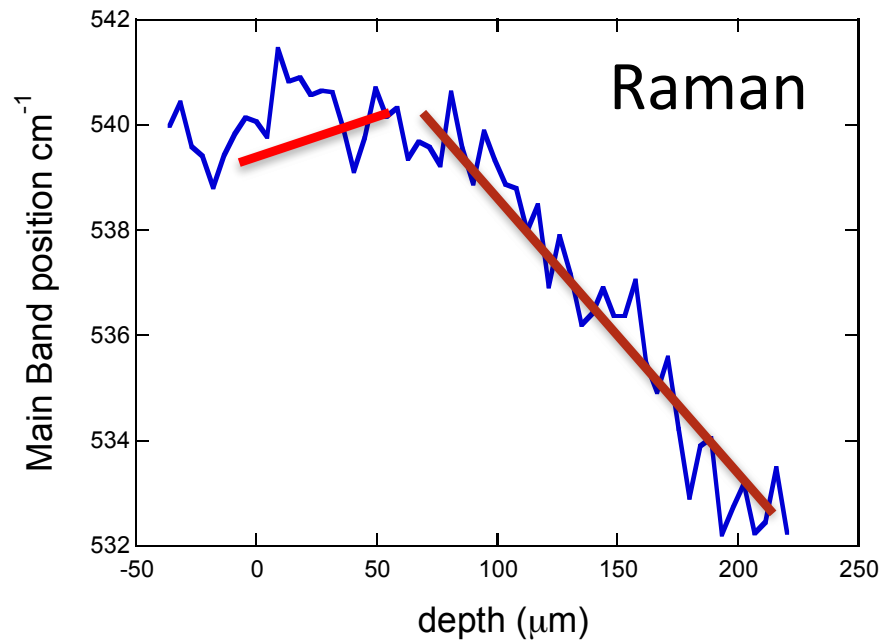
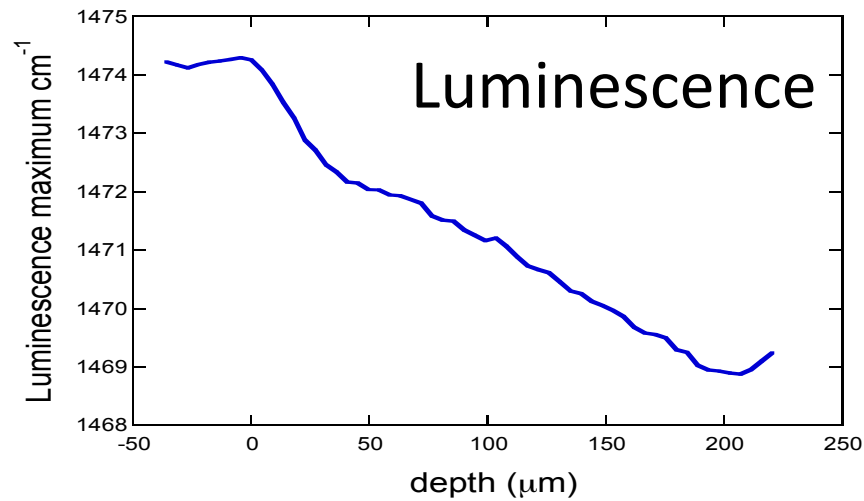


Accroissement de densité de 3,7% pendant la relaxation

$$K = \rho \frac{dP}{d\rho}$$

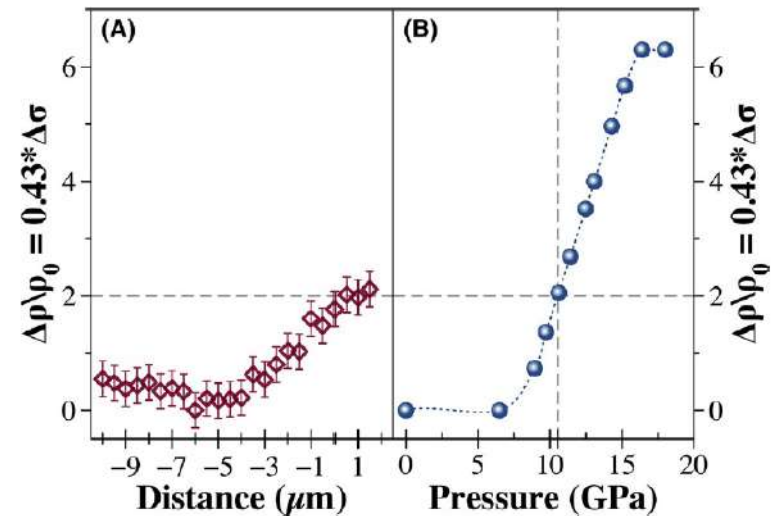
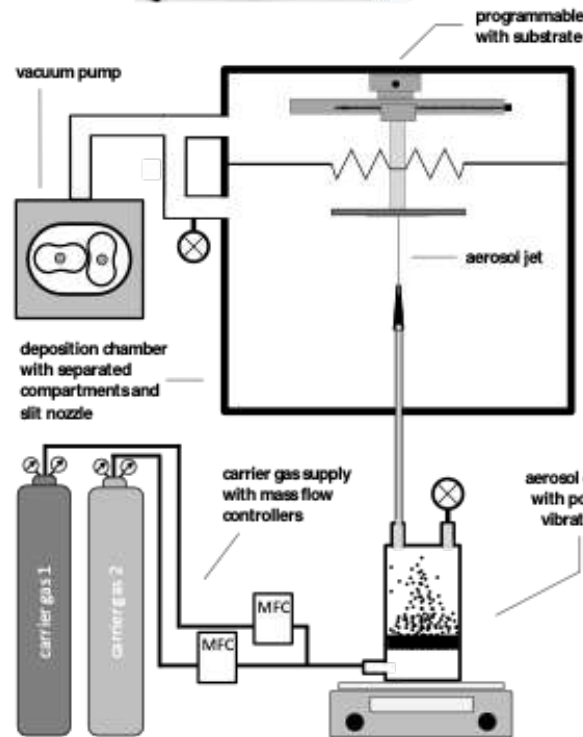
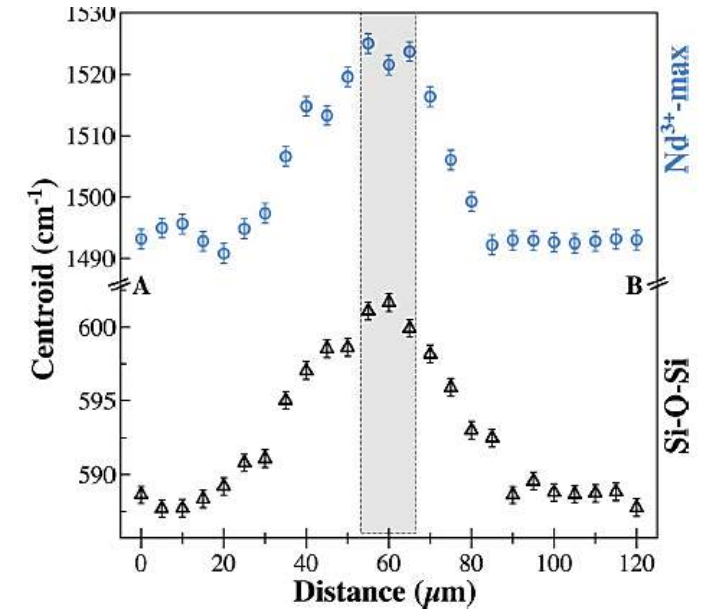
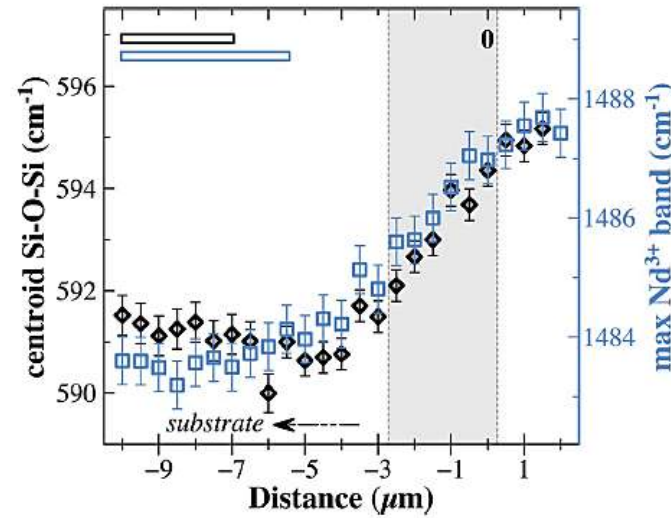
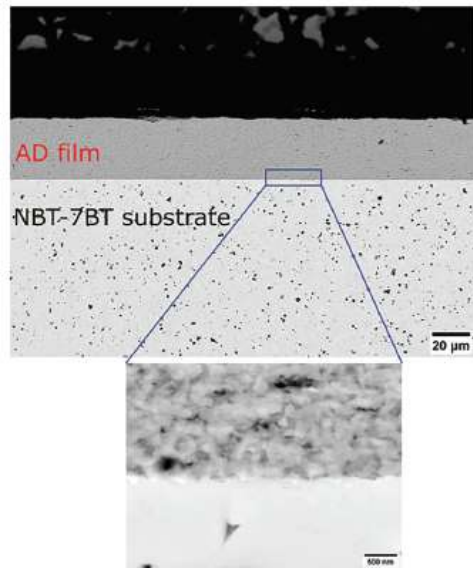
Avec K=40 Gpa alors ΔP= 1,5 GPa

Larmes bataviques



Variation de 1GPa entre la surface et 200 μm en profondeur
En surface un effet aussi lié à la vitesse de refroidissement

Aérosol déposition



Pendant la déposition la pression augmente jusqu'à 10GPa

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- **Tentatives dans la nature**
 - **Tectites**
 - **Fulgurites**
 - **Obsidiennes**



Tectites

- Glass transition temperature:
 - Moldavite: $T_g \approx 740^\circ\text{C}$
 - Chinoises et Thailandaises: $T_g \approx 680^\circ\text{C}$
- Est il possible de détecter un effet par spectroscopie?

Tectite Chinoise



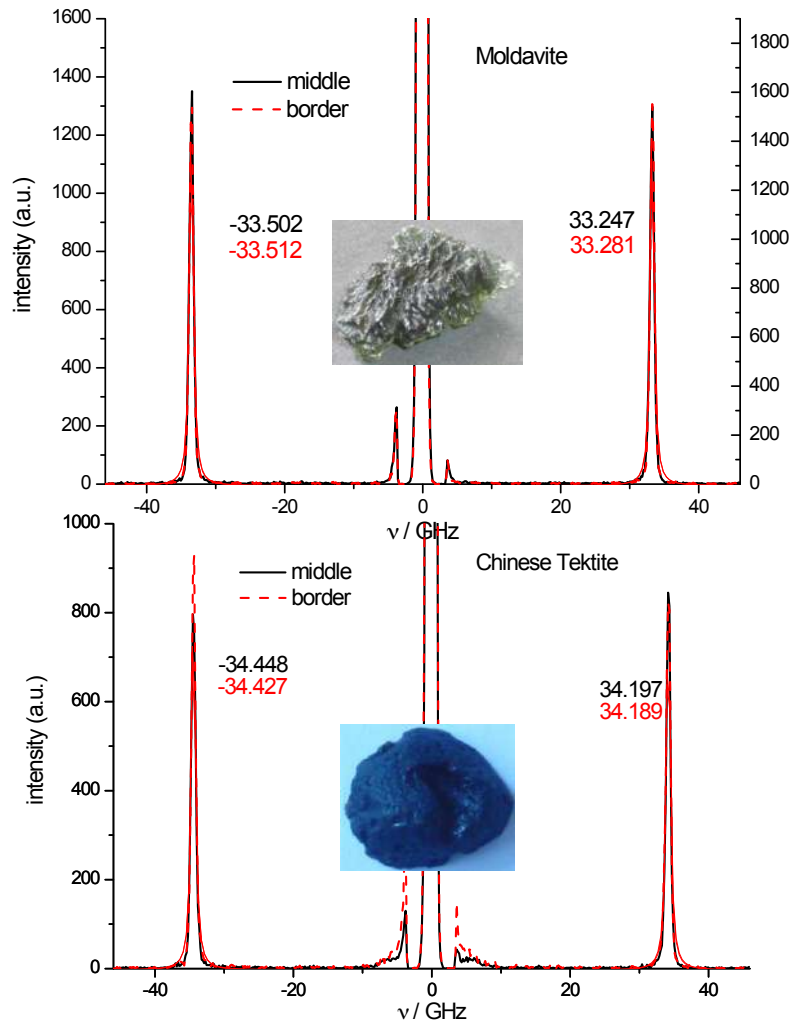
Moldavite



Tectite Thai

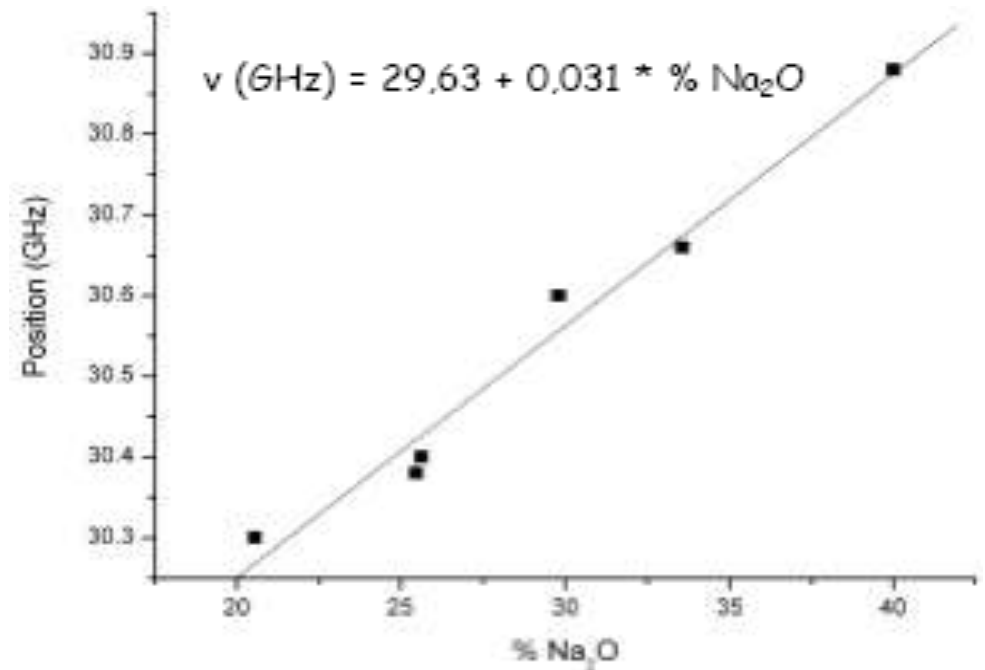


Tectites Brillouin



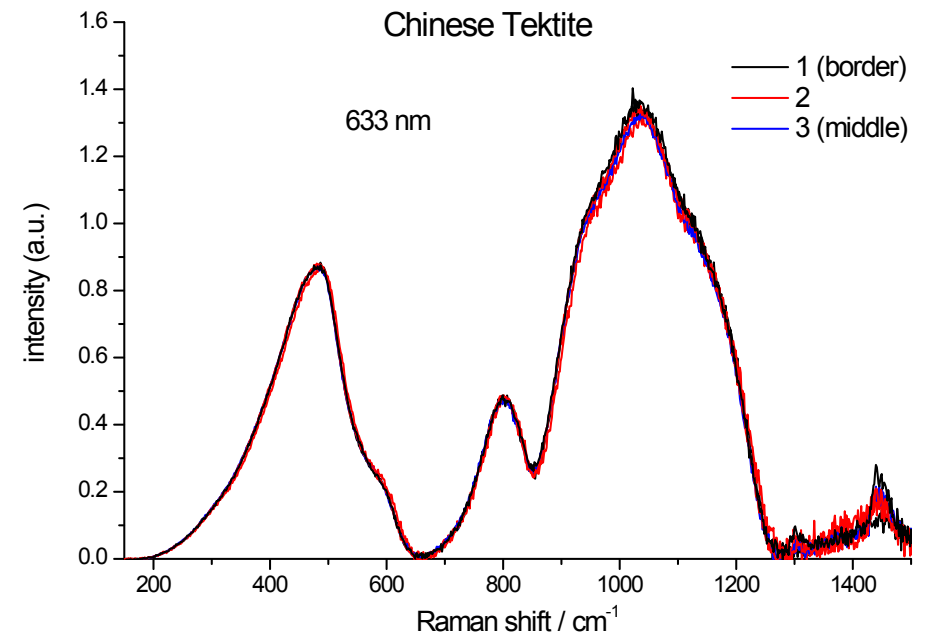
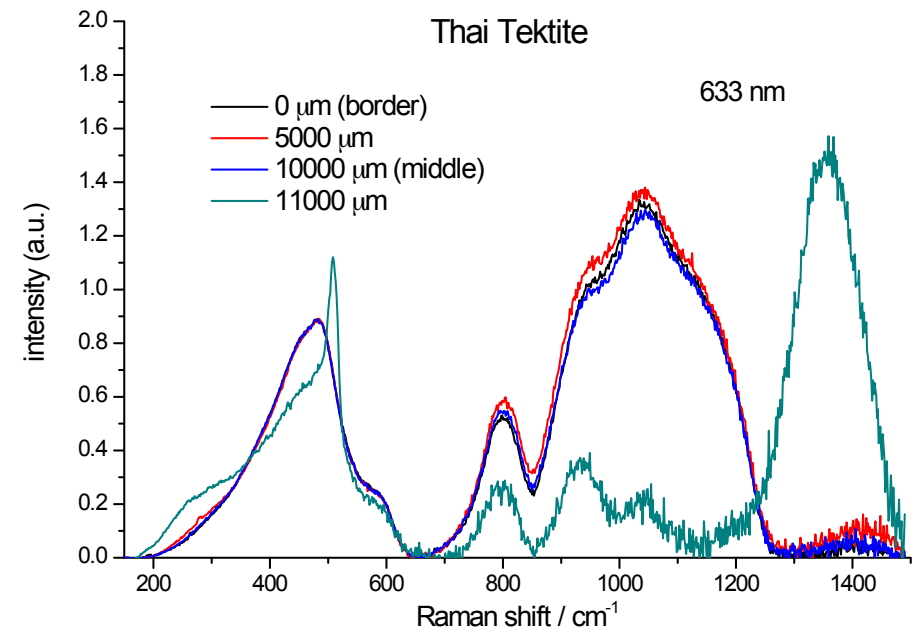
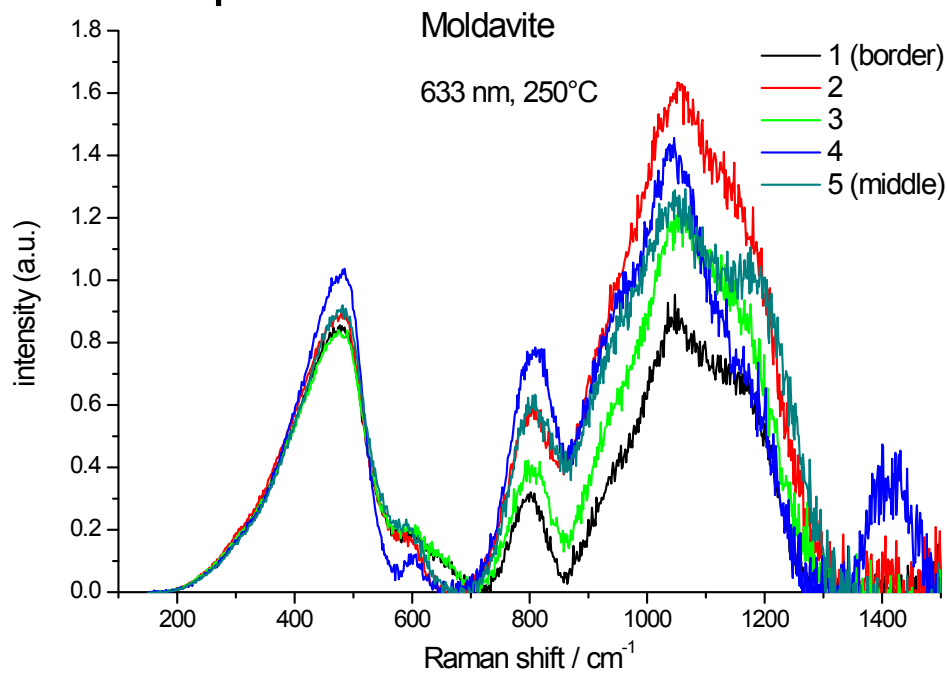
Alkali content ↓

Tektite	ν_{\max} / GHz (middle)	ν_{\max} / GHz (border)
Moldavite	-33.502 33.247	-33.512 33.281
Thai T.	-34.365 34.138	-34.301 34.146
Chinese T.	-34.448 34.197	-34.427 34.189

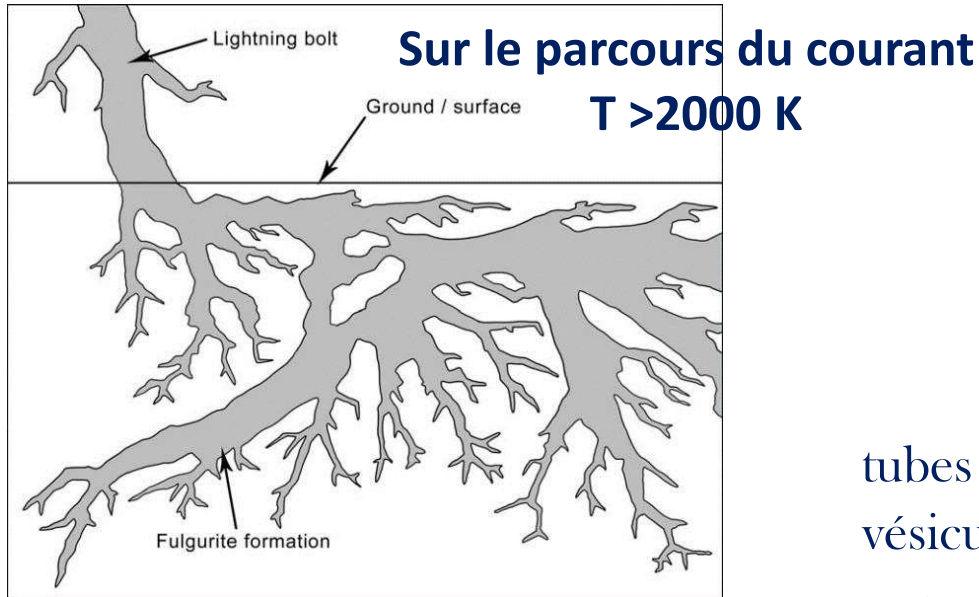


Tectites Raman

- Pas de changements significatifs du bord vers le centre
- Inhomogénéités dominant le spectre
- Cristallisation
- Graphite ?



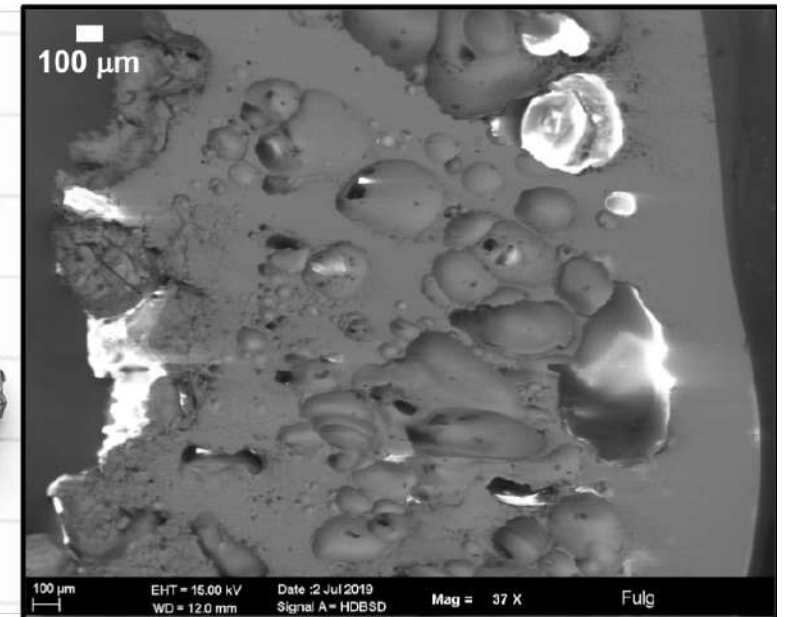
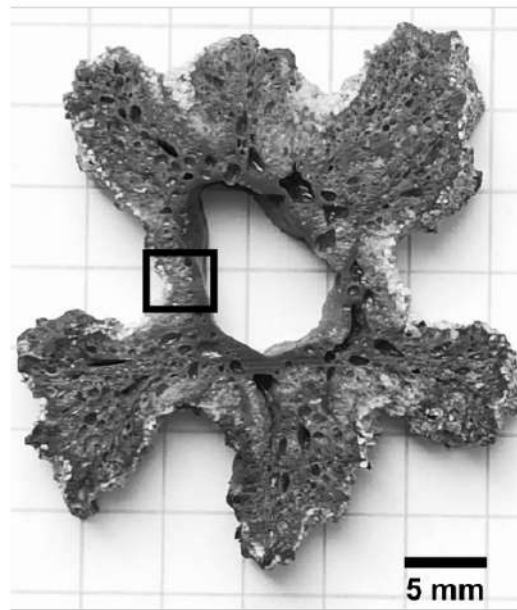
Fulgurites



tubes creux avec beaucoup de vésicules créés par vaporisation

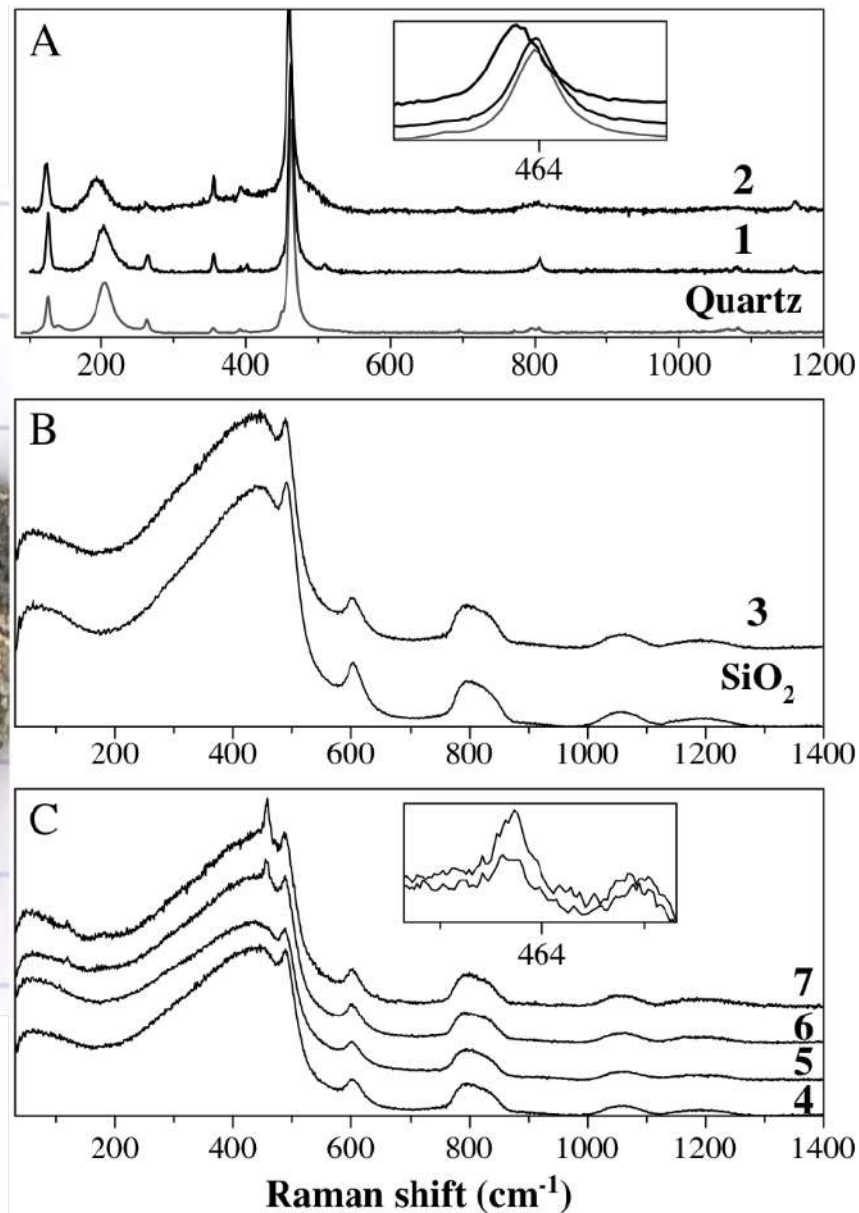
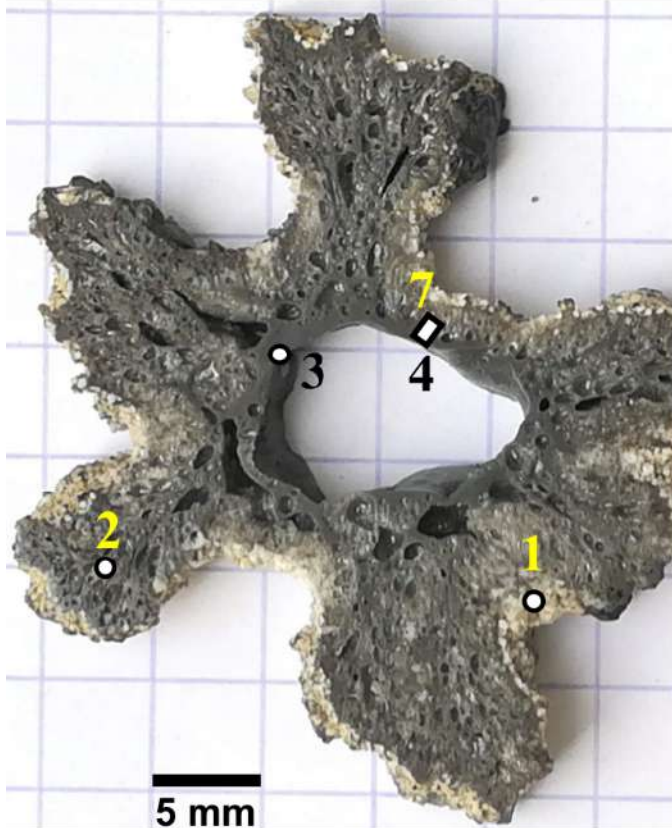
Surface externe irrégulière

Surface interne lisse



*Cicconi & Neville 2019: Natural glasses.
Springer Handbook of Glasses*

Fulgurites Raman



α -Quartz:
décalage
suggérant une
augmentation de
la pression de 25
GPa

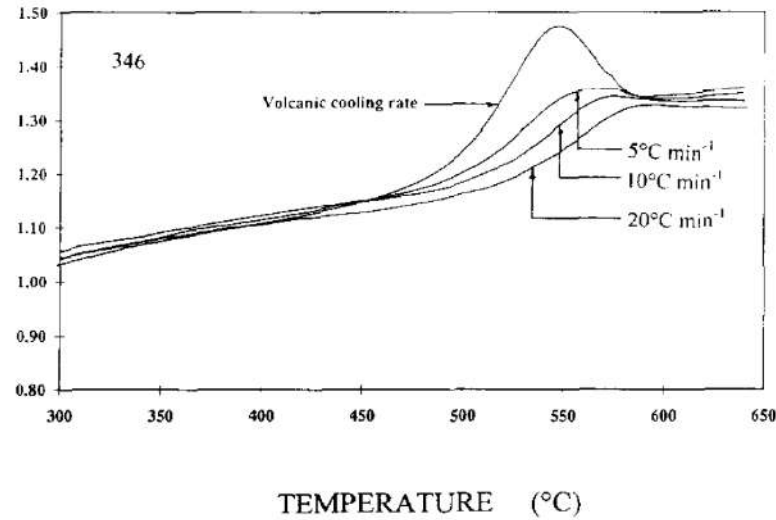
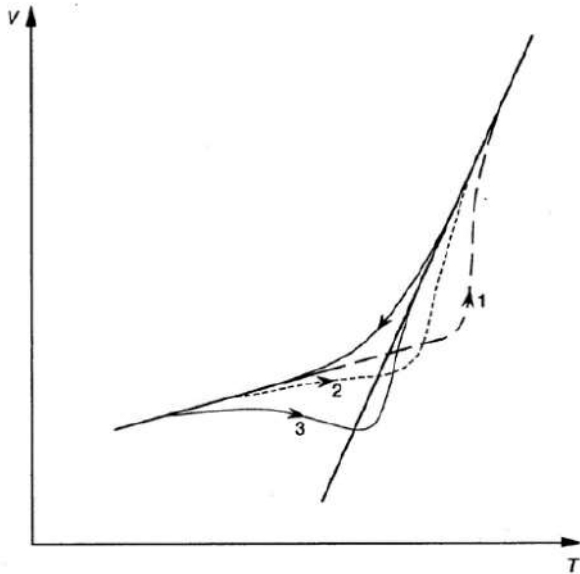
Quasiement
verre de silice
pure
Pas de D1
particulièrement
marquée

*Cicconi et al. 2021: Non-Magmatic Glasses.
Review in Mineralogy and Geochemistry*

Obsidiennes

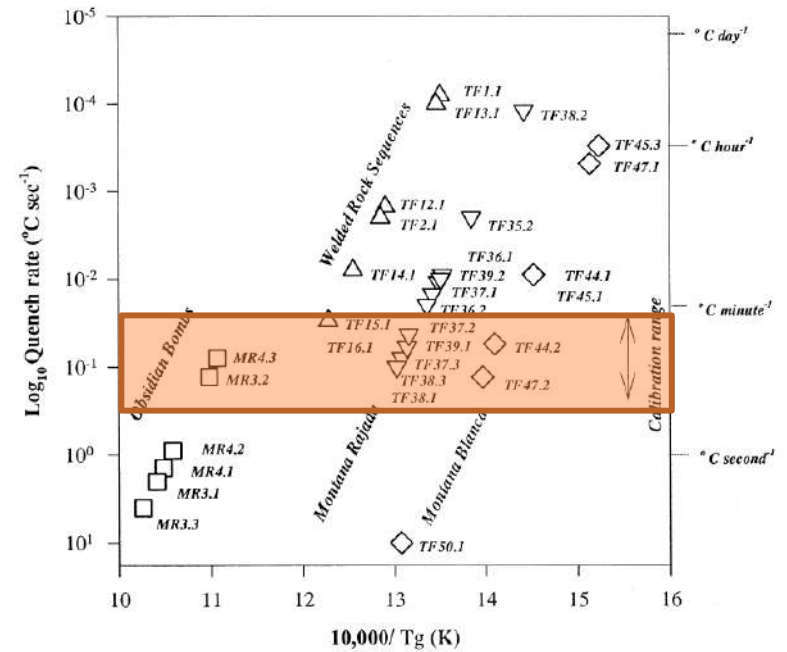
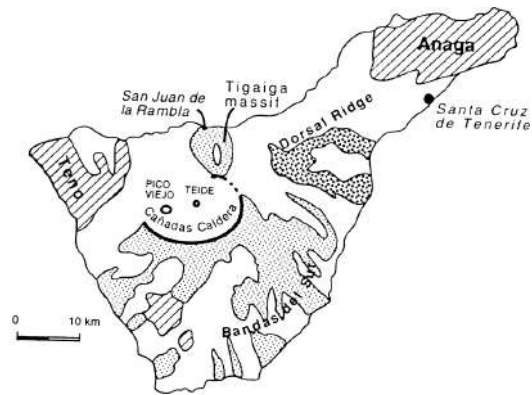


123RF.COM

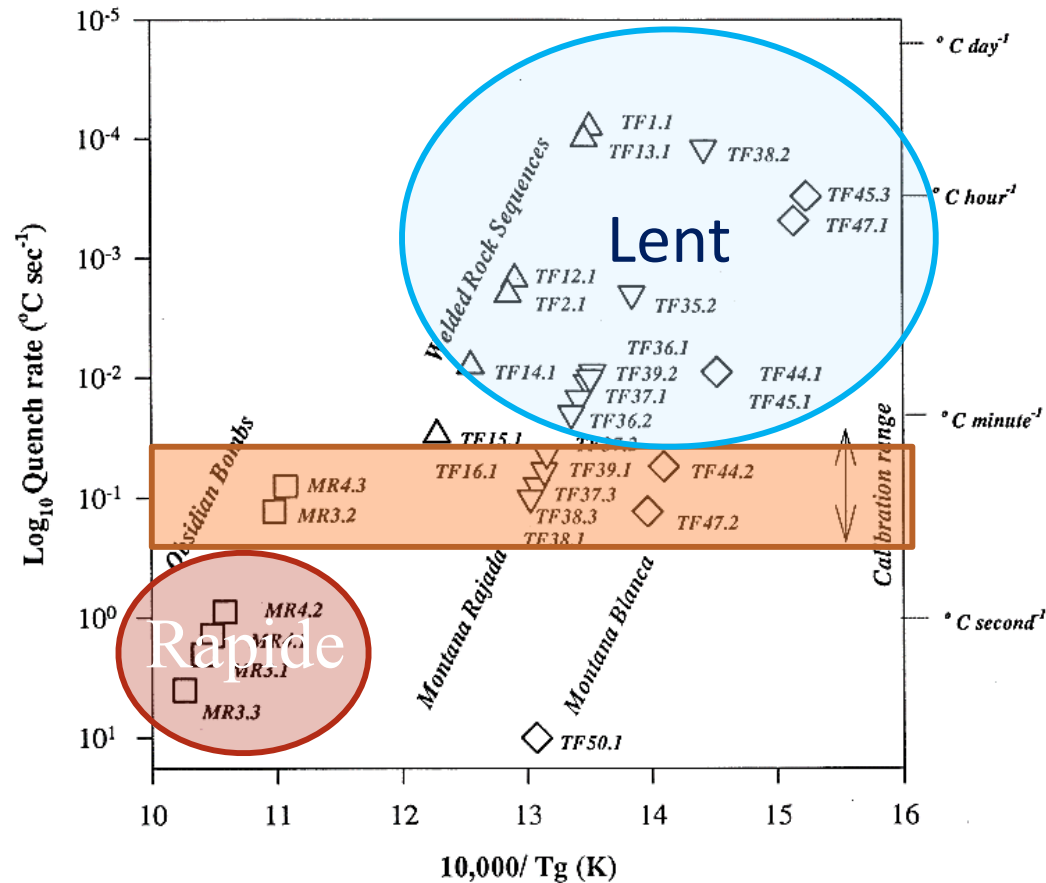


$$-\log_{10} |q| = -\log_{10} |q_0| + \frac{H}{RT_g}$$

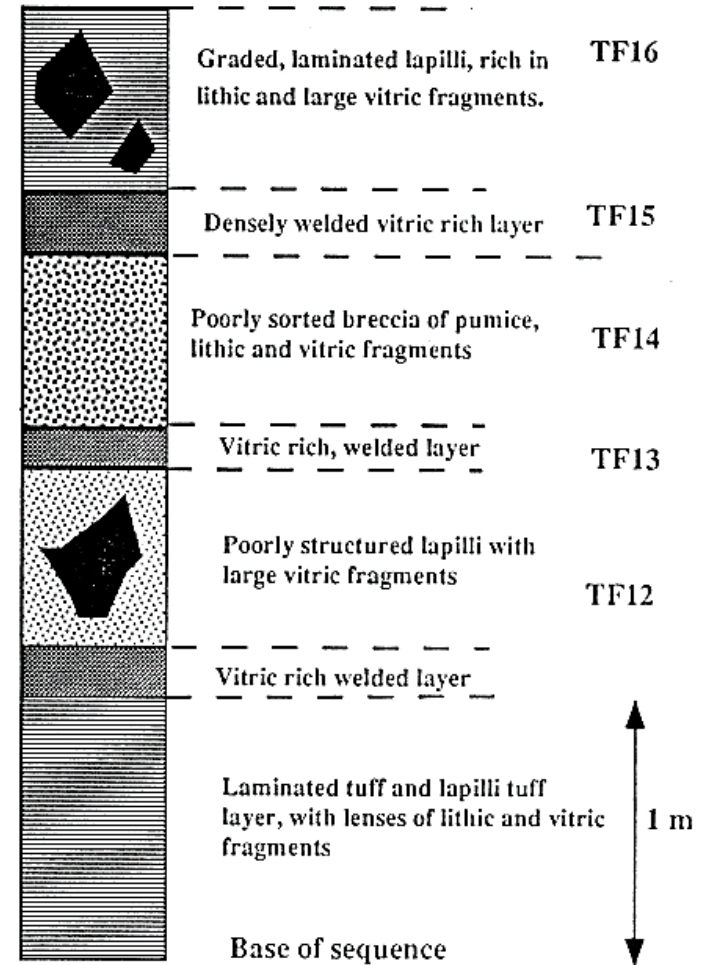
Wilding et al. Contrib.Min.Petrol 1996



Obsidiennes



Barrianco del Rio Sequence

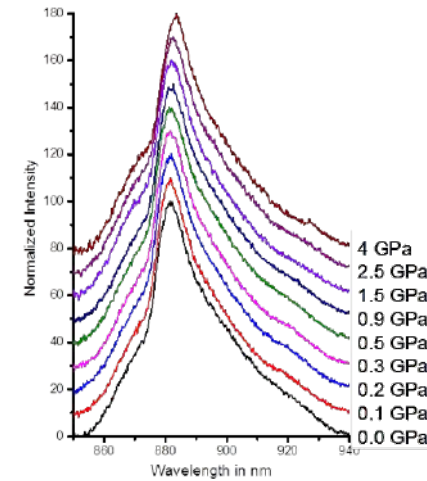


Wilding et al. Contrib.Min.Pet 1996

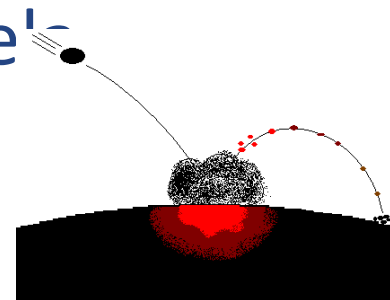
- Moldavite: 2-10°C/s (CTE, Arndt et al. 1976)
- Tektite: 1-10°C/s (DSC, Wilding et al. 1996)

Conclusion

- Le verre a une mémoire
- Cette mémoire peut être lue en utilisant les spectroscopies de vibrations et de luminescence
- Grande variabilité chimique de la nature couvre bien des effets
- Les éruptions volcaniques, les chutes de météorites et la foudre ne sont pas des effets si extrême que ce



Periodic Table of the Elements





VAYAGIF.COM



Lena Bressel, Gérard Pankzer et Bernard Champagnon -ILM Lyon 1
Rita Cicconi, Daniel Neuville – IPG Paris

Tectites

- Glass transition temperature:
 - Moldavite: $T_g \approx 740^\circ\text{C}$
 - Chinoises et Thailandaises: $T_g \approx 680^\circ\text{C}$
- cooling rates:
 - Moldavite: $2\text{-}10^\circ\text{C/s}$ (from thermal expansion measurements, Arndt et al. 1976)
 - Tektite: $1\text{-}10^\circ\text{C/s}$ (from DSC measurements, Wilding et al. 1996)
- possible to detect with spectroscopy?

Chinese Tektite



Moldavite



Thai Tektite



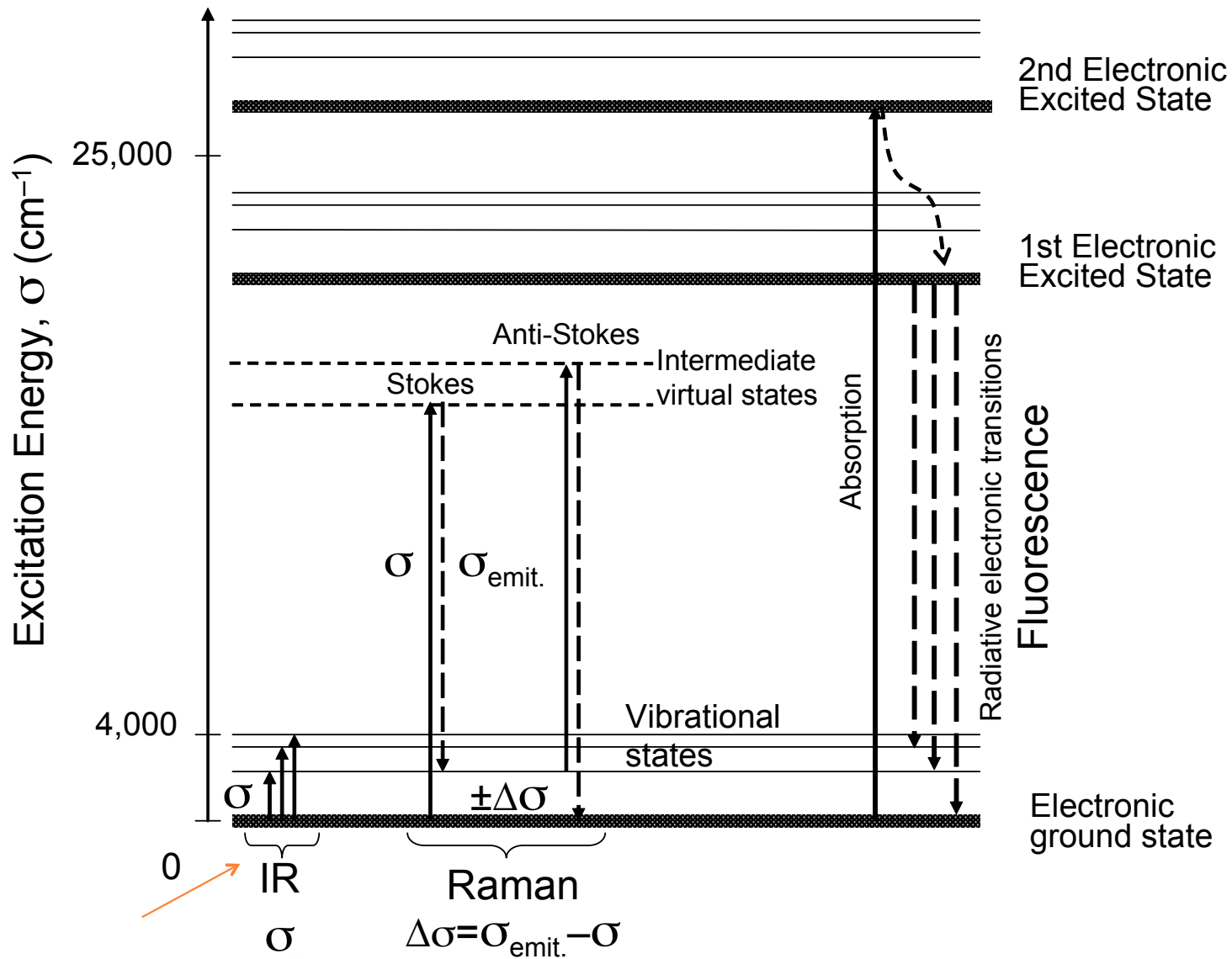
1.1 Who is Prince Rupert



Mystery of Prince Rupert's Drop at 130,000 fps -
Smarter Every Day 86 YouTube

**Rupert, Count Palatine of the Rhine, Duke of Bavaria,
Duke of Cumberland 1619-1682**

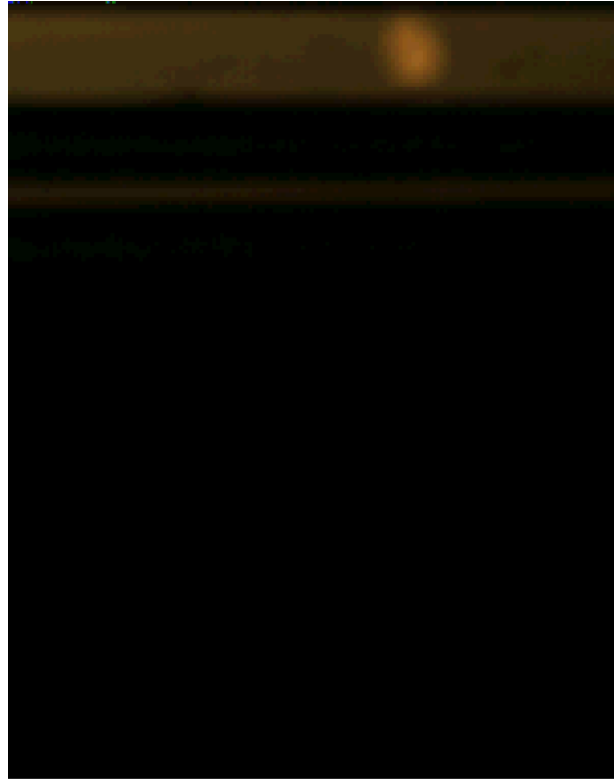
1. Fluorescence / Raman / absorption IR



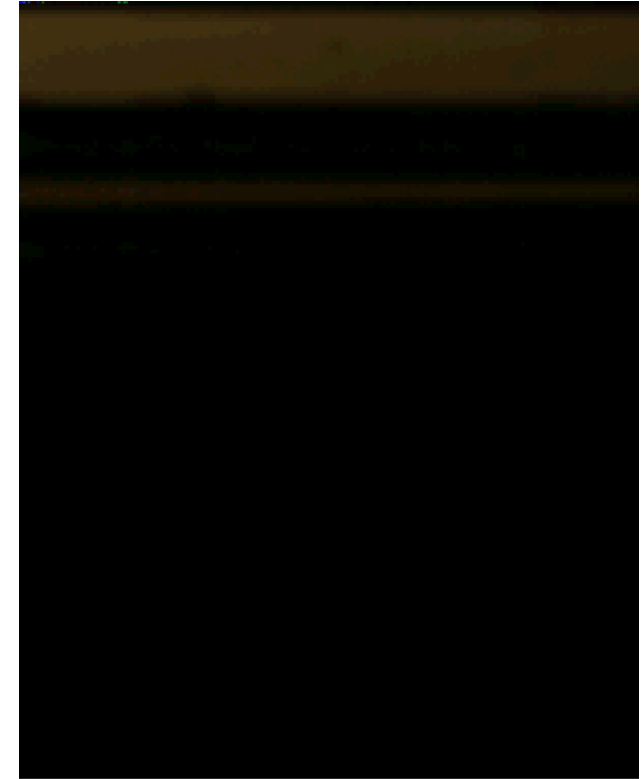
Bologneser Tränen



04.05.2015 18:37:24 0001 2123.2[ms] 608x764, 2800 Hz, 352 µs, *1,
MotionBLITZ EoSens Cube7 #00154, V1.11.25



04.05.2015 18:17:16 0001 0191.0[ms] 608x764, 2800 Hz, 352 µs, *1,
MotionBLITZ EoSens Cube7 #00154, V1.11.25



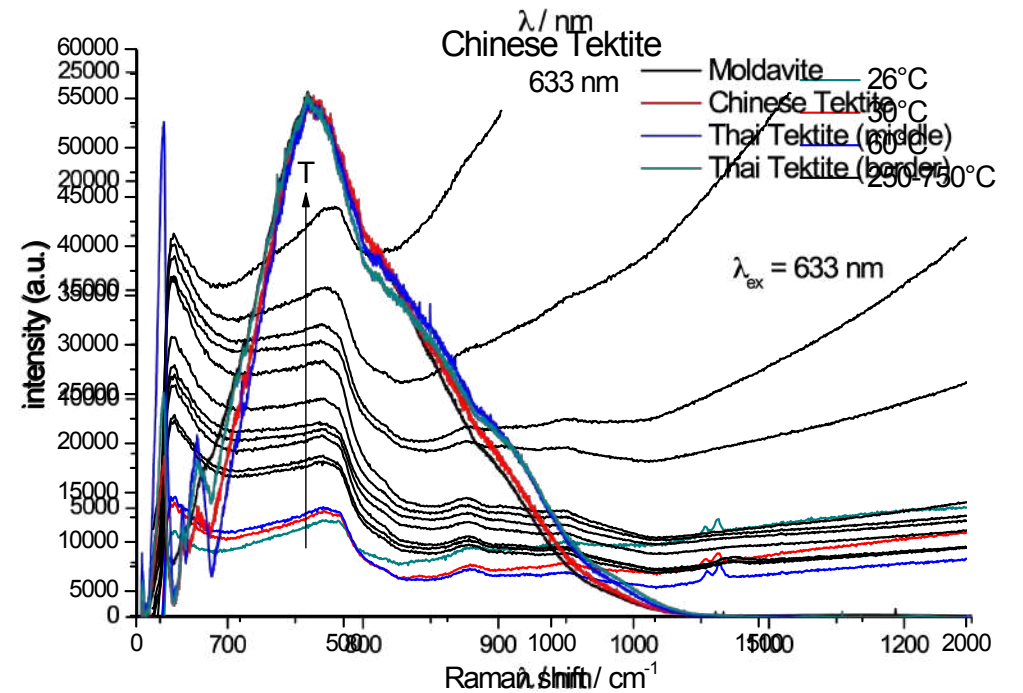
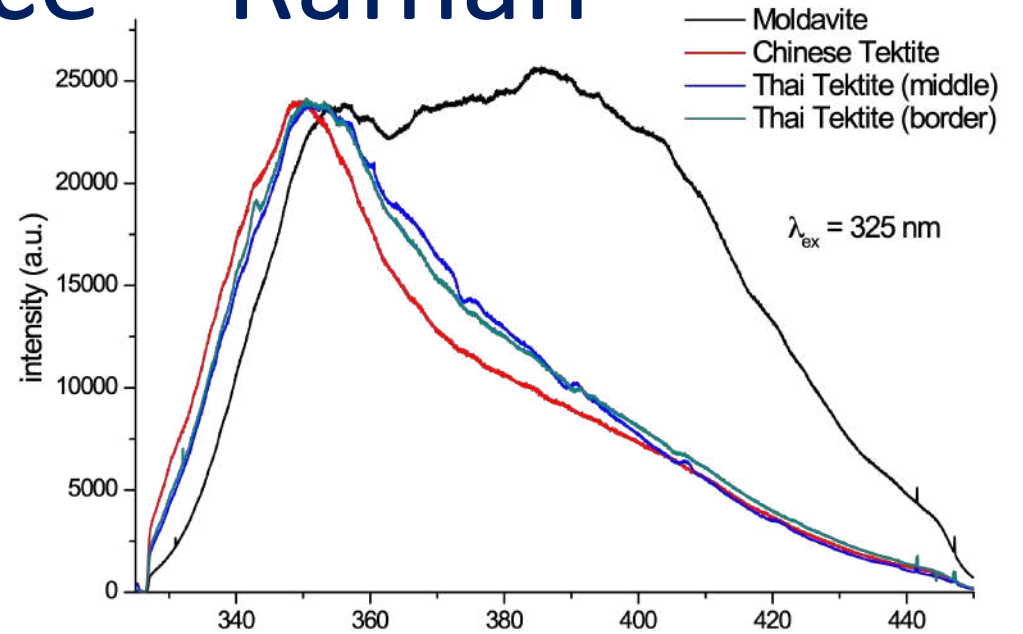
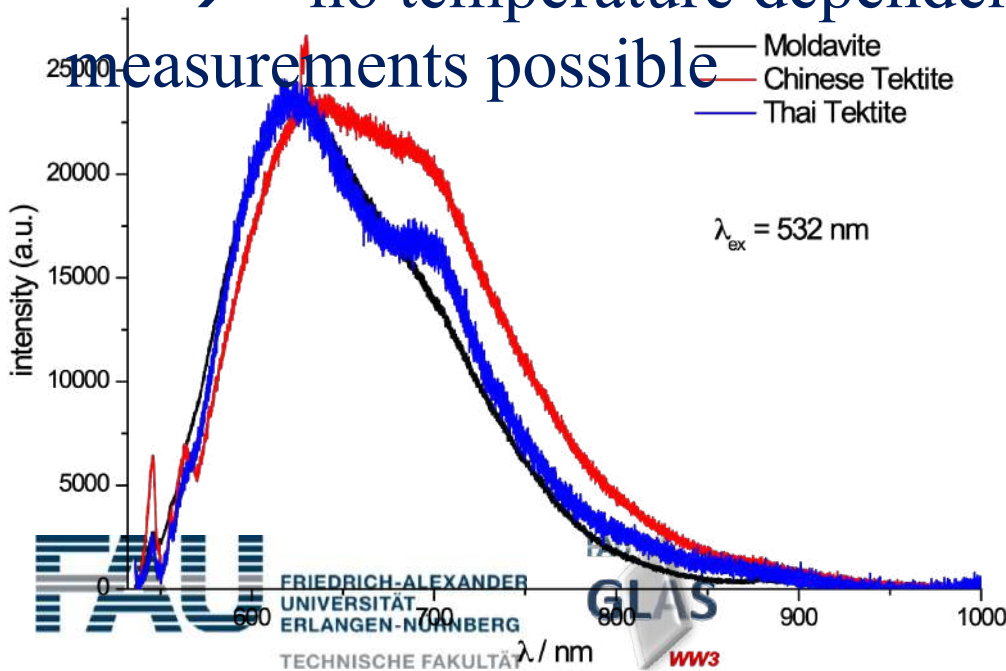
04.05.2015 18:23:20 0001 2669.7[ms] 608x764, 2800 Hz, 352 µs, *1,
MotionBLITZ EoSens Cube7 #00154, V1.11.25

Luminescence – Raman

- strong luminescence (especially at low wavelength)

heating: diminution of luminescence but increasing black body radiation

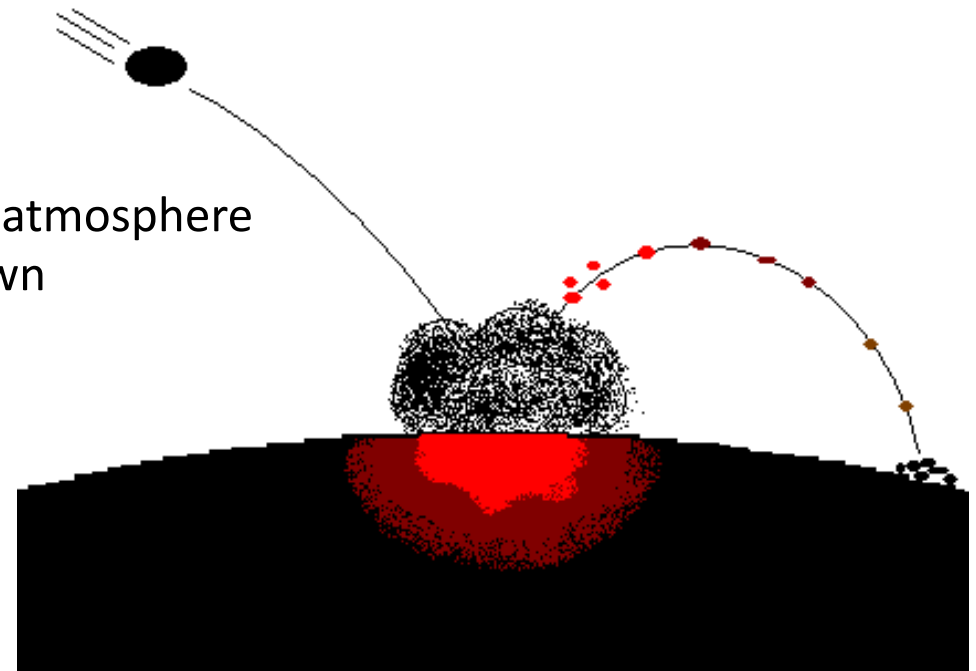
→ no temperature dependent measurements possible

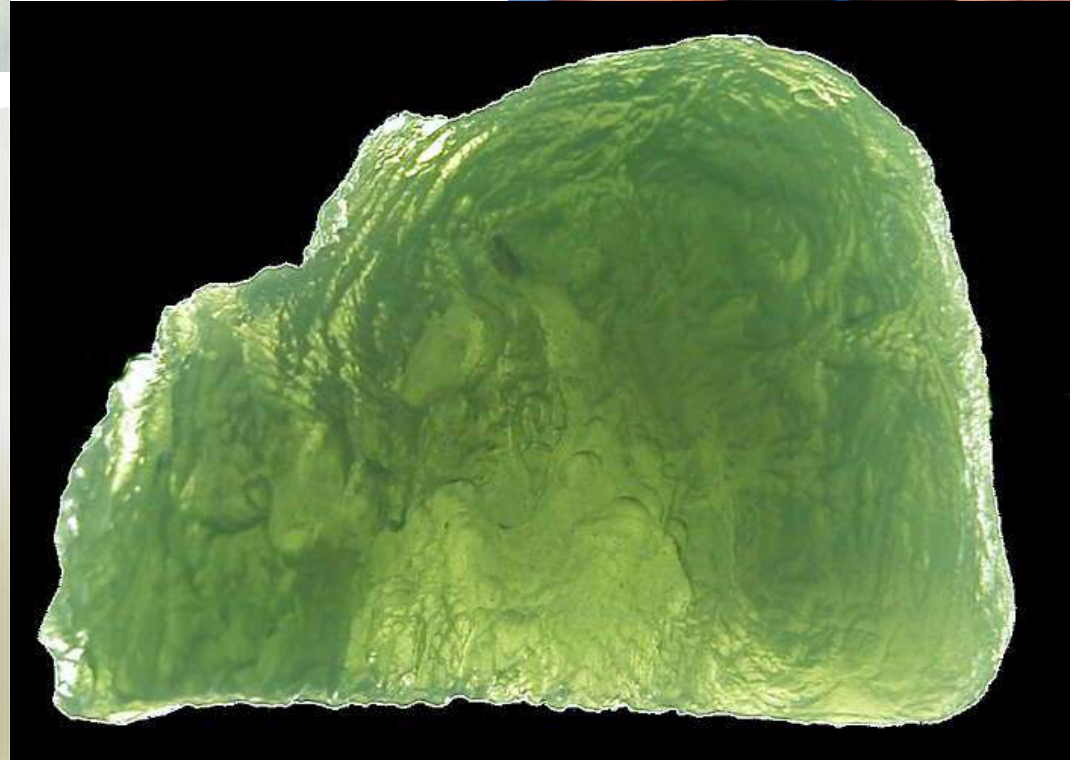
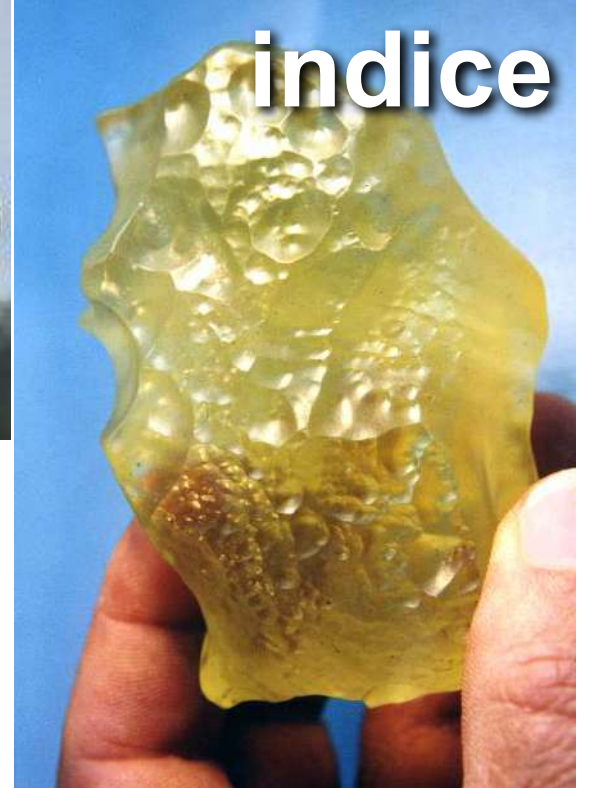


Tektites – Overview

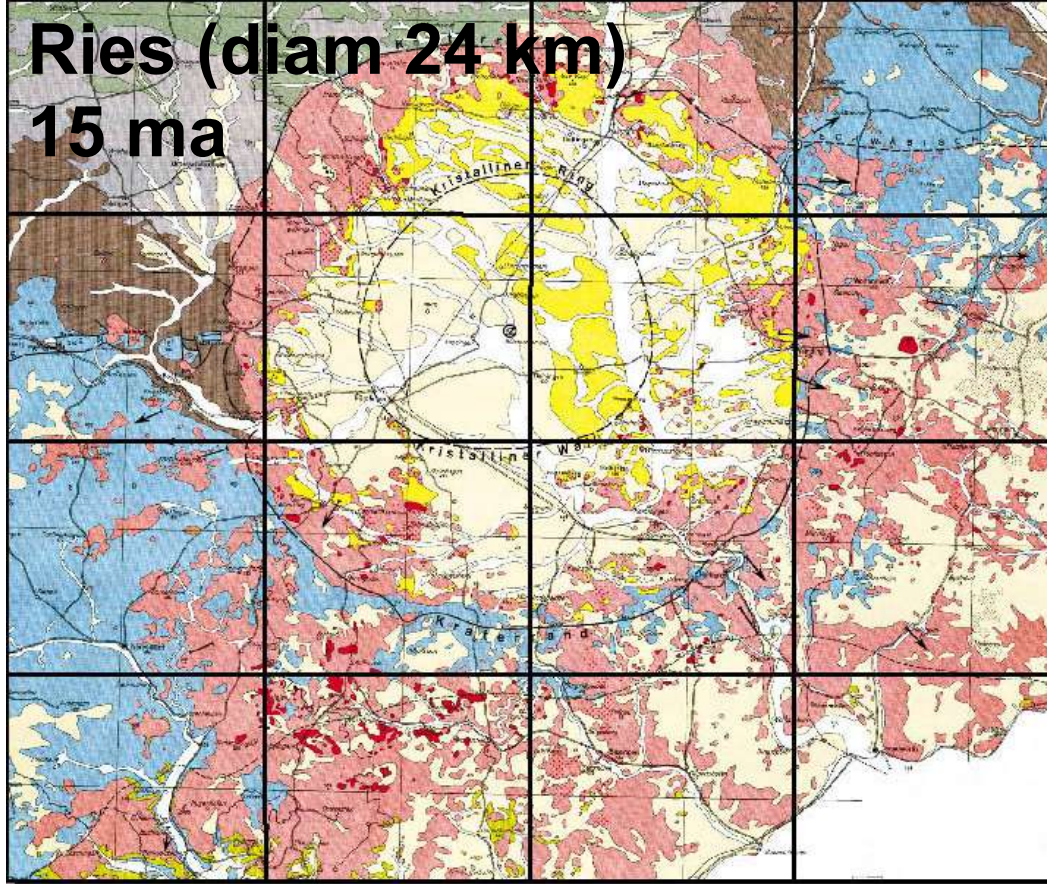
what is this?

- natural glasses
- four known strewn fields (North American, Czechoslovakian, Ivory Coast, Australasian)
- main composition: SiO_2 (70-80%), Al_2O_3 (9-20%), FeO (1-6%), CaO (1-4%), MgO (0.1-3.5%), Na_2O (0.5-2.3%) and K_2O (1-3.5%), MnO/TiO_2 (< 1%)
- origin is still controversial
- believed to result from meteorite impacts
- meteorite hits the surface
- earth liquefies
- drops of the liquefied earth are thrown in the atmosphere
- while flying through the air the drops cool down and solidify into the tektite glasses
- here studied three types of tektites: Moldavites, Chinese tektites, Thai tektites

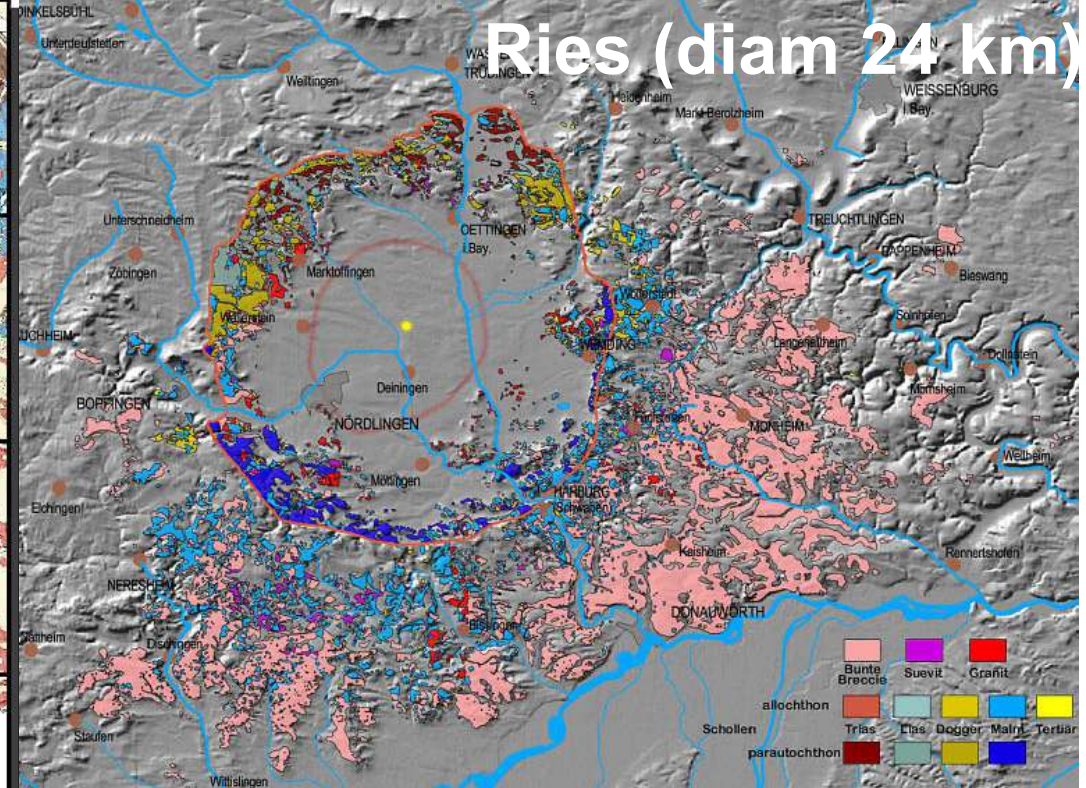




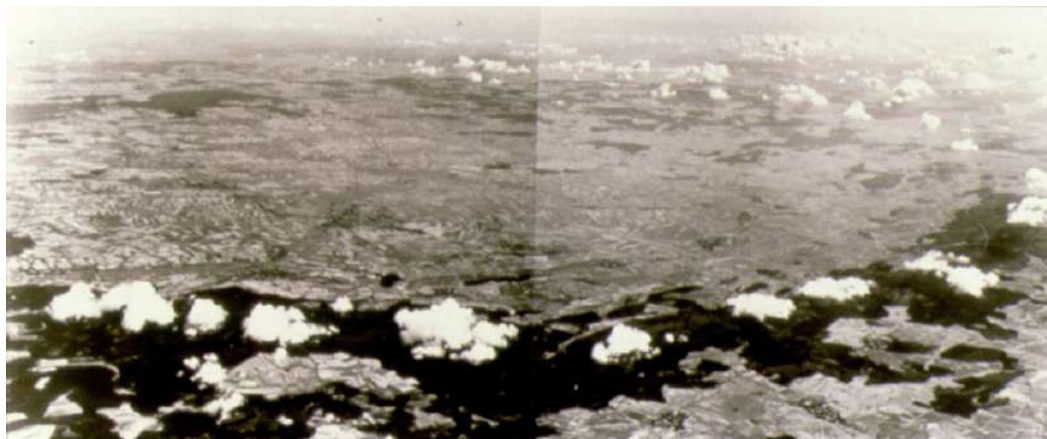
Ries (diam 24 km) 15 ma



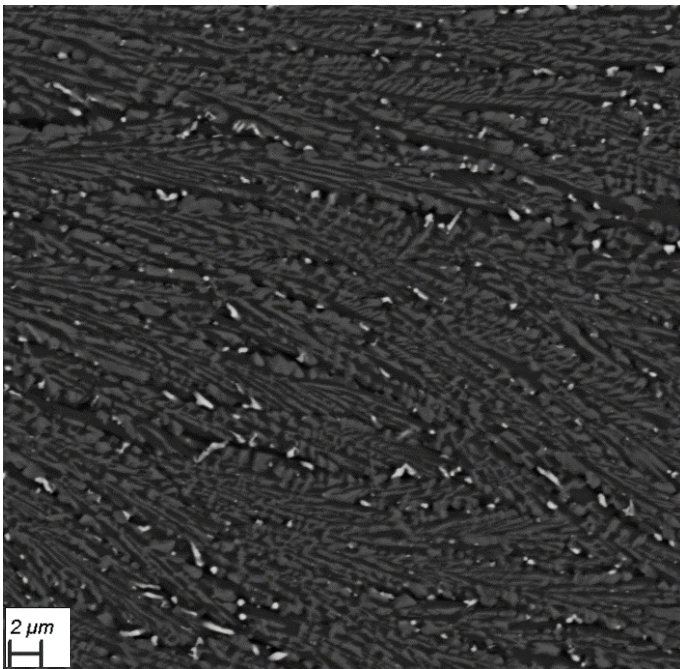
Ries (diam 24 km)



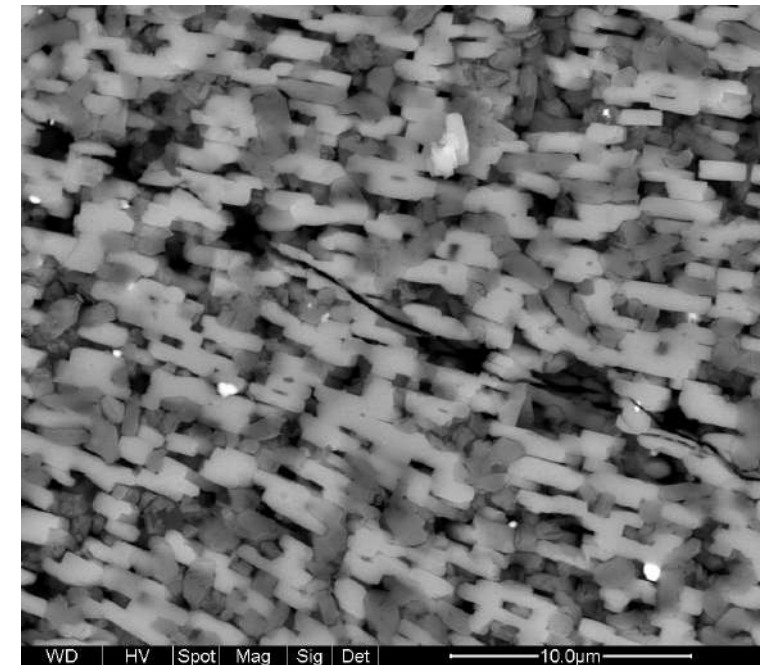
Steinheim (diam 2,5 km)



Rocks



Glass-ceramics



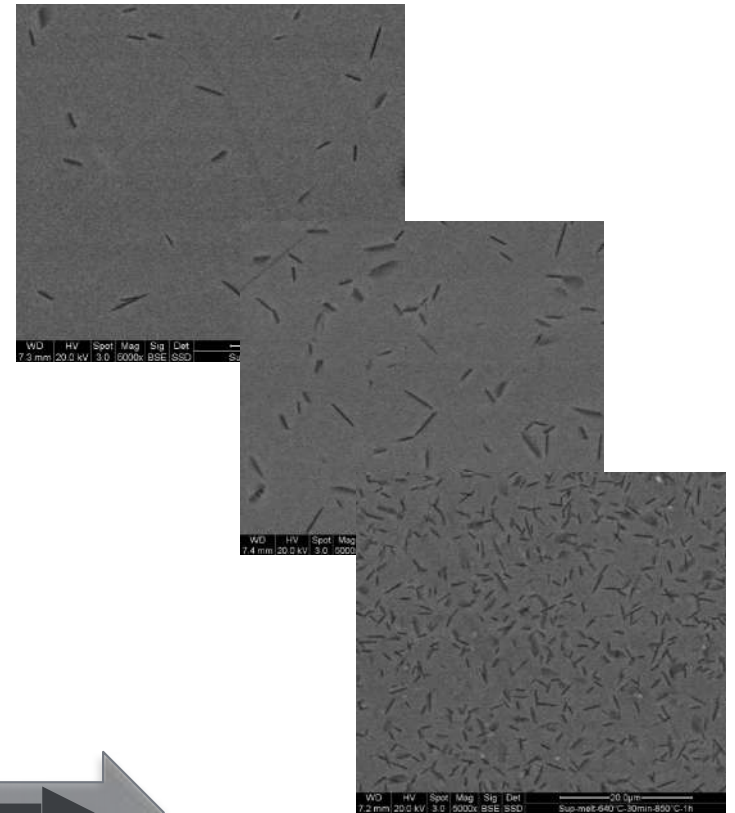
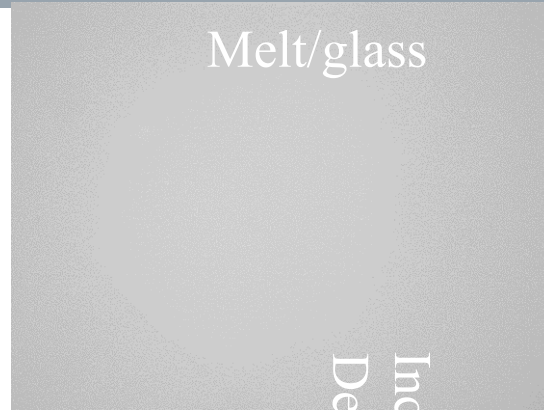
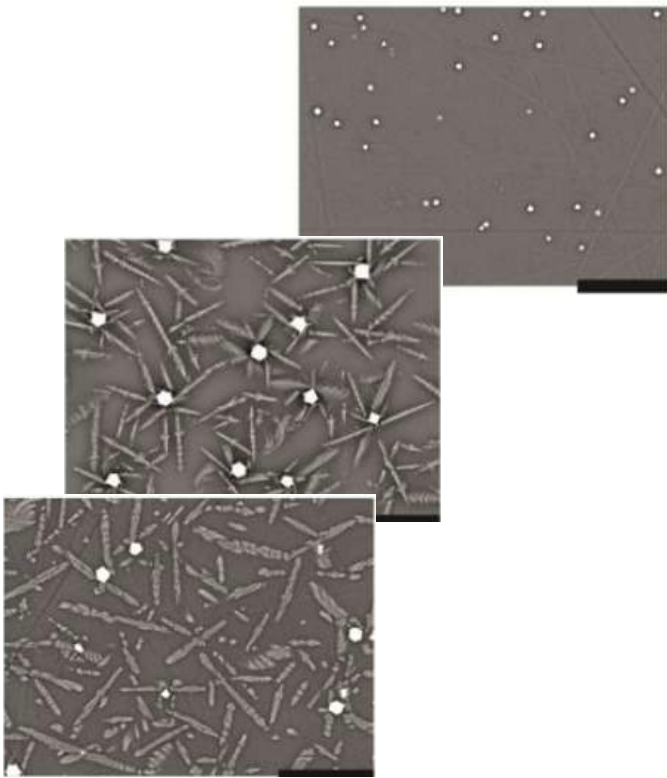
→ History of the volcanic area

→ Mechanical/optical properties

Rocks

Melt/glass

GC

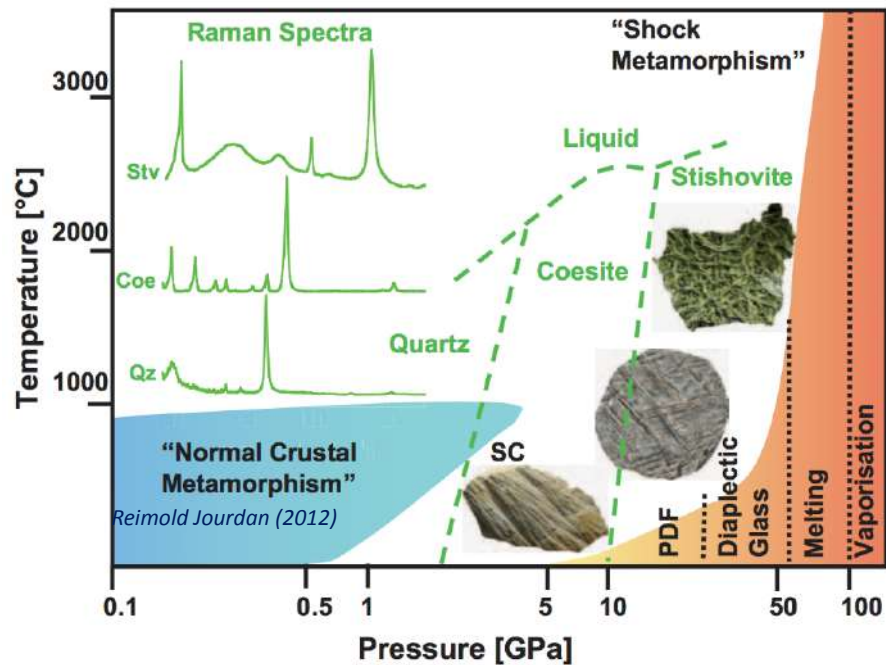


→ History of the volcanic area

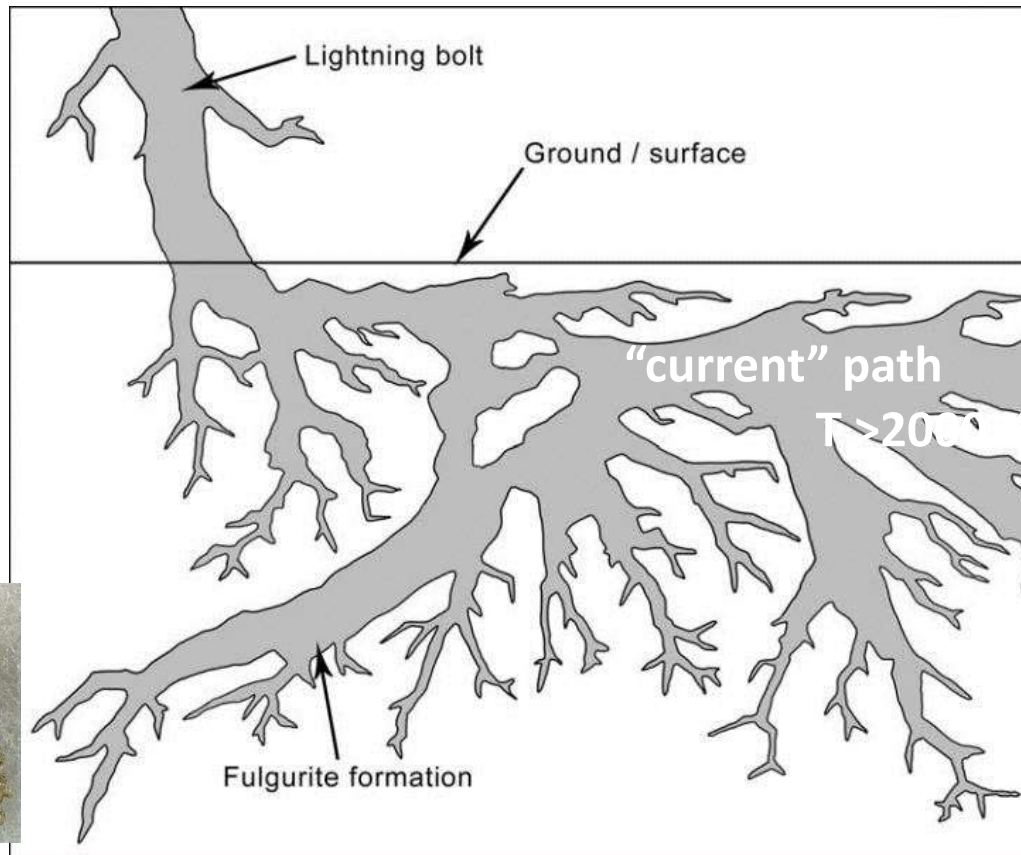
→ Mechanical/optical properties

Investigation of glasses formed under extreme conditions

Hyperquenching, meteorite impacts, lunar glasses and irradiation



Images from: Cicconi & Neuville 2019: *Natural glasses*. Springer Handbook of Glasses
Cicconi et al. 2021: *Non-Magmatic Glasses*. Review in Mineralogy and Geochemistry



Fulgurites

