



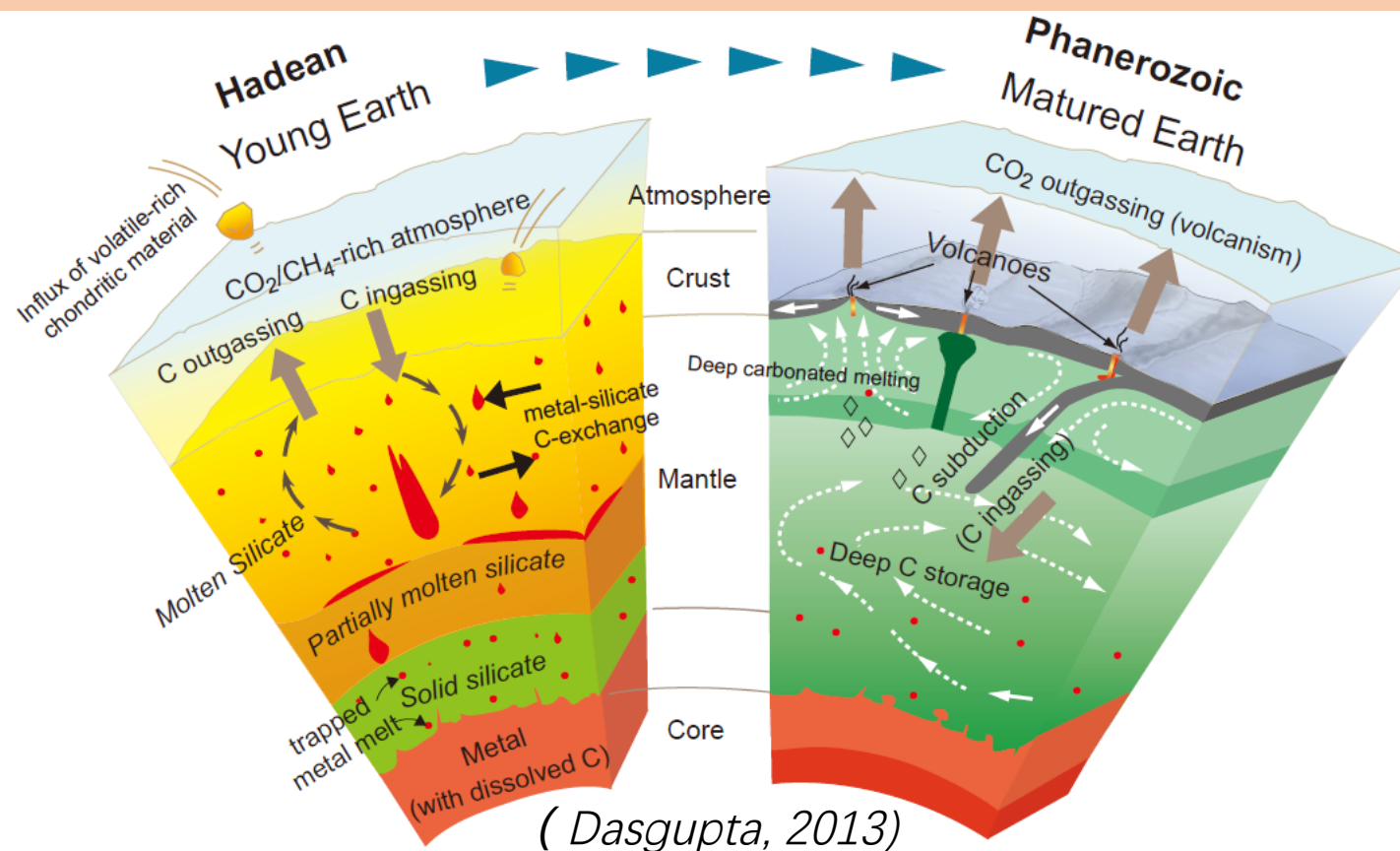
# The role of phlogopite in the deep Earth's water and fluorine cycles

Jiaqi Sun\*, Yan Yang, and Qunke Xia

Key Laboratory of Geoscience Big Data and Deep Resource of  
Zhejiang Province, School of Earth Sciences,  
Zhejiang University, Hangzhou, China

# Volatile cycles (e.g. H,S,C,F...)

- Volatile cycles between the surficial and deep Earth play a critical role in the evolution and habitability of the Earth.
- Most efficient way for volatiles to recycle into the mantle——**SUBDUCTION**





# During Subducting

- *Gradually accepted:*
  - Hydrogen and other volatiles are recycled into the mantle **mainly through subduction**
  - Volatile release depends on **stabilities of the host minerals** in subduction zones
  - Most subducted hydrous minerals are not only important water carriers, but also **other volatiles such as nitrogen and halogens carriers**
- *Still Unclear: The amount, location and mechanism* of these volatiles release during subduction ?
  - *Important and extensively investigated:* Stability of subducted hydrous minerals
  - *Little concerning:* Whether **OTHER VOLATILES** will influence dehydration and stabilities of hydrous phases? (e.g. Nitrogen, Fluorine...)

# Example : Nitrogen-Water cycle



Contents lists available at ScienceDirect

Earth and Planetary Science Letters

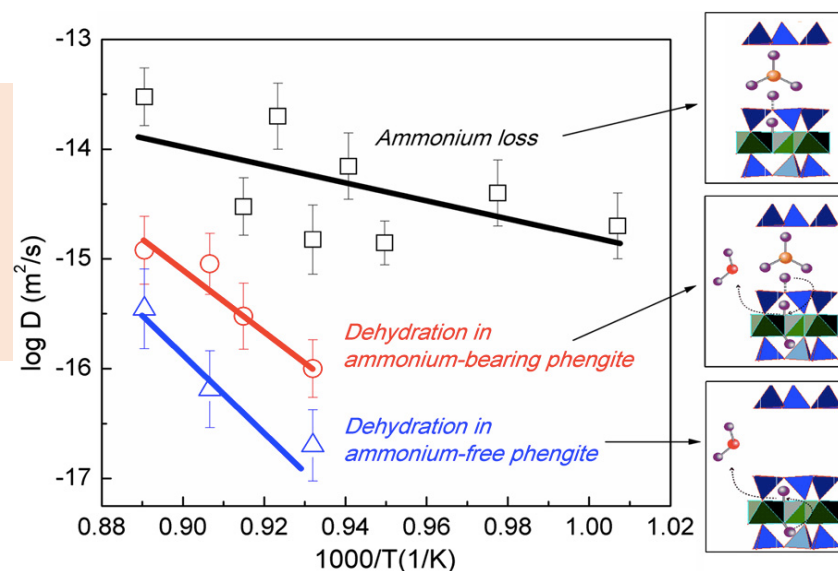
[www.elsevier.com/locate/epsl](http://www.elsevier.com/locate/epsl)

Intimate link between ammonium loss of phengite and the deep Earth's water cycle

Wendi Liu<sup>a</sup>, Yan Yang<sup>a,\*</sup>, Vincent Busigny<sup>b</sup>, Qun-Ke Xia<sup>a</sup>

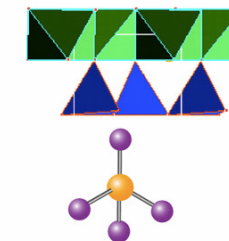
- Ammonium release from phengite:
  - Easier than dehydration
  - Promote dehydration

(Liu et.al, 2019)

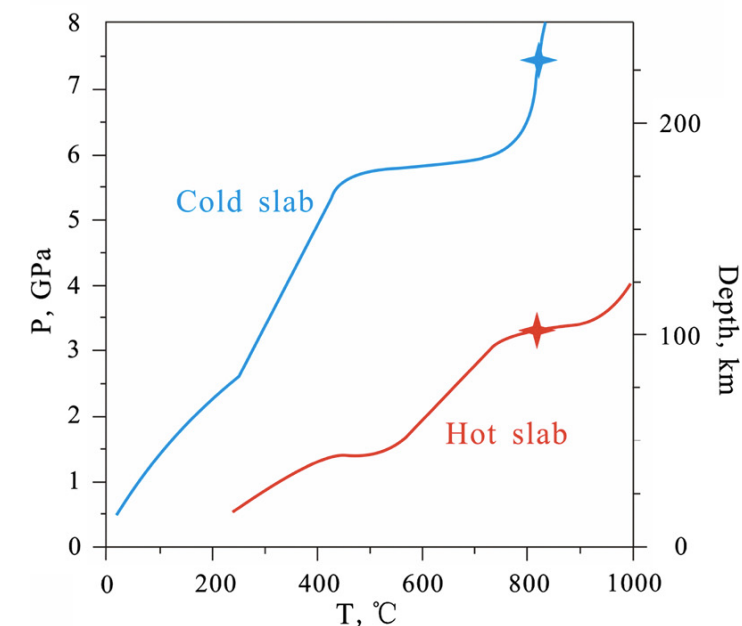
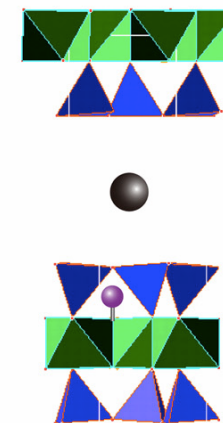


99% ammonium loss

32.5% dehydration



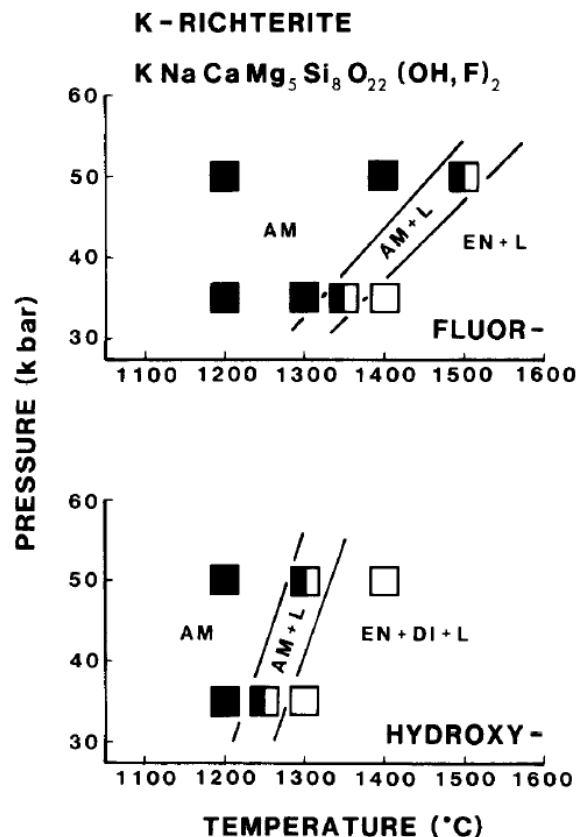
14.5% dehydration



# Fluorine can stabilize hydrous minerals

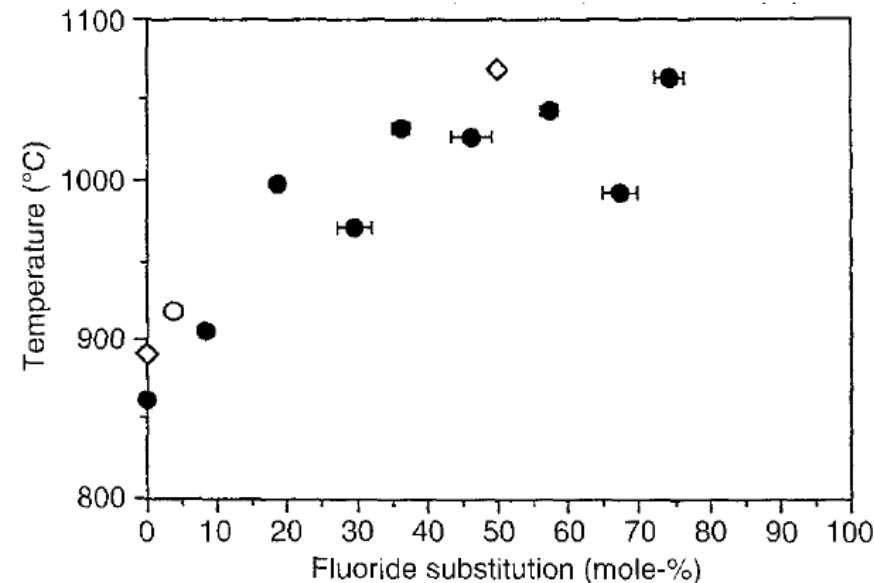
- It has long been noticed that fluorine substituting hydroxyl can make hydrous minerals such as amphibole, talc and clinohumite **MORE STABLE**.

(Foley, 1991)



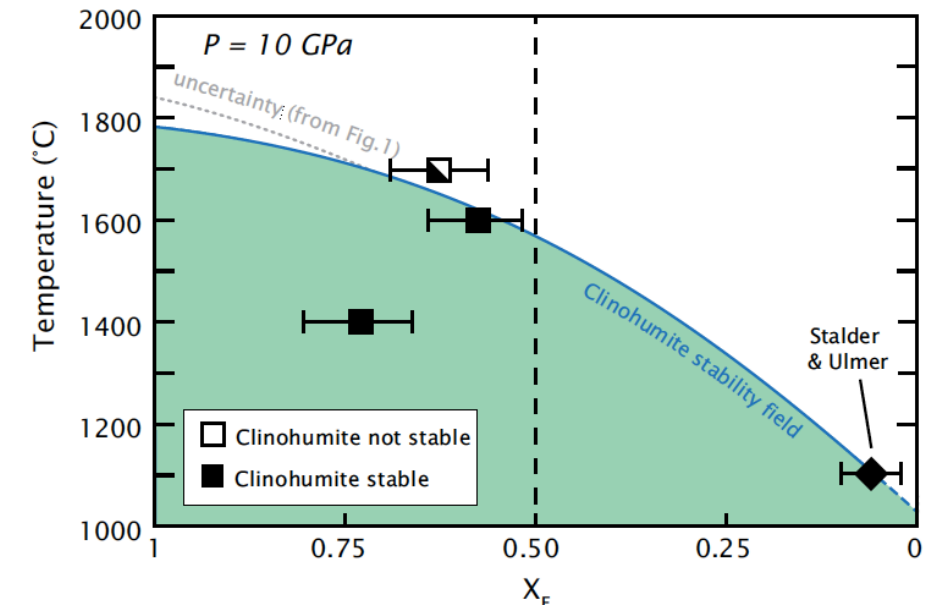
(Rywak & Burlitch, 1996)

The thermal stability of the talcs was studied using DT and TG, powder XRD, FTIR, and fluoride ion-selective electrode analyses. Synthetic talc without fluoride decomposed at 860 °C, whereas talc with 68% fluoride substitution showed essentially no decomposition when heated to 1060 °C. When heated to 1200 °C, 68% fluo-



(Grützner et al., 2017)

We show that even small amounts of  $\text{F}^-$  substituting for  $\text{OH}^-$  are sufficient to stabilize clinohumite to temperatures well above the normal mantle geotherm. Based on this finding we propose that in subduction

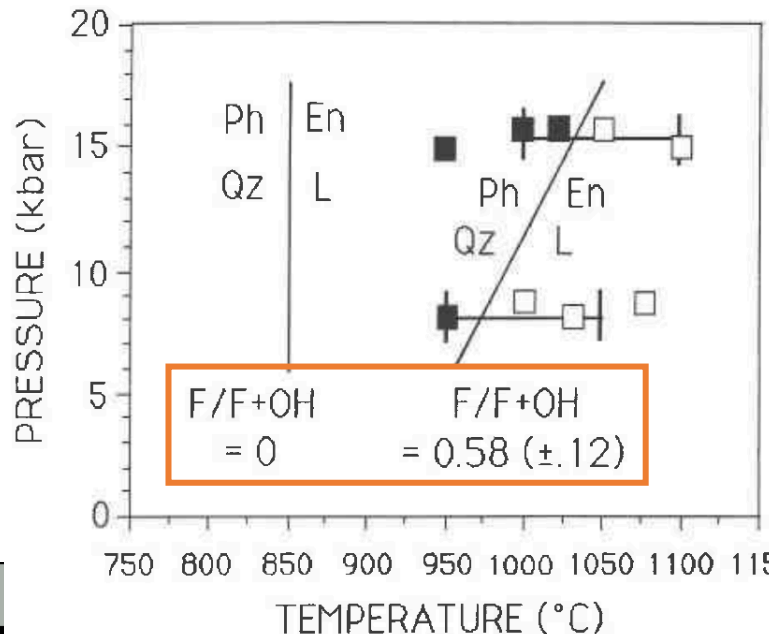


# Fluorine can stabilize phlogopite

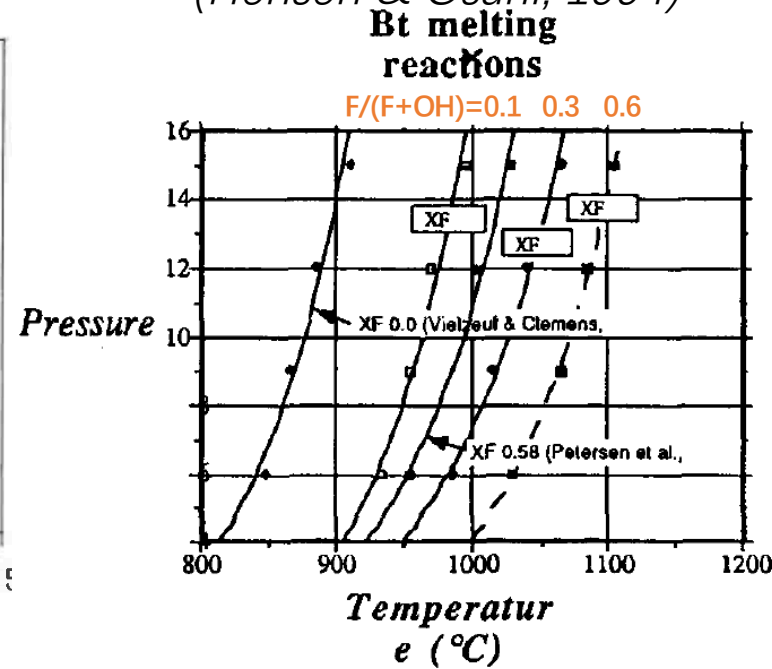
- Phlogopite:
  - ✓ An accessory mineral frequently found in mantle nodules
  - ✓ Fluorine can substitute for hydroxyl in phlogopite easily due to their similarity, thus is an important carrier of fluorine and water down to >200 km depth

Previous studies show that F markedly extends the thermal stability of biotite (phlogopite)

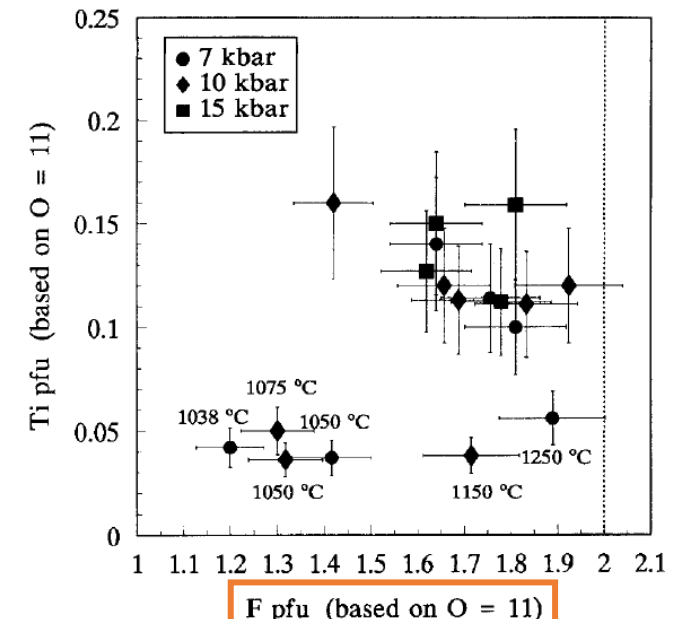
(Peterson et al., 1991)



(Hensen & Osani, 1994)



(Dooley and Patiño Douce, 1996)





# However...

- **Still unclear:**

- × Role of fluorine on the thermal stability ?
- × Mechanism of the stabilization ?



- **What we do:**

- ✓ Systematically investigate effects of fluorine on hydroxyl and lattice of phlogopite at high temperatures, to further understand fluorine effects on the stability of phlogopite.





# How we do ?

- Comparing two natural phlogopite samples with different fluorine contents

F-poor Phlogopite (0.20 wt% F)



F-rich Phlogopite (4.07 wt% F)

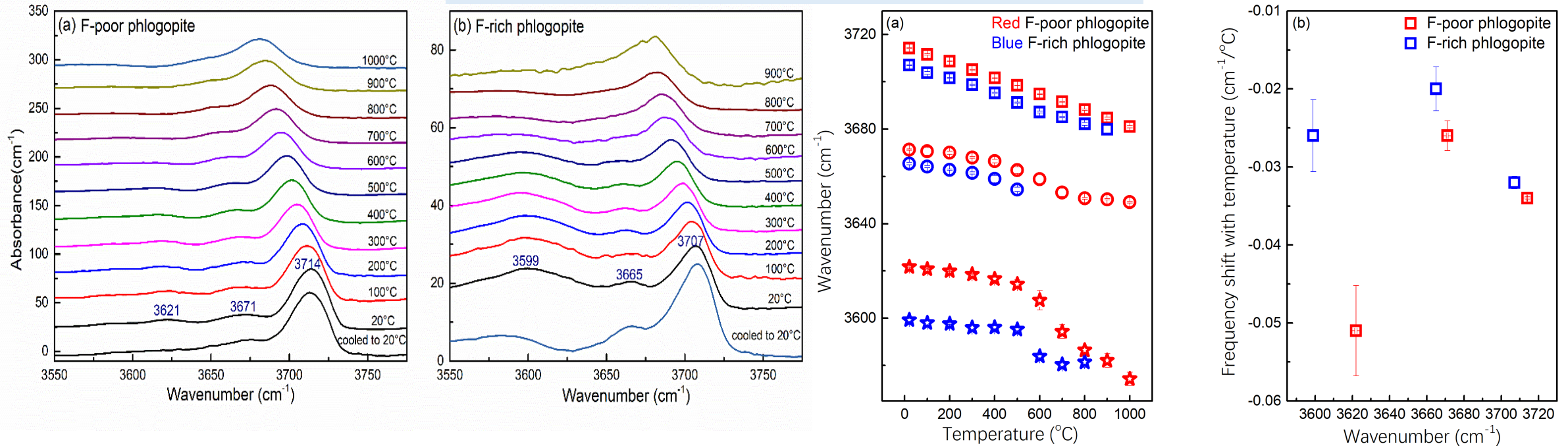


(F content analysed by EMPA in School of Earth Sciences, Zhejiang University, China)



# 1. Fluorine affects hydroxyl of phlogopite

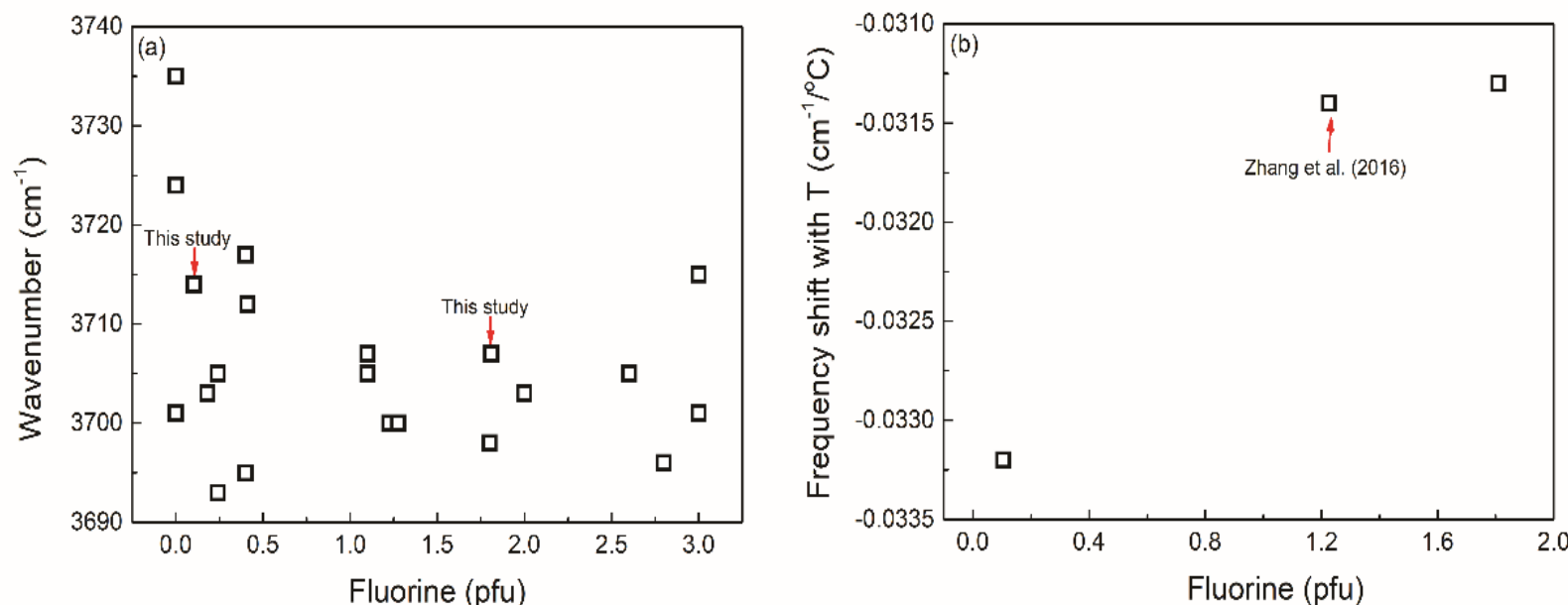
In-situ high-temperature FTIR up to 1000°C



- Three groups of OH band indicating different environments
- No distinct dehydration during the heating process up to 1000°C
- The amplitudes of temperature-induced frequency shifts of the three OH groups are larger for the fluorine-poor phlogopite than fluorine-rich phlogopite, suggesting potential effects of fluorine on O-H bonding strength



Combined with data from previous studies:



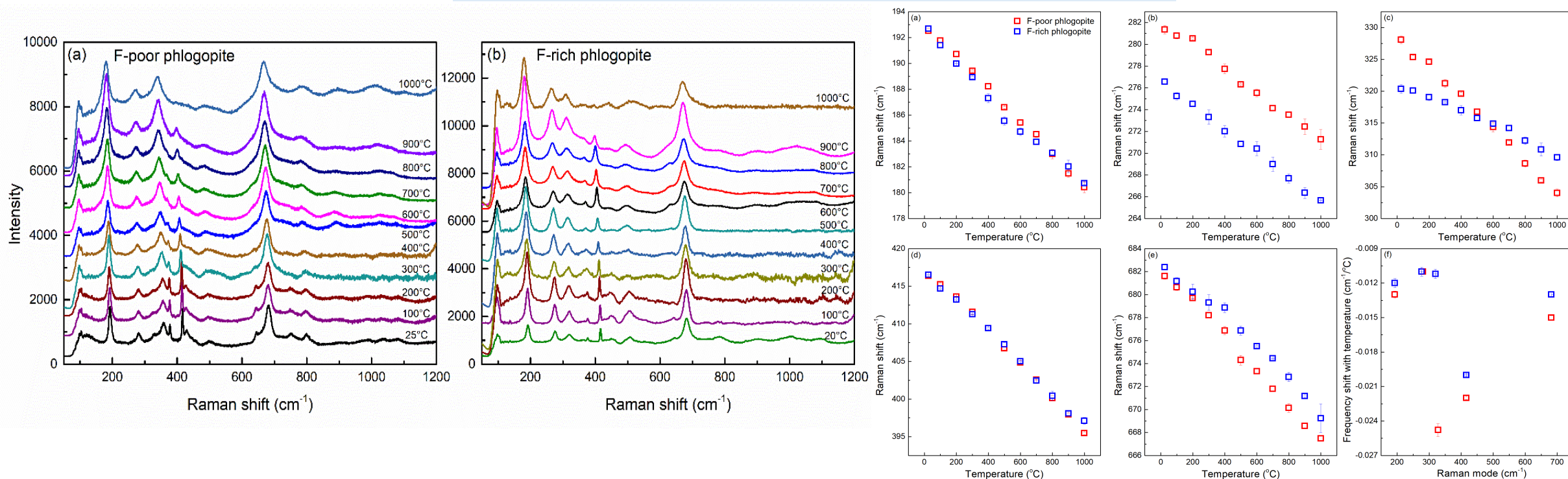
- With fluorine substitution increasing,
  - Frequencies of the OH bands decreases, indicating the enhanced strength of hydrogen
  - Amplitude of temperature-induced frequency shift decreases, indicating lower levels of O-H bonding weakening



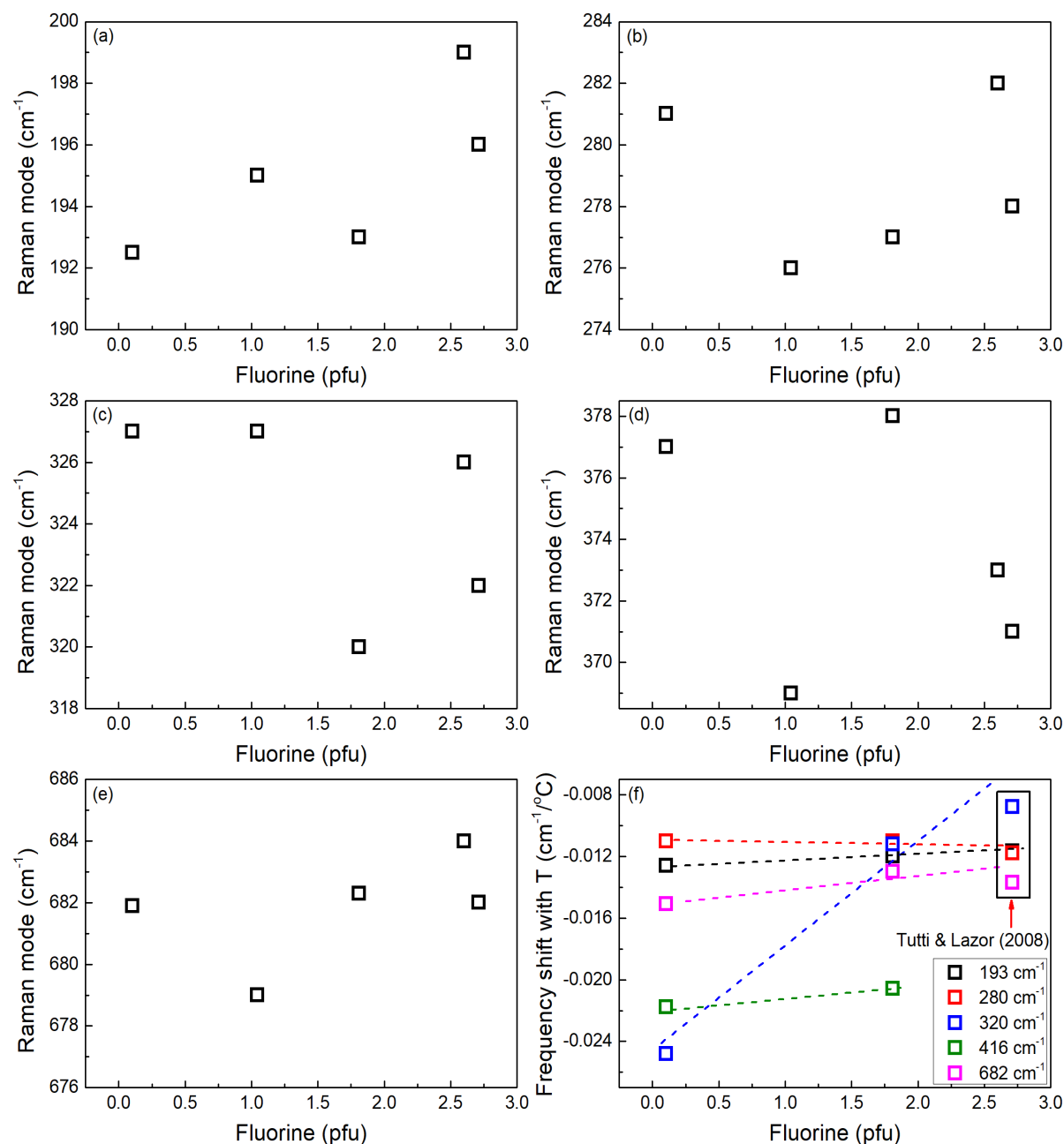
Fluorine can increase the thermal stability of hydroxyl in phlogopite

## 2. Fluorine affects lattice of phlogopite

In-situ high-temperature Raman up to 1000°C



- All modes shift continuously towards lower frequencies, indicating temperature-induced weakening of the lattice.
- No apparent turning points, indicating no structural phase transition occurring during the heating process.
- Temperature-induced frequency shifts for the fluorine-rich phlogopite are uniformly less than the fluorine-poor phlogopite, suggesting potential effects of fluorine on lattice modes of phlogopite.



- Incorporation of fluorine can increase frequencies of the Raman modes at 193 and 682 cm<sup>-1</sup>, suggesting that fluorine substitution can strengthen the lattice
- The amplitudes of temperature-induced frequency shifts of most modes are smaller for the sample with more fluorine, indicating fluorine substitution will delay the weakening of lattice at high temperatures and thus stiffen the lattice.



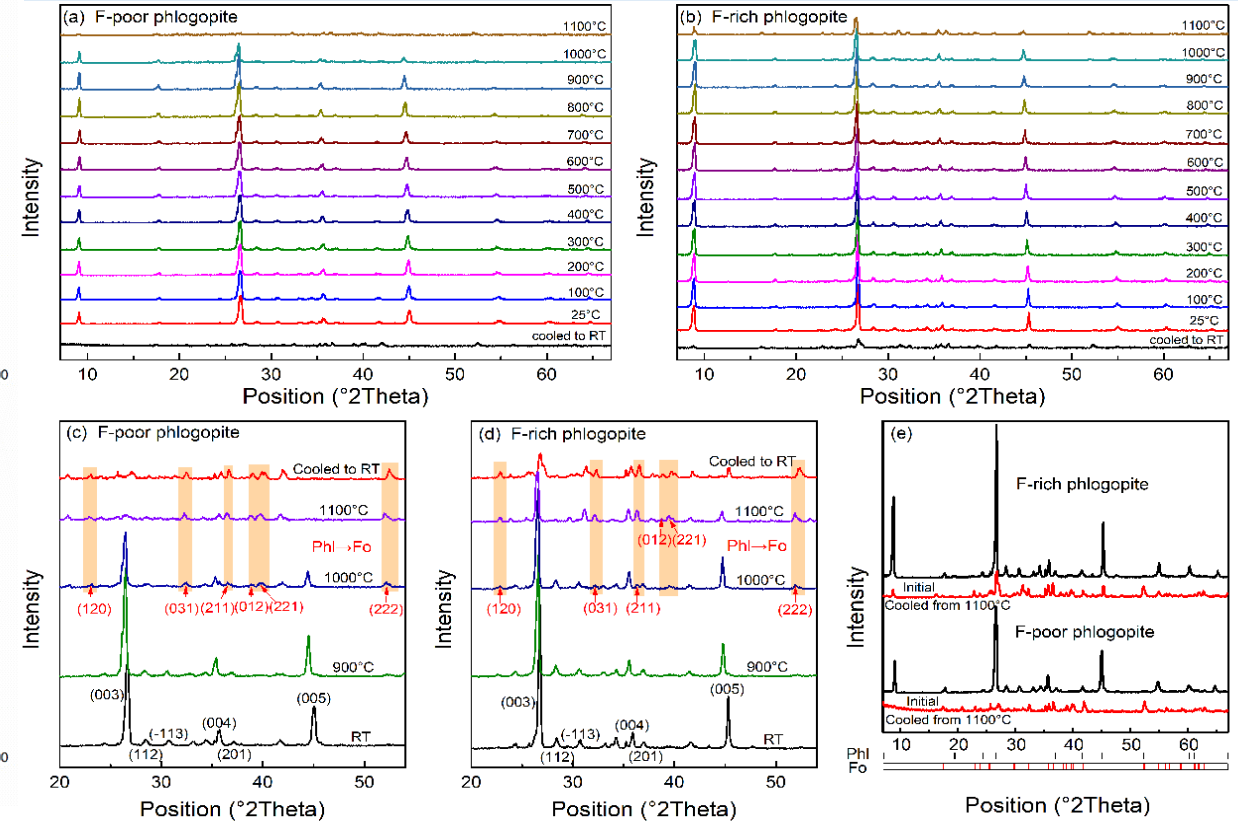
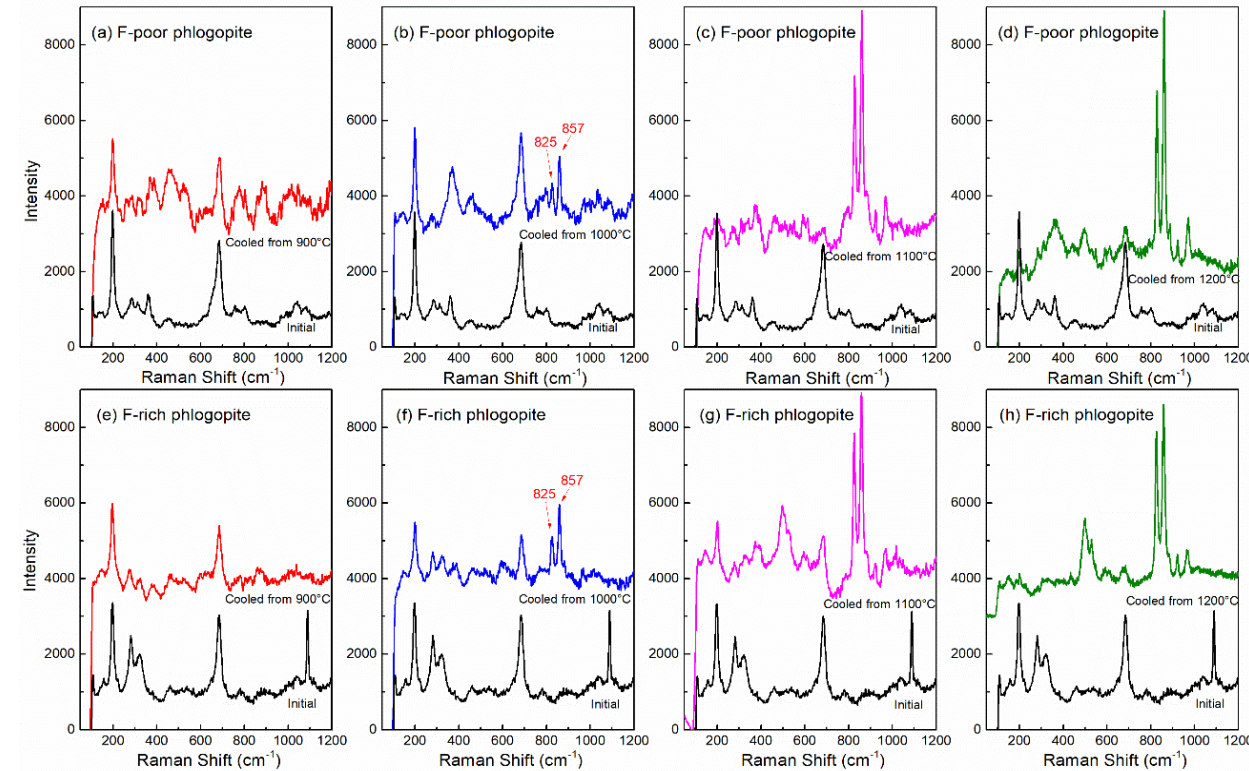
Fluorine can stiffen the lattice of phlogopite



# 3. Fluorine affects stability of phlogopite

High-T Raman up to 1200°C

High-T X-ray diffraction measurements up to 1100°C

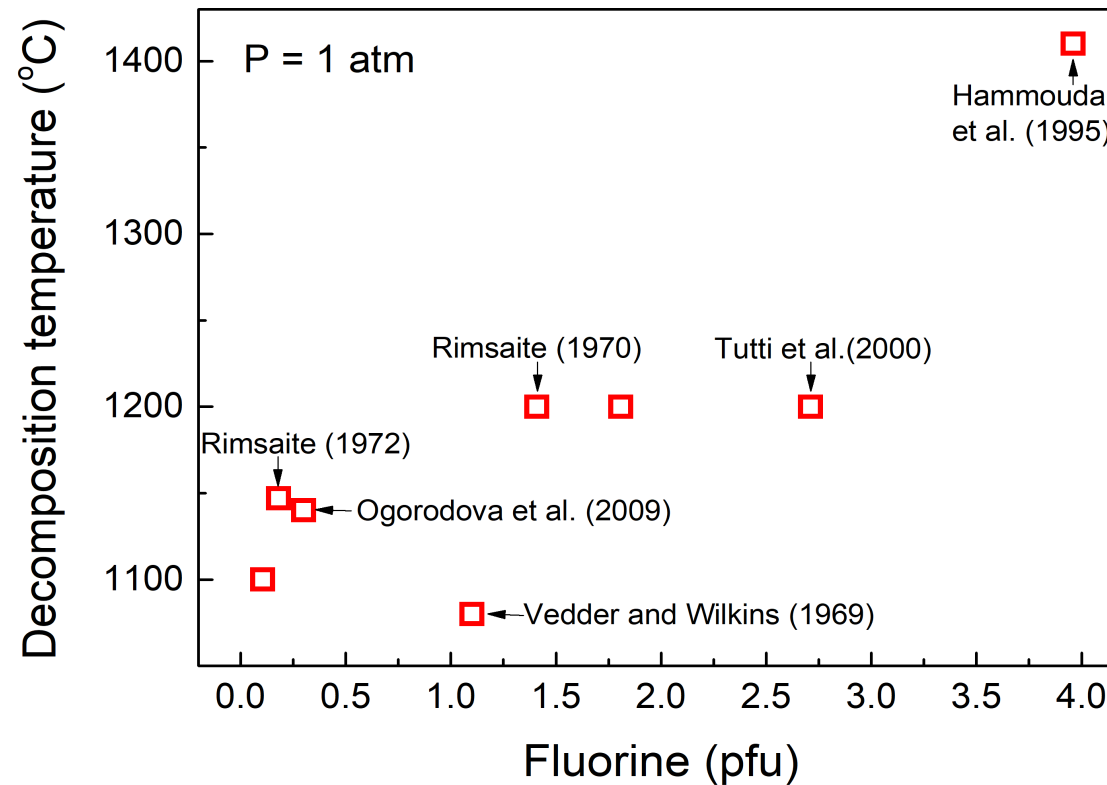


- Both phlogopites begin to decompose after heated to 1000°C
- F-poor phlogopite completely decomposed after heated to 1100°C, while F-rich phlogopite reached 1200°C





Complete decomposition temperature of phlogopite as a function of fluorine content at 1 atm from previous studies



Addition of fluorine can slow down the decomposition of phlogopite at high temperature



# Conclusions

- In situ high temperature infrared spectroscopy, Raman spectroscopy, and X-ray power diffraction results shows that the phlogopite with higher fluorine content has stiffer O-H bonding and lattice, which may be responsible for the stabilizing effect of fluorine to phlogopite at high temperature.
- *Implications:*
  - a) Fluorine-rich hydrous minerals can effectively transport both water and fluorine to the deep Earth;
  - b) Electrical conductivity in the deep Earth need considering effects of fluorine which is not only a charge carrier but also influences hydrogen conductivity.