Effect of saline fluids on chlorine incorporation in serpentine

Solid Earth Sciences(2018) 3, 61-66.

Authors:

Ruifang Huang, Xing Ding, Chiou-Ting Lin, Wenhuan Zhan, Mingxing Ling.

Student ： Liang, Yu-Hsin

Adviser：Prof. Lu, Yi-Chia

Date：2025/01/03

OUTLINE

- **Introduction**
- **Methodology**
- **Results**
- **Discussion**
- **Conclusions**

- Characteristics of Serpentine($Mg_3Si_2O_5(OH)_4$) ：
  - Serpentinization, a low-temperature (≤500°C) hydrothermal alteration of ultramafic rocks (like Olivine) in mid-ocean ridges and subduction zones. (Ulmer et al., 1995; Schmidt et al., 1998)
  - Serpentine is the main secondary mineral.
- Serpentine contains：
  - Contain up to 13.5 wt% water
  - Stable at depths of up to 150 km
  - Mobile fluid elements like **chlorine(Cl^-)**

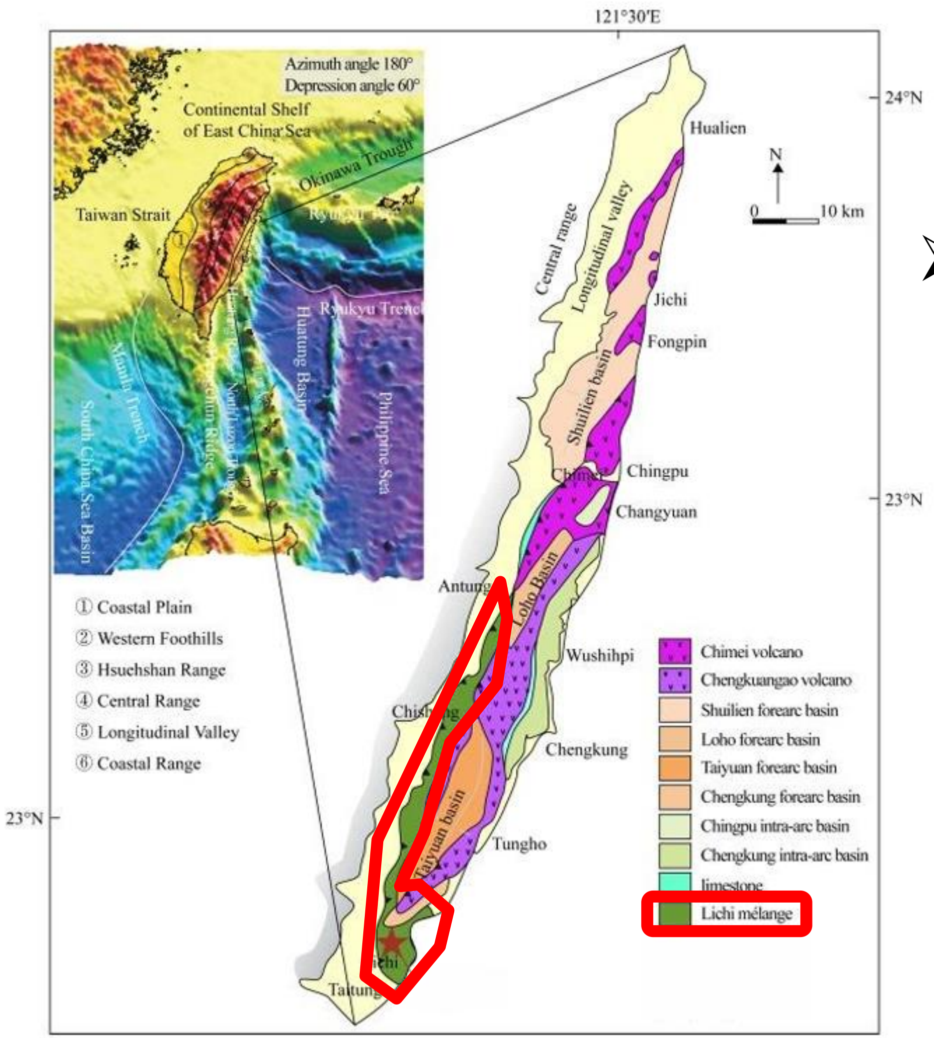
(Hattori et al., 2003)

(Miami Mining Co.,2023)

- Study the effect of different saline concentrations on chlorine content in serpentine.
- Compare chlorine binding forms (weakly-bound vs. structurally-bound) in varying salinity conditions.

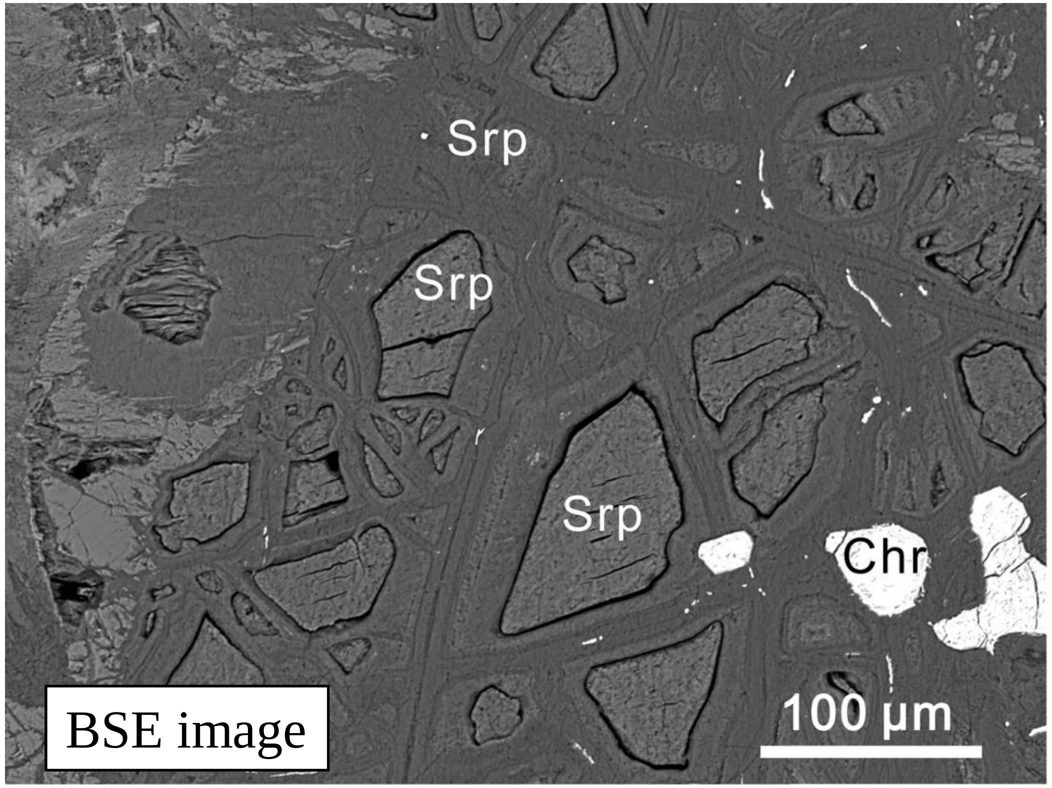
Feature	Weakly-Bound Sites	Structurally-Bound Sites
Location	Surface, pores, or crystal defects	Inside the crystal structure
Existence	Attached to surfaces or within pores	Embedded within the crystal structure
Bond Type	Physically adsorbed	Chemical bonding, replacing OH groups
Stability	Low (easily released)	High (hard to release)

(Sharp et al., 2004; Bonifacie et al., 2008)



(Modified from Huang CY et al., 2000)

- **Sampling Site：**
  Natural serpentinite from the Lichi mélange in eastern Taiwan , a geologically complex subduction zone with mélange rocks, sediment, and serpentinite.
- **Composition：**
  Over 95% serpentine , with minor magnetite(磁鐵礦) & chromite(鉻鐵礦)



Sample Preparation

- Ground Serpentine to 100-177μm
- Prepared **2.93, 8.78, 19.30 wt%** NaCl; 100 mg sample in 10 ml each deionized water

Experimental Conditions

- Normal temperature and pressure, equilibrated for 18, 30, 43 days
- Washed in 20 ml pure water for 24 hours

Analysis

- JEOL JXA-8100 electron microprobe, 15kV, 20nA ,15μm beam
- Cl detection limit：33ppm , calibrated with STD minerals

JEOL JXA 8100 electron microprobe(figure from USTB)

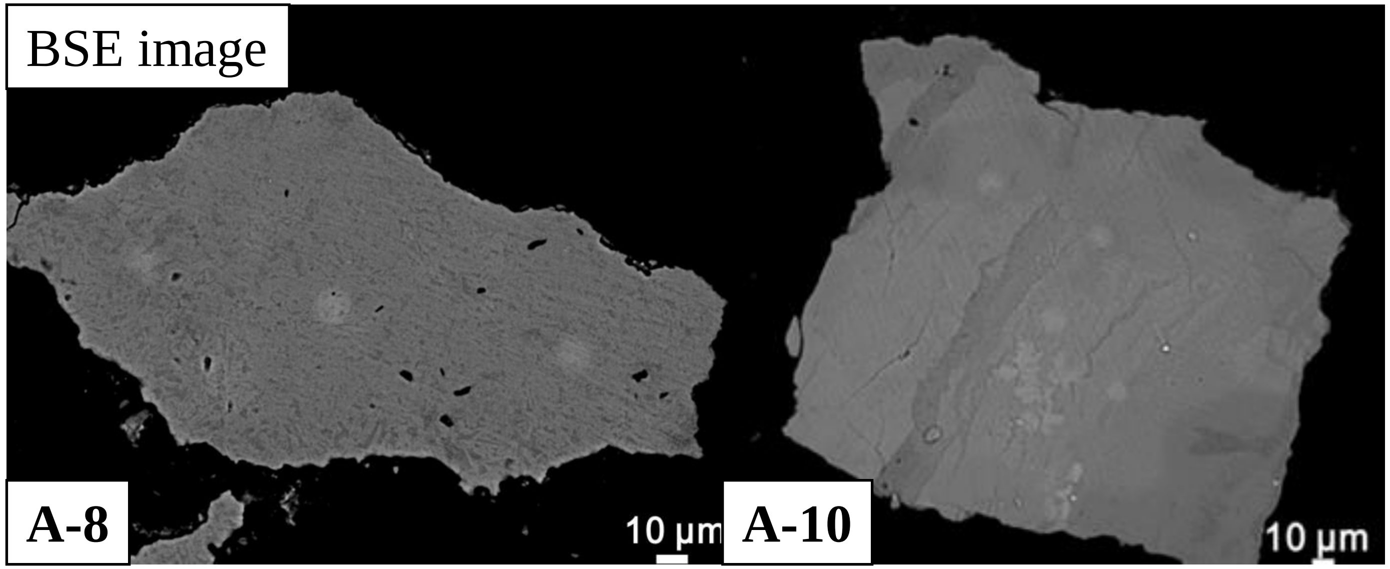
	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	MgO	FeO	CaO	MnO	CoO	NiO	Cl	Total
Average	**42.73**	**0.00**	**0.62**	**0.05**	**38.41**	**3.73**	**0.12**	**0.05**	**0.00**	**0.23**	**0.017**	**85.94**
Stdev	**±1.08**	**0.00**	**±1.14**	**±0.11**	**±1.34**	**±0.66**	**±0.03**	**±0.01**	**0.00**	**±0.06**	**±0.009**	**±1.07**

Sample no.	NaCl solution (wt%)	Days	Cl in serpentine (wt%)
A-8-1	2.93	18	0.077±0.033
A-8-2		30	0.073±0.049
A-8-3		43	0.075±0.055
A-9-1	8.78	18	0.059±0.018
A-9-2		30	0.045±0.016
A-9-3		43	0.059±0.036
A-10-1	19.30	18	0.053±0.015
A-10-2		30	0.054±0.017
A-10-3		43	0.073±0.028

Sample no.	NaCl solution (wt%)	Days *after rebalancing in pure water	Cl in serpentine (wt%)
A-8-4	2.93	45	0.033±0.013
A-9-4	8.78	45	0.032±0.013
A-10-4	19.30	45	0.060±0.021

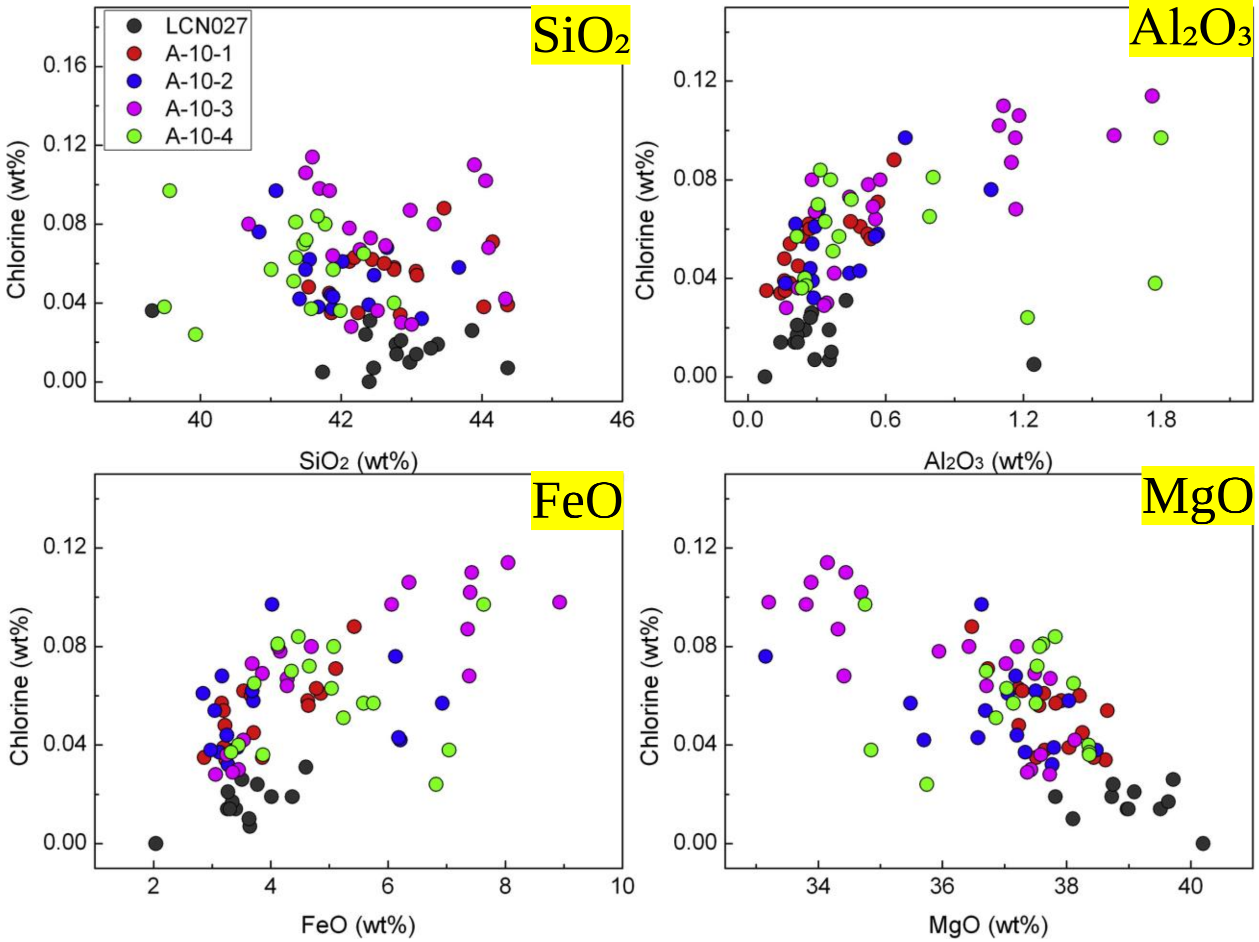
- Previous studies suggest main way for chlorine enters serpentine minerals：
  - Chlorine enters as submicroscopic particles, like $Fe_2(OH)_3Cl$, $MgCl_2 \cdot 6H_2O$ or NaCl.

(Rucklidge et al., 1977; Sharp et al., 2004)



Using BSE imaging, **NO** $Fe_2(OH)_3Cl$, salt minerals, or particles were observed in the images.

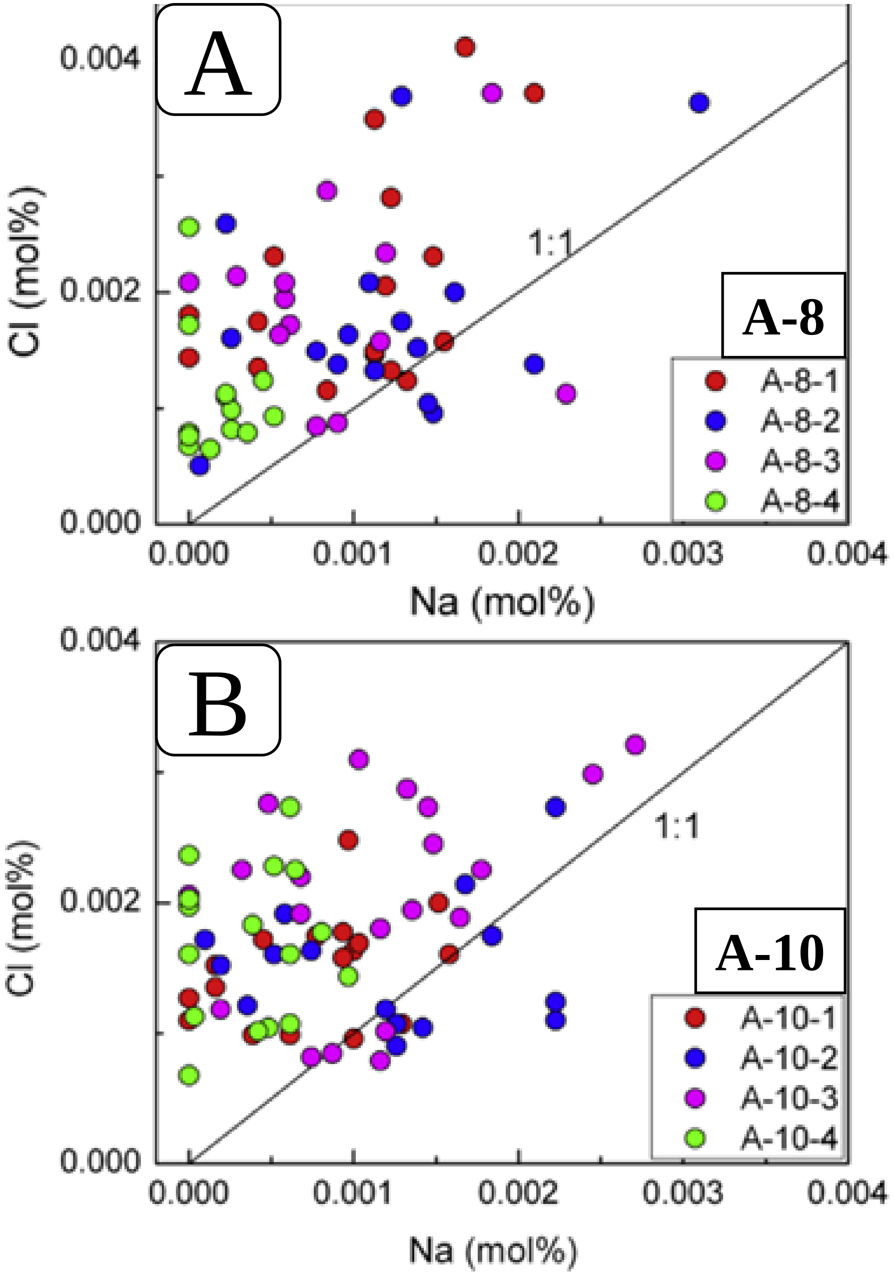
Further studies with SEM and TEM also found no clear evidence of other salt minerals within the serpentine, so these possibilities can be **ruled out**.



A-10(19.30wt%NaCl)

- Negative Correlation with SiO_2 and MgO：Indicates that **more stable** crystal structures make **it harder for chlorine to enter.**
- Positive Correlation with Al_2O_3 and FeO：Al can replace Mg or Si, and Fe can partially substitute Mg. which the substitution destabilizes the crystal lattice, making it easier for chlorine to enter.

- If $MgCl_2 \cdot 6H_2O$ existed, chlorine would show a positive correlation with MgO, which was not observed.



- The 1:1 line indicates equal molar ratios, which would suggest NaCl formation, chlorine and sodium are positively correlated, but most data points fall above the line, ruling out NaCl formation.
- Using the BSE images show **NO** NaCl minerals, confirming **NO** salt minerals formed.

- This study look at the effect of saline solutions on chlorine supply in serpentine under conditions over 18 to 43 days.
  - Low salinity (2.93 wt% & 8.78 wt% NaCl): Chlorine mostly exists in weakly-bound sites, easily released during pure water rebalancing.
  - High salinity (19.30 wt% NaCl): Chlorine is in the main structurally-bound, showing high stability and minimal release after rebalancing in pure water.
- **High-salinity** environments **promote chlorine incorporation into serpentine's structure** as stable, structurally-bound chlorine.
- This highlights serpentine's role as a major chlorine reservoir in subduction zones, helping chlorine transport to Earth's deep interior.

Thanks for your listening

Journal of Asian Earth Sciences 145 (2017) 101–110

Contents lists available at ScienceDirect

Journal of Asian Earth Sciences

journal homepage: www.elsevier.com/locate/jseaes

Full length Article

Influence of temperature, pressure, and fluid salinity on the distribution of chlorine into serpentine minerals

Ruifang Huang[a,b,*], Weidong Sun[a], Wenhuan Zhan[b], Xing Ding[c], Jihao Zhu[d], Jiqiang Liu[d]

[a] *Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 510640 Guangzhou, PR China*
[b] *Key Laboratory of Marginal Sea Geology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, 510301 Guangzhou, PR China*
[c] *State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 510640 Guangzhou, PR China*
[d] *The Second Institute of Oceanography, SOA, Hangzhou 310012, PR China*

Importance of Chlorine：

Chlorine-rich fluids released from serpentine during high-temperature dehydration in subduction zones transport incompatible elements such as Ba, Cs, and Pb into the mantle, promoting partial mantle melting and influencing arc magma composition, while also carrying deep Earth water and element cycling.

(Scambelluri et al., 1997；Hattori and Guillot, 2003；Deschamps et al., 2012)

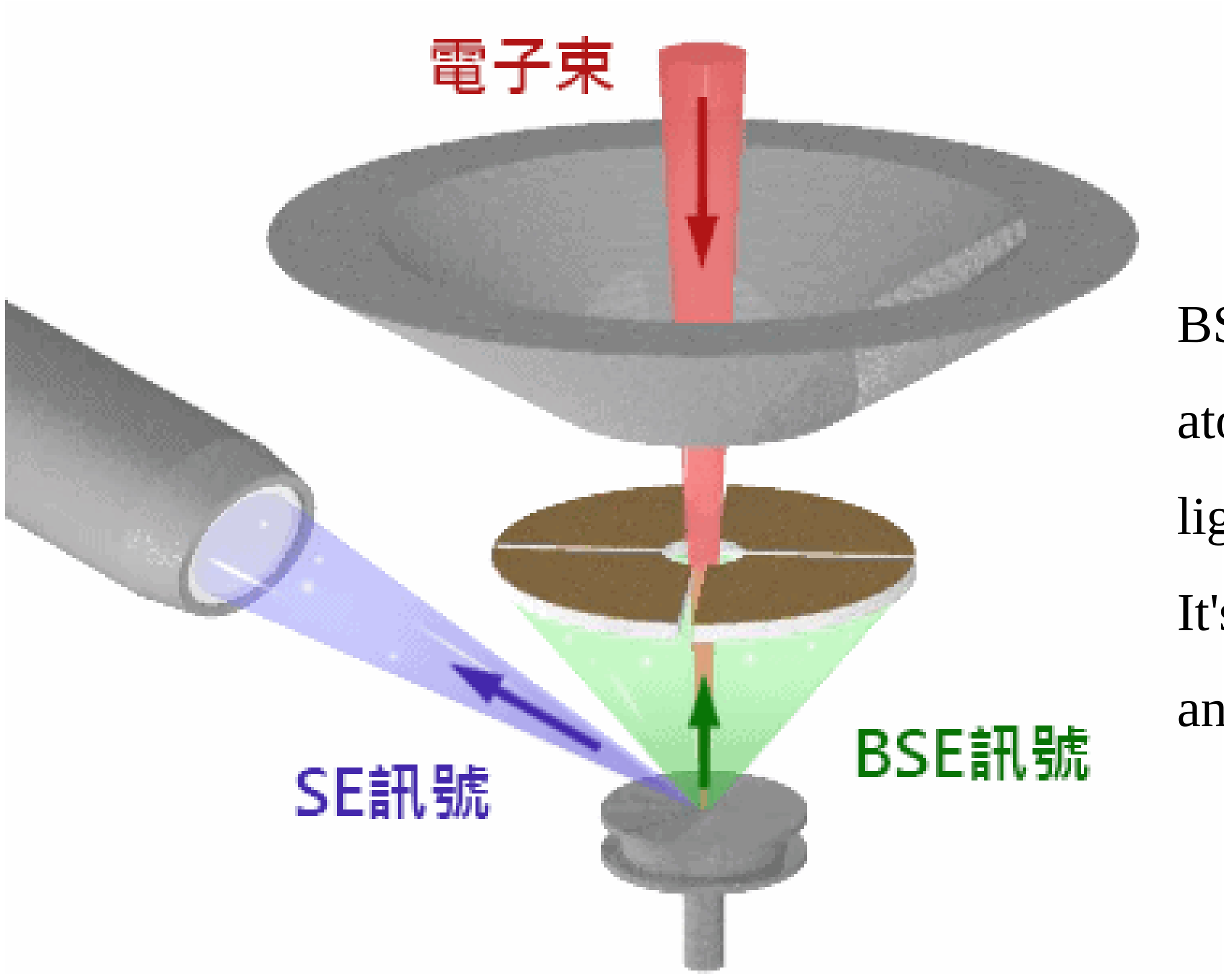
JEOL JXA-8100 electron microprobe：

The instrument uses a high-energy electron beam to excite signals from elements in the sample for analysis.

Settings: A voltage of 15 kV and current of 20 nA make sure stable beam energy and enough penetration, improving accuracy.

Beam Characteristics: The 15-micron beam diameter allows precise analysis of very small areas.

Sensitivity: It can detect trace amounts of chlorine down to 33 ppm, which is critical for studying variations in chlorine content in serpentine.



BSE imaging highlights brightness differences based on atomic number：heavier elements appear brighter, while lighter elements appear darker.

It's ideal for quickly analyzing the chemical composition and structural distribution of rocks, minerals, and materials.

SEM, (Scanning Electron Microscope)

It uses an electron beam to scan a sample's surface, providing high-resolution images of its structure down to the micro- and nanoscale.

It's great for studying tiny details and identifying the elements in a material.