Abundant Volatiles in Sub-continental Lithospheric Mantle

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Outline

1. Our Understanding of the Mantle Volatiles
2. Samples and Method
3. Occurrence Modes of Volatile in Earth Mantle
4. Chemical Compositions of Volatile in the Sub-continental Lithospheric Mantle
5. Summary

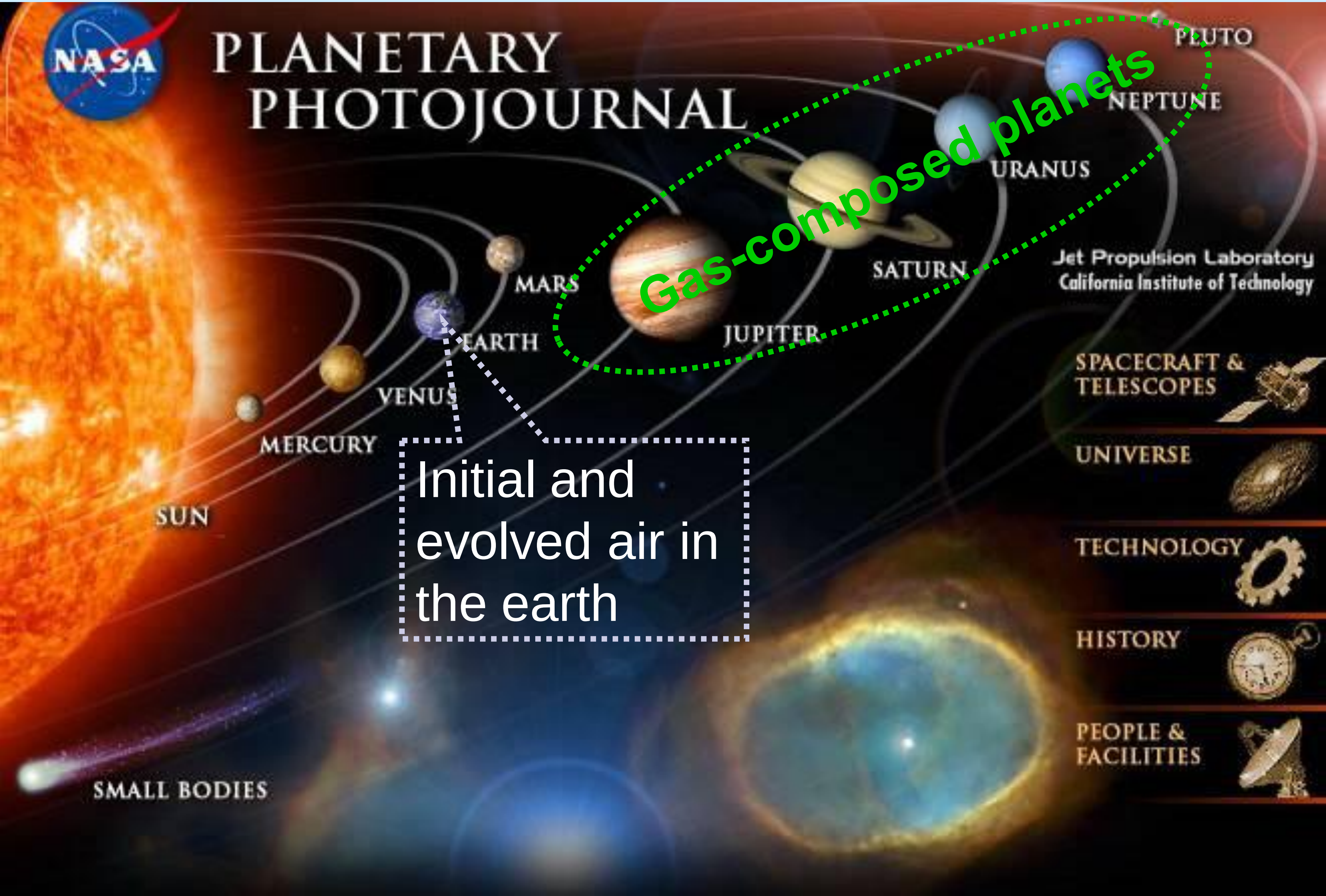
1. Significances of the Volatiles

1.1 Volatiles are major components in the Solar system.

1.2 Volatiles play the important roles in chemical differentiate, heat-mass transport and surface environmental events in the Earth.

1.3 Mantle volatiles vary in stable isotopes and noble gas isotopes with tectonic settings and mantle sources.

1.1 Volatiles in the solar system



Atmosphere compositions of Earth-like planets

	Nitrogen	Oxygen	Argon	Carbon dio	Neon	Helium	Methane
Earth	N2	O2	Ar	CO2	Ne	He	CH4
Gas(Volume/ppm)	780900	209500	9300	300	18	5. 2	1. 5
Gas(Weight/ppm)	755100	231500	12800	460	12. 5	0. 72	0. 94
abundance(ppm by	780840	209460	9340	330	18. 18	5.24	2
Percent Volume	78. 1	20. 9	0. 9	0. 03	0. 0018	0. 0005	0. 0002
Mars(V%)	2. 7	0. 15	1. 6	95			
Venus(V%)	3. 5	<=0.002	0. 007	96. 5	0. 0007	0. 001	

1.2 Significances of Volatiles in Earth Interiors

Volatiles are more active than solid elements during geochemical system, and play important roles in following processes:

1) The **chemical differentiation** of the Earth's mantle primarily by means of mantle degassing, metasomatism, magma generation and evolution

2) The **transport of heat** (Spera, 1981; O'Reilly and Griffin, 2000) and major and trace **elemental exchanging** (Schneider and Eggler, 1986; Eggler, 1987)

3) The **interaction** between atmosphere, hydrosphere of earth with lithosphere mantle (Hilton, 2009).

1.2.1 The Type of Mantle Volatiles

The volatiles are in supercritical state under high temperature and pressure of ambient Earth's mantle, including:

- Inorganic C-H-O-S gases: stable isotopic tracing system;
- Hydrocarbon gases;
- Noble gases: excellent tracers.

1.2.2 Origins of Mantle Volatiles

Volatiles in the mantle are mixtures of primordial volatiles and recycled volatiles with characteristic chemical compositions

- Some volatiles are **primordial** from condensing during Earth formation.
- Some are **recycled** from atmosphere, hydrosphere and crust by plate subduction.
- Some are subsequently **radioactive ingrowths**.

1.2.3 The residence sites of volatiles in the mantle

Mantle volatiles occur in various forms such as:

- free element or molecular species along grain boundaries, dissolved volatiles in melts or interstitial solid solutions, and leak up to the surface (Hilton, 2009).
- complex anions incorporated in carbonate, sulfide or hydrous minerals,
- but most mantle volatiles are stored as fluid inclusions or charged species dispersed in structural site (e.g., OH-), defects or vacancies of nominally anhydrous minerals (NAMs).

1.3 Deriving questions in Mantle volatiles

(1) Volatiles in mantle minerals have long been thought to reside primarily in:

- Various types of fluid inclusions;
- Anion complexes in structural sites of hydrous minerals (e.g., OH- in amphibole, mica and Cl- and F- in apatite etc.) as well as nominally anhydrous minerals (e.g., OH- in Olv, Opx, Cpx,Grt).
- Structural defects and vacancies of mantle minerals.

The main occurrence modes of mantle volatiles is fluid inclusions, or others?

1.3 Deriving questions in Mantle volatiles

(2) Volatiles in the sub-continental lithospheric mantle (SCLM) are still poorly understood, especially in the chemical compositions.

The geochemical implications of chemical compositions of mantle volatiles are variable and depend on …?

2. Methods

2.1 Samples and pretreatments

2.2 Experiments

2.1 Samples for Mantle Volatiles

Mantle volatiles can be rarely sampled directly. Hot-springs, summit fumaroles, mantle derived melts (e.g., basalt, kimberlite and lamprophyre), diamonds, mantle xenoliths, ultramafic intrusions and ophiolitic peridotites are all used to characterize mantle volatiles.

Diamonds that act as an impermeable capsule for a variety of volatiles and fluid inclusions offer a unique insight into the physicochemical evolution of volatiles in deep portions of the SCLM,

Mantle xenoliths brought to the surface by alkali basalts are the only materials that allow us to investigate how volatiles reside in mantle minerals.

Studied samples

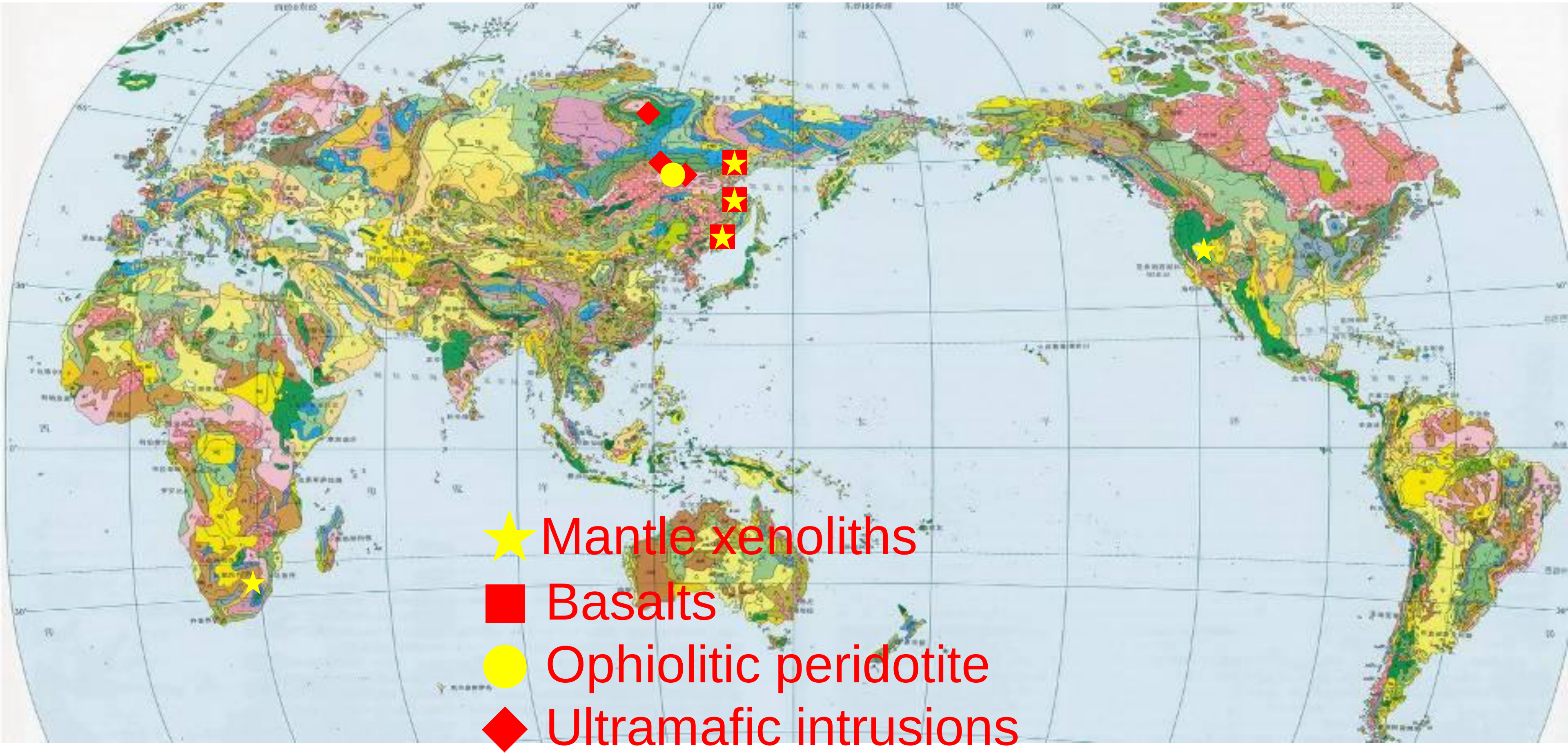
We have collected and measured by same experimental procedures of stepwise heating method the chemical and isotopic compositions of volatiles in:

(1) Mantle xenoliths in basalts and kimberlite in China, USA and south Africa,

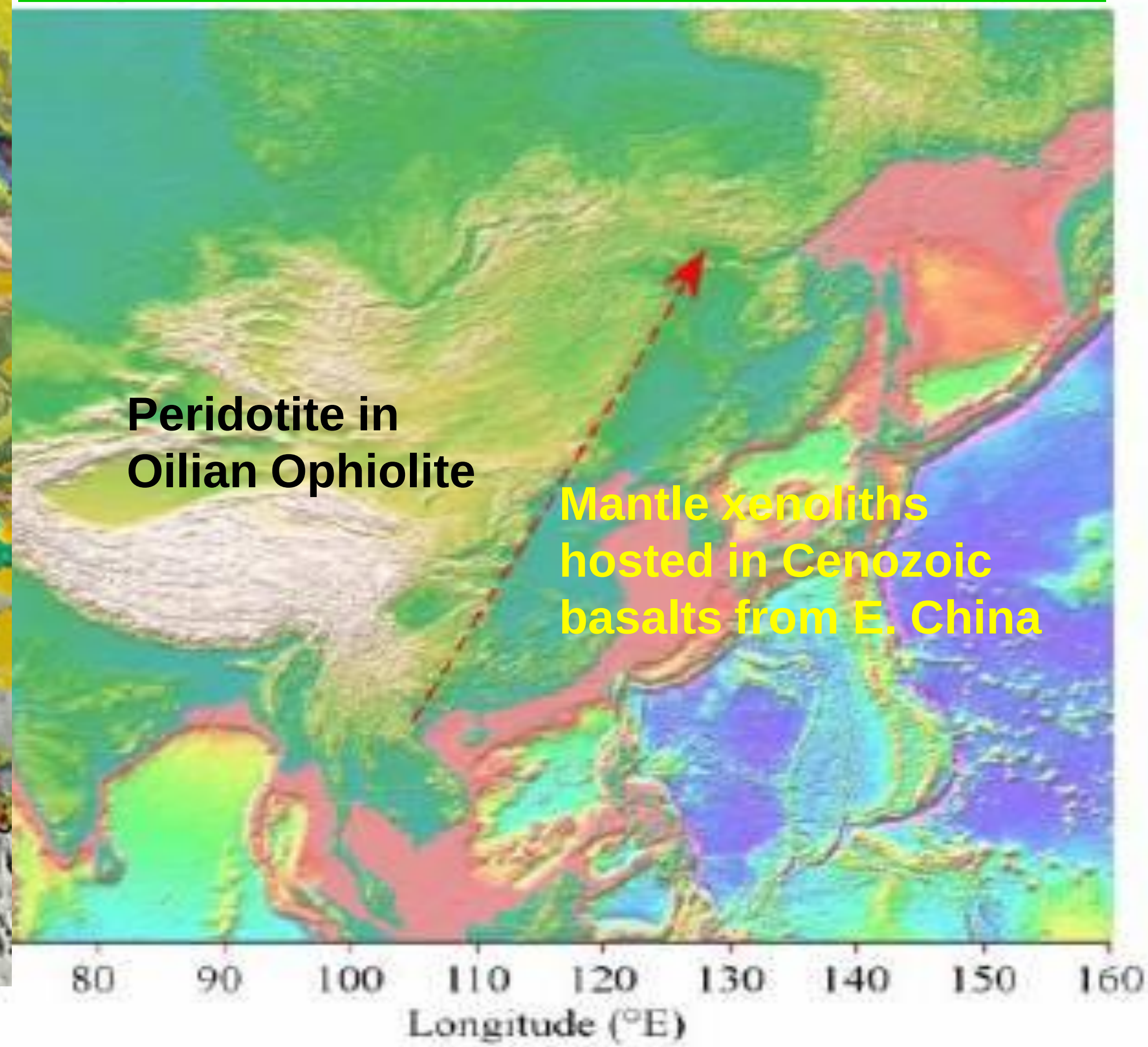
(2) Ophiolitic peridotites from Qilian orogenic belts,

(3) mafic-ultramafic rocks in magmatic Cu-Ni-PGE sulfide deposits in China and Russia.

Localities of studied samples



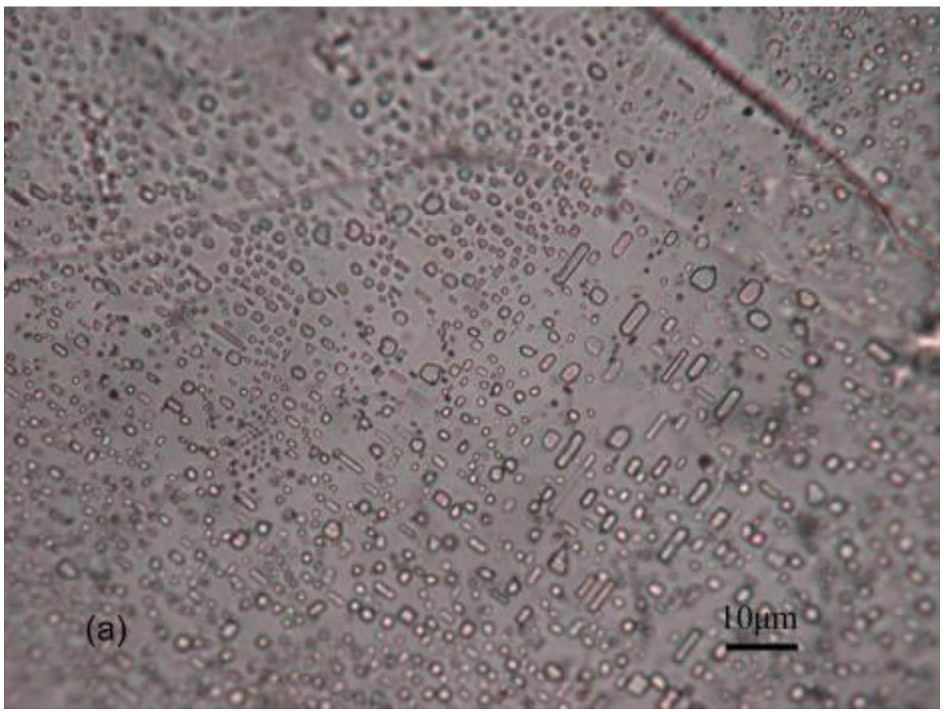
Mantle Xenolith Samples

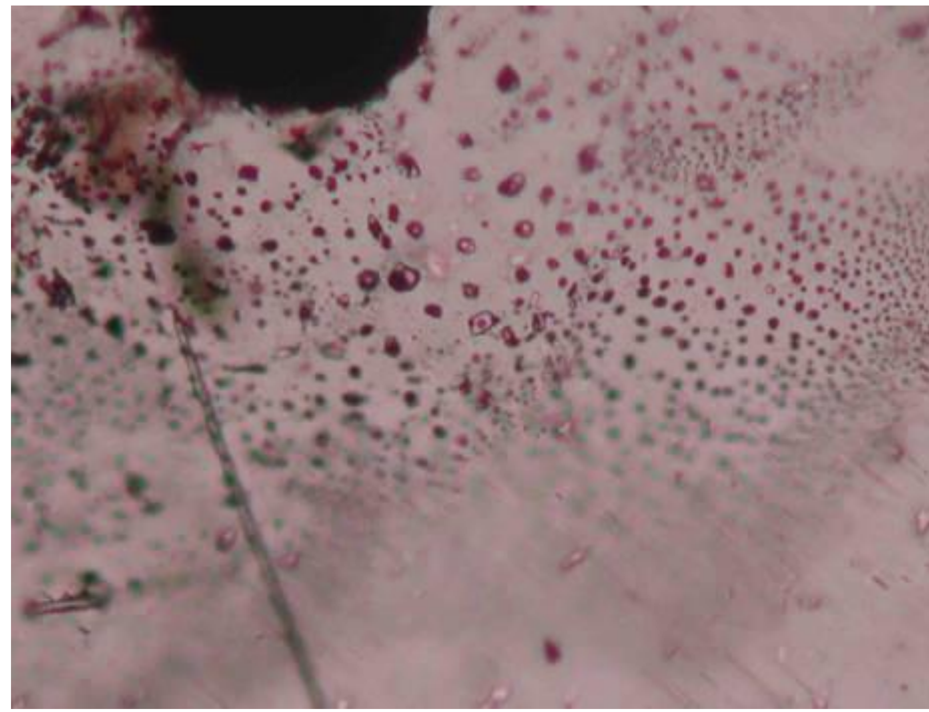


a Portion of world topography

Early stage of fluid inclusions

usually containing melt/glass are small (5~ 20μm in diameter) with regular shapes (e.g., oval, egg or negative crystal), in the cores and distributed along crystal lattices of the host minerals

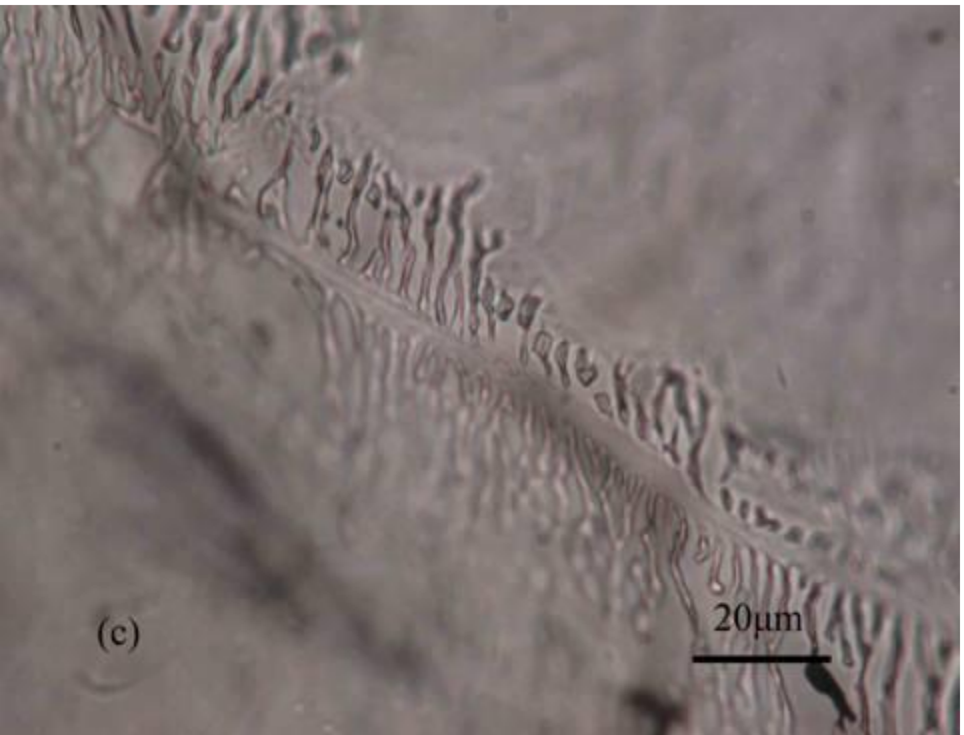


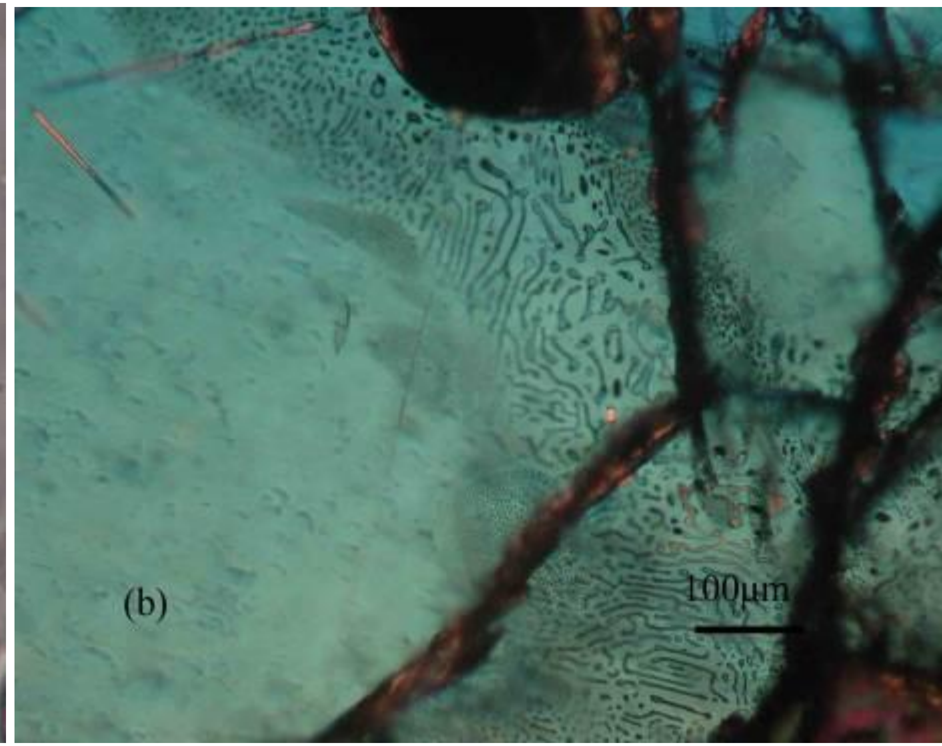


50×20(+)

Late-stage of fluid inclusions

They are large (10 to 100μm in diameter or length) with irregular shapes (e.g., tree-branch, bead-string or tabular), located in healed micro-fractures or cracks at edges of host crystals





50×20(+)

Pretreatments

Olivine (Olv), orthopyroxene (Opx) and clinopyroxene (Cpx) **mineral separates** from the lherzolite and pyroxenite xenolith with crushing size of 0.5-1 mm were **hand-picked** under a binocular to ensure free of alteration. Purity was in excess of 95%.

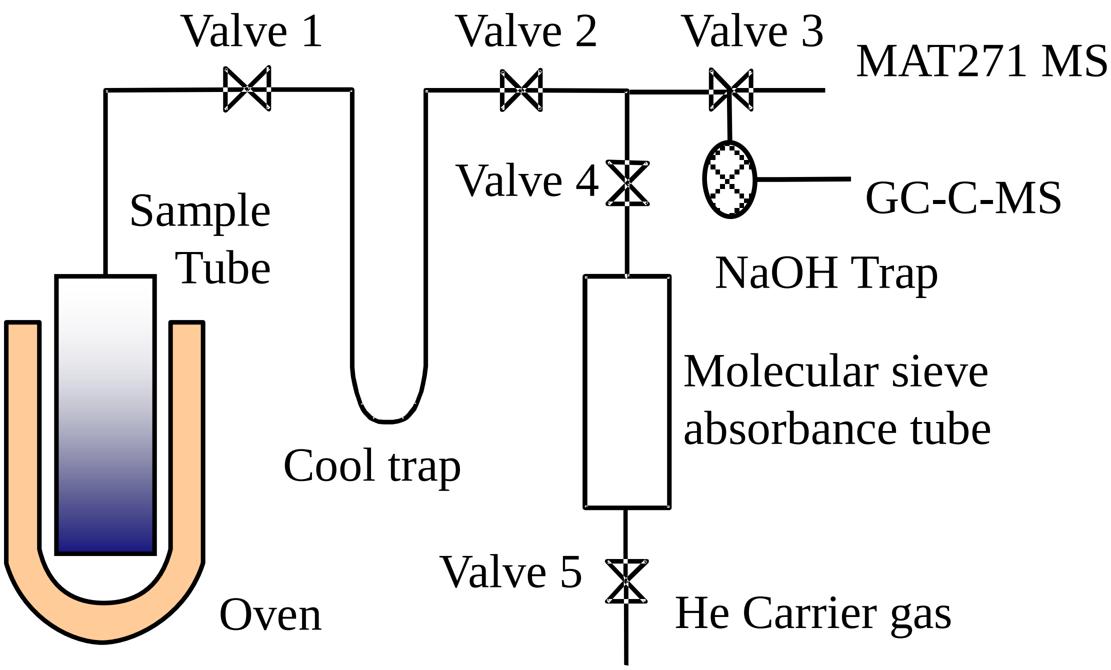
The samples for occurrence modes were divided into six aliquots, and **crushed and sieved** to sizes of 0.9, 0.3, 0.2, 0.1, 0.06 and 0.03mm, respectively.

The mineral separates were **ultrasonically cleaned** with 0.3mol/L HCl, followed by rinsing with distilled water until pH value reaches around 7, then ultrasonically cleaned with analytical grade CH2Cl2 and acetone, respectively, before being finally dried at 110° C.

2.2 Analytical Procedures

- Each sample was loaded into a quartz tube and preheated with high-purity O_2 gas at 200° C for 4 hours and then outgassed under ultrahigh vacuum (1×10^{-8} Pa) for 4 hours prior to analysis.
- Volatiles were extracted by **stepwise heating** from 200 to 1200° C with 100° C increment and 1 hour duration at each increment. After sample is heated for 1 hour at the highest temperature of each step, volatiles are completely released (extra heating yields no more volatile release).
- H_2O in volatiles released have been separated by liquid nitrogen cooled alcohol trap (around -60° C), because H_2O shows high analytical error and large effect to analytical precision of other components.
- The condensed volatile species except H_2O together with other uncondensed volatile species released from sample are introduced to a MAT271 mass spectrometer for volatile concentration measurement, and pumped out at each step after measurement. The analytical errors are typically <10 mol% for main volatile species such as CO_2, CO and H_2.

Apparatus of online vacuum stepwise heating system



Why to use stepwise heating

(1) Stepwise heating can extract volatiles in all residence sites of minerals with the largest yield of bulk volatiles compared with others.

(2) Stepwise heating can distinguish volatiles stored in different residence sites by setting heating temperature intervals according to temperature ranges of homogenization or incipient melting for fluid and melt inclusions.

(3) The reaction between the extracted volatiles and fragments of the host mineral

The possible reaction between molecular carbonic species in the extracted volatiles and fragments of the host mineral during temperature-induced extraction are reversible.

$C + H_2O = CO + H_2$ [1]

$CO_2 + CH_4 = 2CO + 2H_2$ [2]

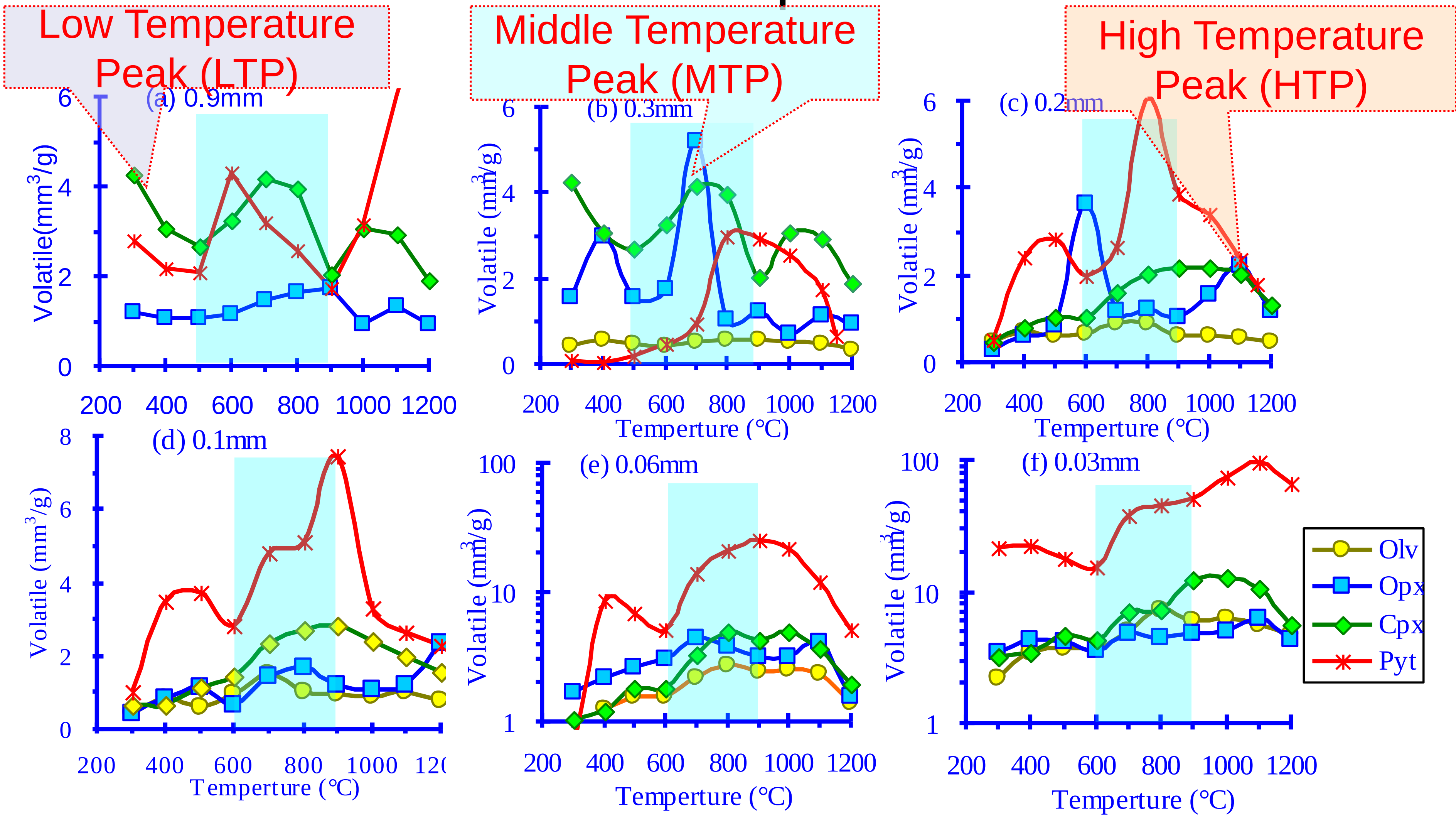
$CH_4 + 2H_2O = CO_2 + 4H_2$ [3]

$2Fe_3O_4 + H_2O = 3Fe_2O_3 + H_2$ [4]

But mantle volatiles were equilibrium in high temperature of ambient mantle conditions.

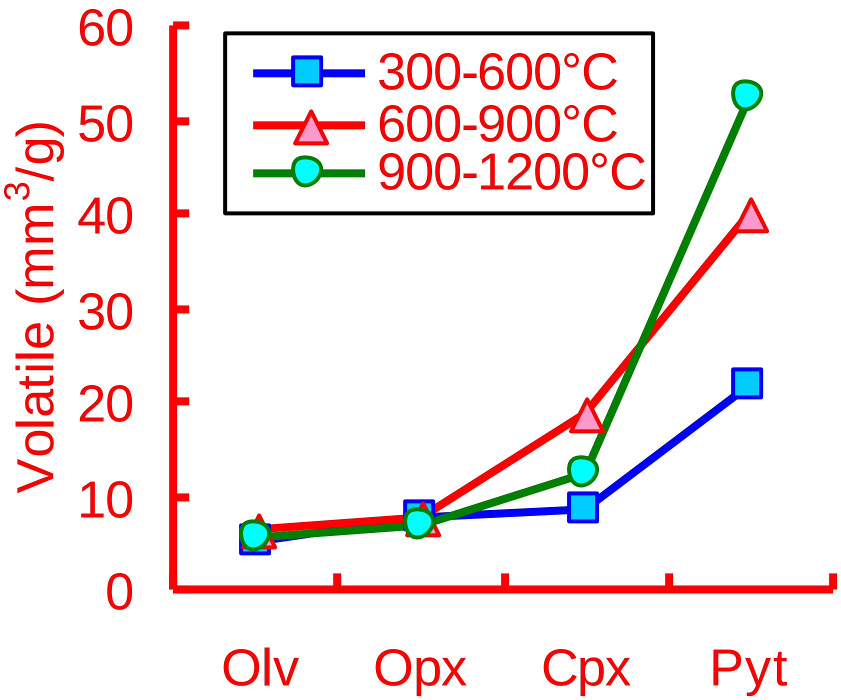
So, the re-equilibrated volatiles in the interior of minerals are generally considered as the re-conversion of equilibrated volatiles at mantle temperatures.

3. The volatiles released in minerals tend to concentrate at three temperature intervals



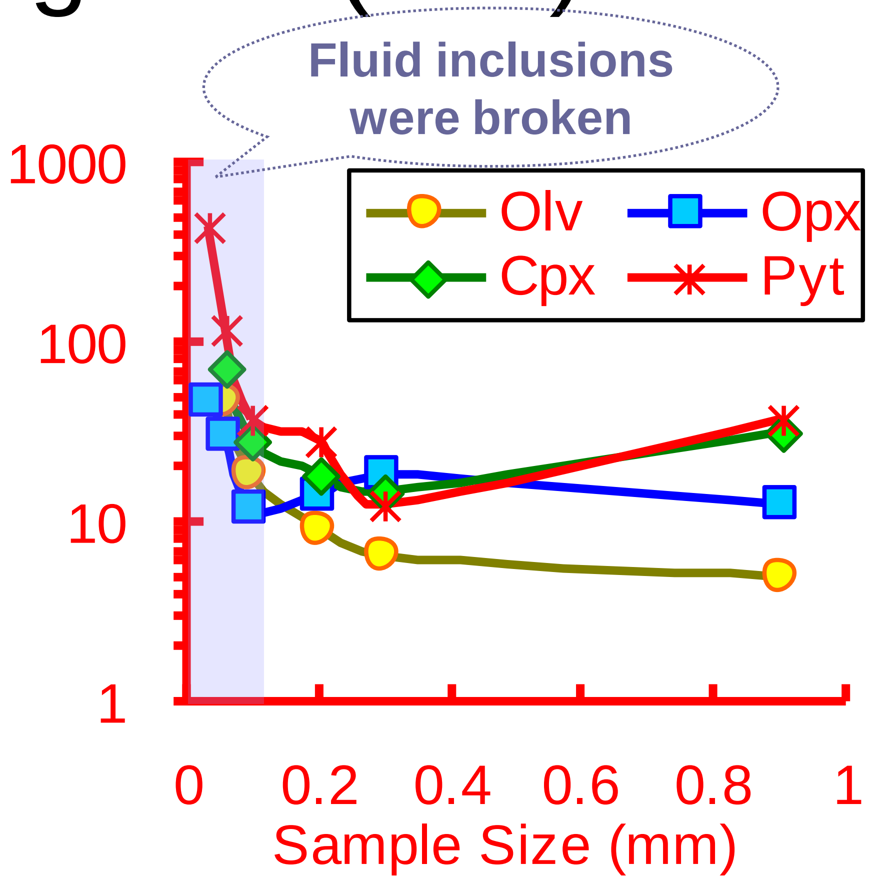
Volatile contents of different type of minerals

The total amount of volatiles released increases from Olv (av. 17.17 mm3/g), to Opx (21.92), to Cpx (39.48) in lherzolite xenoliths, and to Pyt in the pyroxenite xenolith (113.74 mm3/g).



Volatile contents (mm^3.STP/g) as a function of crushing size (mm)

- Volatile contents in mineral separates increased rapidly with crushing size of samples.
- Thus, much of the mantle volatiles must in fact reside in **structural defects and vacancies**, which are volumetrically more important than fluid inclusions (Robert, 2010, DCC).



4. Composition Variations of Mantle Volatiles

The volatiles from different type of mantle-derived rocks by same experimental procedure of stepwise heating MAT271 MS vary with

- tectonic settings,
- mantle depth and
- the type of mantle reservoirs.

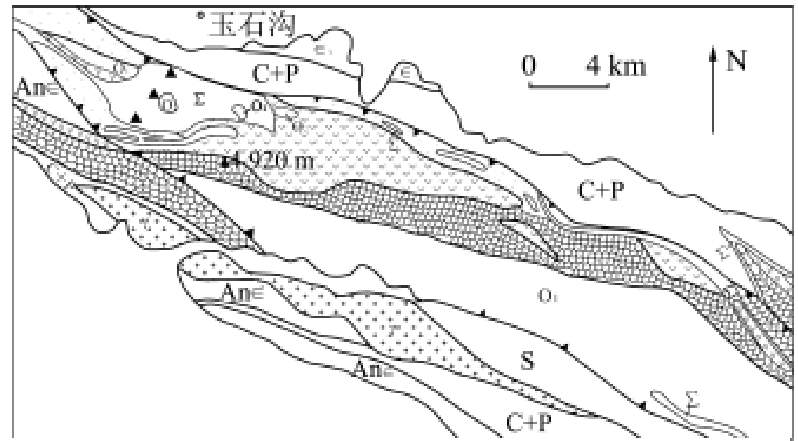
4.1 The mantle volatiles in different tectonic settings

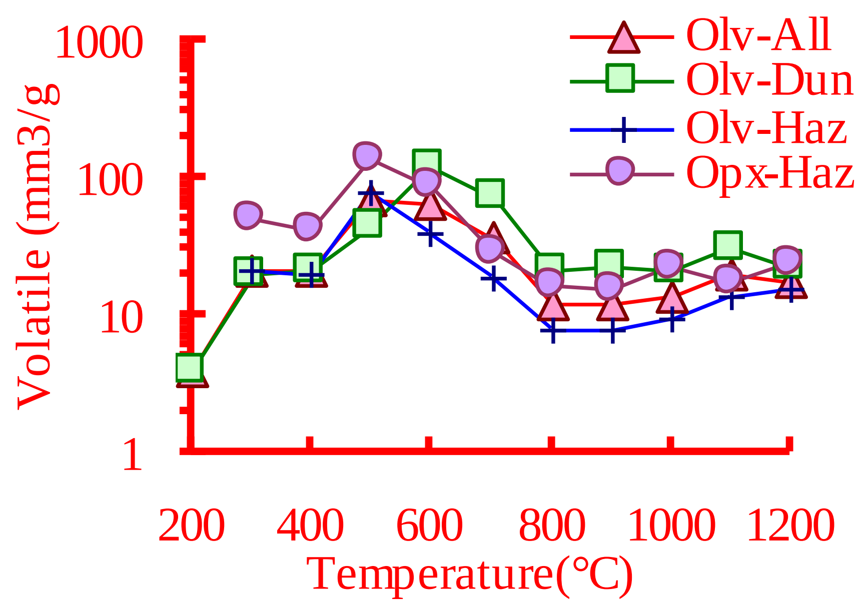
(1) The volatiles in the craton mantle (NCC, SCC) are dominated by CO, CO_2 and H_2; The volatiles in the Su-Lu UHP orogenic belt mantle are dominated by CO_2 and SO_2.

(2) The volatiles in mantle source regions of oceanic basalts are all dominated by H_2O and CO_2 with minor CO, CH_4, N_2 and H_2.

(3) Volatiles in Qilian ancient oceanic lithosphere

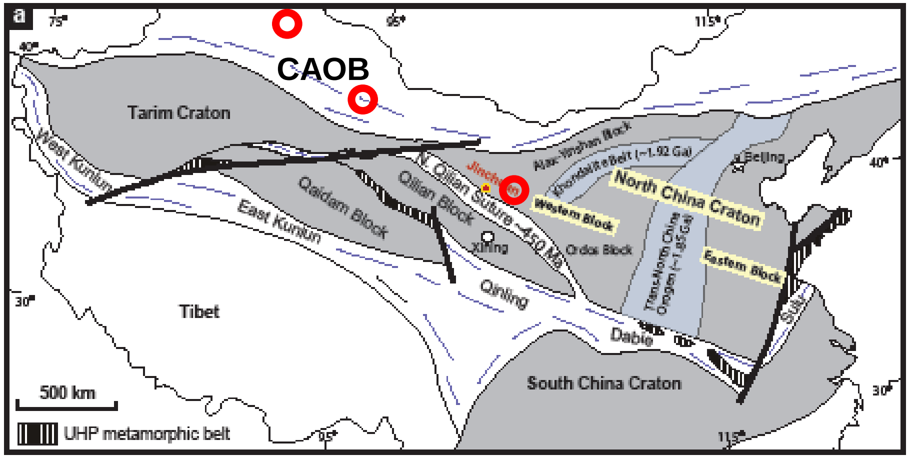
- Volatiles in ancient oceanic lithosphere are recorded in ophiolites are all dominated by CO2.
- Minor volatile are H_2 and CO etc. reduced volatiles in dunite, and SO_2 in harzburgite.

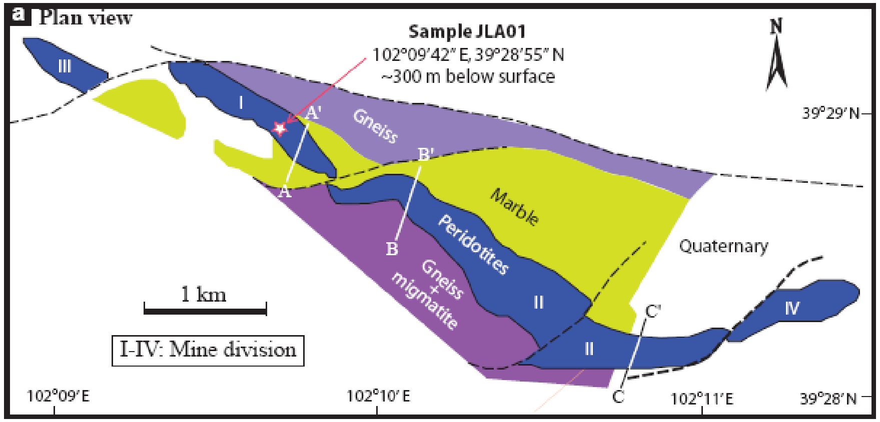


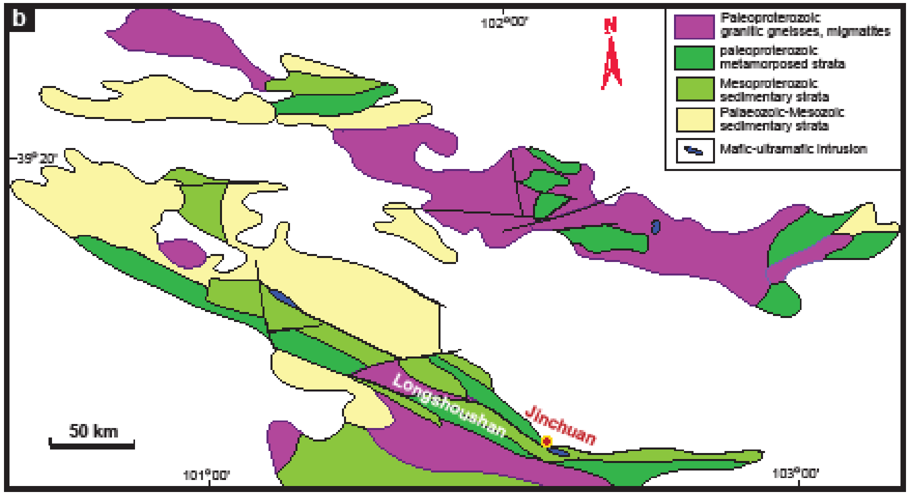


(4) Volatiles in the ultramafic intrusions of Cu-Ni-PGE sulfide deposits

The ultramafic rocks of Jinchuan Cu-Ni-PGE sulfide deposit located **in Craton** show CO_2 and H_2O dominated Volatiles.

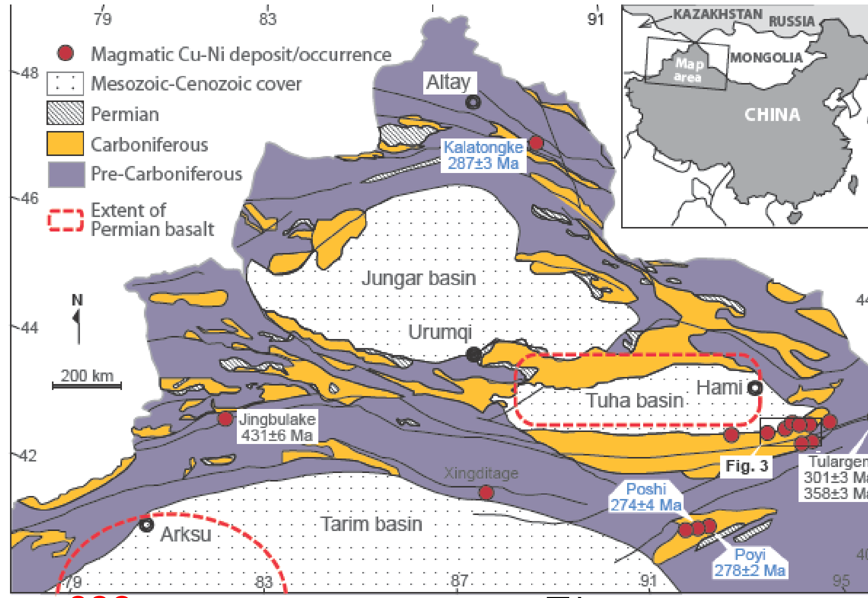




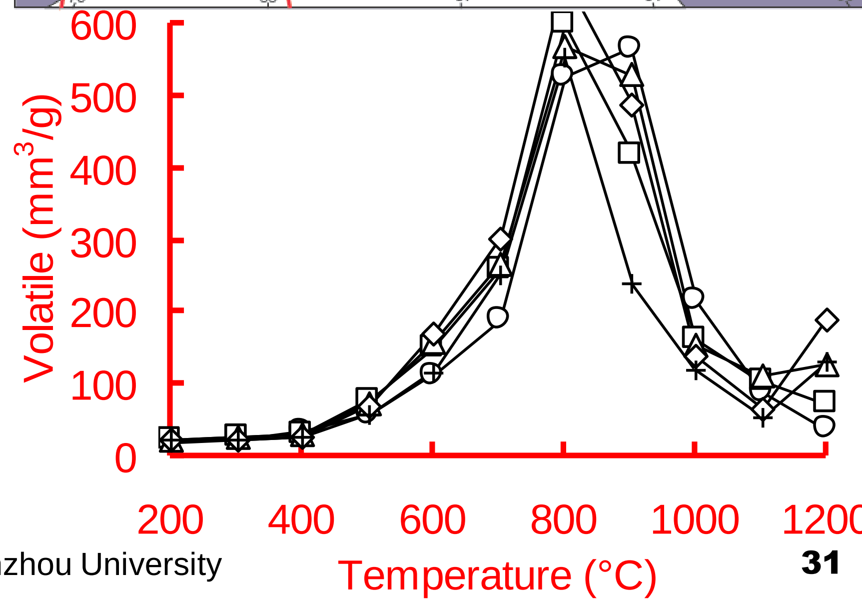


Volatiles in Cu-Ni sulfide deposits in orogenic belt

The ultramafic rocks of Huangshan, Karatongke deposits located **in the CAOB** show H2O and H2 dominated Volatiles.



- The volatiles released at 900-1200° C are composed mainly of CO_2 and SO_2 (39.32 and 34.14mol%, respectively) with minor H_2S and H_2 (16.26 and 1.22mol%).
- The volatiles at 500-800° C are composed of H_2 and H_2S (40.47 and 35.02mol%, respectively) with minor CO_2 (17.60), $CO+N_2$ (2.96) and SO_2 (2.08mol%).



4.2 Volatile compositions in different depth of mantle

(1) Deep Mantle (>150Km)

(2) Degassed Lithospheric Mantle

- The Initial Volatiles in the SCLM
- The Metasomatic Volatiles in the SCLM

(1) Volatiles in Deep Mantle

- Deep portions of mantle lithosphere in the diamond stability field have higher contents of reduced volatile species such as H2 and CO etc.,

Volatile compositions (mm3./g) of fluid inclusions in different types of diamonds

Colored	Location	Type	n	CO_2	N_2	H_2O	H_2	CH_4	CO
Colored	Congo	Cubic	3	215.8	23.6	653.2	19.7	41.5	46.2
	Brazil	Cubic	2	48.0	20.7	832.6	51.7	47.0	0.0
	Mean	Cubic	5	147.1	22.4	726.6	32.8	43.8	27.3
Colorless	Pamir	Octahedron	4	80.6	114.1	210.0	340.1	76.8	178.4
	USA	Dodecahedron	3	144.6	87.1	423.8	201.7	49.2	93.6
	Mean		7	108.0	60.6	264.5	386.7	81.5	98.8

- Summarized from Ivankin et al. (1988),
- Deep portions of mantle lithosphere in the diamond stability field have **higher contents of reduced volatile species** such as H2 and CO etc.,

(2) Degassed Lithospheric Mantle

Volatile compositions (mm3./g) in different depth of mantle

SCLM	Sample	Locality	H_2	CH_4	H_2S	CO	N_2	C_2H_6	CO_2	SO_2
Top part	Pyt	E.China	7.9	1.9	1.5	49.7	7.9	0.13	47.2	26.7
Upper	Sp-Lht	E.China	44.9	1.2	0.5	28.6	1.1	0.02	13.6	0.2
Middle	Sp-Gt-Lht	E.China	4.7	0.6	0.0	2.2	0.7	0.00	24.5	22.6
Low	Gt-Lht	E.China	97.2	1.3	0.1	24.7	1.3	0.00	10.9	1.0
>100Km	Diamond	USA	386.7	81.5		98.8	60.6		108.0	

At shallow levels, the lithospheric mantle as reflected in mantle xenoliths displays varying volatile compositions.

4.3 The Initial Volatiles in the SCLM with different source

The Initial Volatiles in the sub-continental lithospheric mantle (SCLM) refer to volatiles trapped during initial stage of mantle mineral crystallization, and can be characterized by the volatiles released at 600-1200° C from refractory minerals olivine of lherzolite xenoliths.

The Initial Volatiles in SCLM vary with mantle sources.

The Initial Volatiles in the SCLM with different sources (ul·STP /g)

Type of mantle	District	H_2	CH_4	H_2S	CO	N_2	CO_2	SO_2	Total
Primitive Mantle	NCC	2.76	0.12	0.01	7.77	0.41	3.04	0.02	14.13
Depleted Mantle	SCC	3.66	0.19		4.92	0.18	7.49	0.82	17.26
Enriched Mantle	CAOB, W-USA	18.73	0.2		4.6	0.38	6.26	0.18	30.35
Mixed Mantle	Su-Lu	0.12	0.03			1.01	24.66	2.61	28.43

*NCC: northern China craton, SCC: southern China craton, CAOB: North part of northeastern China, Central Asia Orogenic Belt, Su-Lu: Su-Lu UHP.

The Metasomatic Volatiles in the SCLM

The Types of Metasomatic Volatiles:

- Macroscopic metasomatism with conspicuous metasomatic minerals (e.g., amphiboles, phlogopite, apatite etc.)
- Cryptic metasomatism with the enrichments as hydrous melts distributed along grain boundaries (e.g., O'Reilley et al., 1988; Hansteen et al., 1991; Wyllie, 1987).

The metasomatic volatiles have been trapped as metasomatic agents in macroscopic metasomatic minerals or secondary inclusions in the edges and cracks of recrystallized mantle minerals.

Macroscopic metasomatic volatiles

Type	n	CO_2	H_2O	SO_2	H_2S	O_2	CH_4	CO
Hornblendite	1	356.4	11200.0	140.0	65.9	980.0	560.0	240.0
Selvage	1	152.7	14560.0	35.0	131.8	630.0	420.0	240.0
Oikocrysts	6	356.4	12091.9	46.7	175.7	1493.3	490.0	306.7
Megacrysts	2	305.5	10826.7	297.5	230.6	1260.0	350.0	160.0

The amphiboles from mantle xenoliths in Vulcan's Throne, Grand Canyon, Arizona, USA show volatiles of macroscopic metasomatism dominated by H2O with high concentrations of O2, CH4, CO2 and CO. Matson and Muenow (1984).

Cryptic metasomatic volatiles in the SCLM

	Description	Location	Reservoirs	H_2	CH_4	H_2S	CO	N_2	CO_2	SO_2
	Opx,	NCC	PM	83.65	0.77	0.80	31.05	1.09	8.91	0.05
I	Cpx	SCC	DM	138.91	0.92	0.08	32.31	1.01	11.32	0.00
	600-1200	W-USA	EM	13.08	0.29	0.01	7.25	0.23	8.05	1.18
	Olv,	NCC	PM	1.47	0.68	0.07	4.63	0.16	7.81	0.23
	Opx, Cpx	SCC	DM	1.07	0.66	0.00	3.11	0.22	8.64	0.42
	300-600	W-USA	EM	0.21	0.17	0.00	1.64	0.04	5.26	0.00

5. Summary

(1) Much of the mantle volatiles must in fact reside in structural defects/vacancies, which are volumetrically more important than fluid inclusions.

(2) Volatiles in the mantle vary with tectonic settings, depth and mantle reservoirs, and show constraints on origins.

(3) Mantle volatiles in early stage fluid inclusions and structural defects/vacancies are more reduced, dominated by CO and H2 etc, implying lower *f*O2 than current view on the basis of fluid inclusion analysis (pure CO2 inclusions).

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Thanks for Suggestion

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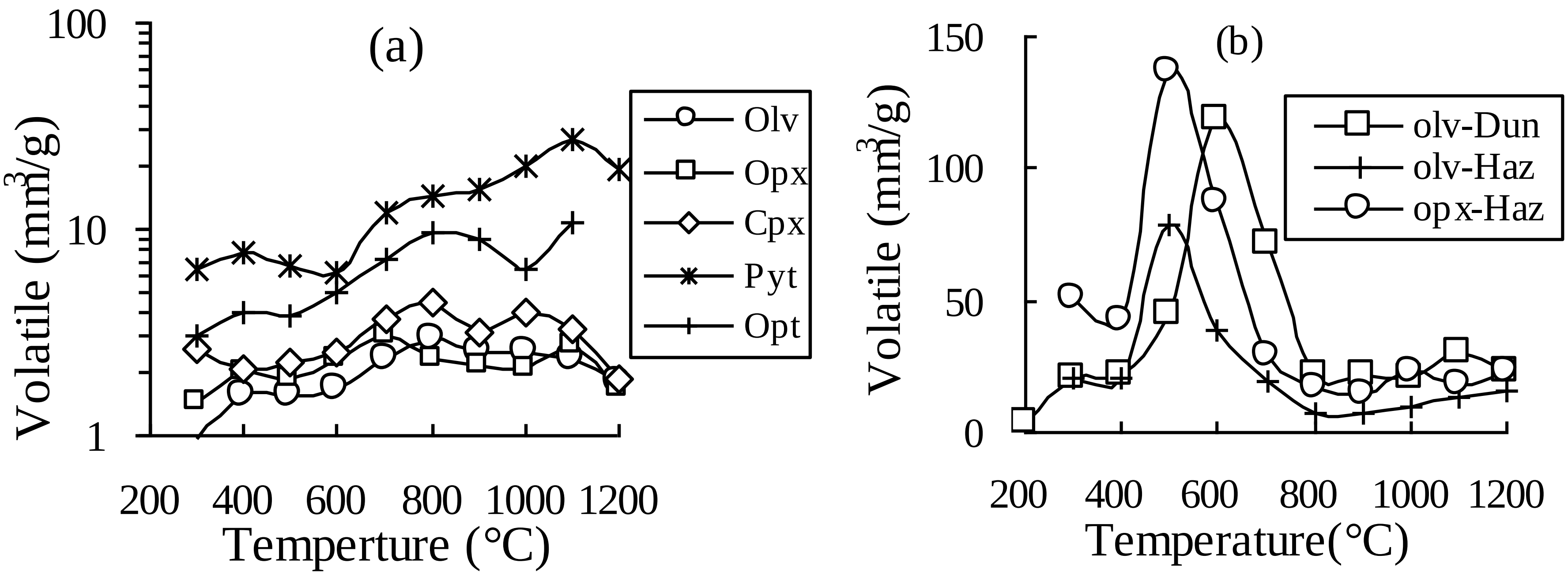
Method

Stepwise heating or laser extraction techniques can extract bulk volatiles trapped in fluid inclusions or structural defects and vacancies for chemical and isotopic analysis with both advantages and limitations



uncertain what the extent of the reaction between molecular carbonic species in the extracted volatiles and fragments of the host mineral during temperature-induced extraction

The volatile species in inclusions were re-equilibrated to the furnace temperatures during heating (Norman and Sawkins, 1987). Pasteris and Wanamaker (1988) showed that CO_2-rich fluid inclusions in olivine, which is volumetrically the most important mineral of the Earth's upper mantle, will react with the olivine at high temperatures and low fO_2 conditions to form CO, in some cases, graphite.

Olivine and orthopyroxene of peridotite with CO_2-rich inclusions from Harzobergite at Yushigou ophiolite show little CO and H_2 contents in temperature-induced extraction, while mantle xenolith from Damaping contains high contents of CO and H_2.

Those indirectly demonstrated that volatile re-equilibration and generation via the reaction with the host mineral and volatiles in the interior of minerals could be ignored under our experimental designs.

Experimental reproducibility

The well-established and ameliorative online vacuum stepwise heating MAT-271 mass spectrometer show many merits in determination of volatiles in mantle xenoliths.

- **Showing good reproducibility.**
- **Minimizing the possibility for new species (H_2 and CO etc.) formation by the following reactions between volatiles released from sample.**

$C+H_2O \rightarrow H_2+CO$

$CO_2+CH_4 \rightarrow 2CO+2H_2$

$CH_4+2H_2O \rightarrow CO_2+4H_2$

$Fe_3O_4+H_2O \rightarrow 3Fe_2O_3+H_2$

Experimental reproducibility and comparability

No.	Rock	Exp. No.	H_2	CH_4	H_2S	CO	N_2	CO_2	SO_2
MP30	B-Pxt	1	7.46	0.00	0.53	81.2	3.1	16.14	0.05
		2	7.08	0.00	0.5	81.51	4.01	16.33	0.07
		3	9.11	0.00	0.65	82.66	3.76	15.47	0.04
		Mean	7.89	0.00	0.56	81.79	3.63	15.98	0.05
Standard deviation			1.08	0.00	0.08	0.77	0.47	0.45	0.01
DF40	Y-Pxt	1	7.13	0.09	0.89	63.76	2.29	42.51	0.93
		2	7.05	0.00	0.86	61.57	2.26	47.86	1.69
		3	7.64	0.00	0.9	64.92	2.15	37.35	1.53
		Mean	7.27	0.03	0.89	63.42	2.23	42.58	1.38
Standard deviation			0.32	0.05	0.02	1.7	0.07	5.26	0.4
	Jade quartzite		0.00	0.61	0.00	4.69	3.65	2.36	0.00
	Eclogite		0.00	0.22	0.00	21.6	2.54	28.54	0.00