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Chapter 5

VOLATILES IN THE MANTLE LITHOSPHERE: MODES OF OCCURRENCE AND CHEMICAL COMPOSITIONS

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Abstract

Volatiles play important roles in chemical differentiation of the Earth, in concentrating economic metals, and in regulating earth's surface environments by means of magmatism, metasomatism, degassing and recycling. Mantle rocks and rocks derived from the mantle such as basalts, mantle xenoliths and ophiolitic peridotites are materials available to investigate the ways in which volatiles may store in the mantle, their compositions, and probable histories. The laser Raman spectroscopy, Infrared spectrometry and ion microprobe in combination with micro-thermometry are non-destructive methods to analyze volatile compositions trapped in fluid inclusions. On the other hand, vacuum crushing and stepwise heating are methods employed to extract the volatiles and measure their chemical and isotopic compositions using mass spectrometry. An improved vacuum stepwise heating technique can effectively separate volatiles in different occurrence modes in mantle materials, which in combination with mass spectrometry can yield excellent and highly reproducible analytical data.

Volatiles in the mantle occur in various forms such as free element or molecular species along grain boundaries, carbonate, sulfide or hydrous minerals, fluid inclusions or charged species dispersed in mineral structures (e.g., OH^-), structural defects or vacancies. Volatiles trapped in structural defects and vacancies are volumetrically significant. Large amount of hydrogen occurs as free H_2 species, not OH^- as previously thought.

Volatiles in the mantle are mixtures of primordial volatiles and recycled volatiles with characteristic chemical compositions. Volatiles in the sub-continental lithospheric mantle (SCLM) vary with depth and mantle reservoirs. Deep portions of mantle lithosphere in the diamond stability field have higher contents of reduced volatile species such as H_2 and CO

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etc., whereas at shallow levels, the mantle lithosphere as reflected in mantle xenoliths displays varying volatile compositions; initial volatiles trapped during primary crystallization stage are dominated by reduced species like CO, H_2. In contrast, metasomatic volatiles are more oxidized such as CO_2 and SO_2 etc.

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; the abundances vary with tectonic settings. MORB are depleted in volatiles as a result of source depletion in its history, whereas abundant volatiles in IAB and BABB are probably originated from subduction devolatilization. OIB may have abundant volatiles inherited form the undegassed mantle with a recycled component. Volatiles in ancient oceanic lithosphere as recorded in ophiolites are all dominated by CO_2 with minor amounts of other volatile species.

Key words: volatiles, occurrence mode, chemical composition, mantle lithosphere.

1. Introduction

1.1. Implications of Mantle Volatiles

The Earth's mantle is an important reservoir for volatiles. Water of various forms, inorganic species (i.e. CO_2 and SO_2 etc.), hydrocarbon (i.e. CH_4 etc.) and noble gases have all been found in mantle xenoliths (Trull et al., 1993; Zhang et al., 1999a,b, 2007), diamond (Ivankin, 1988; Verchovsky et al., 1998; Ratan and Mohapatra, 2006; Frezzotti and Peccerillo,2007), basalts (Byers et al., 1983-1986; Javoy and Pineau, 1991), kimberlite (Canil and Bellis, 2008) and volcanic fumaroles (Yuri, 2000; Zimbelman et al., 2000), which provide convincing evidence for the presence of abundant volatiles in the Earth's mantle (Cartigny et al., 2001; Aubaud et al., 2005; Workman et al., 2006).

Degassing of the Earth's mantle has led to the formation of Earth's atmosphere and hydrosphere (Allegre et al., 1987), and continues to modify our global environment (Self et al., 2006; Moune et al., 2007). Volatiles play important roles in mantle differentiation and evolution by means of mantle metasomatism, magma generation and crust-mantle interactions (Porcelli and Wasserburg, 1995; O'Reilly and Griffin, 2000; Wyllie and Ryabchikov, 2000; Niu and O'Hara, 2003). Volatiles in the Earth's mantle are in the supercritical state under ambient conditions (Wyllie, 1987), and can transport quantities of economically valuable metals from the Earth's deep interiors (Olmez and Finnegan, 1986; Wyllie, 1987; Rubin, 1997; Yuri, 2000). Mantle volatiles continue presently to escape through Earth's crust (Weinlich, 1999; Hilton, 2007, Zhang et al., 2008). Thus, studies of mantle volatiles provide a means for understanding Earth's early history and its continued evolution.

Volatiles in the mantle are "mixtures" of volatiles with different origins. Some are primordial incorporated during Earth formation (Burnard et al., 1997; Hilton, 2007), some are likely recycled from the atmosphere, hydrosphere and crustal materials through lithosphere subduction (Trull et al., 1993; Fyfe, 1997; Zhang et al., 2004, 2007; Ratan and Mohapatra, 2006), and some may be added by nucleogenic or radiogenic ingrowths (Albarede, 2008). To characterize volatiles degassed from the mantle requires a good knowledge of the initial volatile abundances and isotopic compositions in the convective mantle. However, such mantle materials are rare, and the SCLM offers the best sample for such investigations. The types, abundances, compositions and characteristics of volatile species in mantle materials are likely to have diverse identities because of their different origins and complex histories, and can thus be used to decipher their ultimate origins and passageways in the context of crust-mantle recycling and mantle circulation.

1.2. Occurrence Modes of Mantle Volatiles

It has been recognized that volatile species of C-O-H-S composition must exist in the mantle in some physical state (free volatile phase, dissolved volatiles in melts or interstitial solid solutions, complex anions incorporated in minerals). Some volatiles are present as free species dispersed along grain boundaries of mantle minerals, but most mantle volatiles are stored in minerals. Sulfide, carbonates and hydrous phases, such as phlogopite and amphiboles, can hold abundant volatiles, but these phases are volumetrically insignificant and have limited stability fields. Hence, much of the mantle volatiles reside in nominally anhydrous minerals such as olivine, pyroxenes, garnet and other phases at great depths (Bell and Rossman, 1992; Beran and Libowitzky, 2006; Skogby, 2006). Volatiles in nominally anhydrous mantle minerals have long been thought to reside primarily in various types of fluid inclusions. However, the exact ways in which volatiles reside in the mantle minerals remain poorly understood, largely due to difficulties in obtaining representative mantle samples and inaccessibility for direct observations.

Mantle volatiles are conventionally considered to reside as free phases in different types of fluid inclusions in mantle minerals (Roedder, 1965; Anderson et al., 1984; Xia, 1984; Deines, 1992; Andersen and Neumann, 2001), to occur as anion complexes in hydrous minerals (e.g. OH^- in amphibole and mica, and Cl^- and F^- in apatite etc., Chazot et al., 1997; O'Reilly and Griffin, 2000; Aubaud et al., 2007) or to be trapped in structural defects and vacancies of crystals (Freund and Oberheuser, 1986; Bai and Kohlstedt, 1992). Their residence in mantle minerals is thought to reflect different origins by mantle events (Hansteen et al., 1991; Matsumoto et al., 2000; Landis and Rye, 2005). Hence, to identify the occurrence modes of volatiles in mantle minerals is key to understanding their origins.

1.3. Compositions of Mantle Volatiles

Volatiles are most active agents in Earth processes and have chemical and isotopic compositions that are characteristic of different major reservoirs such as the atmosphere, hydrosphere, crust and different mantle source components (e.g. DM, EMI-II and HIMU). Therefore, volatiles have been used as tracers for their origins (Norman and Musgrave, 1994; Eiler et al., 1997; Deines, 2002; Hansteen and Troll, 2003; Shaw et al., 2004; Zhang et al, 2004). Abundant literature exists on stable isotopes and noble gas isotopes of mantle-derived volatiles.

The $\delta^{13}C$ of ~ -5‰ has been identified as a characteristic value of mantle materials, e.g., kimberlite, mantle xenoliths and fresh glasses of mid-ocean ridge basalts (MORB) and ocean island basalts (OIB) (Exley et al., 1986). The $\delta^{13}C$ of diamonds (-27.9‰ to -3.2‰, Deines et al., 1997) and mantle xenoliths (-30‰ to 0 ‰) (Nadeau et al., 1990; Pineau and Methez, 1990; Trull et al., 1993; Deines, 2002) shows bimodal peaks at -5‰ and -25‰, respectively; whose origin remains poorly understood (Deines, 2002). The $\delta^{18}O$ values of "Normal" mantle is widely accepted as ~ +5.5‰ (Kyser, 1986; Mattey et al., 1994) and δD values as -40‰ to -

95‰ (a mean of -80‰, Kyser and O'Neil, 1984; Kyser, 1986), e.g. $\delta^{18}O$ values of oceanic gabbros (+3.3‰ to +5.1‰, Hansteen and Troll, 2003), fresh MORB or OIB glasses (+5.7‰ to +6.0‰, Eiler et al., 1997; Widom and Farquhar, 2003) and olivines in mantle xenoliths and of MORB phenocrysts (+5.2‰ on average, Mattey et al., 1994; Eiler et al., 1997).

Noble gases are inert and do not recycle into the mantle by subduction with the possible exception of Xe (Porcelli and Wasserburg, 1995). Because of the rarity, chemical inertness and significant isotopic fractionation noble gases are important tracers for volatile origins in the context of Earth evolution and specific Earth processes such as magmatism, metamorphism, fluid migration and melt segregation (Allegre et al., 1987; Norman and Musgrave, 1994; Burnard et al., 1998; Farley and Neroda, 1998; Ozima and Podosek, 2002). The shallow upper mantle contains a higher proportion of radiogenic noble gases sampled through mid-ocean ridge basalts (MORB) (e.g. ^{4}He, ^{21}Ne and ^{40}Ar; Allegre et al. 1987; Farley and Neroda, 1998). The depleted MORB mantle (DMM) shows a small range of $^{3}He/^{4}He$ (7-9Ra; O'Nions and Tolstikhin, 1994; Trieloff et al., 2000). Deep mantle plume sources as analyzed in OIB contain relatively high abundances of primordial noble gas isotopes, e.g. ^{3}He, ^{22}Ne, ^{36}Ar and ^{38}Ar (Trieloff et al., 2000).

The stable and noble gas isotopic compositions of volatiles are complex in mantle minerals and show differences between the sub-continental lithospheric mantle (SCLM) as revealed by mantle xenoliths and oceanic (asthenospheric) upper mantle as revealed by oceanic basalts (Inonov et al., 1994; Eiler et al., 1997; Valley and Cole, 2001; Deines, 2002; Ozima and Podosek, 2002; Hansteen and Troll, 2003; Shaw et al., 2004). However, whether there are systematic differences in terms of chemical compositions of the volatiles between the SCLM and upper mantle source regions of oceanic basalts remain poorly understood. Furthermore, theoretical modeling of mantle volatiles are hampered by lacking thermodynamic data at high temperature and pressure.

In this chapter we review our present knowledge about mantle volatiles and their redox state. We also review available mantle volatile data and analytical methods we use to acquire these data. We use a combined techniques of microthermometry, improved vacuum stepwise heating, grain-size reduction, mass spectrometry and infrared spectrum measurements (1) to assess analytical reproducibility of volatile compositions and the superimposed effects of volatiles in different occurrence modes, (2) to characterize occurrence modes of volatiles, and (3) to discuss in details the decrepitation mechanism of inclusions by stepwise heating, and (4) to elucidate chemical compositions of volatiles that vary between different tectonic settings and mantle reservoirs.

2. Samples and Analytical Methods

2.1. Representative Samples

Mantle volatiles can be rarely sampled directly. Hot-springs, summit fumaroles, diamonds, mantle derived melts (e.g., basalt, kimberlite and lamprophyre), mantle xenoliths, ultramafic intrusions and ophiolitic peridotites are all used to characterize mantle volatiles. Hot-springs, summit fumaroles, even natural gases can contain a large quantity of mantle volatiles, although they are always contaminated by crustal and atmospheric components (Kelley, 1996; Charlou et al, 1998; Welhan, 1988). Oceanic basalt glasses, including MORB, OIB, back-arc basin basalt (BABB), and island arc basalt (IAB) can provide volatile compositions of oceanic upper mantle source regions (Welhan, 1988; Kelley and Frueh, 1995; Burnard et al., 1997). Peridotite in the lowest part of ophiolite sequence may be unique samples for the volatiles of ancient oceanic lithosphere (Abrajano et al., 1988; Su et al., 1999; Hu et al., 2007).

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, e.g. Africa, USA and Brazil (Deines, 1980; Eggler and Baker, 1982; Ivankin et al., 1988; Navon, 1991; Verchovsky et al., 1998; Frezzotti and Peccerillo, 2007).

Mantle xenoliths brought to the surface by alkali basalts are interpreted as direct samples of the SCLM to characterize volatiles in the mantle (Mathez, 1987; Litasov et al., 2000). Mantle xenoliths can preserve volatiles intact in primary fluid inclusions or crystal structural defects and vacancies in the interiors of constituent mineral crystals, thus prevent from subsequent contamination by crustal and atmospheric components. This is however not the case for volatiles from volcanoes, hot-springs, summit fumaroles, ultramafic intrusions, basalts or xenoliths hosted in kimberlite or lamproite (Andersen and Neumann, 2001; Deines, 2002). Therefore, mantle xenoliths hosted in alkali basalts are probably the best mantle material for reliable estimation of average compositions of mantle volatiles. Abundant spinel lherzolite, garnet lherzolite, harzburgite, and pyroxenite xenoliths and megacryst from eastern China (Figure 1 of Zhang et al., 2007), central Asia (Inono et al., 1992), Australia (Anderson et al., 1984), Siberia (Ionov et al., 1994), central Europe (Weinlich, 1999) and North America (Nadeau et al., 1990; Tingle et al., 1990) have been collected to analyze the chemical and isotopic compositions of volatiles by various methods.

2.2. Analytical Methods

Ideal sample sets and effective pretreatments are important for obtaining reproducible volatile concentration and isotope data. Less altered olivine (Olv), orthopyroxene (Opx) and clinopyroxene (Cpx) separates or megacrysts were hand-picked under an binocular. They were then ultrasonically cleaned with 0.3mol/L HCl and analytical grade CH_2Cl_2 and acetone, respectively, and rinsed with distilled water until pH value reaches around 7 at first HCl-cleaning step, finally dried up at 110°C prior to analysis. Such sample pretreatment procedure effectively removes carbonate and sulfide hosted in the sample as well as possible surface contaminants and volatiles absorbed on mineral surfaces and cracks (Miller and Pillinger, 1997).

Thin sections have been made for petrography and fluid inclusion observations and micro-thermometry studies. The petrographic microscope equipped with a heating-cooling stage or a high temperature stage is routinely employed to examine the type, size, distribution, and thermal data (e.g., melting and homogenization temperatures) of fluid inclusions (Roedder, 1990; Andersen and Neumann, 2001).

Laser Raman microprobe, or ion microprobe is non-destructive and easy to combine with microthermometry to directly observe and analyze the composition of volatiles trapped in fluid inclusions (Anderson et al., 1984; Bergman and Dubessy, 1984; Pasteris and Wanamaker, 1988; Roedder, 1990; Hansteen et al., 1991; Williams, 1996; Chazot et al., 1997; Workman et al., 2006; Frezzotti and Peccerillo, 2007), but has a relatively high detection limit on the order of 0.x mol% for most of potentially important volatile species of interest, such as water and noble gases (Andersen and Neumannr, 2001), and assume implicitly that mantle volatiles have the same equilibrium phases as those at room temperature. On the other hand, superimposed volatile fractionation during inclusion entrapment leads to volatile heterogeneity among inclusions (Burnard, 1999).

Infrared spectroscopy or Raman spectroscopy can be used directly to analyze volatiles incorporated as anion complexes in minerals (Dixon et al., 1988; Roedder, 1990). For example, the modes of occurrence of H and OH^- in nominally anhydrous mantle minerals have been widely studied using FTIR and ion microprobe (Skogby and Rossman, 1989; Smyth et al., 1991; Bell et al. 1995; Kohn, 1996; Zhang et al., 2005; Aubaud et al., 2007). However, it is not straightforward to determine the abundances and compositions of volatiles trapped in structural defects and vacancies of minerals.

Crushing, 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 (Anderson et al., 1984; Burnard et al., 1997; Marty and Zimmermann, 1999; Matsumoto et al, 2000; Cartigny et al., 2001; Aubaud et al., 2005). In most instances, crushing can extract volatiles in fluid inclusions of large size, thus yielding only a small fraction of volatiles (ca. 5-15% of heating, Landis and Rye, 2005). Stepwise heating or laser extraction could cause reactions among volatile species before or after released, meanwhile reactions between molecular carbonic species in the extracted volatiles and fragments of the host mineral is possible at high temperature (Andersen and Neumannr, 2001). The *pros* and *cons* of volatile extraction by stepwise heating in carbon isotopic measurements have been assessed by Miller and Pillinger (1997).

Vacuum stepwise heating is widely used to extract and analyze volatiles (e.g., species, concentrations and isotopic compositions etc.) in mantle derived melts and mantle xenoliths, which can distinguish volatiles stored in different occurrence modes by setting temperature increments according to incipient melting or homogenization temperatures for melt or fluid inclusions, and can extract volatiles trapped in structural defects and vacancies of crystals at high temperatures, even up to the melting point (Marty and Zimmermann, 1999; Matsumoto et al., 2000).

Volatiles released from mantle minerals at different temperature intervals during stepwise heating show distinct chemical, stable and noble gas isotopic compositions and have been interpreted as reflecting different modes of occurrence and different origins (Nadeau et al., 1990; Pineau and Methez, 1990; Javoy and Pineau, 1991; Trull et al., 1993; Miller and Pillinger, 1997; Deines, 2002; Shaw et al., 2004; Zhang et al., 2004, 2007). For example, volatiles released at high heating temperatures (>800°C) dominated by CO and H_2 with $\delta^{13}C$ value of ~ -5‰ vs. PDB and MORB-like noble gas isotopes are consistent with being fluid inclusions trapped at an early stage of crystal formation (Nadeau et al., 1990; Pineau and Methez, 1990; Trull et al., 1993; Marty and Zimmermann, 1999; Matsumoto et al, 2000; Zhang et al., 2004, 2007) or incorporated in crystal structures (Miller and Pillinger, 1997; Deines, 2002). On the other hand, volatiles released at low heating temperatures (<800°C) dominated by CO_2 with $\delta^{13}C$ values of ~ -25‰ are subject to a wide range of interpretations. These include surface contamination by ubiquitous airborne particulates of biological origin (Miller and Pillinger, 1997), graphitic and organic materials absorbed on sample cracks or surfaces (Pineau and Methez, 1990; Nadeau et al., 1990), mantle heterogeneities (Deines, 2002), and different types of fluid inclusions (Zhang et al., 2004, 2007).

Volatile extraction by vacuum stepwise heating has been widely used for stable and noble gas isotopic measurements, but shows difficulty in precise analysis of volatile concentrations, partly due to (1) reactions among volatile species released at high temperature (Nadeau et al., 1990; Roedder, 1990; Graney and Kesler, 1995; Zhang et al., 2000, 2005), and (2) superimposed effects of volatiles from different occurrence modes; all these often result in poor reproducibility of measured volatile concentrations. Zhang et al. (2000, 2004, 2007) have improved the procedure of stepwise heating to minimize these affects.

2.3. Improved Online Vacuum Stepwise Heating Method

2.3.1. Analytical Procedures

A well-established and improved online vacuum stepwise heating system connected to a MAT-271 mass spectrometer was used to extract volatiles from mineral separates (Zhang et al, 2000, 2007). The complete apparatus of online volatile extracting (Figure 1) are described in Zhang et al (2004, 2007). The efforts were made to use path length and diameter of the inlet ports as small as possible. The inlet ports were heated at a constant temperature of 120°C to minimize adsorption of volatiles onto surfaces. A cold trap held at the liquid nitrogen temperature was adopted during sample heating to condense and isolate H_2O, CO_2 and heavy hydrocarbon species released from the sample from the high temperature area, which can minimize or prevent contributions from reactions among released volatiles (Zhang et al., 2005a). Reactions among these volatiles in the interior of samples could be considered as the reconversion of equilibrated volatiles at mantle temperatures (Zhang et al., 2000).

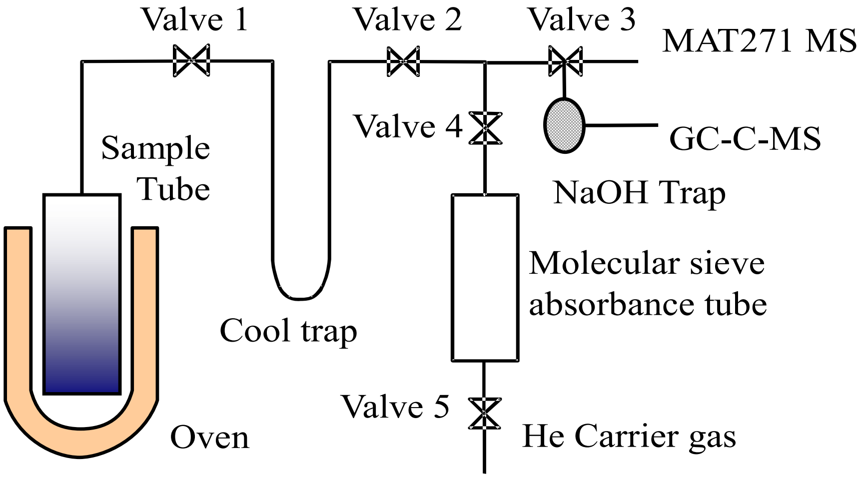

Figure 1. Apparatus of online stepwise heating system.

The improved analytical procedures of volatile concentration were previously described (Zhang et al., 2000, 2004, 2007) and are briefly summarized here. The sample was loaded into a quartz sample tube and combusted in high-purity O_2 gas for 4 hours in a furnace at 200°C to remove possible surface organic contaminant (Shaw et al., 2004), then preheated at 200°C and outgassed under ultrahigh vacuum for 4 hours prior to analysis. Volatiles in a given sample crushing size of mineral separates were extracted by stepwise heating from 200 to 1200°C with 100°C increment and 1 hour duration per step. A cold trap held at the liquid nitrogen temperature was adopted to prevent volatile reactions (see above). After heating for 1 hr at each step, volatiles have been released completely from samples. The condensed volatile species (except for H_2O) in cold trap are released by replacing cold trap into alcohol-liquid nitrogen mixture (ca. -60°C). All the volatiles released are then introduced to a MAT271 mass spectrometer for concentration measurement. The analytical errors are typically < 1 mol% for main volatile species such as CO_2, CO and H_2.

The cold trap at the liquid nitrogen temperature can rapidly trap the released volatiles and minimize the possibility for new species (e.g., H_2 and CO etc.) formation (Hu et al., 2007). The one hr duration of heating is adequate to release volatiles completely as demonstrated by negligible volatile yields for extra heating. The analysis suggests that the released volatiles are stored in the form of fluid inclusions as well as structural sites, defects and vacancies of the constituent minerals.

2.3.2. Analytical Reproducibility of Volatile Concentrations

Measurement of volatile concentrations in mantle minerals has always shown poor reproducibility due to heterogeneous distributions and asynchronous release of volatiles (Matson and Muenow, 1984). Magmatic pyroxenite xenoliths without granoblastic microstructures are often considered to be of magmatic origin under mantle conditions; they have least number of fluid-trapped stages with relatively homogeneous distribution of volatiles because of the simple history (Hansteen et al., 1991; Litasov et al., 2000). Hence, Cpx separates in the pyroxenite xenoliths are ideal samples for carrying out analytical reproducibility tests. On the other hand, the volatiles resided in different sites in host crystal may be released at different heating temperature intervals depending on experimental procedures (Nadeau et al., 1990; Pineau and Methez, 1990; Trull et al., 1993; Zhang et al., 2004, 2007). Therefore, one step heating can effectively eliminate superimposed effects due to asynchronous release of volatiles in different occurrence modes.

Volatiles in Cpx separates from pyroxenite xenoliths in Hanluoba and Dafangshan in eastern China were extracted by one step heating from 200 to 1200°C for 1 hour to test analytical reproducibility. Cpx separates from pyroxenite xenoliths show much higher volatile contents than Cpx from lherzolite minerals, which is consistent with magmatic petrogenesis of pyroxenite xenoliths, because volatiles are enriched as incompatible components in the late crystallized minerals, or are added as the allothigenetic volatiles into the parental melt of pyroxenite. The reproducibility for major volatile species CO_2, CO, H_2 and N_2 is excellent with relative standard deviation < 13.68%. The relative standard deviation is 2.82-12.35% for CO_2, 0.94-2.68% for CO, 4.4-13.68% for H_2, 2.54-13.63% for H_2S, 3.26-12.91% for N_2 (Zhang et al., 2009).

The excellent reproducibility of volatile abundances and compositions in our experiments indicates the effective analytical procedures we applied, including (1) sample pre-treatment to remove carbonate, sulfide and possible volatiles absorbed on mineral surfaces and cracks, (2) effective analytical procedures that rapidly trap released volatiles and prevent formation of new species, and (3) 1 hour duration of heating can release volatiles completely.

3. Occurrence Modes of Volatiles

Volatiles in the mantle occur in various forms, such as a free state of elements (e.g., graphite, diamond etc.; Melton et al., 1972; Melton and Giardini, 1974; Tingle et al., 1990; Deines, 1992) and molecules (e.g., CO_2, H_2O etc.), as structural components in carbonate, sulfide or hydrous minerals (Matson and Muenow, 1984), as fluid inclusions (Roedder, 1965; Andersen and Neumann, 2001) and as some unidentified "species" dispersed in structural defects and vacancies in mantle mineral crystals (Green and Radcliffe, 1975). These occurrence modes have been recognized by petrographic observations and analytical results using Laser Raman microprobe, Infrared spectroscopy and stepwise heating methods.

Mantle volatiles as free species dispersed along grain boundaries in the mantle can percolate through and escape into the crust or leak to the Earth's surface through hot-springs, summit fumaroles, volcano and faults, which are difficult to quantify due to surface contaminations. Graphite, diamond, carbonate, sulfide and hydrous minerals are volumetrically insignificant in the mantle. Therefore, fluid inclusions and structure defects and vacancies in mantle minerals are primary host of mantle volatiles.

Stepwise heating reveals that volatiles are released progressively from mineral separates and tend to concentrate at three temperature intervals of 300-600°C, 600-1000°C and 1000-1200°C in constituent minerals of mantle xenoliths in eastern China (Figure 2a, Zhang et al., 2004, 2007, 2009) and of 200-400°C, 400-800°C and 800-1200°C in harzburgite and dunite of the Yushigou ophiolite in western China (Figure 2b, Hu et al., 2007). The progressive release of volatiles with increasing temperature, the increase of volatile contents with decreasing sample crushing size (Figure 3, Zhang et al., 2009), and the chemical compositional differences of three volatile release peaks (Table 1) suggest that volatiles reside in more than one form in the constituent minerals of mantle xenoliths, e.g., different types of fluid or melt inclusions (Xia, 1984; Deines, 2002; Zhang et al., 2004), and crystal structural defects and vacancies (Freund and Oberheuser, 1986; Bai and Kohlstedt, 1992; Zhang et al., 2004, 2007). Volatiles in different occurrence mode may have complex origins and histories (Burnard et al., 1998).

3.1. Fluid Inclusions

3.1.1. Types of Fluid Inclusions

Fluid inclusions are traditionally thought to be the primary hosts of volatiles present in nominally anhydrous mantle minerals, which were trapped during mantle mineral crystallization (Andersen and Neumann, 2001) or exsolved from the decompressed solid (Green and Radcliffe, 1975). The most common fluid inclusion reported from mantle minerals is pure CO_2 (Murck et al., 1978; Bergman and Dubessy, 1984; Frezzotti and Peccerillo, 2007). The volatile phases in fluid inclusions are often associated with melt (Roedder, 1965; Murck et al., 1978; Andersen and Neumann, 2001).

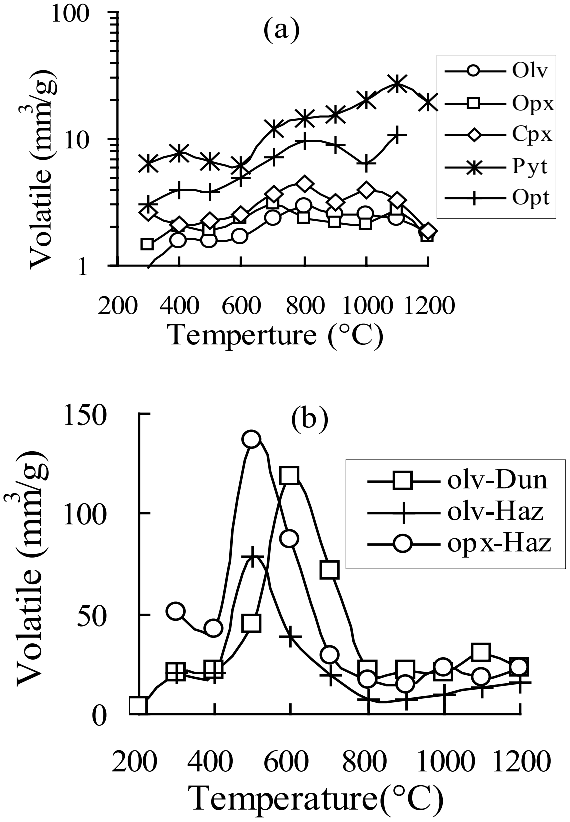

Figure 2. Average abundances of volatiles (mm^3.STP/g) released from mantle xenolith minerals (a) and the Yishugou ophiolitic peridotite (b) in China plotted as a function of heating temperature. Olv, Opx and Cpx are olivine, orthopyroxene and clinopyroxene in lherzolite xenoliths, respectively; Pyt is clinopyroxene in pyroxenite xenoliths, Opt is orthopyroxene megacryst, olv-Dun and olv-Haz are olivine in dunite and harzburgite respectively and opx-Haz is orthopyroxene in harzburgite.

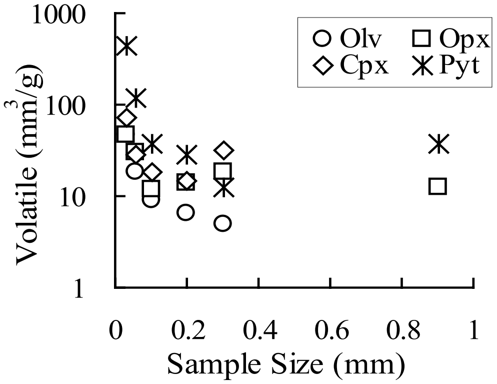

Figure 3. Total volatile contents (mm^3.STP/g) released at all steps plotted as a function of crushing size (mm) of olivine (Olv), orthopyroxene (Opx) and clinopyroxene (Cpx) in lherzolite and pyroxenite (Pyt) xenoliths.

Table 1. Chemical compositions (mm^3.STP/g) of volatiles released at different temperature intervals from constituent minerals of mantle xenoliths in Damaping, eastern China

Temperature	Mineral	Rock	H_2	CH_4	CO	N_2	CO_2	SO_2
300-600°C	Olv	lherzolite	0.90	0.33	1.70	0.08	1.81	0.00
	Opx	lherzolite	0.34	0.42	2.17	0.05	4.56	0.01
	Cpx	lherzolite	1.83	0.48	1.95	1.43	2.60	0.01
	Pyt	pyroxenite	1.29	0.57	6.79	0.23	12.15	0.05
600-1000°C	Olv	lherzolite	1.95	0.01	6.29	0.05	0.42	0.00
	Opx	lherzolite	0.82	0.09	5.00	0.16	3.44	0.12
	Cpx	lherzolite	4.11	0.96	10.21	1.24	2.72	0.79
	Pyt	pyroxenite	12.28	0.15	37.28	5.32	2.48	0.01
1000-1200°C	Olv	lherzolite	0.47	0.00	2.65	0.04	0.35	0.00
	Opx	lherzolite	0.42	0.00	1.99	0.15	1.91	0.11
	Cpx	lherzolite	0.64	0.20	4.81	0.20	0.95	0.17
	Pyt	pyroxenite	2.42	0.00	28.75	2.26	0.68	0.01

The early-stage and late-stage two type fluid/melt inclusions can be readily recognized in mantle xenolith minerals based on the shape, size, distribution pattern and homogenization temperature (Roedder, 1965; Xia, 1984; Zhang et al., 2007).

(1) Early-stage fluid inclusions: Primary fluid inclusions trapped during mantle mineral crystallization show high internal pressure (0.8~ 1.4GPa) (Andersen et al., 1984; Xia, 1984; Navon, 1991), which can result in fracturing of host crystal and leakage of volatiles by rapid decompression or even thermal shock prior to ascent and cooling (Roedder, 1965; Andersen et al., 1984; Tait, 1992; Rosenbaum et al., 1996; Ertan and Leemanr, 1999; Andersen and Neumann, 2001). Some decrepitated and leaked inclusions are recognized by the star-shaped and ragged appearances, and often show signs of partial decrepitation in the form of planar arrays of tiny ellipsoidal inclusions radiating outward from a central spherical bubble (Roedder, 1984; Rosenbaum et al., 1996). Only crystal interiors preserve primary fluid inclusions intact, i.e., early-stage fluid inclusions, which usually are small in size (mostly 5 to 20 μ in diameter) with regular shapes (e.g., oval, egg or negative crystal shape), and are located in the crystal interiors, or distributed along crystal lattices of the host crystals, and have high homogenization temperatures (Xia, 1984; Andersen and Neumann, 2001).

(2) Late-stage fluid inclusions: Primary fluid inclusions distributed along edges of host crystals have been deformed, altered, leaked, or refilled during subsequent mantle metasomatism and other tectono-thermal events (Andersen et al., 1984; Ertan and Leemanr, 1999). The healed irregular or circle micro-fractures at edges of re-crystallized minerals trapped volatiles in subsequent mantle tectonic-thermal events as late-stage fluid inclusions (Roedder, 1965; Xia, 1984; Hansteen et al., 1991; Andersen and Neumann, 2001; Zhang et al., 2007), which are large in size (from 10 to 200μ in diameter or length) with irregular shapes (e.g., tree-branch, bead-string or tabular), and are located in healed micro-fractures or cracks at edges or oriented parallel to the cleavage traces of host minerals with low homogenization temperatures (Xia, 1984).

Volatiles in inclusions are compressible and condensed to the liquid state following an isochore, and form “shrinkage” bubble when mantle xenoliths ascend to surface and cool below entrapment temperature to room temperature (Roedder, 1965), which leads to reduced internal pressures within inclusions. Furthermore, silicate glasses or carbonaceous films deposited and encapsulated at inclusion lining are relatively resistant to volatile exchanges between inclusions and the host crystals (Murck et al., 1978; Xia, 1984; Mathez, 1987; Rosenbaum et al., 1996; Burnard et al., 1997). Depressurized inclusions with silicate glass or carbonaceous lining readily keep their volatiles intact during surface events after ascending and cooling; the volatiles stored can provide information on their origins.

3.1.2. Decrepitation of Fluid Inclusion

The decrepitation of fluid inclusion depends on physical strength of the host crystal as well as pressure difference between the internal fluid pressure in the inclusion and external pressure of the host crystal. The physical strength of the host crystal around the fluid inclusion depends on crystal type, density of cleavages/cracks, and wall thickness of inclusion (e.g., sample crushing size, distance to crystal edges) (Zhang et al., 2007). Mantle minerals such as Olv, Opx and Cpx are brashy (vs. quartz), which leads to reduced physical strength and readily fractured host crystals, thus reducing decrepitation temperatures of fluid inclusions. Small crushing size, presence of micro-cracks and thin walls also facilitate inclusion decrepitation.

During vacuum heating, liquid phases in inclusion are gasified, and the volatiles dissolved in glass/melt and daughter crystal in inclusion are separated into gas phase while glass and daughter crystal begin to melt progressively, which rapidly raises internal pressure in the inclusion as progressively heating due to the high thermal expansion coefficient of volatiles (Lowenstern, 1994), and internal pressure of inclusion will reach the entrapped pressure at homogenization temperature. On the other hand, mantle minerals release very low content of volatiles into the high vacuum line at each heating step, moreover most of the volatiles with low freezing-point are condensed into cold trap (Zhang et al., 2004, 2007), i.e., the pressure of host crystal exterior is very low (~10-200Torr). Therefore, a large pressure gradient exists between the inclusion interior (usually over-pressured) and the crystal exterior (nearly low vacuum) when sample has been heated upto homogenization temperature. The fluid inclusion will decrepitate if the host crystal is not strong enough to withstand large pressure differences at about the range of homogenization temperatures (Tait, 1992).

In principle, inclusions trapped at same stage of tectono-thermal event should simultaneously decrepitate for a given crushing size of sample and release volatiles during stepwise heating due to similar internal pressures, homogenization temperatures, residence sites, and ratios of vapor/liquid or glass (Hansteen et al., 1991; Andersen and Neumann, 2001). For a given crushing size of sample, small size of inclusions, such as early-stage fluid inclusions, are associated with thick walls of fluid inclusions (i.e. greater strength against decrepitation) and will decrepitate at higher temperatures than large size of inclusions, such as late-stage fluid inclusions.

(1) Early-stage fluid inclusions: The early-stage fluid inclusions trapped at ambient mantle P-T conditions of mineral crystallization are expected to decrepitate at a temperature range close to or slightly lower than homogenization temperatures due to anticipated high interior pressures of inclusions (Xia, 1984; Andersen and Neumann, 2001). The volatile release peak at 600-1000°C shows largest intensity for crushing size of 0.06mm, and declines

in intensity for samples of smaller or larger crushing size, indicating the degassing feature of fluid inclusion. The process of sample crushing size reduction is actually to reduce wall thicknesses (i.e. physical strength) of fluid inclusions with a given size range, which facilitates decrepitation of fluid inclusions. The volatile release peak at 600-1000°C are interpreted as decrepitation of early-stage fluid inclusions (Zhang et al., 2007), and are dominated by CO (7.17 mm^3.STP/g on average), which is supported by volatile compositions of same type fluid inclusions (Bergman and Dubessy, 1984) and re-equilibrated experiment of pure CO_2 fluid inclusions (Pasteris and Wanamaker, 1988). Pasteris and Wanamaker (1988) reported that pure CO_2 fluid inclusions were re-equilibated to dominant CO at >1000°C based on their micro- thermometry and laser Raman microprobe study.

(2) Late-stage fluid inclusions: The late-stage fluid inclusions distributed along crystal edges have thin walls of fluid inclusions with weak physical strength, thus are readily decrepitated with reduced decrepitation temperatures. The volatile release peak at 300-600°C decreases in intensity with decreasing crushing size, and nearly disappears at crushing size of 0.03mm, which is about the smallest size of late-stage fluid inclusions (Zhang et al., 2009). This is caused by late-stage fluid inclusions to be broken and outgassed, and lost their volatiles during progressive crushing (Marty and Zimmermann, 1999; Matsumoto et al., 2000; Aubaud et al., 2005), which is supported by the similar compositions of volatiles (i.e., CO_2, ~ 2.99 mm^3.STP/g on average) to those of same type individual fluid inclusions analyzed by *in situ* Laser Raman Probe (Xia et al., 1984; Yang et al., 2001).

3.2. Volatiles in Mineral Structural Defects and Vacancies

Volatiles can also be trapped in structural defects and vacancies (Freund and Oberheuser, 1986; Bai and Kohlstedt, 1992), or dispersed in crystal structure (Green and Radcliffe, 1975) during crystallization, and possess similar chemical compositions to early stage inclusions. The former are similar to nm-sized inclusions below optical resolution, which are attached to crystal defects induced by deformation and exsolution (Green and Radcliffe, 1975; Koch-Müller et al., 2004) and are released at higher heating temperatures to overcome the larger physical strength around structural defects and vacancies than early stage inclusions (Matsumoto et al., 2000).

Grain size reduction experiment reveals that the total contents of volatiles as well as individual volatile species (CO_2, CO, H_2) increase with decreasing sample crushing size, especially increase rapidly towards smaller sample crushing size, which is consistent with increasing grain surface areas (Figure 3, Zhang et al., 2009). Volatile abundances released at the 1000-1200°C interval increase with decreasing sample crushing size and show additional concentration peak in samples of smaller crushing size. The release temperature of 1000-1200°C overlaps the final equilibration temperature ranges of lherzolite xenoliths (987°C to 1296°C, Fan and Hooper, 1989). Their chemical composition dominated by CO with minor H_2 and CO_2 are similar to volatiles released at the 600-1000°C interval for early-stage fluid inclusions. Hence, volatile release peak at the 1000-1200°C interval likely results from degassing of volatiles trapped in crystal defects and vacancies, and are volumetrically significant (Zhang et al., 2009).

3.3. Anion Complexes Incorporated in Crystal Structures

Anion complexes incorporated in crystal structures are considered as another primary occurrence mode of volatiles in hydrous mantle minerals, e.g., OH^- in amphibole and mica, Cl^- and F^- in apatite etc. (Chazot et al., 1997; O'Reilly and Griffin, 2000; Aubaud et al., 2007). Especially OH^- concentrations, incorporation and diffusion mechanism and their effect in olivine, pyroxene, and garnet etc. major mineral phases of upper mantle have been well studied by infrared spectroscopy (IR), NMR, X-ray and neutron diffractions, mass spectrometry (MS), laser Raman spectroscopy, hydrogen diffusion, hydrothermal and dehydrogenation experiments (Ackermann et al., 1983; Freund and Oberheuser, 1986; Kitamura et al., 1987; Smyth et al., 1991; Bai and Kohlstedt,1992; Bell et al,1995; Kohn,1996; Mierdel et al., 2007; Grant et al., 2007) since hydroxyl was first identified in nominally anhydrous minerals (Martin and Donnay, 1972).

The amount of structural OH^- is constrained by the replacement amount of Fe^{3+} by Fe^{2+} in mineral structure and hydrogen partial pressure (P_{H2}) of the formation environment (Skogby and Rossman, 1989; Ingrin et al,1995). OH^- in crystal structure is released when heating temperature is high enough to break OH bond in crystal lattices (Bell et al. 1995; Kohn, 1996). FTIR absorbance peak of OH^- at a wavelength of about $3450cm^{-1}$ in olivine and orthopyroxene shows that OH^- amounts are obviously reduced only when samples have been vacuum degassed at 1200°C (Zhang et al., 2005), which is supported by OH^- solubility and stability experiments (Bell et al. 1995; Kohn, 1996).

3.4. The Superimposed Effects of Volatiles in Different Occurrence Modes

Large size fluid inclusions can be broken and release their volatiles during progressive crushing (Marty and Zimmermann, 1999; Matsumoto et al., 2000; Aubaud et al., 2005). Late stage fluid inclusions with large size are always located at sample edges and can be readily decrepitated at lower temperatures, or broken in smaller crushing size of samples. So the volatiles in late stage fluid inclusions have little superimposed effects on volatile release peaks at high heating temperatures of 600-1000°C and 1000-1200°C.

The early stage fluid inclusions located in crystal edges are readily decrepitated with reduced decrepitation temperatures due to thin wall of fluid inclusions. Some early stage fluid inclusions in crystal interiors could be shifted to sample edges during sample crushing, so more early stage fluid inclusions in sample edges of small crushing size could be released at lower temperatures and have superimposed effects on volatiles at 300-600°C intervals. Early stage fluid inclusions in large crushing size samples are difficult to decrepitate due to thicker wall of fluid inclusions, a little of early stage fluid inclusions in crystal edges show little superimposed effect on volatiles at 300-600°C intervals.

Volatiles trapped in structural defects and vacancies of crystals are released at temperatures high enough to destruct the crystal lattices, so their superimposed effect on concentration peaks of 300-600°C and 600-1000°C is negligible.

4. The Redox State and Volatile Species in the Mantle

4.1. The Redox State in the Mantle

Oxygen fugacity (fO_2) is an important parameter in mantle processes. The redox state of lithospheric mantle is heterogeneous and varies over four log units, e.g., oxygen fugacity (f_{O2}) can vary from 3 log units below and 1 log unit above the fayalite-magnetite-quartz (FMQ) buffer using the olivine-orthopyroxene-spinel oxygen barometry (i.e., FMQ-3 to FMQ+1; Ballhaus, 1993; Wood and Virgo, 1989). The f_{O2} in the mantle may have changed to the more oxidized state over the Earth's history because of mantle degassing and introduction of recycled components (O'Neill and Wall, 1987), and also vary spatially from oceanic to continental mantle (Bernardj and Ltaras, 1992), from orogenic belts (Woodland et al, 1992) to craton (Ballhaus, 1993; Woodland and Koch, 2003), and from deep to shallow mantle.

The redox states in upper mantle become more oxidized from initial Earth to the present (Eggler and Baker, 1982; O'Neill and Wall, 1987). The f_{O2} in the upper mantle could be near nickel precipitation curve (iron-wustite buffer, IW) in olivine during late stage of Earth's formation, and then became more oxidized because oxygen-enriched components (e.g., H_2O, CO_2 and O_2) were added by plate subduction (O'Neill and Wall, 1987). For example, the f_{O2} of isolated samples from Archaean cratonic lithosphere is as low as FMQ-5, fertile spinel peridotite xenoliths (1.5GPa) is around FMQ-2 (Ballhaus, 1993). Heterogeneous redox state of Archean cratons may mostly result from heterogeneous nature of percolating fluids (Thomassota et al., 2007). The fO_2 in upper mantle show highest value nearby subduction zones due to large quantity of oxidized volatiles released (Wood et al., 1990).

The Earth's mantle is degassed along mid-ocean ridges, while is re-hydrated (and possibly re-carbonated) at subduction zones. These processes and the speciation of C-H-O fluids in the mantle are related to the redox state of mantle peridotite. Abyssal spinel peridotites and quenched MORB glasses demonstrated that the redox state in oceanic mantle is more reduced than in the SCLM (Bernardj and Ltaras, 1992; Ionov and Wood, 1992). The f_{O2} values of MORB and OIB range from FMQ-1 (N-MORB) to ~ FMQ +2 (OIB) (Ballhaus, 1993), the outer surface quench glasses of MORB lavas indicated the fO_2 of FMQ-1 to FMQ-2 in the mantle source regions of MORB (Christie et al.,1986). Peridotites from ocean ridges are reduced and have an average fO_2 of about -0.9 log unit relative to FMQ; whereas peridotite xenoliths from continental localities exhibit a fO_2 range from FMQ-1.5 to FMQ +1.5 (Wood et al., 1990). The Earth's interior is more reduced than the redox state reflected by the erupting tholeiitic magmas; basaltic melts are more oxidized than samples from lithospheric upper mantle. An initially highly reduced mafic magma may become oxidized by degassing of C-species under the shallow crust conditions (Mathez, 1984).

The fO_2 is sensitive to pressure, and falls with increasing pressure. The rate of reduction per unit GPa pressure increase may be of the order of 0.6 log unit (Ballhaus, 1995). For example, the fO_2 varies along CCO buffer ($C+O_2=CO_2$) at uppermost portions of upper mantle (Blundy et al., 1991). fO_2 may decrease up to ~3 log units with the upper mantle depth between about 80 and 150 km beneath the Kaapvaal craton in Southern Africa. The $\Delta\log fO_2$ lies just FMQ-4 at ~220 km depth (Woodland and Koch, 2003). Spinel lherzolites from the Baikal rift area have slightly lower fO_2 than depper garnet- and garnet-spinel lherzolites (Ionov and Wood, 1992). fO_2 is expected to decrease further with depth in the asthenospheric mantle, reaches conditions of metal saturation (Fe-Ni precipitation curve in olivine, IW) near the 410 km discontinuity, and meets the necessary condition for 'redox melting' in the deeper portions of the upper mantle (Wood et al., 1990; Woodland and Koch, 2003). The lowest fO_2 is consistent with dominant CH_4, H_2 and other reduced volatiles in fluid inclusions of diamond (Melton et al., 1972; Melton and Giardini, 1974; Eggler and Baker, 1982).

4.2. Volatile Species in the Mantle

Volatile species in the C-H-O system at mantle high pressure and temperature are mixtures of H_2O, CO_2, CO, CH_4, O_2 and H_2 (Bergman and Dubessy, 1984; Saxena and Fei, 1988; Ballhaus, 1993), which are potentially important redox-controlling reactants (Deines, 1992). In the f_{O2} range between IW and FMQ, upper mantle materials contain a number of elements that can attain more than one redox state (Ballhaus, 1995):

$$C+O_2=CO_2 \qquad [1]$$

$$2C+O_2=2CO \qquad [2]$$

$$CH_4+O_2=C+2H_2O \qquad [3]$$

$$2H_2 + O_2 = 2H_2O \qquad [4]$$

Spatial and temporal variations of oxygen fugacity in the mantle place important controls on volatile speciation in the mantle (Deines, 1980). Significant variability of oxygen fugacity in the upper mantle is consistent with the occurrence of both reduced (CH_4 and H_2, or CH_4 and H_2O bearing) and oxidized (CO_2 and H_2O bearing) fluids (Thomassota et al., 2007). The volatile accretion in the Earth are heterogeneous: the primary reduced materials, 99.8% of the solar planet, brought 6% of H, 48% of C and 70% of N of the upper Earth (upper mantle, crust, ocean-atmosphere), a late veneer of CI composition supplied the residual (Javoy, 1997). Mantle volatiles also vary in chemical compositions from continent to ocean, and from deep mantle to shallow mantle due to heterogeneous redox state in the mantle (O'Neill and Wall, 1987; Wood and Virgo, 1989; Bernardj and Ltaras, 1992; Ballhaus, 1993; Javoy, 1997; Woodland and Koch, 2003).

Volatiles identified in mantle samples are often oxidized and consist of CO_2 and H_2O (Roedder, 1984), such as high density CO_2 inclusions in worldwide mantle minerals (Roedder, 1984; Xia, 1984; Andersen and Neumann, 2001; Frezzotti and Peccerillo, 2007), which gives a false notion that CO_2 is a dominant volatile phase in the mantle. With increasing pressure or depth in the lithosphere, elemental carbon becomes progressively refractory and carbon-bearing equilibria become more important for f_{O2} control. Below a realistic lower f_{O2} limit given by the H_2O+ C= CH_4+ O_2 (C-H_2O) equilibrium, a fluid becomes CH_4 rather than CO_2-bearing, and carbonatitic melt is presumably unstable (Ballhaus, 1993). The volatile phase(s) would be dominantly composed of H_2O and CH_4 near the 410 km discontinuity (below FMQ-4) (Ballhaus, 1995; Woodland and Koch, 2003).

Different elements may occur as variably different volatile species with depths in the mantle, e.g., carbon solubility increases with pressure (Shcheka et al., 2006). Volatile speciation in the upper mantle has been examined by sufficient number of abyssal spinel peridotites and quenched MORB glasses as probes of the upper mantle (Bernardj and Ltaras, 1992). C-H-O system is likely to be dominated by CH_4, H_2 and H_2O in deeper upper mantle (>100 km), CH_4 and H_2 are dominant volatiles in the convecting upper mantle, while CO_2 only plays a minor role. CO_2 is unlikely a major contributor to the upper mantle's volatile budget at pressures exceeding 3GPa (Ballhaus, 1995). Primordial mantle volatiles in the asthenosphere were originally CH_4-N_2-rich corresponding to mantle redox melting (Liu and Fei, 2006). For example, diamonds were precipitated from reduced CH_4-bearing fluid(s) within the sub-continental mantle at depths > 150 km and T > 1200 °C (Thomassota et al., 2007). Conditions in the vicinity of mantle plumes are favorable for CH_4 dominant volatile phase in the upper mantle (Bernardj and Ltaras, 1992). But asthenospheric mantle at depths greater than 150 km in Hawaii could have high-density CO_2 (+H_2O+H_2S) volatiles (Frezzotti and Peccerillo, 2007).

5. Chemical Compositions of Volatiles in Sub-Continental Lithospheric Mantle

Volatiles in the sub-continental lithospheric mantle (SCLM) are still poorly understood, especially their chemical compositions. Mantle-derived minerals from different depths provide a rare opportunity to study a deep-seated compositional profile of volatiles in the SCLM. Continental basalts are always contaminated by crustal or atmosperic components during magma ascent, and contain more oxidized volatile species like CO_2 (58.4-79.78 mol%) and SO_2 (2.87-31.35 mol%) (Zhang et al., 1999a, b).

Among mantle minerals, only diamonds possess sufficient strength to encapsulate and transport volatiles trapped at depths in excess of 100 km to the surface (Navon, 1991). The fluid inclusions in different color/shape, corresponding to different origins, have distinct chemical compositions (Melton et al., 1972; Melton and Giardini, 1974; Deines, 1980; Eggler, and Baker,1982; Navon et al., 1988). Colorless diamonds have more reduced volatiles (e.g., higher contents of H_2 and CO etc.) than colored diamonds with recycled components (Table 2, Ivankin et al., 1988), which is similar to initial volatiles in the SCLM with primitive mantle-like reservoir (see below).

Table 2. Chemical compositions (mm^3.STP/g) of volatiles of fluid inclusions in different types of diamonds (summarized from Ivankin et al., 1988)

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

Volatiles in mantle xenoliths record their nature and origin during mantle evolution. Alkali basalts always host mantle xenoliths with fresh Olv, Opx and Cpx minerals or megacrysts. Olv, Opx and Cpx behave in different way during mantle partial melting, magma crystallization and mantle metasomatism due to distinct chemical and physical properties (e.g., initial melting or crystallization temperatures), and hence preserved volatiles from different depths or origins (Albarede, 2008; Zhang et al., 2004, 2007). Volatiles in different occurrence modes of minerals in mantle xenoliths show various origins with information pertaining to the formation and evolution of the Earth's mantle. Based on the chemical and isotopic compositions of volatiles in mantle xenoliths, "initial" and "metasomatic" two types of volatiles in the SCLM can be distinguished.

5.1. The Initial Volatiles in the SCLM

The initial volatiles in the SCLM refer to volatiles trapped in crystals during initial stage of mantle mineral crystallization; they were trapped both in primary fluid inclusions and in structural defects and vacancies of the minerals. Olivine is the most refractory mineral of lherzolite xenoliths that can preserve the initial volatiles intact in crystal interiors, and survived subsequent mantle events. So initial volatiles in the SCLM can be characterized by the volatiles released at 600-1200°C from olivine of lherzolite xenoliths (Zhang et al., 2004).

Initial volatiles in the SCLM beneath eastern China vary in chemical compositions with mantle components defined by Sr-Nd-Pb isotopes (Zhu, 1995; Griffin et al., 1998). The chemical compositions of initial volatiles in different mantle reservoirs from eastern China and western USA are summarized in Table 3 (Zhang et al., 2004, 2005). Initial volatiles in the SCLM is dominated by CO with minor CO_2 and H_2 in primitive mantle-like reservoir (PM), such as the North China Craton; whereas they are dominated by CO_2 with minor SO_2 and H_2 in depleted mantle reservoir (DM), e.g., the South China Craton. Enriched mantle reservoir (EM), e.g., northern part of northeastern China fold belt and western America, display high contents of volatile and H_2 in initial volatiles in the SCLM, suggesting a mantle fluid with high H_2 contents. Initial volatiles in the SCLM with a "mixed" mantle reservoir are primarily composed of CO_2 and SO_2 which are related to recycled continental crustal fluids (Dabie ultra-high pressure metamorphic belt).

Table 3. Chemical compositions (mm^3.STP/g) of initial volatiles in the SCLM in different mantle reservoirs

Mantle	H_2	CH_4	H_2S	CO	N_2	CO_2	SO_2	Total
Primitive Mantle	2.76	0.12	0.01	7.77	0.41	3.04	0.02	14.13
Depleted Mantle	3.66	0.19	0.00	4.92	0.18	7.49	0.82	17.26
Enriched Mantle	18.73	0.20	0.00	4.60	0.38	6.26	0.18	30.35
Mixed Mantle	0.12	0.03	0.00	0.00	1.01	24.66	2.61	28.43

CO_2 contents in initial volatiles in the SCLM with various mantle reservoirs are all much lower than estimated values of primitive mantle (from 5.23-12.5 $\times 10^{-6}$ mol/g) (Zhang and Zindler, 1993; Jambon, 1994). The calculated H_2O contents in depleted and primitive mantle also show high values to be 13.89-64.44 $\times 10^{-6}$ mol/g (O'Neil and Palme, 1998). Low abundances of CO_2 and H_2O in olivine, i.e. initial volatiles in the SCLM, are supported by the fact that CO_2 and H_2O contents in whole rock samples of lherzolite are higher than in olivine, and that LREE-rich volatiles related to CO_2 were preserved mainly in Opx, Cpx or mineral interstices (Xu, 2000). Ultramafic xenoliths from alkali basalts or kimberlites have undergone voaltile fractionation etc. processes within the mantle, so that volatiles in Olv must be considered as the lowest values of initial volatiles in the SCLM. CO_2 and H_2O could be preserved in Opx, Cpx or mineral interstices.

5.2. The Metasomatic Volatiles in the SCLM

5.2.1. The Types of Metasomatic Volatiles

Mantle metasomatism is extensive throughout the SCLM, which may be macroscopic with conspicuous metasomatic minerals (e.g., amphiboles, phlogopite, apatite etc.) or cryptic 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.

The volatiles of macroscopic metasomatism can be infered from volatiles in different types of metasomatic minerals. The amphiboles from mantle xenoliths in Vulcan's Throne, Grand Canyon, Arizona, USA show volatiles of macroscopic metasomatism dominated by H_2O with high concentrations of O_2, CH_4, CO_2 and CO (Table 4, Matson and Muenow, 1984), differing from initial volatiles in the SCLM in the western USA (Zhang et al., 2005b) or volatiles in diamonds with mantle origin (Ivankin et al., 1988). The more oxidized volatile species could be originated from shallow mantle or recycled components.

Table 4. Chemical compositions (mm^3.STP /g) of macroscopic metasomatic volatiles from different types of amphiboles in Arizona, USA (summarized from Matson and Muenow, 1984)

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

Extensive cryptic mantle metasomatism in the SCLM has been widely observed in mantle xenoliths and is defined by the decoupling between enriched trace elements and depleted major elements and Sr-Nd-Pb isotopes (Griffin et al., 1998; Coltorti et al., 2000). Orthopyroxene and clinopyroxene with low melting point are readily altered by metasomatic fluids. The volatiles released at 600-1200°C from Opx and Cpx of mantle xenoliths are predominantly H_2 with minor amounts of CO_2 and CO in eastern China and western USA

(Zhang et al., 2004, 2005b), which can represent one type of volatiles in cryptic mantle metasomatism (Zhang et al., 2004, 2007), and are summarized as Type I in Table 5.

On the other hand, recrystallization of such metasomatized peridotites would incorporate the cryptic metasomatic volatile agents as fluid (or melt) inclusions at the edges and cracks of the recrystallized minerals (Peng et al., 1994). This type of metasomatic volatiles are released at 300-600°C from Olv, Opx and Cpx of mantle xenoliths in eastern China, and are primarily composed of CO_2 and SO_2 (Zhang et al., 2004), which differ from initial volatiles in the SCLM and type I cryptic metasomatic volatiles. So the volatiles released at low temperature interval represent another type of volatiles in cryptic mantle metasomatism, and are summarized as Type II in Table 5.

Table 5. Chemical compositions (mm^3.STP/g) of cryptic metasomatic volatiles in the SCLM in different mantle reservoirs

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

NCC- northern China craton, SCC- southern China craton, W-USA- western margin of USA.

5.2.2. The Residence of H_2 in Metasomatic Volatiles

H_2 is one of the most important volatile components in the solar system. A certain amount of H_2 as one of the primordial components remains in the Earth's interior. H can be incorporated as OH^- in crystal structures of mantle-derived olivine, pyroxene and garnet etc. minerals (Skogby and Rossman, 1989; Smyth et al, 1991; Bai and Kohlstedt, 1992; Ingrin et al, 1995; Bell et al, 1995; Kohn, 1996). Structural OH^- has been considered as the main occurrence mode of H in anhydrous mantle minerals (Martin and Donnay, 1972).

H can enter into or degas from Si-deficient and Fe^{3+}-rich pyroxene structure by the following reaction, which controls the amount of OH^- in pyroxene (Skogby et al., 1989).

$$2Fe^{3+}+2O^{2-}+H_2 = 2Fe^{2+}+2OH^- \qquad [5]$$

Olivine is volumetrically the most important mineral in the upper mantle. The incorporating way of H in olivine could be distinctive from pyroxene, yet little is known about the mechanisms of OH^- incorporation in olivine structure (Grant et al., 2007). OH^- could take octahedral or tetrahedral vacancies in olivine (Freund and Oberheuser, 1986). H may enter into olivine structure by placing a neutral site and incorporating OH^- with vacancy O^{2-}, or placing a metal position with 2 negative charges and forming H (Bai and Kohlsted, 1992). Hydroxyl solubility in olivine depends on fO_2, but current data from relatively high fO_2 experiments overestimate the OH^- solubility in mantle olivine (Grant et al., 2007).

Olv, Opx and Cpx show varying H_2 contents and infrared spectra with grain-size and heating temperature during stepwise heating, (1) H_2 mainly release at two temperature intervals of 600-1000 and 1000-1200°C. (2) H_2 contents decrease from Cpx (av. 3.667mm^3.STP/g), to Olv (av. 3.183 mm^3.STP/g) and to Opx (av. 1.381 mm^3.STP/g). H_2 contents released from olivine increase rapidly with decreasing sample crushing size. H_2 in orthopyroxene and clinopyroxene has the highest content at crushing size of 0.2 and 0.1mm, respectively, and then decreases with decreasing sample crushing size. (3) Infrared absorbance peaks of OH^- in Olv and Opx at a wavelength of about 3450cm^{-1} are not reduced while degassed at 600°C and 900°C compared with samples dried at 120°C, but are obviously reduced after degassed at 1200°C.

Because organic contaminants and gases adsorbed on the sample surface and in cracks and secondary inclusions have been removed completely by our efficient sample pretreatment and analytical procedures, H_2 released from mantle minerals could be derived from three sources: (1) reactions [6-9] among volatiles at high-temperature:

$$C + H_2O = CO + H_2 \qquad [6]$$

$$CO_2 + CH_4 = 2CO + 2H_2 \qquad [7]$$

$$CH_4 + 2H_2O = CO_2 + 4H_2 \qquad [8]$$

$$2Fe_3O_4 + H_2O = 3Fe_2O_3 + H_2 \qquad [9]$$

(2) OH^- in mineral structure and H^0 in structural vacancies, and (3) fluid inclusions.

The efficient analytical procedures, i.e., adopting a liquid-N_2 cold trap etc., can eliminate the contribution of H_2 derived from reactions [6-9] of released volatiles, which are supported by negligible contents of H_2 and CO in analyses of other type samples using the same experimental procedure (Zhang et al., 1999a, b; Hu et al., 2007). New volatile phases formed by possible reactions among volatiles inside fluid inclusions or samples are considered as re-equilibrated volatile compositions at mantle high temperature conditions (Anderson et al., 1984; Pasteris and Wanamaker, 1988; Zhang et al., 2000).

Following lines of evidence indicate that little H_2 released at 600-1000°C has been derived from degassing of structural OH^-:

1) Infrared spectra of Olv and Opx separates from lherzolite xenoliths indicate that OH^- contents are not reduced in samples degassed at 600°C and 900°C compared with samples dried at 120°C, but are obviously reduced when samples are degassed at 1200°C (Zhang et al., 2005).
2) H_2 contents decrease with decreasing sample crushing size in Opx and Cpx, which is inconsistent with increasing sample surface area. H_2 from either structural OH^- or H^0 in structural defects and vacancies should increase by sample crushing (Skogby and Rossman, 1989).
3) H_2 in metasomatic volatiles has heavier δD ranging from -31.1 to -96.4‰ (Zhang et al., 2007) than OH^- in mantle-derived garnet, enstatite and augite (-92 to -113‰, Bell and Ihinger, 2000).

4) H_2 releasing peaks at 600-1000°C show synchronous release with volatiles derived from early stage fluid inclusions.

All these suggest that high concentrations of H_2 released at 600-1000°C may be primarily stored in fluid inclusions; H_2 released at 1000-1200°C could be from the loss of structural OH^-, which is also supported by OH^- solubility and stability experiments (Bell et al., 1995; Kohn, 1996; Grant et al., 2007). Hydroxyl solubility in olivine at low fO_2 (below Fe-FeO) is substantially less than that solubility laws might suggest (Grant et al., 2007). Structural OH^- in pyroxene is more difficult to lose, and could be released when pyroxene has been heated at 1000°C for 24 hrs in air (Bell et al.,1995).

OH^- can be incorporated efficiently in pyroxene structures when pyroxene was heated only in H_2 atmosphere (Skogby and Rossman, 1989), so high concentrations of H_2 from either early stage fluid inclusions or the loss of structural OH^- suggested that an H_2-rich (in free state) volatile may have been involved in the metasomatism of the SCLM in eastern China and western USA.

5.3. The Origins of Volatiles in the SCLM

5.3.1. The Volatiles of Mantle Origin

C, O and H isotopes and concentrations of volatiles in mantle xenoliths should allow faithful identification of various source components in the volatiles. Initial volatiles in the SCLM beneath eastern China are characterized by $\delta D_{H2,\ H2O}$, $\delta^{13}C_{CH4}$ and $\delta^{18}O_{CO2}$ of mantle origin. δD values of H_2O and H_2 (from -33.8‰ to -88.2‰) are restricted to the δD range of "normal" upper mantle, $\delta^{13}C$ values of CH_4 towards the methane $\delta^{13}C$ value from Murchison meteorite and olivine in oceanic gabbros (Yuen et al., 1984; Abrajano et al, 1988; Kelley and Frueh, 1995), suggesting that a large proportion of initial volatiles in the SCLM could be upper mantle origin.

5.3.2. The Origin of H_2 in Metasomatic Volatiles

H_2 in metasomatic volatiles has δD ranging from -31.1 to -96.4‰. Garnet lherzolite from deeper mantle shows higher content of H_2 (145.10 mm^3.STP/g) than spinel lherzolite (Zhang et al., 2007); H_2 contents in Cpx (av. 3.667mm^3.STP/g) are higher than Olv (av. 3.183) and Opx (av. 1.381) etc. crystalized early minerals. All thses prove that H_2 could come from deep mantle at late stage of the SCLM formation and evolution beneath eastern China.

5.3.3. Recycled Crustal Volatiles

The recycled crustal volatiles (RCVs) are identified in both initial volatiles and metasomatic volatiles in the SCLM beneath eastern China based on C-O-H isotopic compositions of volatiles:

1) RCVs in initial volatiles: Initial volatiles released at 600-1200°C from Olv show difference in volatile compositions between North China Craton (NCC, dominated

by CO) and South China Craton (SCC, dominated by CO_2), suggesting different formation and development condition between NCC and SCC. They are characterized by $\delta D_{H2, H2O}$, $\delta^{13}C_{CH4}$ and $\delta^{18}O_{CO2}$ of mantle origin with lighter $\delta^{13}C_{CO2, CO}$, and suggested that a little RCVs were mixed into volatiles of old Cratonic lithosphere during a Proterozoic continental collision (1.9Ga) (Zhang et al., 2008).

2) RCVs in type I cryptic metasomatic volatiles, which are released at 600-1200°C from Opx and Cpx, are dominated by H_2 both in NCC and SCC, suggesting their similar development condition. δD_{H2} and $\delta^{13}C_{CH4}$ with mantle characteristics implied their mantle origin. Lighter $\delta^{13}C$ of CO_2 and CO, and heavier $\delta^{18}O$ of CO_2 suggested that a recycled crustal volatiles with terrigenous features have been involved possibly during a common crust-mantle interaction process during Mesozoic collision of NCC and SCC (Zhang et al., 2008).
3) RCVs in type II cryptic metasomatic volatiles, which were released at 300-600°C from Olv, Opx and Cpx of mantle xenoliths, and composed mainly of CO_2 both in NCC and SCC. Their crustal $\delta^{13}C$ of CO_2 and CO, biogenic $\delta^{13}C$ of CH_4, lighter and variable $\delta^{18}O$ of CO_2, and lighter δD of H_2 suggested the presence of a recycled oceanic crustal volatile during the SCLM thinning, which could be derived from dehydration of the subducted paleo- Pacific lithosphere (or predecessor) that lies horizontally in the transition zone beneath eastern China (Zhang et al., 2007).

6. Chemical Compositions of Volatiles in Oceanic Upper Mantle

The chemical composition of volatiles in oceanic upper mantle (OUM) can be deduced from volatiles of fresh oceanic basaltic glasses because of the inaccessibility of fertile mantle source regions. MORB, OIB, BABB and much of IAB are originated from OUM. Volatiles in modern OUM can be investigated by means of oceanic basalts and mantle xenoliths, mantle xenoliths are reliable samples for mantle volatiles relative to oceanic basalts that are always contaminated by air and seawater during magma generation and ascent, and are in a more oxidized state than OUM (Mathez et al., 1984). The volatiles in ancient OUM can be investigated by means of ophiolitic peridotite or ancient ocean basalts which always altered.

6.1. Modern Oceanic Upper Mantle

Volatiles in modern (refer to currently extant) OUM have been the subject of a small number of broad and global studies. Available volatile investigations in modern OUM are conducted by oceanic basalt glasses and mantle xenoliths, Volatiles within the asthenospheric mantle at depths greater than 150 km in Hawaii could be high-density CO_2 ($+H_2O+H_2S$) in the diamond stability field (Frezzotti and Peccerillo, 2007). Volatiles in oceanic basalts are higher in abundance than in SCLM xenoliths. MORB, OIB and IAB formed under distinct conditions and by different mechanisms show difference in redox state (Ballhaus, 1993), REE, Pb-Sr-Nd isotopes (Hofmann, 1997; Niu and Batiza, 1997; Niu et al., 2003, 2005), and display distinct volatile compositions, C-O-H and noble gas isotopes (Eiler et al., 1995, 1997; Ozima and Podosek, 2002; Hansteen and Troll, 2003). The chemical compositions of volatiles released from different types of oceanic basalt are summarized in Table 6.

Table 6. Chemical compositions (mm^3.STP/g) of volatiles released from different type of oceanic basalts

Type	Ocean	Location*	Rock	n	CO_2	N_2	H_2O	CH_4	CO	Method[#]	Ref.[+]
MORB	Indian	IRT,CIR,SI	Glass	52	172	0.19				Crushing	[a]
		IRT	Basalt	6	28.1	0.18	9.7067			Crushing	[b]
	Pacific	GSC, EPR	Glass	33	99.1	0.02	2940.8	140	320	H-T MS, IR	[c]
		GSC, EPR	Basalt	15	716		2204.4	97	211	H-T MS	[d]
	Atlantic	13.5°N	Popping	5	464		77.907			Crushing	[e]
		FAMOUS	Glass	9	672		2613.3			H-T MS	[f]
OIB	Hawaii	Loihi	Basalt	5	468		7740.4			IR, H-T MS	[g]
		Loihi, Kilauea	Glass	29	295		7831.1			H-T MS	[h]
	Samoa		Glass	18	30.4		11455			IMP	[i]
IAB	Mariana	Arc	Basalt	4	1246		13263			H-T MS	[j]
BABB	Mariana	Trough	Basalt	4	1060		12731			H-T MS	

* IRT- Indian Ridge Triple Junction, CIR-Central Indian Ridge, SI- Southeast Indian, GSC-Galapagos Spreading Center, EPR-East Pacific Rise.

[#] IR- infrared spectroscopy, H-T MS- high temperature mass spectrometry, IMP-Ion microprobe.

[+] Ref. [a] Marty and Zimmermann, 1999; Cartigny et al., 2001; Nishio Y, 2007; [b] Marty and Zimmermann, 1999; [c] Byers et al., 1984; Michael, 1995; Marty and Zimmermann, 1999; Roux et al., 2006; [d] Byers et al., 1983, 1986; [e] Javoy and Pineau, 1991; [f] Delaney et al., 1978; [g] Dixon and Clague, 2001; [h] Muenow et al., 1979; Byers et al., 1985; [i] Workman et al., 2006; [j] Garcia et al., 1979.

6.1.1. Mid-Ocean Ridge Basalts (MORB)

Volatiles in MORB are dominated by H_2O (1284 mm^3.STP/g) and CO_2 (263 mm^3/g) with minor CO, CH_4, N_2, and H_2 components. CO_2 is richer in the crystalline basalts (av. 509 mm^3/g) than in glasses (av. 194.4mm^3/g), whereas H_2O is richer in glasses (av. 2870.6mm^3/g) than in the more crystalline basalts (av. 1289 mm^3/g). The MORB volatiles vary with region (Table 6). Atlantic MORB have higher CO_2 (av. 598 mm^3/g) than Pacific and Indian (av. 292 and 157 mm^3/g, respectively). Pacific MORB show higher content of H_2O (av. 2271 mm^3/g) than Atlantic (av. 1708 mm^3/g). N-MORB and E-MORB also are uniform in H_2O/Ce ratios (av. 155-213) within a region but show significant regional variations. N-MORB and E-MORB sources may share a common heritage (Michael, 1995).

Volatiles in MORB usually are contaminated by recycled atmospheric component and seawater during magmatism. Estimating the volatile species degassed along mid ocean ridges (MORs) requires a good knowledge of the initial volatile characteristics in terms of abundance and isotopic composition of MOR magmas (Pineau and Javoy, 1983; Cartigny et al., 2001). Defining the initial volatile composition of MORB is a key to understanding volatile cycling and mixing in the upper mantle.

The popping rock on Mid Atlantic Ridge (MAR) with typical MORB noble gas isotopic composition ($^3He/^4He$=8Ra, $^{40}Ar/^{36}Ar$= 28000) provides probably so far the best sample of upper mantle volatiles with negligible (3-7%) atmospheric and seawater contamination, and places a constraint on initial volatiles in undegassed MORB at depth of MORB formation. Their vesicles have volatile content of 7.56 cm^3 STP/g, and is mainly composed of CO_2 (94.95%) with minor H_2O (4.93%) and N_2 (0.12%) as well as trace He, Ar, H_2, CO and CH_4 (Javoy and Pineau, 1991). Meanwhile CO_2 is also a dominant volatile in East Pacific Rise (EPR) with an average content of 831.5 mm^3/g (Byers et al., 1986). CO_2 abundances decrease from fractionated ferrobasalt, to andesite and to rhyodacite glasses in Galapagos Spreading Center (GSC) (Byers et al., 1984). These suggested that CO_2 should be a dominant volatile species in initial volatiles of undegassed MORB.

H_2O is the most abundant volatile in MORB, and increases from fractionated ferrobasalt, to andesite and to rhyodacite glasses in GSC (Byers et al., 1984). Average content of H_2O in Pacific MORB glasses increase from 1203 mm^3/g in GSC 95.5°W propagating rift (Byers et al., 1984), to 1493.5 mm^3/g in the EPR at 21°N (Byers et al., 1986), and to 2613 mm^3/g in Woodlark Spreading Center, Southwest Pacific (Muneow et al., 1991). H_2O content should be low in initial volatiles of undegassed MORB. Michael (1995) argued that H_2O in MORB is derived from recycled, subducted, altered oceanic crust. The poor correlation of H_2O/Ce with $^3He/^4He$ imply that H_2O/Ce variations are not related to variations in juvenile H_2O in the source. Higher H_2O/Ce ratios in MORB (e.g., in north MAR, av. 240-280) may be a regional characteristic of the mantle, which might be related to a period of rapid subduction in the past that resulted in depressed isotherms and less dehydration in the slab.

Indian MORB differ from the EPR and MAR MORB by having higher $^{87}Sr/^{86}Sr$ and lower $^{206}Pb/^{204}Pb$ (Schiano et al., 1997; Rehkamper and Hofmann, 1997) because of the effect of Dupal anomaly, which could be due to large-scale mantle contamination either by ancient recycled sediments or by delaminated subcontinental lithosphere (Castillo, 1988; Schiano et al., 1997; Rehkamper and Hofmann, 1997; Regelous et al., 2009). Indian MORB volatiles are mainly composed of CO_2 (9.63-52.4, av. 28.1 mm^3/g) and H_2O (0.005-0.022, av. 0.01mm^3/g) with minor N_2, Ar, CO, CH_4 and H_2, and show the lowest contents of CO_2 and H_2O with unusual $N_2/^{40}Ar$, C/N, and $CO_2/^3He$ ratios in vesicles (120, 26190, and 0.3×10^9, respectively), whereas $N_2/^{40}Ar$, C/N, and $CO_2/^3He$ in the MAR and EPR are 91, 2154600, and 1.5×10^9, respectively (Nishio et al, 1999). Major volatile signatures of Indian MORB could be produced more likely by mantle heterogeneity (Nishio et al, 1999), degassing-induced fractionation or late atmospheric contamination (Cartigny et al, 2001).

EPR and GSC glasses contain trace amounts of reduced carbonaceous species, such as methane (CH_4 <0.01 wt.%) and carbon monoxide (CO, 0.04 wt.%). The abundance of reduced carbon species in GSC glass decrease with increasing magma differentiation (Byers et al., 1983, 1984). Indian MORB also contains minor CO, CH_4 and H_2 (Nishio et al, 1999). These suggested that MORB sources are probably dominantly more reduced state of the upper mantle (below FMQ buffer).

6.1.2. Ocean Island Basalts

Volatiles in ocean island basalts (OIB) are characterized by the lowest CO_2 content (av. 210mm^3 /g) among oceanic basalts and higher H_2O content (9063.3 mm^3 /g) than MORB, but H_2O content in OIB lavas is generally lower than in arc lavas (up to ~6 wt%, Workman et al., 2006). CO_2 in OIB glass (av. 192 mm^3/g) is lower than OIB basalt (468 mm^3/g), whereas H_2O

in OIB glass (9100 mm^3/g) is much higher than OIB basalt (7740 mm^3/g). Volatiles in OIB also vary with region.

Volatile contents of submarine basalt glasses from Loihi and Kilauea, Hawaii range from 0.73 to 1.40 wt%. H_2O contents range from 4355.6 to 12568.9 mm^3/g and CO_2 from 14.8 to 967.3 mm^3/g (Muenow et al., 1979; Byers et al., 1985; Dixon and Clague, 2001). Minor reduced carbonaceous species (CO and CH_4) in most of Loihi alkali samples, combined with lower H_2O contents (av. 0.54 wt.%) of tholeiites in Loihi than in Kilauea indicate a reduced primitive source for Loihi magmas with higher $^3He/^4He$ (Byers et al., 1985).

The extent of OIB lava degassing is depth dependent (Heide and Schmidt, 2003). CO_2 may have been degassed from the tholeiitic and transitional magmas in the storage of a shallow magma chamber prior to eruption. For example, CO_2 content in glass decreases with increasing vesicle abundance in the alkali lavas from Loihi (Byers et al., 1985). Alkalic basalt glasses from the North Arch Volcanic Field, Hawaii have varying H_2O contents from 8586.7 to 17671.1 mm^3/g and CO_2 from 132.4 to 407.3 mm^3/g, which could be related to extensive degassing prior to deep submarine eruption. Estimated bulk volatile contents of the vesicular vent samples are up to 23644 mm^3/g for H_2O and 27490 mm^3/g for CO_2, which are interpreted to have formed by closed system degassing (Dixon et al., 1997).

OIBs from Samoan islands have higher H_2O content (11455 mm^3/g) and lower CO_2 (30.4 mm^3/g) than Hawaii. The Samoan lavas show a large range in H_2O (7840-15928 mm^3/g) and CO_2 (3.1-91.1 mm^3/g) contents (Workman et al., 2006). Volatiles in glasses from seamounts flanking the East Pacific Rise (EPR) are commonly enriched in H_2O, Cl, F and S; H_2O and Cl abundances range from 0.111 to 1.021 wt.% and 0.003 to 0.226 wt.%, respectively (Aggrey et al., 1988a).

6.1.3. Island Arc and Back-arc Basin Basalts

Basalts from back-arc basin (BABB) or island arc (IAB) are similar in chemical composition of volatiles to OIB (Garcia et al, 1979). The volatiles in BABB are slightly lower in H_2O and CO_2 contents than in IAB.

Volatiles in IAB are dominated by H_2O (13263 mm^3/g) with minor CO_2 (1246 mm^3/g), such as Mariana Island arc (Garcia et al, 1979). H_2O contents in Sumisu Rift basalts are at least four times greater than in MORB (Hochstaedter et al., 1990). H_2O is the principal volatile species in Solomon Island arc (av. 336×10^{-6} mol/g) and in Grand Canyon, where total volatiles range from 1.27 to 1.75 wt.% (Dean, 1984). Higher volatile contents in IAB imply partial melting and degassing of the subducted slab in production of island arc magmas.

Volatiles in BABB are also dominated by H_2O (av. 568.33×10^{-6} mol/g) with minor CO_2 (47.33×10^{-6} mol/g). H_2O and CO_2 abundances in glasses display a large range from depleted, primitive MORB to enriched, transitional tholeiites in North Fiji and Lau back-arc basins, and show distinct volatile characteristics from lavas from the Mariana Trough and Scotia Sea (Aggrey et al., 1988b).

6.1.4. The Origins of Volatiles in Modern OUM

The MAR popping rock constrains initial volatiles of undegassed MORB which are mainly composed of CO_2 (94.95%) with minor H_2O. CO_2 contents in oceanic basalts increase from OIB (av. 210 mm^3.STP /g), to MORB (263), to BABB (1060) and to IAB (1246, see Table 6 for details and references). MORB are depleted in volatiles relative to OIB, IAB and BABB; low CO_2 contents in MORB could be caused by magma degassing, whereas high CO_2 contents in BABB and IAB could be responsible by degassing of subducted slabs.

H_2O is the main volatile component of most oceanic basalts. H_2O is most depleted in MORB (1284 mm^3.STP/g), and increases from OIB (9063 mm^3/g), to BABB (12731) and to IAB (13263). So much higher H_2O contents in IAB and BABB could be near surface addition of volatiles (Garcia et al, 1979), but most likely caused by subduction-zone slab dehydration (e.g., Stolper and Newman, 1994) including water released from seafloor serpentinized peridotites (Niu, 2004).

H_2O must be a more important component in the generation and evolution of back-arc basin lavas than in the genesis of mid-ocean ridge basalts. Assimilation- fractional crystallization- degassing allows efficient degassing of mantle-derived volatiles and contribution of crust- and atmosphere- derived volatiles in Manus Basin. Basaltic andesite, dacite glasses with high vesicles (up to 18%) show saturated H_2O (av. 826×10^{-6} mol/g) in the glasses. The volatiles in vesicles consist predominantly of H_2O (average 179×10^{-6} mol/g) with minor amounts of CO_2 (0.18×10^{-6} mol/g) (Marty et al., 2001).

The chemical compositions of volatiles in modern OUM still need more data due to following causes:

(1) Wholly or partially crystalline basaltic lavas but quench glasses from the outer surfaces of lavas show more oxidized state than mantle source regions (Christie et al.,1986), an initial highly reduced mafic magma may be oxidize by degassing of C-species in the conditions of the shallow crust, the volatiles in modern OUM are more reduced phases than volatiles in basalts (Mathez et al., 1984), similar to alkali basalts in eastern China, which composed of more oxidized CO_2 and SO_2 species in volatiles (Zhang et al., 1999) than hosted mantle xenoliths which are dominated by H_2 and CO (Zhang et al., 1999, 2000).

(2) The chemical compositions of volatiles recorded in oceanic basalts depend on the volatile fractionation, which result in heterogeneous volatiles in vesicles, matrix glasses and crystalline phases. Basalt glasses are quenched melts whose volatile contents represent those in the melt. Non-class basalts are partly solidified with significant volatile loss or gain depending on erupting environments. For example, glass-vapor inclusions within phenocrysts in pillow tholeiitic basalts from the Marianas Interarc Basin contain more water than in the adjacent matrix glasses, whereas inclusions in phenocrysts from MORB and Hawaii pillows contain more CO_2 than adjacent matrix glasses (Delaney et al., 1978). The volatile compositions of He, Ar and CO_2 in individual vesicles in basaltic glass from MAR vary from vesicle to vesicle due to Rayleigh-type fractional degassing. Volatile fractionation during vesicle formation may be superimposed on the overall Rayleigh degassing trend in one of the samples (Burnard, 1999).

(3) Different analytical methods may yield different results due to various distributions and occurrence modes of volatiles, e.g., H_2O in MORB from the FAMOUS in the Atlantic, which could be dissolved in melts, trapped in vesicles, or incorporated in structural site of crystalline phases, shows much lower contents by secondary ion mass spectrometry (SIMS) (2.9×10^{-6}mol/g, Roux et al., 2006) than by high temperature mass spectrometry (116.7×10^{-6}mol/g, Delaney et al., 1978). SIMS may detect small proportion of H_2O on spots.

6.2. Ancient Oceanic Upper Mantle

Most of ancient oceanic lithosphere has been subducted into the convective mantle, which result in mantle chemical and isotopic heterogeneity (Fyfe, 1997), thus no fresh samples of ancient OUM are available. Ancient oceanic basalts have been altered or weathered for volatile investigating of ancient OUM. The peridotite in the mantle section of ophiolites may be representative materials of ancient OUM for volatile analysis (Hu et al., 2007; Sachan et al., 2007).

Chemical and stable isotopic compositions of volatiles in ophiolitic assemblages can trace the nature and evolution of volatiles in ancient OUM, e.g., pillow basalts and sheet dykes in the upper crustal section of ophiolites show higher $\delta^{18}O$ values in bulk rock samples (6.8-12.7‰) than the mantle value, whereas gabbro, layer cumulate and peridotite etc. are depleted in ^{18}O, and have lower $\delta^{18}O$ values in bulk rock samples (3.7- 6.2‰). Such variations of oxygen isotopic composition with rock types are caused by water-rock isotopic exchanges at different temperatures (Agrinier et al., 1988; Cartwright and Barnicoa, 1999). The fluid inclusions with high concentration of CH_4 found in some ophiolitic peridotites (Su et al., 1999; Liu and Fei, 2006; Sachan et al., 2007) could trace primary volatile components in ancient OUM, including reduced fluids produced by serpentinization (Rona et al., 1992; Sachan et al., 2007) or volatile fractionation during inclusion entrapment (Burnard, 1999).

Fresh olivine and orthopyroxene in harzburgite and dunite of the Yushigou ophiolite in northwestern China with a $^{206}Pb/^{238}U$ age of 550±17 Ma using zircon of cumulate gabbro (Shi et al., 2004) have been measured for volatile compositions by stepwise heating to reveal the abundances and compositiosn of volatiles in ancient OUM (Hu et al., 2007; Zhang et al., 2008). Three concentration peaks of volatiles at 200-400°C, 400-800°C and 800-1200°C (Figure 2b) appear to correspond to the decrepitation degassing of secondary, metasomatic and primary three types of fluid inclusions, respectively (Su et al., 1999; Hu et al., 2007). The release temperature (400-800°C) of main volatile peak is lower than mantle xenoliths in eastern China (Zhang et al., 2004, 2007).

Table 7. Chemical compositions (mm^3.STP/g) of different type of volatiles in Qilian ancient OUM

Type		H_2	CH_4	C_2H_6	C_3H_8	CO	H_2S	N_2	Ar	O_2	CO_2	SO_2	H_2O
Initial Volatiles	OUM	1.68	0.26	0.23	0.07	2.29	3.48	0.05	0.02	0.18	39.99	13.33	6.44
	Magmatism	19.28	0.07	0.00	0.00	13.53	2.02	0.33	0.02	0.08	59.23	0.61	9.23
Metasomatic Volatiles		3.19	0.61	0.26	0.11	1.70	2.32	0.36	0.01	0.52	201.37	5.60	67.60
Alteration Volatiles		1.16	0.27	0.22	0.17	0.47	1.06	0.00	0.01	0.23	58.65	0.16	7.47

The volatiles in Yushigou ophiolitic peridotite are composed mainly of CO_2 with trace amounts of H_2, N_2, H_2O and SO_2, and vary with types of mineral and rock although Su et al (1999) reported more reduced compositions. Olv in dunite has higher CO_2 (338.42 mm^3.STP/g) with minor H_2O, H_2 and CO (94.52, 27.32 and 15.79mm^3.STP/g, respectively) than Olv in harzburgite (181.96mm^3.STP/g) with trace SO_2, H_2O and CO (32.23, 15.84 and 5.07mm^3.STP/g, respectively). Opx in harzburgite has highest volatile contents and is characterized by highest CO_2 (408.51mm^3.STP/g) with trace H_2O, SO_2, H_2 and CO (16.33, 8.13, 6.51 and 6.04mm^3.STP/g, respectively). The following 3 types of volatiles in the Qilian ancient OUM are identified based on the petrogensis, chemical compositions and C-O-H isotopes of volatiles, combined with the types, size, shapes and homogenization temperature of fluid inclusions (Table 7).

6.2.1. The Initial Volatiles in Qilian Ancient OUM

The volatiles released at 800-1200°C intervals are likely derived from volatiles trapped in primary fluid inclusions and structural defects and vacancies of the minerals, which could represent the initial volatiles in Qilian ancient OUM. The different chemical compositions of volatiles at 800-1200°C intervals between dunite and harzburgite with distinct petrogenesis indicate the presence of following two type of initial volatiles.

(1) The Initial Volatiles in Qilian Ancient OUM

Yushigou ophiolitic harzburgite is interpreted as melting residue (Feng and He, 1995; Song and Su, 1998; Shi et al., 2004). The volatiles released from Olv and Opx of harzburgite at the 800-1200°C interval are characterized by dominant CO_2 (av. 57.95 mm^3.STP/g) and high concentrations of SO_2 (av. 13.33 mm^3.STP/g), which represent the volatiles during initial stage of Qilian ancient OUM formation, and semble volatile compositions of mantle xenoliths from lithospheric mantle in Su-Lu continental subduction belt (Zhang et al., 2004, 2007).

(2) The Initial Volatiles in Magmatism

Yushigou ophiolitic dunite was considered as cumulate from very primitive melt (Feng and He, 1995; Niu, 2005). The volatiles released from olivine in dunite at 800-1200°C interval are characterized by dominant CO_2 (59.23 mm^3.STP/g) with trace H_2 (19.28) and CO (13.53), which may represent initial volatiles of a magmatic event in Qilian ancient oceanic mantle.

The variable $\delta^{18}O$ of CO_2 (4.5-8.8‰) and δD of H_2O (-78.3‰), lighter $\delta^{13}C$ (-21.2 to -23.0 ‰) in Olv of dunite relative to the values of upper mantle suggested that the volatiles may have originated in early SCLM extension stage of Qilian initial ocean (Hu et al., 2007). Heavier δD of H_2O (av. -27.2‰), lighter $\delta^{13}C_{CO2}$ (-29.1~ -19.5‰) and $\delta^{18}O_{CO2}$ (1.0‰) in Olv and Opx of harzburgite than the values of upper mantle indicated possible recycled seawater and crustal components.

The higher volatile contents in dunite Olv than in harzburgite Olv imply that magmatism is consistent with the harzburgite being melting residue and the dunite being cumulate from the primitive basaltic melt. It is also possible that the magmatism may have taken place under volatile-rich conditions. The fluid inclusions with high concentration of CH_4 found in some ophiolitic peridotites (Su et al., 1999) suggest that the CH_4 could come from deeper mantle (Ballhaus, 1995; Su et al., 1999; Woodland and Koch, 2003) and undergone fractionation of volatile species during fluid inclusion entrapment (Burnard, 1999), or perhaps from inorganic synthesizing during serpentinization (Rona et al., 1992; Sachan et al., 2007).

6.2.2. The Metasomatic Volatiles in Qilian Ancient OUM

Mantle metasomatism was involved in Qilian ancient OUM, which is indicated by light REE enriched in harzburgite (Shi et al., 2004). The volatiles as metasomatic agents had been preserved as metasomatic fluid inclusions in healed fractures of constitute minerals in ophiolitic peridotite, which are decrepitated at similar temperature range (400-800°C) to homogenization temperature of metasomatic fluid inclusion (Hu et al., 2007). The metasomatic volatiles in Qilian ancient OUM are characterized by much high volatile concentration and dominant CO_2 (201.37mm^3.STP/g on average) with trace H_2O (67.60), SO_2 (5.60) and H_2 (3.19). Lighter δD_{H2O} (-306.3‰), $\delta^{13}C_{CO2}$ (-15.5~-12.5‰) and $\delta^{18}O_{CO2}$ (1.4~1.9‰, av. 1.6‰) suggest the processes of mantle degassing and addition of seawater.

6.2.3. The Alteration Volatiles in Qilian Ancient OUM

Ophiolitic peridotites have always underdone some low-temperature alteration, i.e. serpentinization and carbonatization with accompanied deformation. Alteration volatiles had been trapped in mineral cleavages or micro-fractures along mineral margins as secondary fluid inclusions that decrepitated at a temperature interval of 200-400°C. The alteration volatiles are mainly composed of CO_2 (58.65 mm^3.STP/g) and relatively high concentration of hydrocarbons, which appear to have been generated as a by-product of Fischer-Tropsch synthesis during a subsequent serpentinization of ultramafic rocks (Abrajano et al., 1988; Charlou et al., 1998; Sachan et al., 2007). Their low contents of volatiles could be caused by the outgassing of secondary fluid inclusions during sample pretreatment before analysis.

7. Summary

Volatiles in lithospheric mantle minerals occur in varied modes. The volatile speciation varies with oxygen fugacity and tectonic settings. The improved vacuum stepwise heating is an effective technique to extract volatiles resided in different sites in mantle minerals. The chemical compositions of mantle volatiles recorded in basalts, diamonds and mantle xenoliths differ from continental to oceanic settings. The main conclusions are as follows.

(1) The occurrence modes of mantle volatiles

1) Volatiles in the mantle occur as free states of elements (e.g., graphite, diamond etc.) and molecules (CO_2, H_2O etc.), as crystal structural components in hydrous and nominally anhydrous minerals or carbonate, or as fluid inclusions or as dispersed forms in structure defects and vacancies in mantle minerals.

2) Volatiles trapped in constituent minerals of mantle xenoliths occur as both fluid inclusions and structural sites, defects and vacancies. Hydrogen mainly occurs as H_2 in fluid inclusions rather than structural OH^- as previously thought. Much of the mantle volatiles may in fact reside in structural defects and vacancies, probably more so than in mineral fluid inclusions.

3) Oxygen fugacity in the mantle is spatially and temporally variable, and controls mantle volatile speciation.

(2) The improved vacuum stepwise heating technique

1) The improved vacuum stepwise heating can effectively separate volatiles in fluid inclusions from crystal structural defects and vacancies for analysis, and shows excellent analytical reproducibility of volatile compositions. Volatiles derived

from fluid inclusions of different stages have little superimposed effects on each other.

2) Fluid inclusions can release volatiles by progressive crushing and stepwise heating. Late-stage fluid inclusions with large size can be broken completely by crushing to small grain size or released at lower temperatures by stepwise heating.
3) The decrepitation temperature of fluid/melt inclusion depends on physical strength of crystals and pressure difference between the interior and exterior of the inclusions. The early-stage fluid inclusions are preserved intact in mineral interiors of mantle xenoliths, and are expected to be decrepitated at temperatures similar to or slightly lower than the homogenization temperature due to high anticipated internal pressures of inclusions and brickle constituent minerals.
4) Volatiles trapped in structural defects and vacancies are released at higher heating temperatures close to the formation temperatures of mantle minerals.

(3) Chemical compositions of volatiles in the SCLM

1) The volatiles in the SCLM are a mixture of volatiles of various origins, and vary with depth and mantle reservoirs. Volatiles in the deeper mantle corresponding to diamond stability field have higher contents of reduced volatile species such as H_2 and CO, whereas volatiles in the SCLM recorded in mantle xenoliths vary with mineral species and mantle reservoirs.
2) Mantle xenoliths show volatiles of different origin as revealed by the varying chemical and isotopic compositions of volatiles. Some volatiles are primordial and some are of metasomatic origin. Initial volatiles in the SCLM, i.e., volatiles at a primary stage of upper mantle crystallization, are associated with mantle reservoirs. Initial volatiles in the SCLM are dominated by CO with minor CO_2 and H_2 in primitive mantle-like reservoir indicted by Nd-Sr-Pb isotopes, and have high contents of volatile and H_2 in enriched mantle reservoir; whereas initial volatiles in the SCLM are dominated by CO_2 with minor SO_2 and H_2 in depleted mantle reservoir, and are primarily composed of CO_2 and SO_2 in a "mixed" mantle reservoir related to recycled crustal fluids. Most of the initial volatiles are of mantle origin.
3) The metasomatic volatiles in the SCLM result from subsequent mantle events, either exhibiting high contents H_2 from depths or containing oxidized species like CO_2 and SO_2 resulting from recycled crustal volatiles.

(4) Chemical compositions of volatiles in OUM

1) Volatiles in modern OUM could be more in reduced species than volatiles in modern oceanic basalts, which are dominated by H_2O and CO_2 with minor CO, CH_4, N_2 and H_2. H_2O is most depleted (57.32×10^{-6}mol/g) in MORB, and increases from OIB ($404.61\ \times10^{-6}$ mol/g), to BABB (568.33) and to IAB (592.08), whereas CO_2 content increases from OIB (9.36×10^{-6} mol/g) to MORB (11.72), to BABB (47.33) and to IAB (55.63). MORB are overall depleted in volatiles. Enriched volatiles in OIB, IAB and BABB are probably related to recycled volatiles by subduction.

2) Very few data of volatiles in ancient OUM are available. The volatiles released from several olivine and orthopyroxene samples of peridotites in the Yushigou ophiolite, western China reveal that CO_2 is a major constituent in the volatiles in ancient OUM. The volatiles vary in chemical composition, depending on mineral species and rock types. Initial volatiles of Qilian ancient OUM are characterized by dominant CO_2 (mean 57.95mm^3.STP/g) and high concentrations of SO_2 (mean 13.33 mm^3.STP/g). Initial volatiles of magmatism are dominated by CO_2 (59.23 mm^3.STP/g) and characterized by high concentrations of H_2 (19.28) and CO (13.53), volatiles in a metasomatism in Qilian ancient OUM are mainly composite of CO_2 (201.37 mm^3.STP/g on average) and trace H_2O (67.60), SO_2 (5.60) and H_2 (3.19).

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References

Abrajano, T. A.; Sturchio, N. C.; Bohlke, J. K.; Lyon, G. L.; Poreda, R. J.; Stevens, C. M. Methane- hydrogen gas seeps, Zambales Ophiolite, Philippines: Deep or shallow origin? *Chemical Geology* 1988, 71, 211-222.

Ackermann, L.; Cemič, L.; Langer, K. Hydrogarnet substitution in pyrope: a possible location for “water” in the mantle. *Earth and Planetary Science Letters* 1983, 62, 208-214.

Aggrey, K. E.; Muenow, D. W.; Batiza, R. Volatile abundances in basaltic glasses from seamounts flanking the East Pacific Rise at 21°N and 12-14°N. *Geochimica et Cosmochimica Acta* 1988a, 52, 2115-2119.

Aggrey, K. W.; Muenow, D. W.; Sinton, J. M. Volatile abundances in submarine glasses from the North Fiji and Lau back-arc basins. *Geochimica et Cosmochimica Acta* 1988b, 52, 2501-2506.

Agrinier, P.; Javoy, M.; Girardeau, J. Hydrothermal activity in a peculiar oceanic ridge: oxygen and hydrogen isotope evidence in the Xigaza ophiolite (Tibet, China). *Chemical Geology* 1988, 71, 313-335

Albarede, F. Rogue mantle helium and neon. *Science* 2008, 319, 943-945.

Allegre, C. J.; Staudacher, T.; Sarda, P. Rare gas systematics: formation of the atmosphere, evolution and structure of Earth’s mantle. *Earth and Planetary Science Letters* 1987, 81, 127-150.

Andersen, T.; Neumann, E. R. Fluid inclusions in mantle xenoliths. *Lithos* 2001, 55, 301-320.

Anderson, T.; O’Reilly, S. Y.; Griffin, W. L. The trapped fluid phase in upper mantle xenoliths from Victoria, Australia: implication for mantle metasomatism. *Contributions to Mineralogy and Petrology* 1984, 88, 72-85.

Aubaud, C.; Pineau, F.; Hekinian, R.; Javoy, M. Degassing of CO_2 and H_2O in submarine lavas from the Society hotspot. *Earth and Planetary Science Letters* 2005, 235, 511- 527.

Aubaud, C.; Withers, A. C.; Hirschmann, M. M.; Guan, Y.; Leshin, L. A.; Mackwell, S. J.; Bell, D. R. Intercalibration of FTIR and SIMS for hydrogen measurements in glasses and nominally anhydrous minerals. *American Mineralogist* 2007, 92, 811- 828.

Bai, Q. and Kohlstedt, D. L. Substantial hydrogen solubility in olivine and implications for water storage in the mantle. *Nature* 1992, 357*,* 672-674.

Ballhaus, C. Redox states of lithospheric and asthenospheric upper mantle. *Contributions to Mineralogy and Petrology* 1993, 114*,* 331-348

Ballhaus, C. Is the upper mantle metal-saturated? *Earth and Planetary Science Letters* 1995, 132, 75-86.

Bell, D. R. and Rossman, G. R. Water in Earth's mantle. *Science* 1992, 255*,* 1391-1397.

Bell, D.R., and Ihinger, P.D. The isotopic composition of hydrogen in nominally anhydrous mantle minerals. *Geochimica et Cosmochimica Acta* 2000, 64, 2109-2118.

Bell, D. R.; Ihinger, P. D.; Rossman, G. R. Quantitative analysis of trace OH in garnet and pyroxenes. *American Mineralogist* 1995, 80, 465-474.

Beran, A. and Libowitzky, E. Water in natural mantle minerals II: Olivine, garnet and accessory minerals. *Reviews in Mineralogy and Geochemistry* 2006, 62, 169-191.

Bergman, S. C.; Dubessy, J. CO_2-CO fluid inclusions in a composite peridotite xenolith: implications for upper mantle oxygen fugacity. *Contributions to Mineralogy and Petrology* 1984, 85, 1-13.

Bernardj, W. and Ltaras, B. Determination of methane stability in the upper mantle and lower crust. *American Journal of Science* 1992, 290, 1-24.

Blundy, J. D.; Brodholt, J. P.; Wood, B. J. Carbon-fluid equilibria and the oxidation state of the mantle. *Nature* 1991, 349, 321-324.

Burnard, P. The bubble-by-bubble volatile evolution of two mid-ocean ridge basalts. *Earth and Planetary Science Letters* 1999, 174, 199-211.

Burnard, P. G.; Farley, K. A.; Turner, G. Multiple fluid pulses in a Samon harzburgite. *Chemical Geology* 1998, 147*,* 99-114

Burnard, P. G.; Graham, D.; Turner, G. Vesicle-specific noble gas analysis of "popping rock": implications for primordial gases in earth. *Science* 1997, 276, 568-571.

Byers, C. D.; Garcia, M. D.; Muenow, D. W. Volatile in pillow rim glasses from Loihi and Kilauea Volcanoes, Hawaii. *Geochimica et Cosmochimica Acta* 1985, 49*,* 1887-1896.

Byers, C. D.; Garcia, M. O.; Muenow, D. W. Volatile in basaltic glasses from the East Pacific Rise at 21°N. *Earth and Planetary Science Letters* 1986, 79, 9-20.

Byers, C. D.; Muenow, D. W.; Garcia, M. O. Volatile in basalts and andesites from the Galapagos spreading center, 85° to 86°W. *Geochimica et Cosmochimica Acta* 1983, 47, 1151-1558.

Byers, C. D.; Christie, D. M.; Muenow, D. W.; Sinton, J. M. Volatile contents and ferric-ferrous ratios of basalt, ferro-basalt, andesite, and thyodacite glasses from Galepagos, 95.5°W propagating rift. *Geochimica et Cosmochimica Acta* 1984, 48, 2239-2245.

Canil, D. and Bellis, A. J. Phase equilibria in a volatile-free kimberlite at 0.1 MPa and the search for primary kimberlite magma. *Lithos* 2008, doi:10.1016/j.lithos.2008.02.011.

Castillo, P. R. The Dupal anomaly as a trace of the upwelling lower mantle. *Nature* 1988, 336, 667-670.

Cartigny, P.; Jendrzewjewski, N.; Pineau, F.; Petit, E.; Javoy, M. Volatile (C, N, Ar) variability in MORB and the respective roles of mantle source heterogeneity and degassing. *Earth and Planetary Science Letters* 2001, 194, 241-257.

Cartwright, I. and Barnicoat, A. C. Stable isotope geochemistry of Alpine ophiolites: a window to ocean-floor hydrothermal alteration and constraints on fluid-rock interaction during high-pressure metamorphism. *Int J. Earth Sciences* 1999, 88, 219-235.

Charlou, J. L.; Fouquet, Y.; Bougault, H.; Donval, J. P.; Etoubleau, J.; Jean-Baptiste, P.; Dapoigny, A.; Appriou, P.; Rona, P. A. Intense CH_4 generated by serpentinization of ultramafic rocks at the intersection of the 15° 20'N fracture zone and the Mid-Atlantic Ridge. *Geochimica et Cosmochimica Acta* 1998, 62, 2323-2333.

Chazot, G.; Lowry, D.; Menzies, M. Oxygen isotopic composition of hydrous and anhydrous mantle peridotites. *Geochimica et Cosmochimica Acta* 1997, 61,161-169.

Christie, D. M.; Carmichael, I. S. E; Langmuir, C. H. Oxidation states of mid-ocean ridge basalt glasses. *Earth and Planetary Science Letters* 1986, 79, 397-411.

Coltorti, M.; Beccaluva, L.; Bonadiman, C. Glasses in mantle xenoliths as geochemical indicators of metasomatic agents. *Earth and planetary science letters* 2000, 183, 303-320.

Deines, P. The carbon isotopic composition of diamonds relationship to diamond shape, color, occurrence and vapour composition. *Geochimica et Cosmochimica Acta* 1980, 44, 943-961.

Deines, P. Mantle carbon: concentration, mode of occurrence and isotopic composition. In *Early organic evolution: Implications for mineral and energy resources*. Schidlowski, M. et al. eds.; Springer-Verlag: Berlin, 1992, pp133-146.

Deines, P. The carbon isotope geochemistry of mantle xenoliths. *Earth Science Reviews* 2002, 58, 247-278.

Deines, P.; Harris, J. W.; Gurney, J. J. Carbon isotope ratios, nitrogen content and aggregation state, and inclusion chemistry of diamonds from Jwaneng, Botswana. *Geochimica et Cosmochimica Acta* 1997, 61, 3993-4005.

Delaney, J. R.; Muenow, D. W.; Graham, D. G. Abundance and distribution of water, carbon and sulfur in the glassy rims of submarine pillow basalts, *Geochimica et Cosmochimica Acta* 1978, 42, 581-594.

Dixon, J. E. and Clague, D. A. Volatiles in Basaltic Glasses from Loihi Seamount, Hawaii: Evidence for a relatively dry plume component. *Journal of Petrology* 2001, 42, 627-654

Dixon, J. E.; Clague, D. A.; Wallace, P.; Poreda, R. Volatiles in alkalic basalts from the North Arch volcanic field, Hawaii. *Journal of Petrology* 1997, 38, 911-939.

Dixon, J. E.; Stolper, E.; Delaney, J. R. Infrared spectroscopic measurements of CO_2 and H_2O in Juan de Fuca Ridge basaltic glasses. *Earth Planetary Science Letters* 1988, 90, 81-107.

Eggler, D. H. and Baker, D. R. Reduced volatiles in the system C-O-H: Implications to mantle meting, fluid formation and diamond genesis, In *Advances in Earth and Planetary Sciences, High pressure research in geophysics,* Akimoto, S. and Manghnani, M.H., Eds.; Ceter for Academic Pub.: Reidel, Dordrecht, Holland, 1982; 12, pp237-250.

Eiler, J. M.; Farley, K. A.; Valley, J. W.; Stolper, E. M.; Hauri, E. H.; Craig, H. Oxygen isotope evidence against bulk recycled sediment in the mantle sources of Pitcairn Island lavas. *Nature* 1995, 377, 138-141.

Eiler, J. M.; Farley, K. A.; Valley, J. W.; Hauri, E.; Craig, H.; Hart, S. R.; Stolper, E. Oxygen isotope variations in ocean island basalt phenocrysts. *Geochimica et Cosmochimica Acta* 1997, 61, 2281-2293.

Ertan, I. E. and Leeman, W. P. Fluid inclusions in mantle and lower crustal xenoliths from the Simcoe volcanic field, Washington. *Chemical Geology* 1999, 154, 83-95.

Exley, R. A.; Mattey, K. P., Clague, K. A., Pillinger, C. T. Carbon isotope systematics of a mantle "hot spot": a comparison of Loihi Seamount and MORB glasses. *Earth and Planetary Science Letters* 1986, 78, 189-199.

Fan, Q.-C. and Hooper, P. R. The mineral chemistry of ultramafic xenoliths of eastern China: Implications for upper mantle composition and the palaeogeotherms. *Journal of Petrology* 1989, 30, 1117-1158.

Farley, K. A. and Neroda, E. Noble gases in the Earth's mantle. *Annu. Rev. Earth Planetary Science Letters* 1998, 26, 189-218.

Feng, Y.-M. and He, S.-P. Research for geology and geochemistry of several ophiolites in the North Qilian Mountains,China. *Acta Petrologica Sinica* 1995, 11, 125-146 (in Chinese)

Freund, F. and Oberheuser, G. Water dissolved in olivine: a single-crystal infrared study. *Journal of Geophysical Research* 1986, 91, 745-761.

Frezzotti, M.-L. and Peccerillo, A. Diamond-bearing COHS fluids in the mantle beneath Hawaii. *Earth and Planetary Science Letters* 2007, 262, 273-283.

Fyfe, W. S. Deep fluids and volatile recycling: crust to mantle. *Tectonophysics* 1997, 275, 243-251.

Garcia, M. O.; Liu, N. W. K.; Muenow, D. W. Volatiles in submarine volcanic rocks from the mariana Island Arc and Trough. *Geochimica et Cosmochimica Acta* 1979, 43, 305-312.

Graney, J. and Kesler, S. E. Factors affecting gas analysis of inclusion fluid by quadrupole mass spectrometry. *Geochimica et Cosmochimica Acta* 1995, 59, 3977-3986.

Grant, K. J.; Brooker, R. A.; Kohn, S. C.; Wood, B. J. The effect of oxygen fugacity on hydroxyl concentrations and speciation in olivine: Implications for water solubility in the upper mantle. *Earth and Planetary Science Letters* 2007, 261, 217-229

Green, H. W. and Radcliffe, S. V. Fluid precipitates in rocks from the Earth's mantle. *Geol. Soc. Am, Bul.*1975, 86, 846-852.

Griffin, W. L.; Zhang, A.; O'Reilly, S. Y.; Ryan, C. G. Phanerozoic evolution of the lithosphere beneath the Sino-Korean craton. In: Flower, M., Chung, S. L., Lo, C. H., Lee, Y. Y. (eds.), Mantle dynamics and plate interactions in east Asia. *Amer. Geodynamics Series* 1998, 27, 107-126.

Hansteen, T. H. and Troll, V. R. Oxygen isotope composition of xenoliths from the oceanic crust and volcanic edifice beneath Gran Canaria (Canary Islands). *Chemical Geology* 2003, 193, 181-193.

Hansteen, T. H.; Andersen, T.; Neumann, E. R.; Jelsma, H. Fluid and silicate glass inclusion in ultramafic and mafic xenoliths from Hierro, Canary Islands. *Contributions to Mineralogy and Petrology* 1991, 107, 242-254.

Heide, K. and Schmidt, C. M. Volatiles in vitreous basaltic rims, HSDP2, big island, Hawaii. *Journal of Non-Crystalline Solids* 2003, 323, 97-103.

Hilton, D. R. The leaking mantle. *Science* 2007, 318, 1389-1390.

Hochstaedter, A. G.; Gill, J. B.; Kusakabe, M.; Newman, S.; Pringle, M.; Taylor, B.; Fryer, P. Volcanism in the Sumisu Rift, I. Major element, volatile, and stable isotope geochemistry. *Earth and Planetary Science Letters* 1990, 100, 179-194.

Hofmann, A W. Mantle geochemistry: the message from oceanic volcanism. *Nature* 1997, 385, 219-229.

Hu, P.-Q.; Zhang, M.-J.; Tang, Z. L. Chemical and stable isotopic compositions of volatiles in mantle peridotites of the Yushigou Ophiolite in Qilian orogenic belt, western China. *Acta Petrologica Sinica* 2007, 23, 169-176.

Ingrin, J.; Hercule, S.; Charton, T. Diffusion of hydrogen in diopside: results of dehydration experiments. *Journal of Geophysical Research* 1995, 100, 15489-15499.

Inono, D. A.; Hoefs, J.; Wedepohi, K. H.; Wiechert, U. Contents and isotopic composition of sulfur in ultramafic xenoliths from Central Asia. *Earth and Planetary Science Letters* 1992, 111, 269-286.

Ionov, D. A. and Wood, B. J. The oxidation state of subcontinental mantle: oxygen thermobarometry of mantle xenoliths from central Asia. *Contributions to Mineralogy and Petrology* 1992, 111, 179-193.

Ionov, D. A.; Harmon, R. S.; France-Lanord, C.; Greenwood, P. B.; Ashchepkov, I. V. Oxygen isotope composition of garnet and spinel peridotites in the continental mantle: Evidence from the Vitim xenolith suite, southern Siberia. *Geochimica et Cosmochimica Acta* 1994, 58, 1463-1470.

Ivankin, P. F.; Argunov, K. P.; Boris, Ye. I. Stages of kimberlite development and evolving conditions of diamond formation. *International Geology Review* 1988, 30, 268-274.

Jambon, A. Earth degassing and large-scal geochemical cycling of volatile elements In: Carroll, M. R. and Holloway, J. R. (eds.) Volatiles in magmas. Mineralogical Scociety of America, *Reviews in Mineralogy* 1994, 30, 479-517.

Javoy, M. Major volatile elements of the earth: their origin, behavior and fate. *Geophysical Research Letters* 1997, 24, 177-180.

Javoy, M. and Pineau, F. The volatiles record of a "popping" rock from the Mid-Atlantic Ridge at 14ºN: chemical and composition of gas trapped in the vesicles. *Earth and Planetary Science Letters* 1991, 107, 598-611.

Kelley, D. S. Methane-rich fluids in the oceanic crust. *Journal of Geophysical Research* 1996, 101, 2943-2962.

Kelley, D. S. and Frueh-Green, G. Methane concentrations and isotopic compositions in Layer 3 of the Oceanic crust. *EOS* 1995, 76, 675.

Kitamura, M.; Kondoh, S.; Morimoto, N.; Miller, G. H.; Rossman, G. R.; Putnis, A. Planar OH-bearing defects in mantle olivine. *Nature* 1987, 328, 143-145.

Kohn, S. C. Solubility of H_2O in nominally anhydrous mantle minerals using ^{1}H MAS NMR. *American Mineralogist* 1996, 81, 1523-1526

Koch-Müller, M.; Matsyuk, S. S.; Wirth, R. Hydroxyl in omphacites and omphacitic clinopyroxenes of upper mantle to lower crustal origin beneath the Siberian platform. *American Mineralogist* 2004, 89, 921-931.

Kyser, T. K. Stable isotope variations in the mantle. In: Valley, J. W., Taylor, Jr., H.P., O'Neil, J.R. (Eds.), Stable isotopes in high temperature geological processes. *Reviews in Mineralogy* 1986, 16, 141-164.

Kyser, T. K. and O'Neil, J. R. Hydrogen isotope systematics of submarine basalts. *Geochimica et Cosmochimica Acta* 1984, 48, 2123-2133.

Landis, G. P. and Rye, R. O. Characterization of gas chemistry and noble-gas isotope ratios of inclusion fluids in magmatic-hydrothermal and magmatic-steam alunite. *Chemical Geology* 2005, 215, 155-184

Litasov, K. D.; Foley, S. F.; Litasov, Y. D. Magmatic modification and metasomatism of the subcontinental mantle beneath the Vitim volcanic field East Siberia: evidence from trace element data on pyroxenite and peridotite xenoliths from Miocene picrobasalt. *Lithos* 2000, 54, 83-114.

Liu, W.; Fei, P. -X. Methane-rich fluid inclusions from ophiolitic dunite and post-collisional mafic- ultramafic intrusion. *Earth and Planetary Science Letters* 2006, 242, 286-301

Lowenstern, J. B. Dissolved volatile concentrations in an oreforming magma. *Geology* 1994, 22, 893-896.

Marty, B. and Zimmermann, L. Volatiles (He, C, N, Ar) in mid-ocean ridge basalts: Assment of shallow-level fractionation and characterization of source composition. *Geochimica et Cosmochimica Acta* 1999, 63, 3619-3633.

Marty, B.; Sano, Y.; France-Lanord, C. Water-saturated oceanic lavas from the Manus Basin. *Journal of Volcanology and Geothermal Research* 2001, 108, 1-10.

Mathez, E. A. Carbonaceous matter in mantle xenoliths: composition and relevance to the isotopes. *Geochimica et Cosmochimica Acta* 1987, 51, 2339-2347.

Mathez, E. A.; Dietrich, V. J.; Irving, A. J. The geochemistry of carbon in mantle peridotites. *Geochimica et Cosmochimica Acta* 1984, 48, 1849-1859.

Matson, D. W. and Muenow, D. W. Volatiles in amphiboles from xenoliths, Vulcan's Throne, Grand Canyon, Arizona, USA. *Geochimica et Cosmochimica Acta* 1984, 48, 1629-1636.

Matsumoto, T.; Honda, M.; McDougall, I.; O'Reilly, S. Y.; Norman, M.; Yaxley, G. Noble gases in pyroxenites and metasomatised peridotites from the Newer Volcanics, southeastern Australia. *Chemical Geology* 2000, 168, 49-73.

Mattey, D.; Lowry, D.; Macpheson, C. Oxygen isotope composition of mantle peridotite. *Earth and Planetary Science Letters* 1994, 128, 231-241.

Martin, R.F.; Donnay, G. Hydroxyl in the mantle. *American Mineralogist* 1972, 57, 554-570.

Melton, C. E. and Giardini, A. A. The composition and significance of gas released from natural diamonds from Africa and Brazil. *American Mineralogist* 1974, 59, 775-782.

Melton, C. E.; Salotti C.A.; Giardini, A. A. The observation of nitrogen, water, carbon dioxide, methane and argon as impurities in natural diamonds. *American Mineralogist* 1972, 57, 1518-1523.

Michael, P. Regionally distinctive sources of depleted MORB: evidence from trace elements and H_2O. *Earth and Planetary Science Letters* 1995, 131, 301-320.

Mierdel, K.; Keppler, H.; Smyth, J. R.; Langenhorst, F. Water solubility in aluminous orthopyroxene and the origin of Earth's asthenosphere. *Science* 2007, 315, 364-368.

Miller, M. F. and Pillinger, C. T. An appraisal of stepwise heating release of fluid inclusion CO_2 for isotopic analysis. *Geochimica et Cosmochimica Acta* 1997, 61, 193-205.

Moune, S.; Sigmarsson, O.; Thordarson, T.; Gauthier, P.-J. Recent volatile evolution in the magmatic system of Hekla volcano, Iceland. *Earth and Planetary Science Letters* 2007, 255, 373-389

Muenow, D.W.; Graham, D.G.; Liu,N.; Delaney, J.R. The abundance of volatiles in Hawaiian tholeiitic submarine basalts, *Earth and Planetary Science Letters* 1979, 42, 71-76.

Muneow, D. W.; Perfit, M. R.; Aggrey K. E. Abundances of volatiles and genetic relationships among submarine basalts from the Woodlark Basin, southwest Pacific. *Geochimica et Cosmochimica Acta* 1991, 55, 2231-2239.

Murck, B. W.; Burruss, R. C.; Hollister, L. S. Phase equilibria in fluid inclusions in ultramafic xenoltihs. *American Mineralogist* 1978, 63, 40-46.

Nadeau, S.; Pineau, F.; Javoy, M.; Francis, D. Carbon concentrations and isotopic ratios in fluid inclusion-bearing upper mantle xenoliths along the northwestern margin of North America. *Chemical Geology* 1990, 81, 271-297.

Navon, O. High internal pressures in diamond fluid inclusions determined by infrared absorption. *Nature* 1991, 353, 746-748

Navon, O.; Hutcheon, I. D.; Rossman, G. R.; Wasserburg, G. J. Mantle-derived fluid in diamond micro-inclusions. *Nature* 1988, 335, 784-789.

Nishio, Y.; Ishii, T.; Toshitaka, G.; Sano, Y. Volatile element isotopic systematics of the Rodrigues Triple Junction Indian Ocean MORB. *Earth and Planetary Science Letters* 1999, 170, 241-253.

Niu, Y. L., Bulk-rock major and trace element compositions of abyssal peridotites: Implications for mantle melting, melt extraction and post-melting processes beneath ocean ridges, *Journal of Petrology* 2004, 45, 2423-2458.

Niu, Y. L. and Batiza, R. Trace element evidence from seamounts for recycled oceanic crust in the eastern equatorial Pacific mantle. *Earth and Planetary Science Letters* 1997, 148, 471-484.

Niu, Y. L. Generation and evolution of basaltic magmas: Some basic concepts and a new view on the origin of Mesozoic-Cenozoic basaltic volcanism in eastern China. *Geological Journal of China Universities* 2005, 11, 9-46.

Niu, Y. L.; O'Hara, M. J.; Pearce, J. A. Origin of ocean island basalts: A new perspective from petrology, geochemistry and mineral physics considerations. *Journal of Geophysical Research* 2003, 108, 10.1029/ 2002JB002048.

Norman, D. I. and Musgrave, J. A. N_2-Ar-He compositions in fluid inclusions: indicator of fluid source. *Geochimica et Cosmochimica Acta* 1994, 58, 1119-1131.

O'Neill, H. S. C. and Wall, V. J. The olivine-orthopyroxene-spinel oxygen geobarometer 'the nickel precipitation curve' and the oxygen fugacity of the earth's upper mantle. *Journal of Petrology* 1987, 28, 1169-1191.

O'Reilly, S. Y. and Griffin, W. L. Apatite in the mantle: implications for metasomatic processes and high heat production in Phanerozoic mantle. *Lithos* 2000, 53, 217-232.

O'Reilly, S.Y. and Griffin, W. L. Mantle metasomatism beneath western Victoria, Australia: I, Metasomatic processes in Cr-diopside lherzolites. *Geochimica et Cosmochimica Acta* 1988, 52, 433-447.

Ozima, M. and Podosek, F. A. *Noble gas geochemistry*. Cambridge University Press: Cambridge, 2001; pp1-280.

Olmez, I. and Finnegan, D. L. Iridium emission from Kilauea volcano. *Journal of Geophysical Research* 1986, 91, 653-663.

O'Nions, R. K. and Tolstikhin, I. N. Behaviour and residence time of lithophile and rare gas tracers in the upper mantle. *Earth and Planetary Science Letters* 1994, 124, 131-138.

Pasteris, J. D. and Wanamaker, B. J. Laser Raman microprobe analysis of experimentally re-equilibrated fluid inclusions in olivine: Some implications for mantle fluids. *American Mineralogist* 1988, 73, 1074-1088.

Peng, L.-G., Liu, R.-X., Fan, Q.-C., Fluid and melt inclusion releases of pyrolite xenoliths from the shore of southern China. *Acta Petrologica Sinica* 1994, 10,440-448. (in Chinese with English abstract).

Pineau, F. and Mathez, E. A. Carbon isotopes in xenoliths from the Hualalai volcano, Hawaii, and the generation of isotopic variability. *Geochimica et Cosmochimica Acta* 1990, 54, 217-227.

Pineau, F. and Javoy M., Carbon isotopes and concentrations in mid-oceanic ridge basalts, *Earth and Planetary Science Letters* 1983, 62, 239-257.

Porcelli, D. and Wasserburg, G. J. Mass transfer of helium, neon, argon and xenon through a steady-state upper mantle. *Geochimica et Cosmochimica Acta* 1995, 59, 4921-4937.

Ratan, K., and Mohapatra, M. H. “Recycled” volatiles in mantle-derived diamonds. *Earth and Planetary Science Letters* 2006, 252, 215-219.

Regelous, M.; Niu, Y. L.; Abouchami, W.; Castillo, P. R. Shallow origin for South Atlantic Dupal Anomaly from lower continental crust. *Lithos* doi:10.1016/j.lithos.2008.10. 012.

Rehkamper, M. and Hofmann, A. W. Recycled ocean crust and sediment in Indian Ocean MORB. *Earth and Planetary Science Letters* 1997, 147, 93-106.

Roedder, E. Liquid CO_2 inclusions in olivine-bearing nodules and phenocrysts from basalts. *American Mineralogist* 1965, 50, 1746-1782.

Roedder, E. Fluid inclusions. *Reviews in Mineralogy* 1984, 12, 1-164.

Roedder, E. Fluid inclusion analysis-prologue and epilogue. *Geochimica et Cosmochimica Acta* 1990, 54, 495-507.

Rosenbaum, J. M.; Zindler, A.; Rubenstone, J. L. Mantle fluids: evidence from fluid inclusions. *Geochimica et Cosmochimica Acta*, 1996, 60, 3229-3252.

Roux, P. J.; Shirey, S. B.; Hauri E. H.; Perfit M. R.; Bender, J. F. The effects of variable sources, processes and contaminants on the composition of northern EPR MORB (8-10°N and 12-14°N): Evidence from volatiles (H_2O, CO_2, S) and halogens (F, Cl). *Earth and Planetary Science Letters* 2006, 251, 209-231.

Rubin, K. H. Degassing of metals and metalloids from erupting seamount and mid-ocean ridge volcanoes. *Geochimica et Cosmochimica Acta* 1997, 61, 3525-3542.

Sachan, H. K.; Mukherjee, B. K.; Bodnar, R. J. Preservation of methane generated during serpentinization of upper mantle rocks. *Earth and Planetary Science Letters* 2007, 257, 47-59.

Saxena, S. K. and Fei, Y.-W. Fluid mixtures in the C-H-O system at high pressure and temperature. *Geochimica et Cosmochimica Acta* 1988, 52, 505-512.

Schiano, P.; Birck, J.L.; Allegre, C.A. Osmium- strontium- neodymium- lead isotopic covariations in mid-ocean ridge basalt glasses and the heterogeneity of the upper mantle. *Earth and Planetary Science Letters* 1997, 150, 363-379.

Self, S.; Widdowson, M.; Thordarson, T.; Jay, A. E. Volatile fluxes during flood basalt eruptions and potential effects on the global environment: A Deccan perspective. *Earth and Planetary Science Letters* 2006, 248, 518-532

Shaw, A.M.; Hilton, D.R.; Macpherson, C.G.; Sinton, J.M. The CO_2-He-Ar-H_2O systematics of the Manus back-arc basin. *Geochimica et Cosmochimica Acta* 2004, 68, 1837-1856.

Shcheka, S. S.; Wiedenbeck, M.; Frost, D. J.; Keppler, H. Carbon solubility in mantle minerals. *Earth and Planetary Science Letters* 2006, 245, 730-742.

Shi, R.-D.; Yang, J.-S.; Wu, C.-L. The evidence of SHRIMP age formed Late Sinina of Yushigou ophiolite in North Qilian mountains, China. *Acta Geol. Sin.* 2004, 78, 649-657.

Skogby, H. Water in natural mantle minerals I: Pyroxenes. *Reviews in Mineralogy and Geochemistry* 2006, 62, 155-167.

Skogby, H. and Rossman, G. R. OH^- in pyroxene: an experimental study of incorporation mechanisms and stability. *American Mineralogist* 1989, 74, 1059-1069.

Smyth, J. R.; Bell, D. R.; Rossman, G. R. Incorporation of hydroxyl in upper mantle clinopyroxene. *Nature* 1991, 351, 723-735.

Song, S.-G. and Su, L. Plastic rheology of the Yushigou mantle peridotite and implications for dynamics of Paleao-Plate movement in the North Qilian Mountains. *Acta geologica Sinica* 1998, 72, 131-141

Su, L.; Song, S.-G.; Wang, Z.-H. CH_4-rich fluid inclusions in the Yushigou mantle peridotite and their implications, North Qilian Mountains, China. *Chinese Bulletin Science* 1999, 44, 1992-1995.

Stolper, E. and Newman, S. The role of water in the petrogenesis of Mariana trough magmas. *Earth and Planetary Science Letters* 1994, 121, 293-325.

Tait, S. Selective preservation of melt inclusions in igneous phenocrysts. *American Mineralogist* 1992, 77, 146-155.

Thomassota, E.; Cartignya, P.; Harrisc, J. W.; Viljoend, K.S. Methane-related diamond crystallization in the Earth's mantle. *Earth and Planetary Science Letters* 2007, 257, 362-371.

Tingle, T. N.; Hochella, M. F.; Becket, C. H.; Malhotra, R. Organic compounds on crack surfaces in olivine from San Carlos, Arizona, and Hualalai Volcano, Hawaii. *Geochimica et Cosmochimica Acta* 1990, 54, 477-485.

Trieloff, M.; Kunz, J.; Clague, D. A.; Harrison, D.; Allegre, C. J. The nature of pristine noble gases in mantle plumes. *Science* 2000, 288, 1036-1038.

Trull, T.; Nadean, S.; Pineau, F.; Polve, M.; Javoy, M. C-He systematics in hotspot xenoliths: Implications for mantle carbon contents and carbon recycling. *Earth and Planetary Science Letters* 1993, 118, 43-64.

Valley, J. W. and Cole, D. R. *Stable isotope geochemistry*. Mineralogical Society of America, 2001; pp1-662.

Verchovsky, A. B.; Fisenko, A. V.; Semjonova, L. F. C, N and noble gas isotopes in grain size separates of presolar diamonds from Efremovka. *Science* 1998, 281, 1165-1167.

Weinlich, F. H. An active subcontinental mantle volatile system in the western Eger rift, central Europe. *Geochimica et Cosmochimica Acta* 1999, 63, 3653-3671

Welhan, J. A. Methane and hydrogen in mid-ocean-ridge basalt glasses: analysis by vacuum crushing. *Can. J. Earth Science* 1988, 25, 38-48.

Widom, E. and Farquhar, J. Oxygen isotope signatures in olivines from Sao Miguel (Azores) basalts. *Chemical Geology* 2003, 193, 237-255.

Williams, A. E. Mass spectrometric analysis of volatiles in fluid inclusions: aliquot calibration valve to simulate inclusion rupture. *Chemical Geology* 1996, 131, 155-165

Wood, B. J. and Virgo, D. Upper mantle oxidation state: Ferric iron contents of lherzolite spinels by 57Fe Mössbauer spectroscopy and resultant oxygen fugacities. *Geochimica et Cosmochimica Acta* 1989, 53, 1277-1291

Wood, B. J.; Bryndzia, L. T.; Johnson, K. E. Mantle oxidation state and its relationship to tectonic environment and fluid speciation. *Science* 1990, 248, 337-345.

Woodland, A. B.; Kornprobst, J.; Wood, B. J. Oxygen thermobarometry of orogenic lherzolite massifs. *Journal of Petrology* 1992, 33, 203-230.

Woodland, A. B. and Koch, M. Variation in oxygen fugacity with depth in the upper mantle beneath the Kaapvaal craton, Southern Africa. *Earth and Planetary Science Letters* 2003, 214, 295-310.

Workman, R. K.; Hauri, E.; Hart, S. R.; Wang, J. H.; Blusztajn, J. Volatile and trace elements in basaltic glasses from Samoa. *Earth and Planetary Science Letters* 2006, 241, 932-951.

Wyllie, P.J.; Ryabchikov, I. D. Volatile components, magmas, and critical fluids in upwelling mantle. *Journal of petrology* 2000, 41, 1195-1206.

Wyllei, P. J. Metasomatism and fluid generation in mantle xenoliths, In *Mantle xenoliths*. Nixon, P. H., ed.; John Wiley and Sons Ltd, 1987; pp599-621.

Xia, L.-Q. Highly dense CO_2 fluid inclusions in peridotitic inclusions in some alkali-basalts from east China. *Acta Mineral. Sin.* 1984, 4, 133-142 (in Chinese with English abstract).

Xu, Y.-G. The distributions of trace elements in spinel- and garnet- peridotite. *Science in China (D)* 2000, 30, 307-314.

Yang, X.-Y.; Zheng, Y.-F.; Liu, D.; Dai, J. Study on chemical compositions of fluid inclusions from peridotite and eclogites in Eastern China: The geodynamic implications.. *Phys. Chem. Earth* 2001, 26, 705-718

Yuen, G.; Blair, N.; Des Marais, D. J.; Chang, S. Carbon isotope composition of low molecular weight hydrocarbons and monocarboxylic acids from Murchison meteorite. *Nature* 1984, 307, 252-254.

Yuri, A. T.; Alain, B.; Juan, G. Native gold in mineral precipitates from high-temperature volcanic gases of Colimma volcano, Mexico. *Applied Geochemistry* 2000, 15, 337-346.

Zhang, M. -J.; Hu, P. -Q.; Niu, Y. L., Su, S. -G. Chemical and stable isotopic constraints on the origin and nature of volatiles in sub-continental lithospheric mantle beneath eastern China. *Lithos* 2007, 96, 55-66.

Zhang, M. -J.; Hu, P. -Q.; Zheng, P. The occurrence modes of H_2 in mantle-derived rocks, In *Mineral Deposit Research,* Mao, J.; Bierlein, F. P. eds., Springer: New York, 2005a; *Chapter*19, pp73-76.

Zhang, M. -J.; Hu, P. -Q.; Wang, X.-B.; Liu, G. The fluid compositions of lherzolite xenoliths in Eastern China and Western American. *Geochim. Cosmochim. Acta* 2005b, 69*A*, 146.

Zhang, M.-J.; Wang, X. -B.; Liu, G.; Zhang, T. -W.; Bo, W. -R. The compositions of upper mantle fluids beneath Eastern China. *Acta Geologica Sinica* 2004, 78, 125-130.

Zhang, M. -J.; Wang, X. -B.; Li, L. -W. An appraisal of different experimental methods in the determination of fluid composition in mantle-derived rocks. *Geological Review* 2000, 46, 160-166. (in Chinese with English abstract)

Zhang, M. -J.; Wang, X. -B.; Liu, G.; Wen, Q. -B. Fluid compositions and carbon and oxygen isotope geochemistry of Cenozoic alkali basalts in Eastern China. *Chinese Journal of Geochemistry* 1999a, 18, 276-282.

Zhang, M.-J.; Wang, X.-B.; Liu, G.; Li, L.-W. The compositions of the fluids in alkali basalts and mantle-derived xenoliths in eastern China. *Acta Geologica Sinica* 1999b, 73, 162-166. (in Chinese with English abstract).

Zhang, M. -J.; Niu, Y. L.; Hu, P. -Q.; Li, L. -W. Huge amounts of volatiles in lithospheric mantle. *Chemical Geology* 2009, *(in submitted).*

Zhang, M. -J.; Meng G. -L.; Hu, P. -Q.; Li, L. -W.; Li, G. -Z. Chemical composition of mantle volatiles in ancient Qilian ocean -Evidence from Yushigou ophiolitic peridotites. *Journal of Lanzhou University* 2008, 44, 1-8. (in Chinese with English abstract)

Zhang, T. -W.; Zhang, M. -J.; Bai, B. -J.; Wang, X. -B.; Li, L. -W. Origin and accumulation of carbon dioxide in the Huanghua depression, Bohai Bay basin, China. *AAPG Bulletin* 2008, 92, 341-358.

Zhang, Y. and Zindler, A. Distribution and evolution of carbon and nitrogen in Earth. *Earth and Planetary Science Letters* 1993, 117, 331-345.

Zhu, B. -Q. The mapping of geochemical provinces in China based on Pb isotopes. *Journal of Geochemical Exploration* 1995, 55, 171-181.