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Metamorphic chemical geodynamics of continental subduction zones in China

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Abstract
Ultrahigh-pressure (UHP) terranes as well as UHP metamorphic minerals and rocks represent a special natural laboratory to investigate the geodynamics and fluid regime during subduction and exhumation of continental crust. Studies of UHP rocks have represented a new frontier in the earth sciences during the past two decades, significantly advancing our understanding of geological processes in continental subduction zones. This is particularly so from intensive studies of geochemical records in deeply subducted continental crustal rocks from the Dabie-Sulu orogenic belt in China. Such studies have addressed the following issues: the time and duration of UHP metamorphism, the origin and activity of metamorphic fluid during continental collision, and element mobility in continental subduction zones. This extends metamorphic chemical geodynamics of subduction zones from the oceanic crust to the continental crust, enabling important contributions to development of the plate tectonic theory.

Keywords: Continental subduction, UHP metamorphism, plate tectonics, metamorphic geochemistry, chemical geodynamics

1. Introduction
The study of ultrahigh-pressure (UHP) metamorphism and continental deep-subduction was initiated by findings of coesite (Chopin, 1984; Smith, 1984) and diamond (Sobolev and Shatsky, 1990; Xu et al., 1992) in metamorphic rocks of supracrustal origin. These findings have provided compelling evidence that segments of the continental crust were subducted to mantle depths in excess of 100 km and returned to the surface during continental collision orogeny. This challenges the precept in the plate tectonics theory that the continental crust cannot be subducted to mantle depths because of its lower density than the oceanic crust. Thus far, 22 coesite- and diamond-bearing UHP terranes have been recognized in the world; most of them are of Phanerozoic ages (Chopin, 2003; Liou and Ernst, 2008). These UHP terranes lie within major continental collision belts and extend for several hundred km or more; most are in Eurasia (e.g., Alps, Norway, Erzgebirge, Kokchetav, Tianshan, Himalaya, Dabie-Sulu), with rare examples in Africa, South, Central and North America and Antarctica. These deep processes would not only result in phase changes and mineralogical reactions within UHP slabs, but also bring about crust-mantle interactions in continental subduction zones.

A group of Chinese earth scientists were involved in the study of UHP terranes as soon as coesite (Okay et al., 1989, Wang et al., 1989) and diamond (Xu et al., 1992) were identified in eclogites from the Dabie orogen, east-central China. Besides Dabie, five additional coesite- and diamond-bearing

UHP terranes have been discovered in China, including Sulu (Enami and Zang, 1990), North Qaidam (Yang et al., 2001), Altun Tagh (Liu et al., 2002), Western Tianshan (Zhang et al., 2002), and North Qinling (Yang et al., 2003). Some special textures of mineral exsolution were also discovered in UHP metamorphic rocks (Ye et al., 2000; Song et al., 2005; Liu et al., 2007a, b), suggesting a possible origin of these rocks from depths in excess of 200 to 300 km. These six UHP terranes occur from east to west along the central orogenic belt of China, forming in the Early Paleozoic and Early Mesozoic, respectively. All UHP rocks consist mainly of felsic and intermediate gneissic rocks with minor eclogites and garnet peridotites. Nevertheless, the mafic-ultramafic rocks appear to have originated from different tectonic settings and were subjected to coeval UHP metamorphism, deformation, and retrogression with their enclosing granitic gneisses and supracrustal rocks. Since UHP eclogites and garnet peridotites more easily preserve petrological and geochemical relics of the UHP stages, they have been studied more intensively to constrain the major processes attending continental subduction, collision and subsequent exhumation. This is particularly so for these rock types in the Dabie and Sulu terranes (e.g., Wang et al., 1995; Cong, 1996; Li et al., 1999; Jahn et al., 2003; Zheng et al., 2003a, 2009a; Xu et al., 2006; Zhang et al., 2009a).

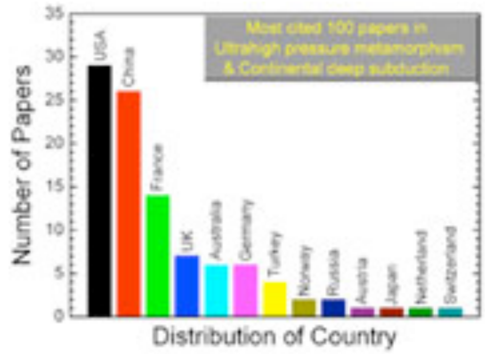

Figure 1
(see appendix for larger image)

The study of UHP metamorphism and continental deep-subduction has greatly promoted the development of solid earth sciences in China. As illustrated by Fig. 1, there are 26 papers in principal affiliation with Chinese institutions that are among the most cited 100 papers for this increasingly recognized topic. While in the past Chinese scientists failed to make their own contributions to the establishment of the plate tectonics theory, at present they highly contribute to its development with respect to continental dynamics. This paper mainly focuses on the progress in metamorphic chemical geodynamics based on studies of UHP rocks from the Dabie-Sulu orogenic belt since no equivalent studies of deeply subducted continental crustal rocks are available from the other UHP terranes in the world.

2. Timing of UHP metamorphism

Determining the age of UHP metamorphism holds the key to unraveling the geodynamics of continental subduction and exhumation. This is particularly so for UHP eclogites in the Dabie-Sulu orogenic belt that resulted from subduction of the South China Block beneath the North China Block. This belt contains one of the largest (>30,000 km^2) and best-exposed two UHP metamorphic terranes (Carswell and Compagnoni, 2003).

There are three very important geochemical anomalies in the Dabie-Sulu UHP rocks: excess argon in phengite (Li et al., 1994), a negative oxygen isotope anomaly (Yui et al., 1995; Zheng et al., 1996), and a positive Nd isotope anomaly (Jahn et al., 1996). These provide us an excellent opportunity to study the physico-chemical changes that occurred during subduction and exhumation of the continental crust.

Geochronology of UHP metamorphic event is a key to understanding subduction and exhumation of the continental crust. Because eclogite has mineral paragenesis of garnet + omphacite + phengite ± rutile, mineral Sm-Nd isochrons have been successfully used to date eclogitization. By means of this classic method, Li et al. (1993) first determined that the Dabie-Sulu UHP metamorphism occurred in the Triassic. Later TIMS and SIMS zircon U-Pb dating gave Early Paleozoic and Neoproterozoic ages for some eclogites in this region, casting doubt on reliability of the Triassic age for UHP metamorphism. Finally, it has been realized that the optical purity of eclogitic minerals is critical to success the Sm-Nd isochron dating (Li et al., 2000). Furthermore, inspection of mineral O isotope equilibrium in the isochron minerals provides a test to the validity of mineral Sm-Nd isochrons in UHP eclogites and gneisses (Zheng et al., 2002, 2003b; Xie et al., 2004). Consequently, the Triassic eclogite-facies UHP metamorphic event is verified by SHRIMP U-Pb dating of metamorphically grown zircons in combination with identification of either mineral inclusions (Liu and Xu, 2004; Liu et al., 2004a, b) or REE distribution patterns (Li et al., 2005), or both (Liu et al., 2006a, 2006b, 2008).

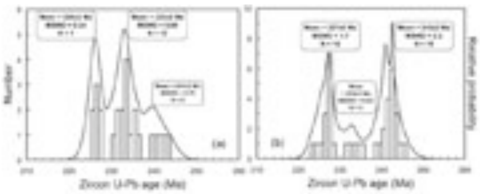

Figure 2
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While the Dabie-Sulu UHP metamorphic event is resolved as having occurred in the Triassic, there are two contrasting views on its exact age. Hacker et al. (1998, 2000) suggested an age of ~245 Ma based on zircon U-Pb dates, whereas Li et al. (2000) preferred an age of 226±2 Ma based on mineral Sm-Nd isochrons. This controversy has more recently been resolved by SHRIMP U-Pb dating of coesite-bearing domains of metamorphic zircon (Wan et al., 2005; Liu et al., 2006a, 2008), bracketing the UHP metamorphic event between 241±2 Ma and 226±2 Ma (Fig. 2a). In doing so, the identification of mineral inclusions in metamorphically grown zircon has played an important role in distinguishing the peak UHP phase from HP eclogite- and amphibolite-facies metamorphic events.

3. Duration of the UHP metamorphism

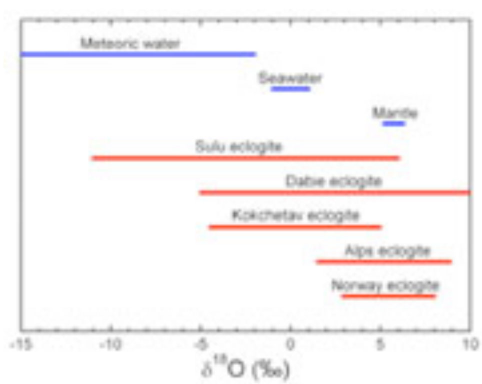

Figure 3
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Highly negative $\delta^{18}O$ values are a very remarkable feature observed in UHP metamorphic rocks from the Dabie-Sulu orogenic belt (Fig. 3). They occur not only in rock-forming minerals of UHP eclogite, granitic gneiss and quartz schist (Rumble and Yui, 1998; Zheng et al., 1998, 1999; Fu et al., 1999; Tang et al., 2008a), but also in granitic minerals such as garnet (Zheng et al., 2007a) and zircon (Tang et al., 2008b). The negative oxygen isotope anomalies represent four global extremes, including the most negative $\delta^{18}O$ values for (1) metamorphic minerals (Rumble et al., 2003; Zheng et al., 2003a), (2) intrusive minerals (Zheng et al., 2007a), (3) zircon of magmatic origin (Zheng et al., 2004; Valley et al., 2005; Tang et al., 2008b), and (4) zircon of metamorphic origin (Zheng et al., 2004). These low $\delta^{18}O$ values have been interpreted to record the meteoric isotope signature of the cold paleoclimate that predates the snowball Earth event in the middle Neoproterozoic (Zheng et al., 2007a).

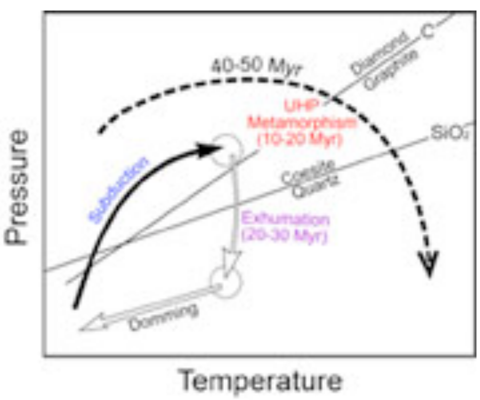

Figure 4
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Preservation of the extreme ^{18}O depletion in the Dabie-Sulu UHP rocks provides a key example of chemical competition between thermodynamics and kinetics during UHP metamorphism at mantle depths. While the thermodynamics always tends to decline the $\delta^{18}O$ difference between the supracrustal protolith and the mantle in order to drive them toward O isotope homogenization, the kinetics requires enough time for the homogenization to be completed at given P-T conditions (depending on the amount of fluid passing through the UHP rocks and driving fluid-mineral O exchange). The competition between the two physico-chemical parameters determines the final status of the $\delta^{18}O$ values recorded in the UHP mineral assemblages. Accordingly, Zheng et al. (1998) estimated a timescale of 10 to 20 Myr for the UHP metamorphism at mantle depths (Fig. 4) based on the preservation of negative O isotope anomaly in the UHP minerals and the kinetics of mineral O transport by diffusion and dissolution-recrystallization under UHP conditions. This estimate is quantitatively confirmed by SHRIMP U-Pb dating on different types of metamorphic zircon (Fig. 2), which indicates that entire UHP metamorphic event in the coesite stability field lasted 15±2 Myr (Hacker et al., 2006; Liu et al., 2006b; Wu et al., 2006). Thus, both subduction and exhumation processes of the continental crust take place at faster rates than those of the oceanic crust, with short residence time of supracrustal rocks at mantle depths. These processes were imaged as if frying an icecream by boiling oil without melting (Zheng et al., 2003a). This interpretation also removes the doubt that the occurrence of negative $\delta^{18}O$ UHP rocks could indicate their formation by dynamic collision of two continental blocks at lower crustal levels without one of them being deeply subducted to mantle depths.

4. Fluid regime in continental subduction zones

Numerous studies have revealed the widespread existence of diverse water species in minerals at UHP conditions (Zheng, 2009b), including structural hydroxyl and molecular water (occurring as aqueous inclusions of different size) in the minerals usually considered stoichiometrically anhydrous (namely the nominally anhydrous minerals). The presence of molecular water in metamorphic minerals was detected by the micro-FTIR and TEM techniques (Su et al., 2002; Wu et al., 2004; Meng et al., 2009). Total water and molecule water were quantified by total and stepwise extraction analyses, respectively, using the TC/EA-MS online technique (Chen et al., 2007a; Gong et al., 2007a). Further distinction in the fluid origin between the structural hydroxyl and molecular water can be made by the hydrogen isotope analysis, because the molecular water is depleted in deuterium relative to the structural hydroxyl at thermodynamic equilibrium (Chen et al., 2007a; Gong et al., 2007b). Thus, the UHP minerals would act as water sinks (with the maximum water solubility at the peak UHP conditions) during the subduction on one hand, and as water sources during exhumation on the other hand (Zheng, 2009b). Occurrence of coesite pseudomorph as inclusion in allanite from allanite-quartz veins within UHP eclogite indicates fluid flow in the UHP regime (Zhang et al., 2008).

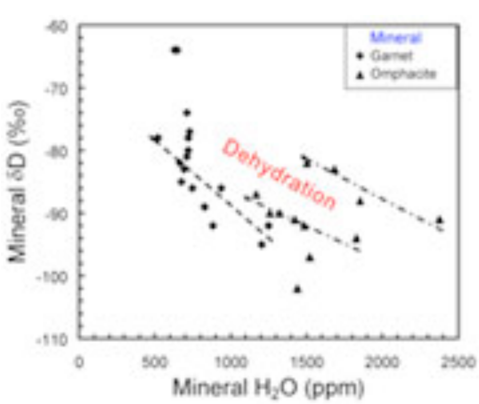

Figure 5
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Many studies have been devoted to petrology, stable isotopes, fluid inclusions and mineral water contents in the Dabie-Sulu UHP metamorphic rocks. The results indicate that the scale of fluid flow is very small during the UHP metamorphism of continental crustal rocks (Zheng et al., 1999; Rumble et al., 2000; Fu et al., 2001). Inspection of the relationship between the distance, petrography and $\delta^{18}O$ values of adjacent samples from the main hole of Chinese Continental Scientific Drilling (CCSD) reveals O isotope heterogeneities between the different and same lithologies on scales of 20 to 50 cm (Chen et al., 2007b), corresponding to the maximum scales of fluid mobility during the continental collision. However, the fluid activity became significantly large during the initial exhumation because waters derived from the decomposition of hydrous UHP minerals and the exsolution of structural hydroxyl and molecular water in nominally anhydrous UHP minerals can be accumulated to form the retrograde fluid (Chen et al., 2007a; Sheng et al., 2007; Zheng, 2009b). This is indicated by negative correlations between water concentration and hydrogen isotope composition of omphacite and garnet from UHP eclogites (Fig. 5). The decreasing water contents of omphacite and garnet with increasing δD values are caused by a solubility decrease of the D-depleted molecular water in the two UHP minerals with decreasing pressure.

It has been well established that subduction of the altered basaltic oceanic crust and overlying sediments is characterized by significant release of aqueous fluid from metamorphosing slabs (Peacock, 1990; Jarrard, 2003; Bebout, 2007). However, this appears not to be the case for the deep subduction of continental crust. In particular, the exhumation of deeply subducted continental crust is characterized by profound flux of aqueous fluid out from UHP metamorphic minerals due to the decomposition of hydrous minerals and the exsolution of structural hydroxyl and molecular water from nominally anhydrous minerals (Zheng, 2009b). This recognition provides a resolution to the controversy on the origin of retrograde fluid in subduction zones. The traditional viewpoint holds that fluids enhancing retrograde alteration of HP and UHP metamorphic rocks originate from external infiltration at shallow depths (e.g., Yardley et al., 2000; Guiraud et al., 2001; Proyer, 2003). In contrast, retrograde fluids is suggested to derive from the decomposition of hydrous minerals and the exsolution of structural-bound hydroxyl within UHP minerals during decompression exhumation (e.g., Vallis and Scambelluri, 1996; Zheng et al., 1999; Li et al., 2004). A study of fluid inclusions in rutile from UHP eclogites gave a narrow range of homogenization temperatures but a wide range of salinities for aqueous inclusions that were trapped during the exhumation (Ni et al., 2008). This suggests mixing of two fluids, with the high salinity one from the decomposition of hydrous minerals but low salinity one from the exsolution of structural hydroxyl and molecular water.

5. Element mobility in deeply subducted continental crustal rocks

By comparing the composition of HP metamorphic rocks to their protoliths, a number of studies indicate considerable removal of LILE and/or LREE from metabasites during subduction of the oceanic crust to eclogite-facies conditions (e.g., Becker et al., 2000; Scambelluri et al., 2001; John et al., 2004). On the other hand, mafic rocks do not lose significant amounts of trace elements during HP metamorphism up to eclogite-facies (e.g., Chalot-Prat et al., 2003; Spandler et al., 2004; Volkova et al., 2004). This implies the decoupling between dehydration and trace element loss during prograde HP metamorphism. Therefore, it has been intriguing how elements are liberated from subducting crusts. This principally concerns the degree and mechanism of element transport with respect to open or closed systems during prograde HP-UHP metamorphism in oceanic subduction zones. It is possible that the subducting slab does not release abundant fluid until a major dehydration reaction like antigorite breakdown (Ulmer and Trommsdorff, 1995; Schmidt and Poli, 1998; Scambelluri and Philippot, 2001), and thus rocks behave as relatively closed systems up to HP-UHP conditions (Spandler et al., 2004). After that, the fluid moves and enhances element mobility and melting or supercritical fluid production in other rock reservoirs like mafic or pelitic rocks. Because the high solubility of trace elements occurs in hydrous melts and supercritical fluids (Kessel et al., 2005; Hermann et al., 2006), their formation or not during subduction-zone metamorphism may play a critical role in dictating the coupling or decoupling of dehydration and trace element loss (Zhao et al., 2007; Xia et al., 2008).

SHRIMP U-Pb dating on different types of zircons from UHP metamorphic rocks indicates that zircon growth is dictated by episodic activity of metamorphic fluid during subduction and exhumation of the continental crust (Li et al., 2004; Wu et al., 2006; Zhao et al., 2006; Zheng et al., 2007b), suggesting Zr and Si mobility at mantle depths in subduction zones. Furthermore, omphacite, garnet, paragonite, kyanite, rutile and zircon is present in UHP kyanite-quartz vein within eclogite (Li et al., 2004; Zheng et al., 2007b; Wu et al., 2009), indicating relative enrichment of Na, Si, Al, HFSE and HREE in metamorphic fluid. The high solubilities of Al, HFSE and HREE are required to precipitate sufficient amounts of garnet, kyanite, rutile and zircon from the fluid as a response to changes in temperature, pressure or chemical potential. It can only be achieved by a substantial extent of Al-Si complexing with relative enrichment of HFSE and HREE in the supercritical aqueous fluid (Wu et al., 2009; Zheng, 2009b).

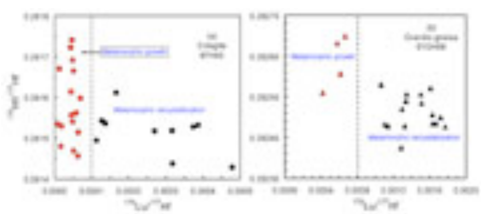

Figure 6
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Zheng et al. (2005) made a combined in-situ study of U-Pb and Lu-Hf isotopes in zircon from UHP eclogite and granitic gneiss, leading to the first finding of decreased $^{176}Lu/^{177}Hf$ ratios but increased $^{176}Hf/^{177}Hf$ isotope ratios for metamorphic growth (Fig. 6). This finding has been confirmed by later studies (Wu et al., 2006; Liu et al., 2008), suggesting chemical exchange between zircon-grown medium and HREE-rich garnet. With the advance of combined LA-MC-ICPMS and LA-ICPMS techniques, simultaneous in-situ analyses of trace elements, U-Th-Pb and Lu-Hf isotopes can be made in the same volume of a single zircon (Yuan et al., 2008; Xie et al., 2008). This provides insights into metamorphic zirconology with implications for fluid action on the recrystallization and growth of zircon during subduction-zone metamorphism. As a consequence, metamorphic recrystallization is subdivided into three mechanisms of solid-state transformation, replacement alteration and dissolution reprecipitation, and the metamorphic growth into new precipitation from aqueous fluid or hydrous melt (Xia et al., 2009, 2010; Chen et al., 2010).

From geochemical analyses of mid-T/UHP eclogite and granitic gneiss from core samples of the CCSD main hole, Zhao et al. (2007) found large variations in the abundance of elements like SiO_2, LREE and LILE at the contact between eclogite and granitic gneiss, indicating their mobility between different slice components. On the other hand, Tang et al. (2007) observed high LILE mobility but REE and HFSE immobility within UHP eclogites in which trace element distribution equilibrium is approached between garnet and clinopyroxene. It is known that the supercritical fluid attending the UHP conditions mainly comprises $SiO_2 + Al_2O_3 + CaO + MgO + FeO + Na_2O + H_2O$, and is enriched in LREE, HFSE, P, V, Sr, Ba and Pb (Zhang et al., 2008). From a comprehensive study of metamorphic zirconology, Xia et al. (2010) suggested that a supercritical fluid transported LREE, HREE, Th, U and HFSE in accessory minerals to recrystallized zircons during subduction-zone metamorphism.

Variable extents of fluid/melt metasomatism are evident at contacts between contrasting lithological units (e.g., Malaspina et al., 2006a, b; Zhao et al., 2007). This is particularly so for some UHP peridotites, in which melt-peridotite reactions at UHP conditions represent an analogue to crust-mantle interaction in continental subduction zones. However, there is no documentation that these orogenic peridotites belong to the mantle wedge above the subducted continental slab. In other words, it is only assumed to be the mantle wedge without any demonstration of its origin (e.g., Zheng et al., 2008; Zhang et al., 2009b). Available Re-Os isotope data argue against the assumption of mantle wedge for the peridotites (Yuan et al., 2007; Zheng et al., 2009b). In this regard, the observed metasomatism in the UHP peridotites has nothing to do with not only the crust-mantle interaction but also fluid mobility and output from the continental slab.

6. Concluding remarks

The plate tectonics theory, which has influenced nearly all branches of the earth sciences, has its roots in the great upsurge of research on the oceanic crust and its deep subduction. By introducing the basic idea that the oceanic crust is recycled from the Earth's surface into the mantle, Armstrong (1968) first recognized the very important implications of geochemical recycling for crust and mantle evolution. Chemical geodynamics, firstly proposed by Allegre (1982) and further propogated by Zindler and Hart (1986), is primarily a field focusing on mantle geochemistry. Now it has been developed as an integrated study of the chemical structure and tectonic evolution of geospheres, extending from geochemical recycling in oceanic subduction zones to HP and UHP metamorphic reworking in both oceanic and continental subduction zones (Bebout, 2007; Zheng et al., 2009a). This enables to trace the possible contribution of deeply subducted continental crust to mantle geochemical heterogeneity.

Through independent and cooperative research efforts, Chinese geochemists have contributed to elucidate of many important problems by seeking answers to questions such as: (1) which geochemical processes occur during subduction and exhumation of the continental crust? (2) how can geochemical records be used to distinguish in-situ from exotic UHP rocks with respect to the enclosing country rocks? (3) what kind of crust-mantle interaction takes place when continental slices are subducted to mantle depths? (4) how does the dehydration of UHP metamorphic minerals during exhumation provide internally-derived fluid for metamorphic veining and amphibolite-facies retrogression? (5) how does the dehydration melting of UHP metamorphic rocks during exhumation produce varying degrees of migmatization and even K-rich magmatism? (6) which mechanism and rate of ascent prevent UHP mineral assemblages from being completely obliterated by metamorphic overprinting and partial melting during exhumation? (7) how can we recognize and distinguish post-collisional melting products with contrasting sources between the subducted and obducted continental lithospheres? (8) how can we quantify element mobility via aqueous fluid, hydrous melt and supercritical fluid during the continental subduction-zone metamorphism? As a consequence, contributions from the Chinese geochemical community have greatly facilitated the understanding of geodynamic processes attending the overall evolution of convergent plate margins: from oceanic crust subduction to continental collision (Zheng et al., 2009c).

Acknowledgments

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Appendix - Figure 1

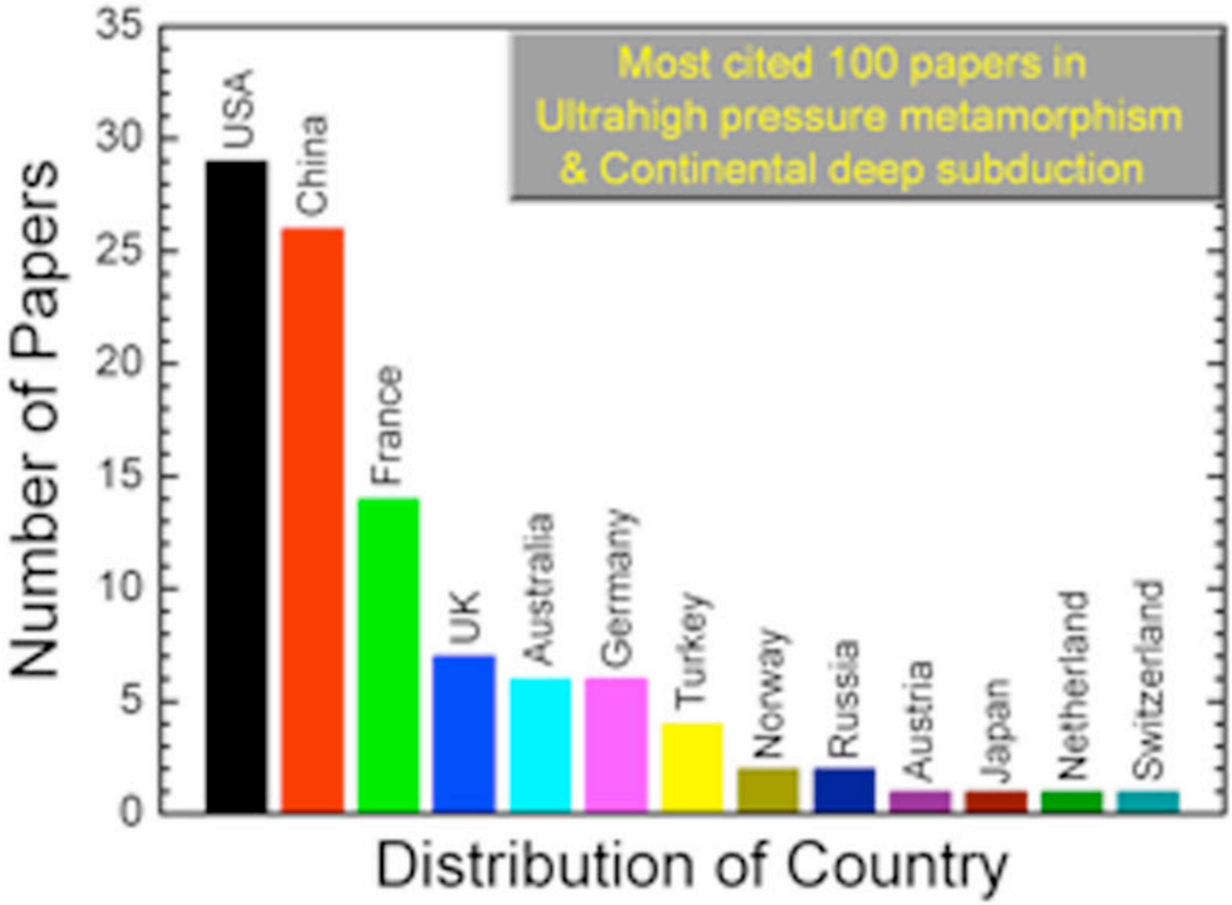

Figure 1. Frequency histogram of countries publishing the most cited 100 papers in ultrahigh pressure metamorphism and continental deep subduction (after Zheng, 2009a).

Appendix - Figure 2

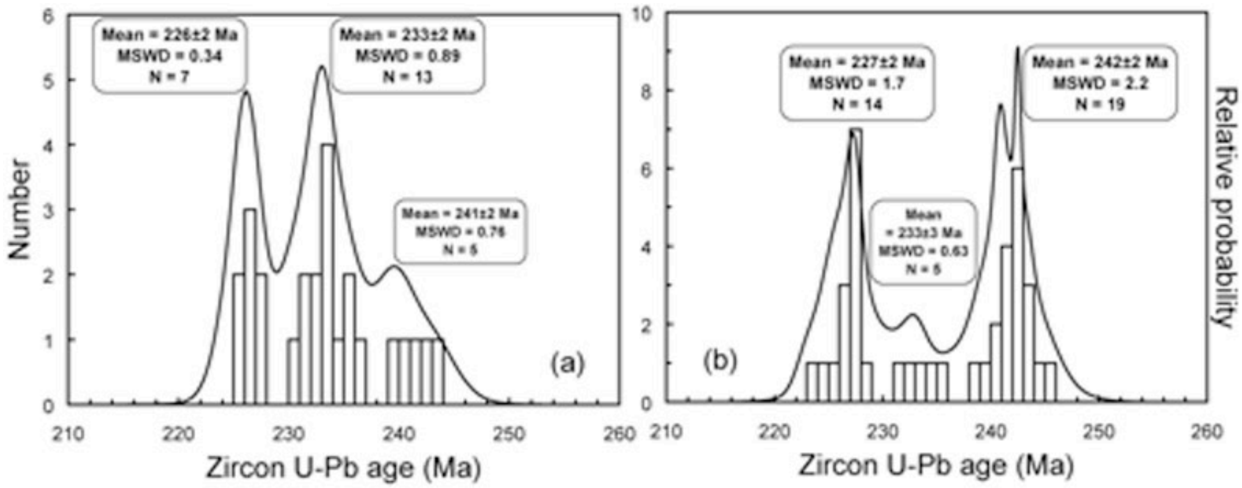

Figure 2. Histograms of SHRIMP U-Pb ages for zircon from UHP metamorphic rocks in the Dabie-Sulu orogenic belt (after Zheng et al., 2009a). (a) Dates for coesite-bearing domain of metamorphic zircons, and (b) dates for metamorphic zircons without corresponding identification of coesite inclusions in the dating domain.

Appendix - Figure 3

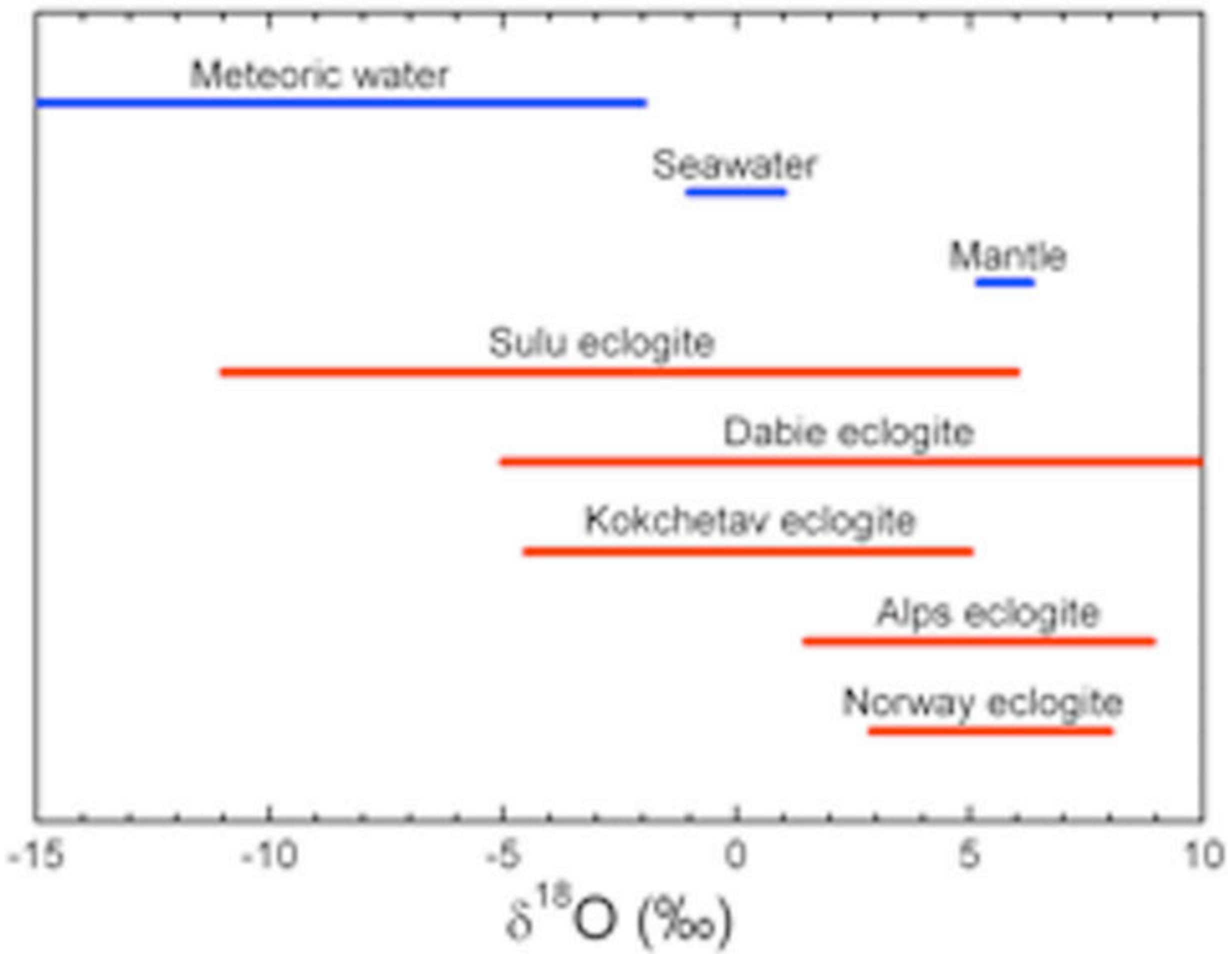

Figure 3. Comparison of oxygen isotope compositions for the Dabie-Sulu UHP eclogites with the other eclogites in the world (revised after Zheng et al., 2003a).

Appendix - Figure 4

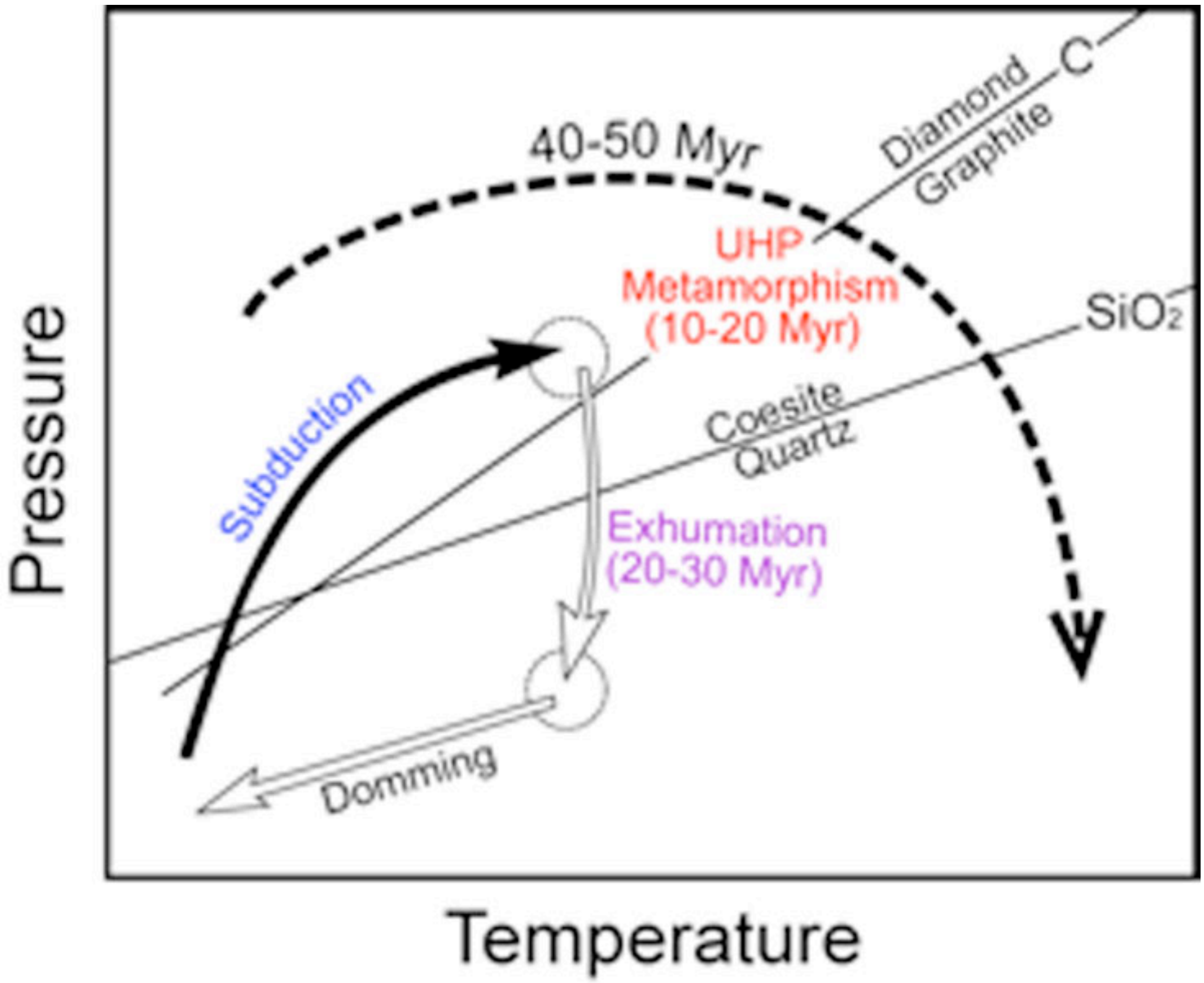

Figure 4. Schematic diagram showing timescales of UHP/HP metamorphism in the Dabie-Sulu orogenic belt due to continental subduction to and exhumation from mantle depths (after Zheng, 2008).

Appendix - Figure 5

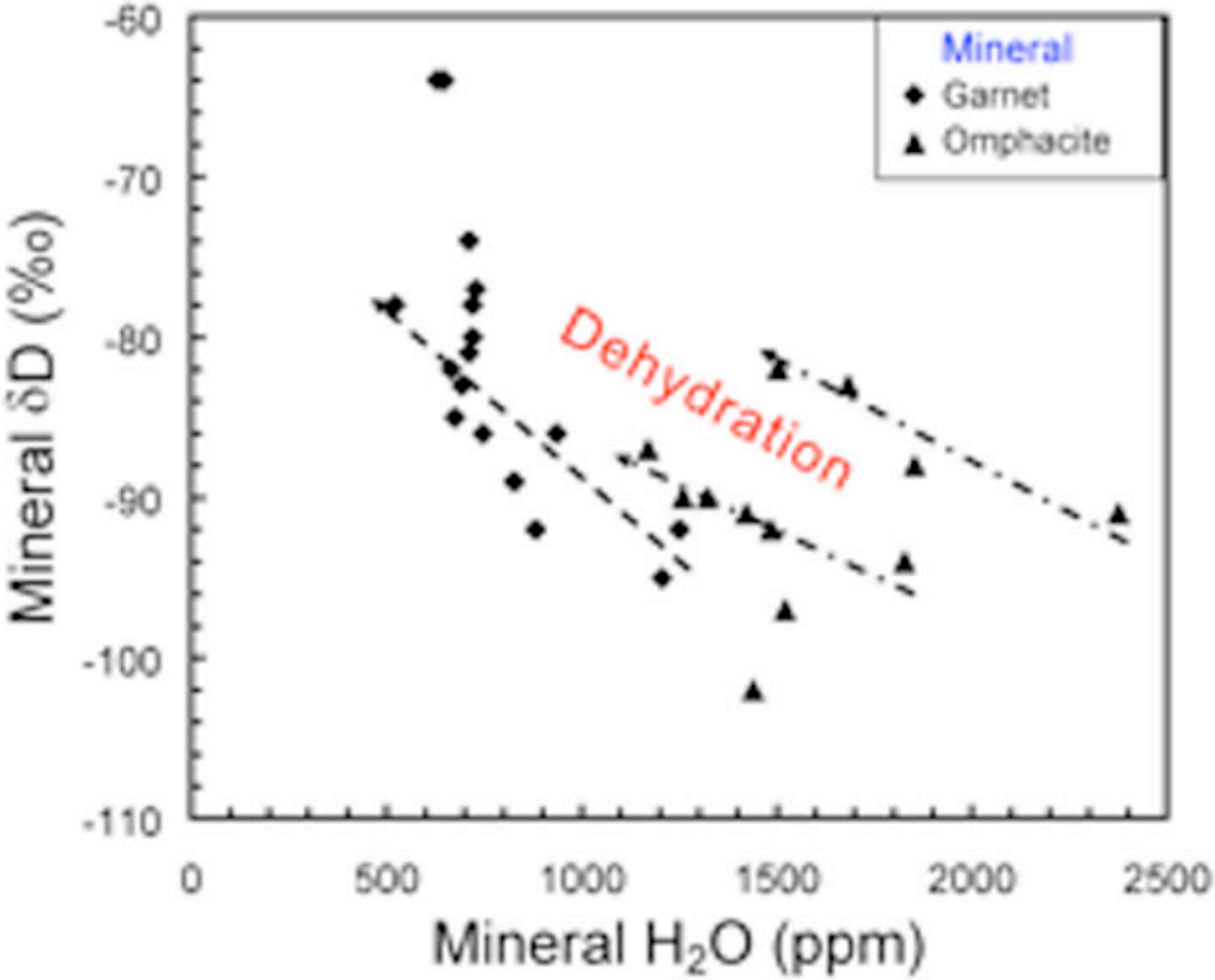

Figure 5. The relationship between water concentration and hydrogen isotope composition of omphacite and garnet from UHP eclogite in the main hole of CCSD, the Sulu orogen (data after Chen et al., 2007a). The decrease in total water concentration is associated with the increase in δD values, pointing to the preferential loss of D-depleted molecular water during exhumation.

Appendix - Figure 6

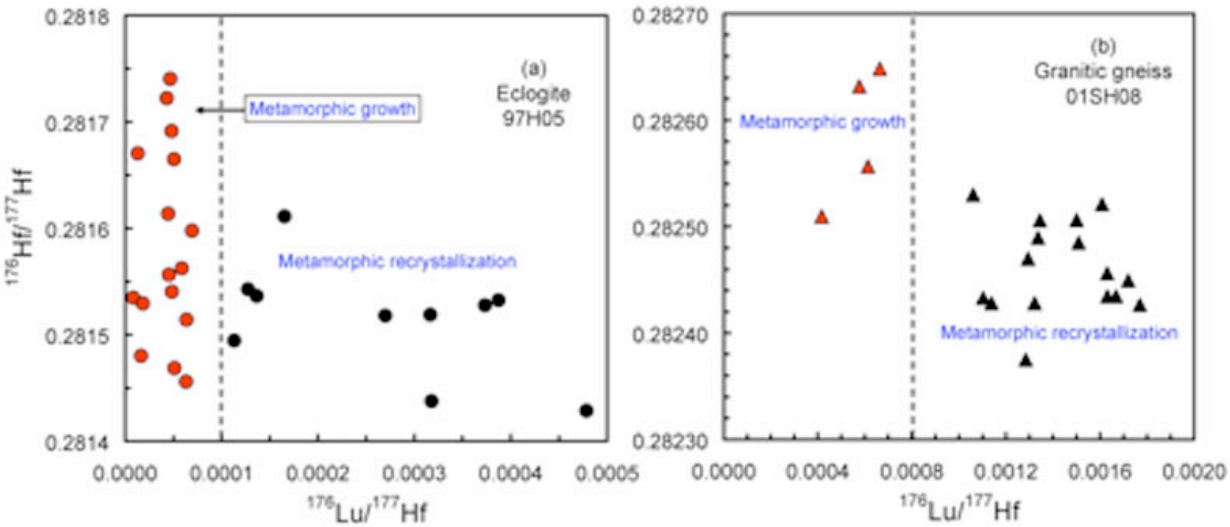

Figure 6. Zircon Lu-Hf isotopic relationship between metamorphic domains of different origins for UHP eclogite and granitic gneiss from the Dabie orogen (revised after Zheng et al., 2005). While metamorphically grown zircon is characterized by decreased $^{176}Lu/^{177}Hf$ ratios but increased $^{176}Hf/^{177}Hf$ isotope ratios, metamorphically recrystallized zircon remains almost unchanged in both $^{176}Lu/^{177}Hf$ and $^{176}Hf/^{177}Hf$ isotope ratios.

About the Author

Yong-Fei Zheng is a professor of geochemistry and director of the Key Laboratory of Crust-mantle Materials and Environments in Chinese Academy of Sciences. He obtained a Dr. rer. nat. in 1991 from Geochemical Institute at University of Goettingen in Germany. His primary research interest concerns the fundamentals of isotope geochemistry and their applications to high-temperature geological systems. His current research largely focuses on chemical geodynamics and fluid regime of continental subduction zones. He was elected as a Fellow of the Mineralogical Society of America in 2005 and a Member of the Chinese Academy of Sciences in 2009. He also serves as associate editors for Terra Nova and Geochemical Journal, and a member of editorial boards for Chemical Geology, Lithos, Ore Geology Review and Journal of Asian Earth Sciences.