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Mineralogy, petrology, U-Pb geochronology, and geologic evolution of the Dabie-Sulu classic ultrahigh-pressure metamorphic terrane, East-Central China†

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ABSTRACT

The Dabie-Sulu Triassic collisional orogen in eastern Asia was created by northward subduction of the Yangtze continental-crust capped plate beneath the Sino-Korean craton. Eclogites, garnet peridotites, and surrounding country rock gneisses and marbles were all subjected to in situ UHP metamorphism, as indicated by the presence of rare but widespread coesite inclusions in eclogitic minerals and in zircon crystals in the country rocks, as well as by virtually identical metamorphic ages of various UHP rock types. Metamorphic *P*-*T* estimates, combined with investigations of mineral exsolution textures and high-*P* polymorphs, indicate that recovered depths of continental subduction may have exceeded 200 km. Parageneses of mineral inclusions in zoned zircon domains combined with U-Pb ages delineate a well-constrained *P*-*T*-time path, suggesting exhumation rates of 5–10 km/Myr. A similar *P*-*T*-time trajectory has been established for the microdiamond-bearing Kokchetav Massif. Thus far, however, diamond inclusions have not been confirmed from coesite-bearing zircon domains of Dabie-Sulu UHP rocks despite numerous detailed studies. Oxygen isotopes of minerals from many outcrop samples and the Chinese Continental Scientific Drilling (CCSD) project main hole cores indicate that $\delta^{18}O$ depletion took place in a volume of Proterozoic protoliths exceeding 100 000 km^3 along the northern edge of the Yangtze craton. Evidently, passive-margin sediments and bimodal igneous rocks that had formed during rifting and breakup of the supercontinent Rodinia were subjected to extensive meteoric water-rock interactions attending terminal Neoproterozoic Snowball Earth conditions. Such hydrothermal alteration volatilized and depleted C from the relatively oxidized protoliths, accounting for the rare occurrences of graphite and apparent lack of microdiamond in Dabie-Sulu UHP rocks.

Keywords: UHP metamorpism, Dabie-Sulu, coesite, zircon, *P*-*T*-time path, fluid-rock interactions

INTRODUCTION: UHP METAMORPHISM AND RECENT FINDINGS

Ultrahigh-pressure (UHP) metamorphism refers to the recrystallization of continental and oceanic crustal rocks at pressures high enough to form coesite and/or diamond at a minimum $P >$ 2.7 GPa at $T > 600$ °C. Figure 1 shows relevant *P*-*T* conditions defining both UHP and HP (high pressure) metamorphism; in addition, geotherms of about 5 °C/km (extremely cold subduction zones) and 20 °C/km (old descending plates) are illustrated. UHP and HP metamorphic conditions are separated by the quartz-coesite phase boundary; the graphite-diamond boundary further subdivides the UHP regime into diamond (±coesite) and graphite (±coesite) *P*-*T* fields. Occurrences of the UHP analog of rutile as well as supersilicic titanite, and/or K-bearing clinopyroxene, and aragonite + magnesite inclusions in garnet from Kokchetav microdiamond-bearing gneisses suggest subduction depths of ~190–280 km (e.g., see review by Schertl and Sobolev 2012). The recent interpretation of stishovite pseudomorphs in a pelitic gneiss from western China suggests that some continental materials might have been exhumed from an even greater depth (>350 km?) than commonly accepted (Liu L. et al. 2007, 2009). Prior to the initial discoveries of coesite in UHP rocks in 1984 and microdiamond in 1990, coesite, diamond, stishovite, and other UHP minerals had only been reported from meteorite impact craters and mantle xenoliths (Chopin 1984; Smith 1984; Sobolev and Shatsky 1990).

Discovery of tracts of upper continental crust metamorphosed under mantle *P*-*T* conditions has enriched and extended our understanding of plate tectonics (Ernst and Liou 1995). The recognition of deep continental subduction responsible for the formation and subsequent return of UHP rocks to the surface from depths >100 km in collisional mountain belts has been intensively studied in the Earth sciences for the last three decades. A continuing explosion of research on global continental UHP terranes reflects their significance with regard to mantle dynamics and the tectonics of continental evolution, crustal subduction, collision, exhumation, mantle-slab interactions, and geochemical recycling. Thus far, more than 20 coesite-bearing, 10 diamond-bearing, and three majoritic garnet-bearing UHP regions have been documented globally (for reviews, see Liou et al. 2009; Dobrzhinetskaya and Faryad 2011).

Among many recent exciting discoveries of UHP minerals in continental collisional zones since 2010, several new occurrences

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of microdiamond, and other UHP minerals have been reported. New findings include, but are not limited to: (1) microdiamond inclusions in oceanic-crust derived garnetites from the ophiolitic UHP unit in the Italian Western Alps (Frezzotti et al. 2011). (2) Microdiamond (±coesite) inclusions in garnet, kyanite, and zircon as well as multi-grain clusters within garnet from Variscan HP granulites of the North Bohemian crystalline massif (Kotková et al. 2011). (3) Inclusions of polycrystalline diamonds associated with nano-scale fluid inclusions at the boundaries of microdiamonds in zircon grains from the Erzgebirge Grt-Phe-Ky UHP gneiss in Germany (Dobrzhinetskaya et al. 2012). And (4), microdiamond and disordered graphite inclusions within garnet and pyroxene lamellae in a coarse chromian spinel grain of a spinel-garnet peridotite (~6 GPa, 1000 °C) associated with a HP granulite in the Bohemian Massif (Naemura et al. 2011). These findings reveal that: (1) microdiamonds and other UHP phases are more common than previous thought in both Alpine- and Pacific-type orogens; (2) the Bohemian microdiamond in HT granulites implies that vast regions of crystalline basement have been subducted to great mantle depths not only in central Europe but also elsewhere; and (3) the close association of garnet peridotites with UHP granulites suggests that these peridotite bodies became interdigitated with deeply subducted continental crust under UHP conditions rather than being tectonically emplaced at shallow crustal levels. (Abbreviations of minerals are after Whitney and Evans 2010.)

Moreover, a great range of UHP minerals including diamond, possible coesite pseudomorphous after stishovite, Fe-Ti alloys, osbornite (TiN), cubic boron nitride (cBN), TiO_2II, moissonite (SiC), zabonite ($FeTiSi_2$), and Cr-spinel containing exsolution lamellae of coesite + diopside recently have been confirmed as nano- to micro-scale inclusions in podiform chromitite from the Luobusa ophiolite, Tibet (Yang et al. 2007, 2012; Li et al. 2009; Dobrzhinetskaya et al. 2009; Yamamoto et al. 2009). In situ occurrences of microdiamond (±moissonite) inclusions in chromite grains have been recently recognized in numerous ophiolitic massifs along the 1400 km long Yarlung-Zangbo suture zone between India and Asia, and in the Polar Ural Mountains (Yang and Robinson 2011). The unexpected occurrence of these reduced UHP minerals suggests that the chromitites formed at P > 9–10 GPa at depths of >250–300 km. The presence of UHP minerals within ophiolitic chromitite has been considered "forbidden" by conventional concepts of ophiolite genesis under high-T, low-P conditions in mid-oceanic ridges or back-arc spreading axes. These findings have renewed interested in the exploration of UHP rocks. Occurrences of UHP minerals and rocks in both ophiolitic and granulite terranes should lead to another research renaissance involving the integrated efforts of geophysicists, geochemists, mineral physicists, and geologists over the next decades. The goal of our review is to summarize recent findings of the petrochemical, mineralogic and geochronologic studies on Dabie-Sulu UHP rocks—the largest and perhaps best understood UHP belt—and to discuss some still controversial issues.

Dabie-Sulu UHP rocks and minerals

Figure 2 shows the Triassic Dabie-Sulu UHP collisional terrane situated between the Sino-Korean and Yangtze cratons. This belt has benefited from intensive multidisciplinary investigations in terms of manpower and resources, including the first CCSD 5 km bore-hole project, which was completed in 2005. Blocks, boudins, and layers of eclogite and garnet peridotite occur as enclaves in UHP gneisses. Rare but widely dispersed occurrences of coesite inclusions in zircon grains from felsic gneisses, marbles, quartzites, and eclogites from both surface and core samples indicate that the supracrustal rocks (>90% felsic gneisses, <10% mafic eclogites) were subducted to depths

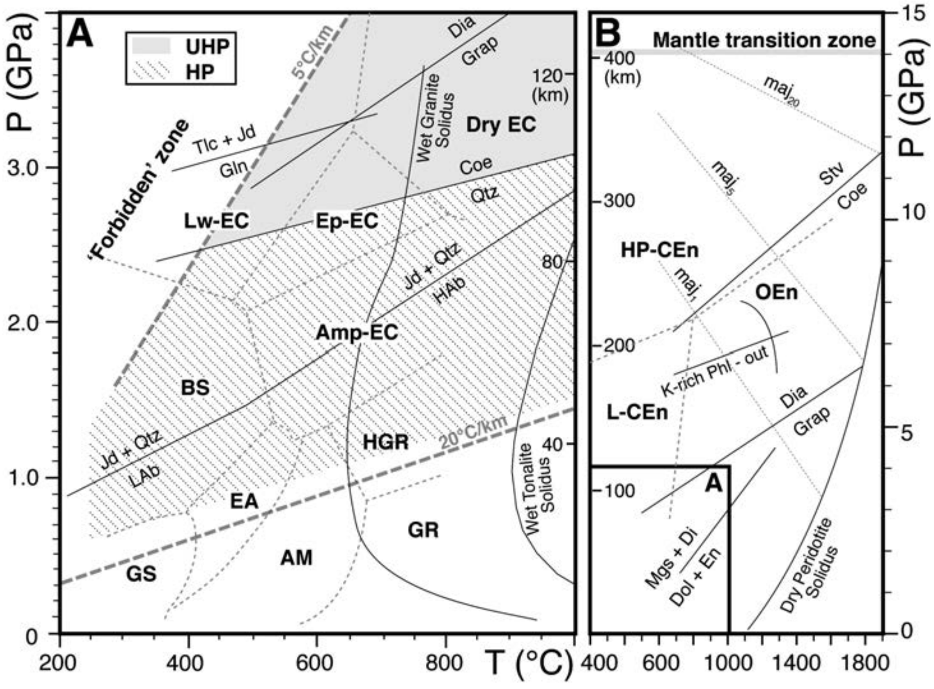

FIGURE 1. (**a**) P-T regimes assigned to various metamorphic types: (1) ultrahigh-P, (2) high-P, (3) low-P, and (4) ''forbidden zone'' and stabilities of coesite, diamond, jadeite, and K-cymrite (modified after Liou et al. 2004). (**b**) P-T stabilities of additional UHP index minerals including pseudomorphic stishovite, majoritic garnet, high-P clinoenstatite, and pseudomorphic K-cymrite are shown [modified from Fig. 1 of Liou et al. (2009)].

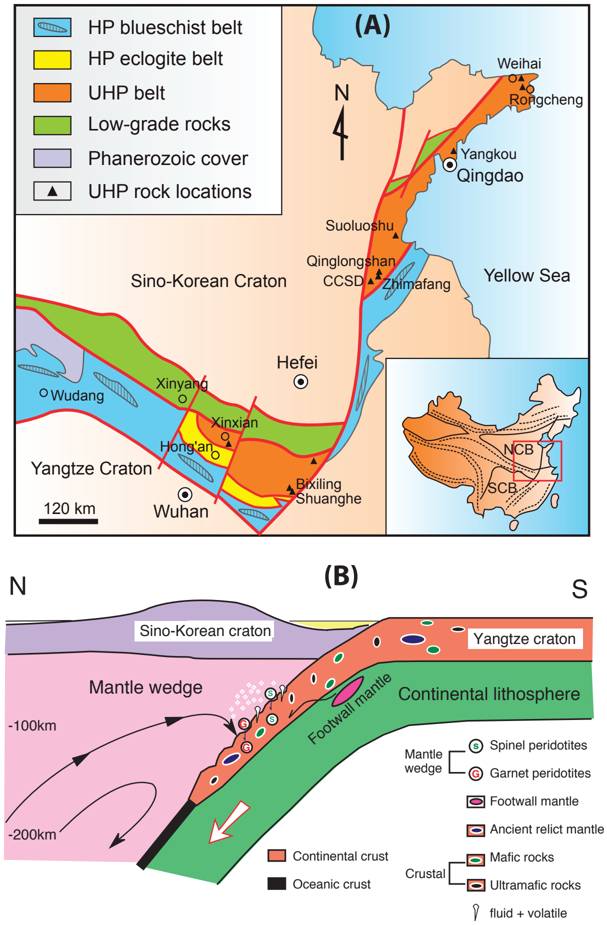

FIGURE 2. (**a**) A sketch map of general geology in the Dabie-Sulu orogen of central-east China: NCB and SCB in the insert denote the North China Block (a part of the Sino-Korean craton) and South China Block [modified from Fig. 1 of Zhang and Liou (1994)]; (**b**) Tectonic model for Triassic subduction of the Yangtze beneath the Sino-Korea cratons showing the tectonic setting for mantle-derived (Type A) and crustal hosted (Type B) garnet peridotite [modified from Fig. 2 of Zhang et al. (1998)].

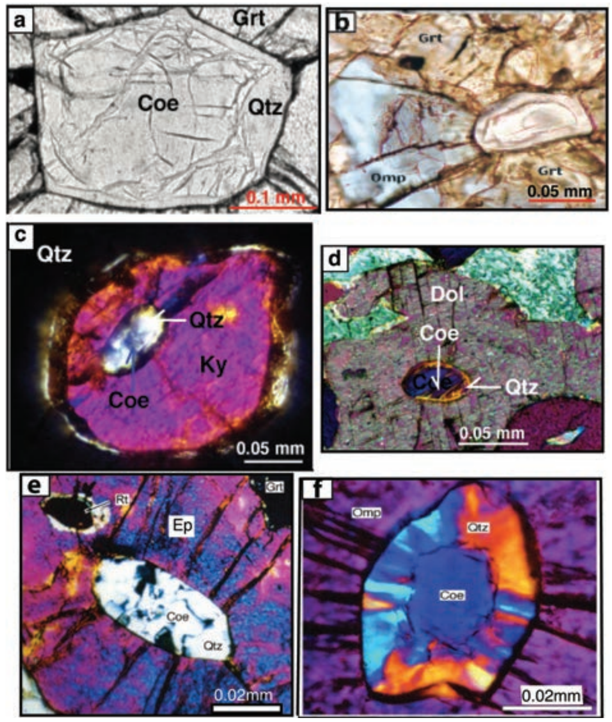

FIGURE 3. Photomicrographs of coesite or coesite pseudomorphs in Dabie-Sulu UHP rocks: (**a**) coesite inclusion in garnet from the Weihai eclogite (Zhang et al. 1995c); (**b**) intergranular coesite from Yangkuo eclogite (Zhang and Liou 1996); (**c**) coesite inclusion in kyanite from the Donghai Ky-quartzite (Zhang et al. 2002a); (**d**) coesite inclusion in dolomite from a Dabie eclogite (Zhang and Liou 1996); (**e**) coesite pseudomorph in epidote (Zhang et al. 1995a); and (**f**) inclusion of coesite + palisade quartz in omphacite from a Dabie eclogite (Liou and Zhang 1998). (**a**–**b**) Plane-polarized light (PPL), (**c**–**f**) cross-polarized light (XPL).

>100 km (e.g., Liu and Liou 2011). Drill-core samples show that the Sulu UHP slab is >5 km thick, and geologic cross sections suggest that the Dabie slab is at least 10 km thick (Hacker et al. 2000); the Dabie-Sulu UHP terrane extends for >2000 km, is about 50 km wide, and represents the geographically largest UHP metamorphic belt (>30 000 km^2) in the world. Characteristic features of common and unusual Dabie-Sulu UHP minerals were summarized by Liou et al. (1998). This complex is famous for the widespread occurrences of coesite inclusions in Grt, Omp, and Ky from various supracrustal rocks; the Dabie-Sulu terrane is also unique in its occurrences of intergranular coesite, coesite inclusions in dolomite and in epidote/zoisite, UHP OH-rich topaz, and talc (Zhang and Liou 1996; Zhang et al. 1995a, 1995b, 2002a). Garnet peridotites and many other mineralogic, petrologic, and geochemical features were summarized in previous reviews (Liou et al. 1998, 2009; Zhang et al. 1994, 2000, 2009b) (also see several photomicrographic examples in Fig. 3). The most common UHP rocks are described below.

Eclogites

Eclogitic rocks are widespread as mafic lenses, blocks and layers in gneiss (type A), peridotite (type B), and marble (type C). The CCSD 5 km main bore-hole revealed a total cumulate thickness of eclogite of about 1600 m (Zhang et al. 2006). Type A eclogites are the most abundant (>90%) and contain inclusions of both coesite and its pseudomorphs in Grt, Omp, Ky, Zo, Ep, and even in dolomite (e.g., Schertl and Okay 1994; Zhang and Liou 1994a, 1996; Zhang et al. 1995a, 2009b). Type B eclogites consist mainly of Grt + Omp + Rt with rare inclusions of Coe/Qtz (Zhang et al. 2009a). Type C eclogites are characterized by the presence of magnesite and dolomite. Zircon separates from most eclogites, except Type B specimens contain rare but widespread coesite inclusions. Phengite, zoisite/epidote are the most abundant hydrous phases in eclogite; talc, lawsonite, OH-rich topaz, and sodic amphibole (including nyboite and glaucophane), as “peak” or eclogite-facies phases are present in some unusual UHP rocks, such as: (1) talc-bearing eclogite (Liou and Zhang 1995; Zhang et al. 1995a, 1995b); (2) nyboite-bearing eclogite (Hirajima et al. 1992); (3) glaucophane-bearing Ky eclogite (Zhang and Liou 1994; Wei et al. 2010); (4) lawsonite-bearing eclogite (Li et al. 2004); (5) OH-rich topaz-bearing Ky-rich quartzite (Zhang et al. 2002a); (6) corundum-bearing eclogite and garnetite (e.g., Zhang et al. 2004); and (7) whiteschist (Rolfo et al. 2000).

Dabie-Sulu eclogites show a significant range in bulk composition, suggesting that they probably were derived from heterogeneous mantle and crustal sources (Jahn et al. 2003). Banded/layered structures reflect distinct compositional variations, in turn caused by magmatic and/or metamorphic differentiation, as well as due to possible modification of bulk-rock composition before, during, and after UHP metamorphism. Furthermore, most type A eclogites have low MgO and CaO contents in comparison with the other two types of eclogite; they are enriched in LREE related to HREE, and show negative anomalies in Nb, Zr, and Ti in spidergrams, except for Rt-rich eclogite from the CCSD main hole. These features indicate a continental basalt affinity for most type A eclogites. Type B eclogites are characterized by higher MgO (most >10 wt%) and variable REE patterns (Zhang et al. 2000, 2005, 2009b) as well as negative $\varepsilon_{Nd}(t)$ (–5 to –7) (Jahn 1998), and may represent Proterozoic intrusives of asthenosphere-derived melts, long-term enriched mantle segregations, or were subjected to crust contamination. A few "eclogites" (or garnet clinopyroxenites) within a meta-lherzolite body in the North Dabie have basaltic protoliths with MORB and E-MORB affinities; they may have been subjected to multistage metasomatism related to the influx of Si-depleted, Mg-enriched fluids produced during serpentinization of the host lherzolite prior to subduction (Malaspina et al. 2006; Zhang et al. 2011a). Type C eclogites are rich in CaO (>15 wt%), suggesting contamination by country rock marble (Zhang and Liou 1998b), or possibly due to metasomatism (Jahn 1998; Wu et al. 2006).

Garnet peridotites

Garnet peridotites are widespread as a minor but tectonically significant component of the Dabie-Sulu UHP terrane (Liou et al. 2007; Zhang et al. 1994, 2000). Dabie-Sulu garnet peridotites consist of garnet lherzolite, harzburgite ± minor wehrlite, and dunite occurring as blocks or lenses from meter to kilometer size in quartzofeldspathic gneisses and as lenses or layer in metabasaltic eclogites. They are classified as mantle-derived (type A) and crust-hosted (type B), based on structural, geochemical and isotopic characteristics. Type B igneous intrusions occur as minor ultramafic cumulates associated with dominant metagabbroic layers of various compositions, whereas Type A peridotites represent depleted, metasomatized mantle fragments, some of which contain minor eclogite and/or garnet clinopyroxenite pods.

Most Sulu peridotites are mantle-derived type A peridotites, and consist of Ol, En, Di, Grt ± Mgs, Phl, and Ti-clinohumite (Zhang et al. 2000). Type A peridotitic minerals have mantle $\delta^{18}O$ isotopic values of 4.5 to 6.5‰ (Zhang et al. 1998, 2000, 2007; Zhang Z. et al. 2005; Zhao et al. 2007). Major elements of Grt peridotites show a wide bulk compositional range, possibly resulting from complex processes including metasomatism and/or crustal contamination (Zhang et al. 1994, 2000, 2007; Yang and Jahn 2000; Malaspina et al. 2009; Zhang et al. 2011a). This suggestion is supported by several petrologic facts: (1) occurrences of hydrous and carbonate phases (phlogopite, Ti-clinohumite, and magnesite); (2) very high K_2O (up to 3.4 wt%) and/or FeO (>10 wt%) contents, high $^{87}Sr/^{86}Sr$ (0.7081–0.7100) values, and low $^{143}Nd/^{144}Nd$ (0.5123–0.5124) ratios; and (3) LREE-enriched and HFSE-depleted distribution patterns. Petrochemical and stable isotopic investigations have shown that Phl- and Mgs-bearing peridotites were subjected to multiple stages of metasomatism (Zhang et al. 2007, 2008, 2009a; Malaspina et al. 2009; Zhang et al. 2011). Microtextures of peridotitic minerals (Zhang et al. 1999) such as clinoenstatite lamellae in orthoenstatite (Zhang et al. 2002b), coarse-grained clinopyroxenes with 25 vol% exsolved garnet and 4 vol% ilmenite (Zhang and Liou 2003), and exsolved needles of pyroxene, rutile, and apatite along garnet (111) planes suggest the former occurrence of majoritic garnets, implying great mantle depths (Ye et al. 2000; Zhang and Liou 2003; see Hwang et al. 2011 for an alternative view). The UHP clinoenstatite and majoritic garnet may have formed in the mantle wedge before tectonic insertion into the downgoing continental lithospheric plate, and then were recrystallized during subduction-zone metamorphism.

Country rocks

Dabie-Sulu eclogites and garnet peridotites are enclosed within various country rocks including granitic gneiss, paragneiss, marble, pelite, and quartzite. Gneisses are most abundant; for example, in the recovered continuous 5 km CCSD main hole cores, the cumulative thickness of orthogneiss layers is about 2428 m, making up 47% of the core total. Orthogneiss consists of the amphibolite-facies assemblage Ksp + Pl + Qtz ± minor epidote, biotite, amphibole, garnet, phengite, and magnetite. As described below, almost all zircon separates from both surface and core gneiss samples contain minute coesite inclusions, suggesting these country rocks all were subjected to in situ UHP metamorphism (for review, see Liu and Liou 2011). Some granitic orthogneisses are interpreted as differentiation products of basaltic magma (e.g., Zhang Z. et al. 2006).

On the other hand, the paragneisses are compositionally and texturally much more heterogeneous. Relatively pure marble consists mainly of dolomite and calcite ± minor magnesite; impure layers contain minor diopside, tremolite, phlogopite, epidote, allanite, amphibole, garnet, rutile, and magnetite. Marble is ubiquitous as stratigraphically continuous units or as blocks in gneisses; carbonate lenses range from 20 to 500 m in length, and are about 10–200 m thick, have poorly exposed contacts with adjacent gneissic rocks and contain centimeter to meter sized eclogite blocks. Primary compositional layers with distinct color bands are preserved.

Zircon, the best mineral for reconstructing the *P-T*-time path

Inasmuch as mineralogical and geochemical tracers of metamorphism are almost completely obliterated in matrix assemblages of UHP rocks, reflecting retrogression during exhumation, unreactive zircon most faithfully preserves the record of the complex evolutionary history. The internal structures of zircon grains from various Sulu-Dabie UHP rocks revealed by cathodoluminescence (CL) imaging display distinct zonations that comprise an inherited (magmatic or detrital) core, prograde and peak (UHP) annuli, and in many cases, an outermost retrograde rim domain. Each zone contains distinctive but minute mineral inclusion assemblages that have been identified by laser Raman spectroscopy and/or electron microprobe analyses. The inherited cores contain low-P, protolithic mineral inclusions (Qtz, Pl), prograde domains preserve Qtz eclogite-facies inclusion assemblages, UHP domains carry coesite eclogite-facies inclusion assemblages, and the outmost retrograde rims exhibit amphibolite-facies inclusion assemblages (see Liu and Liou 2011 for summary and references, and Fig. 4 for a few examples).

Numerous sensitive high-resolution ion microprobe (SHRIMP) and inductively coupled plasma mass spectrometry (ICP-MS) U-Pb and Lu-Hf analyses of zircon separates from Dabie-Sulu UHP rocks combined with mineral parageneses and compositions of inclusion phases preserved in the different zircon domains have been used to constrain the metamorphic history of recrystallization. Examples of simplified P-T-time paths are summarized in Figure 5. In favorable cases, four discrete episodes of pre-subduction protolith, prograde, UHP and retrograde stages can be delineated: (1) Neoproterozoic protolith ages (800–750 Ma); (2) 246–244 Ma early-stage Qtz eclogite-facies prograde metamorphism; (3) 240–220 Ma UHP metamorphism; and (4) 215–205 Ma amphibolite-facies decompression/retrogression. Neoproterozoic supracrustal rocks together with minor mafic-ultramafic rocks of the Yangtze craton were subjected to a prograde subduction-zone metamorphism at 570–690 °C and 1.7–2.1 GPa, then UHP metamorphism at 750–850 °C and 3.4–4.0 GPa, followed by decompression to amphibolite-facies retrograde metamorphism at 550–650 °C and 0.7–1.05 GPa. The estimated subduction and exhumation rates for the Sulu-Dabie UHP terrane are up to 5–9 and 5–11 km/Myr, respectively. Evidently, the subduction zone is a "two-way street" with exhumation velocities comparable to rates of lithospheric underflow.

Fluid is an essential phase for element transport, nucleation, and growth of metamorphic zircon, and its role in the crystallization of Dabie-Sulu zircon grains has been detailed by Zheng et al. (2003, 2011). At Yangkou Beach, South Sulu, both gabbroic minerals and textures (Zhang and Liou 1997) and intergranular coesite (Fig. 3) (Liou and Zhang 1996) coexist in a 10 m long, very dry eclogite block. In this nearly anhydrous metabasaltic system, zircon grains are fine grained, showing limited metamorphic growth, thus retain Neoproterozoic U-Pb ages and isotopic compositions (Zheng et al. 2004). Majoritic garnet inferred from some exsolution lamellae of Cpx, Opx, ilmenite, and apatite in garnet (Ye et al. 2000) has also been reported from the Yangkou Beach eclogite.

Most ultramafic rocks contain extremely low-Zr contents. However, rare zircon crystals have been found in a few Sulu metasomatized garnet peridotites and/or the enclosing eclogites (Fig. 4). These zircon crystals are metamorphic in origin, showing rounded isometric forms without inherited cores, and yield SHRIMP U-Pb ages of 220–240 Ma, consistent with UHP ages of 230 ± 10 Ma for the country rocks described above (Zhang et al. 2005; Zhao R. et al. 2006, 2007; Zhang Z. et al. 2006, 2011b).

Oxygen- and hydrogen isotope characteristics and nature of the UHP fluids

Stable isotopic characteristics of the Dabie-Sulu UHP rocks have been extensively investigated (for reviews, see Rumble et al. 2002; Zheng et al. 2003; Zheng 2009 and references therein) since the first finding of anomalously low-$\delta^{18}O$ values in garnet, omphacite (–10‰) and quartz (–7‰) from Sulu coesite-bearing

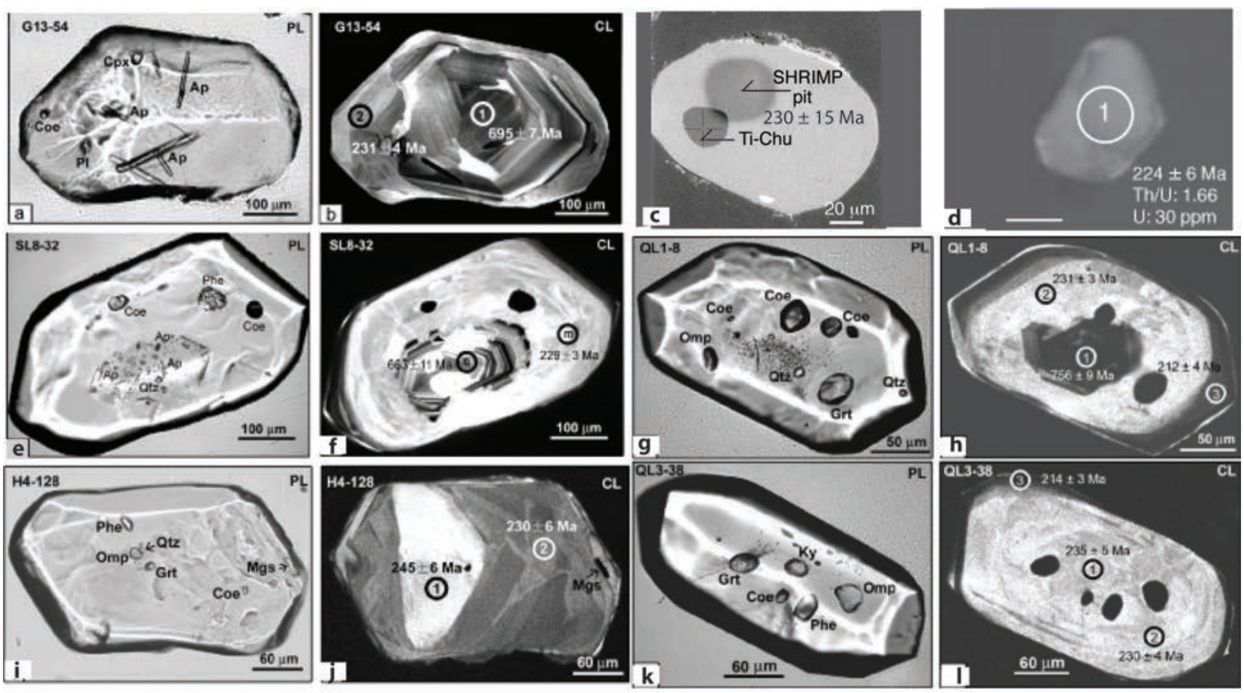

FIGURE 4. Examples of plain light (PPL) and CL images of zoned zircons with mineral inclusions from Sulu UHP rocks: (**a–b**) eclogite; (**e–f**) orthogneiss, (**g–h**) paragneiss, (**i–j**) marble, (**k–l**) quartzite (from Liu and Liou 2011), (**b**) back-scatter image of zircon from metasomatic garnet peridotite with inclusion of Ti-clinohumite (from Zhang et al. 2005), and metamorphic zircon from eclogite block enclosing within garnet peridotite (from Zhao et al. 2007). SHRIMP ages are also shown.

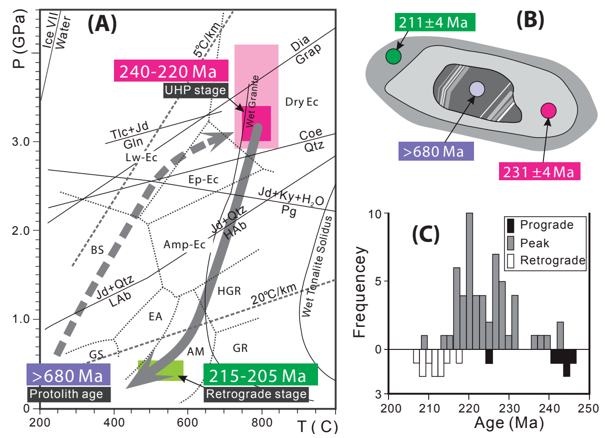

FIGURE 5. (**a**) Simplified *P–T* time paths for Dabie-Sulu eclogite and garnet peridotites. (**b**) Schematic zoned zircon domains with SHRIMP U-Pb ages for Sulu paragneiss. (**c**) Histogram of ages for the 3-stage recrystallization of Dabie-Sulu UHP rocks [modified after Liou et al. (2009)].

eclogites (Yui et al. 1995; Zheng et al. 1996). These are much lower values than those in previously reported metamorphic minerals worldwide. The low values have been attributed to intensive hydrothermal alteration of the Late Proterozoic protoliths, followed by limited fluid interactions during subduction and exhumation of the UHP rocks. Two examples are illustrated below:

Figure 6 shows petrologic and oxygen isotopic profiles of the 5 km CCSD main-hole cores (after Zhang Z. et al. 2006). Several features are apparent. (1) Depleted negative $\delta^{18}O$ values of UHP rocks occur at depths to 3200 m, whereas deeper samples exhibit normal $\delta^{18}O$ values. A depth of 3200 m may be considered as the minimum depth range of Neoproterozoic oxidation. (2) In the depleted zone, UHP rocks with low-$\delta^{18}O$ values are restricted mainly to contacts between the various eclogite, orthogneiss, and paragneiss layers. Such zones may once have been the main lithologic boundaries between the igneous and sedimentary country rocks, and provided fluid channels for intensive hydrothermal alteration. Several U-Pb dates of the protoliths yield age ranges between 700 to 800 Ma (e.g., Zhang Z. et al. 2009). (3) Continuous spatial variations of depleted to normal $\delta^{18}O$ rocks, regardless of their lithology, suggest that the protoliths underwent water-rock interactions before subduction, and that these rocks constituted a structurally coherent terrane during Triassic subduction and exhumation. (4) A preserved depleted zone of 3.2 km together with the widespread distribution of low-$\delta^{18}O$ rocks exposed over a surface area exceeding 15 000 km² (e.g., Zheng et al. 2003, 2011; Zhang Z. et al. 2008, 2011b) indicates that a huge quantity of continental crust (>46 000 km³) interacted with cold meteoric water, suggesting correlation with the Neoproterozoic global "Snowball Earth" event.

Figure 7 is an $\delta^{18}O$ vs. δD diagram for some analyzed hydrous phases from Dabie-Sulu UHP rocks together with standard values for seawater, magmatic waters, meteoric waters, and crustal metamorphic rocks. Recently analyzed Iceland epidotes and fluids from geothermal wells on the landward extension of the Mid-Atlantic Ridge by Pope et al. (2009) are also plotted for comparison. Hydrous minerals from Sulu eclogites and quartz schists exhibit limited δD ranges of –127 to –83‰ for phengite, –81 to –93‰ for amphibole, and –66 to –49‰ for zoisite, despite large variations in $\delta^{18}O$ values (–9.1 to +5.1‰ for phengite and –10.7 to –2.9 ‰ for zoisite). Those from the Dabie eclogites and paragneisses have δD values of –109 to 61‰ for micas, –100 to –72‰ for amphiboles, and –75 to –37‰ for epidote/zoisite (Zheng et al. 2009). The δD values of Dabie UHP phengites are considerably higher than those from Sulu, probably due to different extents of Neoproterozoic water-rock interactions (e.g., Fig. 8). The nearly identical isotopic values between the Iceland geothermal epidotes and the Sulu-Dabie hydrous phases support the suggestion of Neoproterozoic fluid-rock interactions under "Snowball Earth" conditions. A schematic model showing rift-

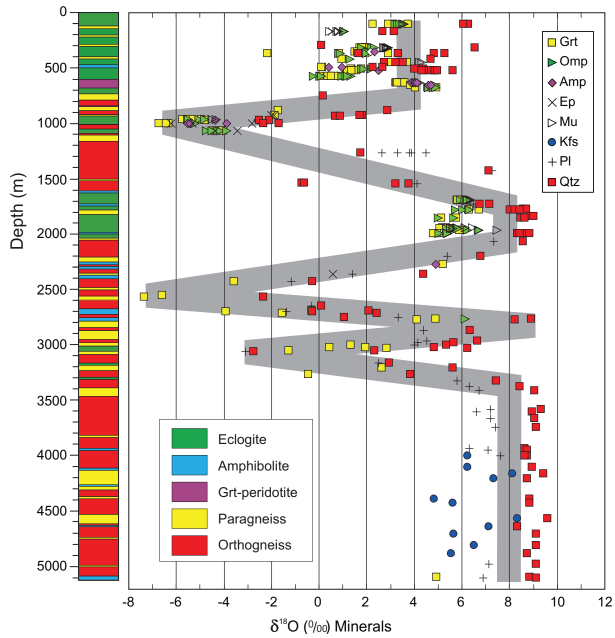

FIGURE 6. Petrologic (left) and oxygen isotopic (right) profiles of the 5000 m depth main hole of the Chinese Continental Scientific Drilling Project (modified after Zhang Z. et al. 2006).

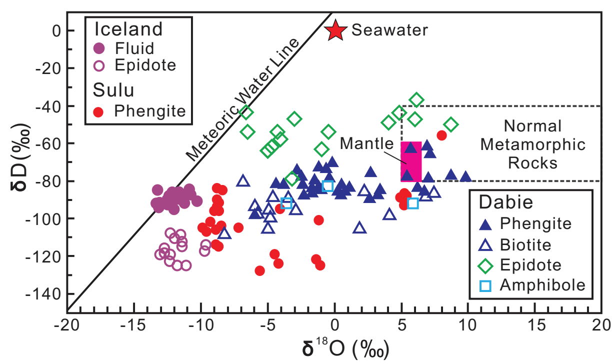

FIGURE 7. A $\delta^{18}O$ vs. δD diagram of Dabie-Sulu hydrous phases from UHP rocks [modified after Zheng et al. (2003) and Zheng (2009)] and Iceland geothermal epidotes (Pope et al. 2009) together with the standard values for seawater, magmatic waters, meteroric waters, and normal metamorphic rocks.

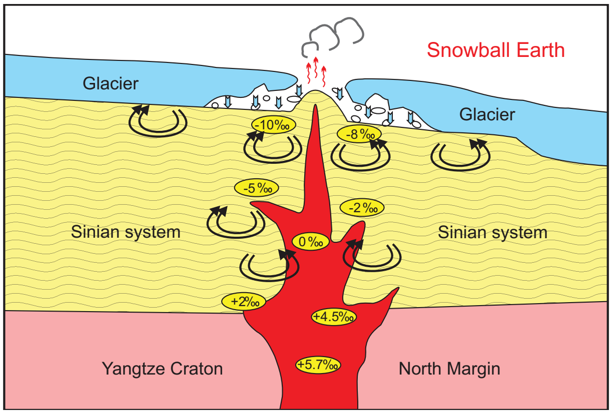

FIGURE 8. Schematic diagram showing rift-magmatism in the northern margin of the Yangtze craton at mid-Neoproterozoic time that resulted in melting and infiltration of glacier ice and triggered extensive fluid-rock interactions [modified after Zhang Z. et al. (2011b)].

magmatism, various extents of interactions with cold meteoric waters, and possible oxidation of crustal rocks along the northern margin of the Yangtze craton is illustrated in Figure 8, modified after Zheng et al. (2003).

The oxygen isotopic results described above indicate that aqueous fluid circulation during Triassic deep subduction and early exhumation stages was limited, and was characterized by local, channelized fluid-rock interactions; most UHP rocks were internally buffered, so preserved their protolith isotopic signatures. However, infiltration by external fluids may have occurred during exhumation and caused local partial melting of some UHP rocks and formation of late retrograde phases and greenschist-facies veins (e.g., Zong et al. 2010; Zheng et al. 2011; Gao et al. 2012).

In short, during the prolonged metamorphic evolution of Dabie-Sulu UHP rocks, fluid-rock interactions occurred at various stages. The nature of the fluids has been documented through numerous studies of fluid inclusions in prograde and retrograde phases (e.g., for summary see Zhang Z. et al. 2011b and references). Seven stages of fluid-rock interactions of the Sulu UHP rocks were recently outlined by Zhang Z. et al. (2011b). (1) Initial intense hydrothermal alteration of bimodal magmatic rocks and their country rocks by meteoric waters of extremely low-$\delta^{18}O$ compositions occurred during Snowball Earth time attending the breakup of Rodinia. (2) Progressive dehydrations and prograde metamorphism of supracrustal rocks at shallow subduction depths from the zeolite-, blueschist-, through epidote–amphibolite- to eclogite-facies conditions occurred attending the Triassic subduction. A series of dehydration reactions resulted in the formation of H_2O and CO_2-H_2O fluids of relatively low salinity. (3) Such processes continued to mantle depths; minor amounts of fluid were incorporated into a few UHP volatile-bearing minerals, including phengite, epidote/zoisite, glaucophane, talc, magnesite, and lawsonite, and into nominally anhydrous minerals (NAMs) such as garnet, omphacite, and rutile. Inasmuch as H_2O was stored in these host minerals, the concentrations of other components and salinities in the CO_2–H_2O fluid phase increased. (4) During fluid-rock interactions at the peak-stage of UHP metamorphism, minor amounts of silicate-rich supercritical fluid were generated and normally immobile elements may have been mobilized. (5) Rehydration during exhumation from mantle to crustal depths resulted in extensive exsolution of structural water from UHP NAMs as well as the dehydration of lawsonite. The resulting fluid probably released large quantity of dissolved elements to form epidote, sodic amphibole, and HP vein minerals, and caused local partial melting (e.g., Zong et al. 2010; Gao et al. 2012; Zheng et al. 2011). (6) During late-stage retrogression at mid-crustal depths, dehydration of phengite and sodic amphibole and the minor addition of an external fluid resulted in pervasive amphibolite-facies recrystallization. (7) The final stage greenschist-facies retrogression was associated with channelized fluid infiltration at shallow crustal depths along ductile shear zones and resulted in the formation of numerous low-*P* quartz veins.

Long duration of UHP and retrograde metamorphism

Numerous geochronological data for Sulu-Dabie felsic, mafic, and ultramafic rocks are summarized in Figure 5c. (1) U-Pb zircon studies have yielded Triassic ages (245–205 Ma) from various Sulu gneisses and eclogites (see summary in Liu and Liou 2011). This 245–205 Ma interval is also consistent with earlier studies that produced Sm-Nd isochron ages (228–209 Ma) for Dabie eclogite and Grt clinopyroxenite (221–236 Ma) by Jahn et al. (2003). (2) Zircon rims that contain low-*P* inclusions such as Qtz and Ab from gneisses yield Late Triassic ages (213–208 Ma) (Liu F. et al. 2001, 2004, 2005, 2008, 2010), representing the amphibolite-facies retrograde event. SHRIMP U-Pb ages of rare Sulu garnet peridotites and their included eclogites range from 238 to 218 Ma (Li et al. 2008; Zhang et al. 2005, 2009b; Zhao R. et al. 2006; Zhang Z. et al. 2006, 2011a); these ages lie within the UHP metamorphic age range (240–220 Ma) for Dabie-Sulu gneisses and eclogites. Such consistent ages from mafic-ultramafic rocks and country rock gneisses demonstrate that the entire section was subjected to coeval UHP-HP metamorphism over an interval of 10–20 Myr.

A large age range exists in samples from different areas and even in adjacent samples from the same region, resulting from several factors. (1) An insufficient number of spot analyses may result in a bias when calculating weighted mean ages of mafic-ultramafic rocks. (2) Absence of inclusions in most zircon grains makes it difficult to pin down the metamorphic conditions for each zircon growth zone. (3) Zircon grains may have recrystallized under different *P-T* conditions in the subduction zone, and their inclusions only reflect the latest *P-T* conditions that reset the U-Pb system. (4) Zircon grains may have grown at different times during protracted residence times of these mafic-ultramafic bodies at UHP-HP conditions. The close proximity and similar petrological-geochemical characteristics of analyzed mafic-ultramafic rocks exclude the possibility that they record different metamorphic events, and were later juxtaposed against one to another. Instead, the mafic-ultramafic rocks underwent prolonged HP-UHP metamorphism between 240 to 220 Ma, similar to the UHP recrystallization intervals determined for the country rock gneisses and in situ eclogites.

As noted above, evidence for 15–20 Myr duration under UHP-HP conditions (Fig. 5c) has been suggested by a growing number of U-Pb, Sm-Nd, and Rb-Sr ages from Dabie-Sulu UHP rocks (e.g., Hacker et al. 1998, 2006; Wu et al. 2006; Zheng 2009; Brouwer et al. 2011). One possible explanation for such a long interval is the episodic growth of zoned zircon grains during prograde and retrograde stages at UHP conditions in the presence of an aqueous fluid. However, UHP zircon domains show marked contrasts in terms of CL patterns, U and Th contents, Th/U ratios, abundance of mineral inclusions, and compositions of omphacite inclusions. The linking of zircon growth to specific metamorphic conditions is not an easy task, and the recrystallization of UHP rocks from prograde, peak, and retrograde stages could pass through the coesite stability field for a considerable length of time. Unless the specific *P-T* conditions for each stage can be determined, the extent to which any of these ages represent prograde, peak and retrograde UHP stages of zircon growth remains somewhat uncertain (e.g., O'Brien 2006; Schmidt et al. 2008).

Alternatively, the large age range of SHRIMP ages for Sulu UHP rocks may instead imply the juxtaposition of several UHP slices during exhumation from mantle to crustal depths. In fact, a successive subduction-exhumation model has been used to explain a ~30 Myr long diachronous exhumation of HP-UHP rocks in the western Dabie terrane (Liu X. et al. 2004). Individual slices of the subducting Yangtze slab have been exhumed from different depths and the successive descent of underlying slices was accompanied by nearly concomitant uplift of some of the overlying slices.

Discussion

SHRIMP U-Pb zircon ages and *P-T*-time paths

Since the discovery of coesite and microdiamond, respectively, in 1984 and 1990, studies of UHP rocks have defined a new frontier in the Earth sciences (Chopin 1984; Smith 1984; Sobolev and Shatsky 1990). A central issue for UHP terranes involves study of the nucleation and growth of zircon, because it seems to be the best container for preserving UHP minerals and represents the best time recorder for the protolith, prograde, UHP, and retrograde stages. The sources of Zr, Si, and REE components as well as the roles of fluid transport during various stages of metamorphism for subsolidus zircon growth domains need to be documented by kinetic modeling and documentation of the characteristics of fluid inclusions in the different $ZrSiO_4$ zones. Moreover, the precise *P-T* conditions for its growth, particularly those dating spots by ion microprobe have been extremely difficult to determine. Evidence linking zircon growth to specific metamorphic conditions is lacking, and the extent to which any of the ages represent UHP conditions or distinct phases of zircon growth remains somewhat uncertain. The Ti-in-zircon geothermometer (e.g., Watson and Harrison 2005; Fu et al. 2008) using an ion-probe in conjunction with spot age analysis should be applied to provide better temperature-time constraints. However, a recent study by Timms et al. (2011) indicates that chemical exchange between zircon and the surrounding matrix can occur; accordingly, Ti-in-zircon thermometry and U-Pb geochronology from deformed zircon grains may not yield exact information relating to the *P-T* conditions and timing of zircon crystallization. Timms et al. (2011) suggested that open behavior of the Ti-Th-U system occurred shortly after zircon growth, but prior to the accumulation of significant radiogenic lead.

Furthermore, linking inclusions in zircon in UHP rocks with the age of growth and/or breakdown of major minerals such as garnet, pyroxene, or phengite is not straightforward. Inclusions identified by optical microscopy and confirmed by micro-Raman typically lie in the interior of the zircon grains and do not appear on the polished surface. This means that the relationship between CL-defined growth zones, REE patterns of these zones, SHRIMP ages, and the positions of the UHP indicator phases in some cases is unclear.

As stated above, most previous geochronologic constraints on metamorphic evolution of the Dabie-Sulu UHP rocks have relied on measured U-Pb ages of various zircon domains; compilation of these ages shown in Figure 5c led to suggestions of long durations for both subduction and exhumation (e.g., Liou et al. 2009; Kylander et al. 2012). This approach has been critically evaluated using new garnet Lu-Hf ages of 223–215 Ma for the CCSD main hole eclogites by Schmidt et al. (2008, 2011); this interval lies between the prograde HP eclogite-facies recrystallization and the amphibolite-facies retrogression. According to Schmidt et al. (2011), improved garnet Lu-Hf data provide better age constraints for HP and UHP rocks, reflecting the preservation of Lu growth zoning in metamorphic garnet, even in cases where major elements in the same grain appear to have been homogenized; thus, the garnet Lu-Hf ages apparently are extremely robust, and resist resetting by diffusive loss along the cooling path. Schmidt et al. (2011) urge combining the results from zircon U-Pb and garnet Lu-Hf ages to more accurately constrain the metamorphic evolution of the Dabie-Sulu UHP rocks.

Fluids and the growth of zircon domains

The presence of fluid is essential for at least episodic growth of zircon grains. Primary fluid inclusions together with coesite mineral inclusions were identified in the same zircon domains from some CCSD main hole eclogite, paragneiss, and orthogneiss core samples (e.g., Liu and Xu 2004). SHRIMP U-Pb dating of these coesite-bearing zones indicates that both fluid and coesite were trapped during the UHP metamorphism. However, surviving coesite and fluid are present as discrete single-phase inclusions; coesite would be totally transformed to quartz in the presence of minor aqueous fluid during decompression, reflecting rapid H_2O-induced back reaction (Mosenfelder et al. 2005). Fluid inclusion studies need to be pursued to characterize the temporal and spatial resolutions of such micro- to nano-size inclusions in zircon grains because the results would provide important information on the compositions and geochemical evolution of metamorphic fluids and fluid-rock interactions (e.g., Zheng et al. 2011).

Oxygen isotope analyses of zircon grains from Dabie-Sulu eclogites and their country rocks indicate that ~50% of the separated zircon grains have substantially negative $\delta^{18}O$ values. Ion-probe micro-spot oxygen isotopic data of 3–4 distinct domains of Dabie-Sulu zircon separates should be undertaken. These data could be used to differentiate the characteristics of fluids in various stages and to assess the rate of oxygen isotopic diffusion (Valley and Kita 2009).

Lack of microdiamonds in Dabie-Sulu UHP rocks

Comprehensive investigations of zircon separates from more than 2000 diamond-grade UHP rocks of the Kokchetav Massif have been reported (for review, see Katayama and Maruyama 2009); microdiamond inclusions are widespread in zircon UHP domains, whereas graphite occurs both as cores and rims of the microdiamond inclusions and as inclusions in retrograde zircon domains. Inclusions of microdiamond in Dabie eclogitic garnets have been reported (Xu et al. 1992, 2005; Okay 1993). However, an extensive search of more than 50 000 zircon grains from 3000 Dabie-Sulu UHP outcrop and drill core rock samples by different investigators have failed to reveal the occurrence of any microdiamond inclusions. The absence of microdiamond and paucity of graphite from Dabie-Sulu UHP rocks probably reflects the presence of relatively oxidized protoliths, in turn, resulting from extensive meteoric water-rock interactions during Snowball Earth time as described above.

Concluding remarks

A steady stream of new UHP mineral occurrences has been reported from continental basement rocks such as exposed in Bohemia and in mafic-ultramafic ophiolite terranes. During the last three decades, efforts have focused on the characterization of UHP rocks through mineralogic, petrologic geochemical, and geochronologic studies. Zircon is now recognized as the best container recording the *P-T*-time path of UHP rocks. Fortunately, it occurs at least sparsely in nearly all UHP rocks, including some ultramafics. Many new micrometer-size inclusions, including fluids and nano-phases have been identified. Subduction depths of supracrustal rocks are now recognized to extend from the coesite through the diamond *P-T* stability at ~150 km, and perhaps to the fields of majoritic garnet and stishovite as deep as 300–350 km. With new analytical tools characterized by high spatial, temporal, and energy resolutions, we anticipate additional petrologic, geochemical, and isotopic surprises. Integrated approaches for isotopic systems including Hf-Lu dating and tracers, and for nano-phase characterization need to be pursued. New findings, combined with precise field, mineralogic, and petrologic data will surely extend our interpretations of geotectonic models and the controlling mantle dynamics.

This review has undoubtedly overlooked many important UHP contributions inasmuch as more than dozen relevant papers and special issues appear each month in regional and international journals. We apologize for this, but hope that our review will spur additional research on the exciting, evolving topic of UHP metamorphism and continental subduction.

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