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Fluid-rock Interaction and Mass Transport during Continental Collision in the Dabie-Sulu Orogenic Belt

HUANG Jian and XIAO Yilin

CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, PR China

Fluid activity and its associated element mobility in oceanic subdutcion zones have been extensively studied, and much outstanding achievement has been gained over the past twenty years (e.g., Spandler and Pirard, 2013). However, only limited attention has been paid so far to the role of fluids during subduction and exhumation of the continental crust (e.g., Zheng et al., 2011). Hydrous veins represent channelized fluid flow with very high fluid/rock ratios and provide a direct evidence for fluid/rock interactions during metamorphism (e.g., Huang et al., 2012). Ultrahigh pressure (UHP) metamorphic rocks and its associated hydrous veins from the Dabie-Sulu UHP metamorphic belt present an excellent natural laboratory to study the nature of fluid phases and element mobility in continental collision zones (e.g., Zheng et al., 2011). Thus, a combined study of petrology, bulk rock and mineral geochemistry, and isotope systematics of hydrous veins and their host eclogites can play a robust constraint on elemental and isotopic fractionations during subduction and exhumation of the continental crust.

Niobium and Ta concentrations in UHP eclogites and rutile from these eclogites and associated HP veins collected at the Bixiling complex in the Dabie orogen have been determined to constrain the mechanism and effective distance of Nb-Ta mobility and fractionation during fluid/rock interaction in continental subduction-zone metamorphism. Niobium and Ta concentrations in the eclogites away from veins (EAVs) range from 0.42 to 3.97 ppm and 0.03 to 0.24 ppm, respectively. The EAVs display bulk Nb/Ta ratios ranging from 14.0 to 19.2, which fall in the range defined by their refered protolith gabbros from the Yangtze Block (Fig. 1a). Their average Nb/Ta ratio of 16.9 ± 0.8 (2s.e. n = 12) is very similar to that of the gabbros (16.2 ± 0.6, 2s.e. n=78). These observations indicate transformation of gabbro to UHP eclogite did not lead to the fractionation of Nb-Ta. More importantly, in the log[Nb] vs. log[Ta] diagram, the slope of 0.965 ± 0.038 for Nb and Ta is very close to 1 and suggests negligible Nb/Ta fractionation during partial melting, magma differentiation, Triassic

subduction, and subsequent eclogitisation. In constrast, Nb/Ta ratios of rutile from eclogites close to veins (ECVs, the distance between vein and eclogite is ≤ 25cm) are highly variable from 17.8 to 49.8, which are systematically higher (by up to 17) than those of rutile from the veins (Fig. 1b). These observations demonstrate that Nb and Ta were mobilized and fractionated during localized fluid flow and intensive fluid-rock interaction. Thus, high fluid/rock ratios and secular fluid flow is the mechanism for Nb-Ta mobility and fractionation, but the scale of mobility is limited (Huang et al., 2012).

In order to further understand the role of fluids on elemental and isotopic fractionations in the deeply subducted continental crust, whole-rock and mineral geochemistry as well as Li-B-O-Sr-Nd-Pb isotopes on four carefully selected sample sets with contrasting lithological boundaries in UHP metamorphic rocks from the Chinese Continental Scientific Drilling Program (CCSD) in the Sulu orogen has been carried out to investigate geochemical modification as a result of fluid flow during progressive dehydration, peak metamorphism, and subsequent exhumation (Xiao et al., 2011). A HP vein (sample set 1) representing dehydration during prograde metamorphism shows an enrichment of Rb, Ba, Th, LREE and other incompatible elements that are complementary to those of its host eclogite, suggesting that vein-formation was initiated by locally-derived fluids that leached elements from the dehydrated host rock. These fluids are aqueous fluids with low contents of silicates at an early stage, but under UHP conditions become fluid phases that have intermediate compositions between aqueous fluids and hydrous melts. A second sample set (sample set 2) consists of garnet peridotite (a mantle segment), eclogite (a crustal segment), and a transition zone between them.

* Corresponding author. E-mail: jianhuang@ustc.edu.cn

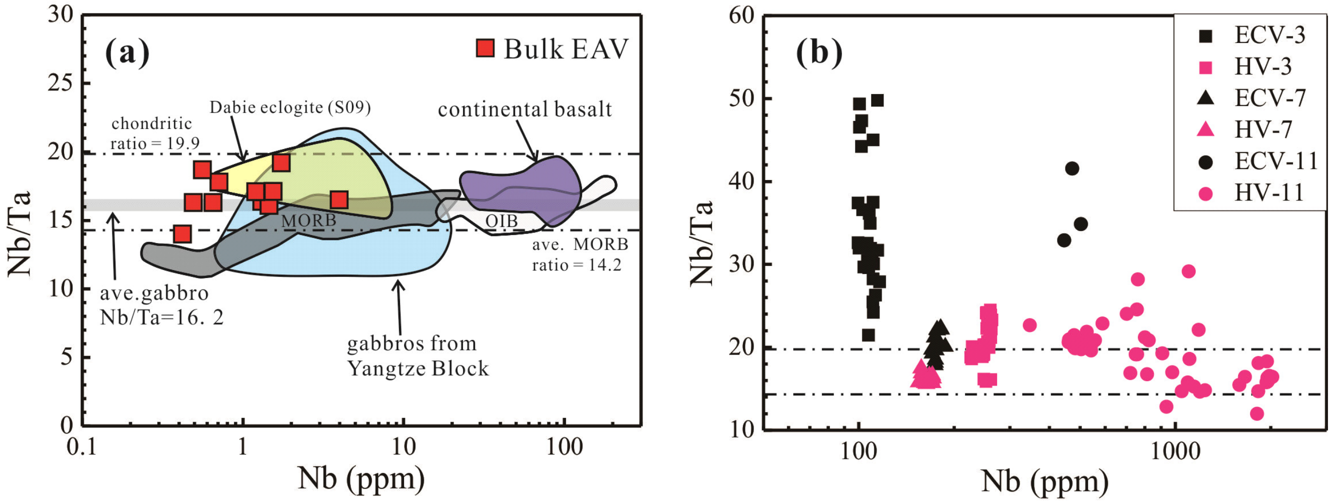

Fig. 1. (a) Plot of Nb (ppm) versus Nb/Ta for the EAV eclogites at Bixiling from the Central Dabie Zone. Also shown are data for chondrite, MORBs, OIBs and continental basalts (data from Münker *et al*., 2003) as well as gabbros (protolith for eclogites) (data from Zhao and Zhou, 2007; Dong *et al*., 2011) and Dabie eclogites determined using the ID method (Schmidt *et al*., 2009, S09); (b) Comparison of rutile from the HP veins (HV) and their host eclogites (ECV) at Bixiling from the Central Dabie Zone. Sample ECV-3 was collected 10 cm from a quartz vein; ECV-7 20 cm from another quartz vein (08bxl07v); ECV-11 5 an epidote-quartz vein (HV-11). Dash dot lines denote the revised chondritic Nb/Ta ratio (upper) and average MORB ratio (lower), respectively (Münker *et al*., 2003).

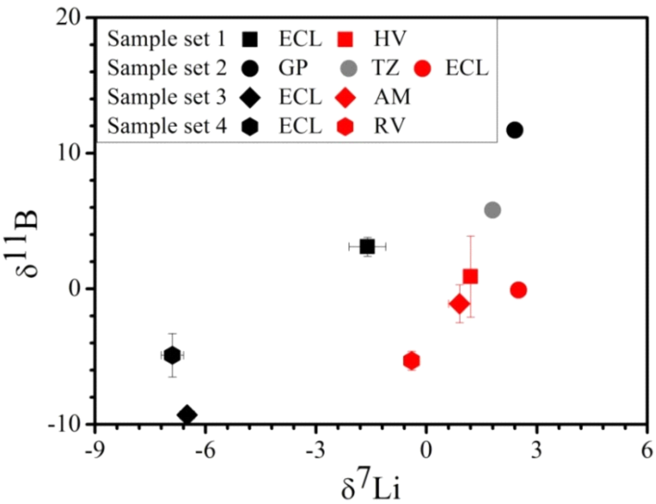

Fig. 2. Variations of both $\delta^{7}Li$ and $\delta^{11}B$ in the metamorphic rocks and veins from the CCSD. Sample set 1 includes a HP vein (HV) that originated from locally-derived fluids during prograde metamorphism and its host eclogite (ECL); sample set 2 consists of a garnet-peridotite (GP), an eclogite and a transition zone (TZ) between them; sample set 3 is composed of a eclogite and its retrograde product amphibolte (AM); and sample set 4 comprises a eclogite and a retrograde amphobilite vein (RV). It is noted that Li and B behave differently during various stages of UHP metamorphism.

Abundant hydrous minerals (i.e., chlorite and amphibole), compositionally different clinopyroxene grains in the transition zone clearly reveals the addition of fluids enriched in silicate component from the subducting slab to the mantle. Another two sample sets (sample sets 3 and 4) composed of retrograde amphibolite and relatively fresh eclogite were chosen to study fluid-assisted retrogression of UHP metamorphic rocks, demonstrating that internally-derived fluids are mainly responsible for the formation of amphibolites and that heavier Li was added to the rock system during exhumation. The overall large variations of $\delta^{7}Li$ from -6.9 to +2.5‰ and $\delta^{11}B$ from -9.3 to +11.7‰ in the studied samples (Fig. 2) are indicative of significant Li and B isotopic fractionations during different metamorphic stages of the UHP rocks. As Li and B budget is controlled by liquids, temperature, mineral assemblages, mineral-fluid reactions, and diffusive processes, they behave differently during UHP metamorphism. This is evident from the contrasting isotopic fractionation of Li and B in samples representing prograde metamorphism and those representing near-peak metamorphism and isotopic composition of the two elements (Fig. 2).

Three distinct types of high-P-T fluids (i.e., aqueous fluids, hydrous melts and supercritical liquids) have been experimentally identified under subduction-zone metamorphic conditions (e.g., Kessel et al., 2005). Different lithological contacts are the most favorable place for fluid activity (e.g., Xiao et al., 2011) and thus for mass transport during metamorphism. Aiming to better understand the nature and action of supercritical liquids and the associated element mobility at UHP metamorphic conditions, geochemical analyses of minerals and whole-rocks for major and trace elements as well as Sr-Nd-O isotopes on samples along a profile across the boundary between amphibolite retrogressed from UHP eclogite and its country rock granitic gneiss from the South Dabie low-T/UHP Zone have been conducted (Huang et al. under review). Compared to the other amphibolites further away from the boundary, amphibolite at the transition to gneiss has much higher light ion lithophile elements (e.g., LILE:

K, Rb, Sr, Ba, Pb, Th and U), high field strength elements (e.g., HFSE: Zr, Hf, Nb, Ta and Ti) and REE, slightly lower SiO_2, MgO and CaO, but very similar Cr and Ni contents. Magma differentiation and/or crustal contamination during igneous processes of the protolith formation in the Neoproterozoic should not result in lower concentrations for both MgO and SiO_2, rather these igneous processes would produce a negative correlation between MgO and SiO_2.Thus, the observed geochemical variations at the contact are probably not related to protolith heterogeneity, but rather should be the result of geochemical modification during metamorphism. This is also supported by a significant variation of initial $^{87}Sr/^{86}Sr$ ratios from 0.7004 to 0.7056 at t_1 = 780 Ma (protolith age), but a very limited range of initial $^{87}Sr/^{86}Sr$ ratios from 0.7061 to 0.7070 at t_2 = 230 Ma (metamorphism age).

Aqueous fluids are too dilute to transport trace elements, especially HFSE (e.g., Hermann et al., 2006), and amphibolite-facies retrogression of eclogite is known to have no significant effect on their major and trace elements (e.g., Xiao et al., 2011). Also, metasomatism of Si-rich hydrous melts from partially melted granitic gneiss should increase the silica content of the amphibolite at the contact, which is not observed. Thus, supercritical liquids are a good agent to explain the observed major and trace element variations, because such liquids can vary continuously in composition from dilute aqueous to silicate melt-like fluids, but have a much greater capacity to dissolve various types of solutes, including silicates and conventionally fluid-immobile elements such as HFSE and HREE (e.g., Kessel et al., 2005). Based on the P-T path of the South Dabie Zone and pressures for the 2nd critical endpoint in the granite- and basalt-H_2O systems, we speculate that supercritical liquids preferentially originated in the granitic gneiss under UHP conditions and dissolved trace element-rich accessory minerals (e.g., allanite, garnet and rutile) and finally became enriched in LILE, REE and HFSE. Therefore, such liquids containing much higher trace element concentrations accumulated at the contact and caused the abrupt increase of trace element concentrations of the eclogite at the contact. This feature has been preserved through retrograde metamorphism during exhumation. This interpretation is supported by multiphase solid inclusions of amphibole ± paragonite ± clinozoisite ± quartz ± K-feldspar ± calcite ± garnet ± rutile ± zircon ± apatite within garnet in the amphibolite.

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Key words: fluid-rock interaction, UHP metamorphism, element mobility, isotope fractionation, continental collision

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