SMP10-01 Room:A05 Time:May 26 14:15-14:30

The fundamental tool for locating new examples of ultra-high pressure metamorphism: your eyes!

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In the space of just over 30 years ultra-high pressure (UHP) metamorphic rocks of continental origin, with characteristic indicators coesite and/or microdiamond, have gone from being an enigmatic, difficult to explain local feature of eclogite-bearing terranes to become an integral feature of numerous subduction-collision orogens the world over. The recognition of the over 100 km depths reached by crustal rocks as well as the extraordinary rates at which these rocks exhume are now accepted features of modern studies in geodynamics. Surprisingly, however, in the present-day scientific world of phenomenal computer power and seemingly unlimited automated analysis and data production, the investigation of UHP rocks, including the search for possible new coesite, microdiamond or minerals recording even deeper subduction (e.g. K-Hollandite or Stishovite) still requires skills in fieldwork and optical microscopy: aspects that are fast disappearing from modern earth science curricula. The search for coesite in the Himalaya was initiated by geothermobarometric calculations using published analyses for phengite-bearing eclogite to indicate rocks that had potentially experienced coesite-depth pressures. The prediction of UHP conditions was confimed after fieldwork in Pakistan unearthed fine-grained eclogites with multiple coesite inclusions (found optically and confirmed by micro-Raman) in omphacite. Soon after, the predicted UHP was also confirmed in the Indian Himalaya (Tso Morari). In the Variscan Orogenic belt, typified by high temperature metamorphism and granulites, UHP metamorphism was not to be expected. However, an important UHP indicator is the widespread presence of garnet peridotite with granulites of granitic composition. With a knowledge of the optical microstructures from well documented microdiamond samples it was possible to work systematically through existing thin section collections of the granulites and identify inclusions in garnet, kyanite and zircon of microdiamond, and its breakdown product graphite, by reflected light microscopy. Again, micro-Raman was used to confirm these finds. In a third example, from the Norwegian Western Gneiss Region, left-over eclogite zircons from a geochronology study were mounted and polished and tiny rounded inclusions investigated by micro-Raman. In this study it was much harder to find coesite inclusions as they appear very similar optically to quartz, apatite and other phases and in addition the connection to the primary rock texture is lost. In summary, preserved UHP minerals make up only a tiny fraction of material collected even from well documented UHP terranes. Skills in the field (you must collect the right rock!) and skill on the microscope (you must learn the features of UHP minerals from good standard samples in order to find the phases in new rocks) are still the most reliable and efficient way to expand our database of UHP samples and advance our knowledge of these exciting rocks.

Keywords: UHP metamorphism, coesite, microdiamond, Himalaya, Variscan

SMP10-02 Room:A05 Time:May 26 14:30-15:00

The origin of oriented mineral inclusions in garnet/clinopyroxene of UHP rocks: Insight from the TEM study

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The phase formed by a solid-state exsolution process generally occurs as oriented lamellae, plates, needles, or short prisms with definite crystal forms and follows specific crystallographic orientation relations (CORs) with the host mineral to reduce the kinetic barriers for nucleation and growth and also to minimize the interfacial and the strain energy. Accordingly, oriented inclusions to be categorized as exsolution products must be ascertained by rigorous crystallographic, energetics and mass balance examinations. Oriented mineral inclusions are known to occur in garnet and clinopyroxene of various ultra-high pressure (UHP) rock types, e.g. garnet peridotite, eclogites, metapelites, and gneisses, and are usually considered to be the exsolution products upon P-T decreasing and have been taken as important UHP indicators. Our TEM study in the past few years, however, showed that the geneses of such tiny oriented inclusions within UHP garnet/clinopyroxene are rather complicated. They could occur either as single-phase inclusions or multiple-phase inclusion pockets with specific phase-assemblage, following either single or multiple CORs, or even without any specific COR with the mineral host. These observations, along with the energetic and mass balance considerations, do suggest that these tiny oriented inclusions in UHP garnet/clinopyroxene might have various petrogenetic origins, including solid-state exsolution, co-precipitation, cleaving-infiltration-healing, and metasomatic alteration. Only through very detailed petrographic, chemical and crystallographic studies as demonstrated in our previous studies of the kokchetavite-bearing multiple-phase needles/prisms in clinopyroxene (Hwang et al., 2004; 2013a), the rutile needles in garnet (Hwang et al., 2007, 2014; Proyer et., 2013), the ilmenite/spinel plates in clinopyroxene of garnet pyroxenite (Hwang et al., 2011), the orthopyroxene blades in peridotite garnet (Zhang et al., 2011; Hwang et al., 2013b), can the true origins of such oriented inclusions in UHP minerals be deciphered.

Hwang et al., 2004. *Contrib. Mineral. Petrol.*, **148**, 380?389. Hwang et al., 2007. *J. Metamorph. Geol.*, **25**, 349-362. Hwang et al., 2011, *Contrib. Mineral. Petrol.*, **161**, 901-920. Hwang et al., 2013a. *J. Asian Earth Sci.*, **63**, 56-69. Hwang et al., 2013b. *J. Metamorph. Geol.*, **31**, 113?130. Hwang et al., 2014. *J. Metamorph. Geol.*, DOI: 10.1111/jmg.12119. Proyer et al., 2013. *Contrib. Mineral. Petrol.*, **166**, 211-234. Zhang et al., 2011. *J. Metamorph. Geol.*, **29**, 741?751.

Keywords: oriented inclusion, ultra-high pressure rock, garnet, clinopyroxene, TEM

SMP10-03 Room:A05 Time:May 26 15:00-15:15

Unusual mineral inclusions in the Luobusa chromitite: Evidence of ultra-deep origin and recycled crustal materials

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Podiform chromitites in Luobusa ophiolite, southern Tibet, yield a wide variety of unusual minerals, including UHP minerals (micro-diamond, coesite, moissanite), highly reduced minerals (native elements, carbide, nitride, alloys), and crustal minerals (quartz, corundum, sillimanite, kyanite, zircon etc.). We reported unusual silicate lamellae (coesite, clinopyroxene and MgSiO3 phase) exsolved from chromite using TEM analysis (Yamamoto et al., 2009), and unusual ancient crustal zircon separates from chromitites using LA-ICPMS and Laser-Raman analysis (Yamamoto et al., 2013). To deduce long history of mantle convection, micro-inclusions preserved in refractory minerals can provide potential mineralogical and geochemical evidence.

Coesite as an exsolution in chromite is diagnostic UHP evidence and clinopyroxene exsolution in chromite is possible evidence of former CF-type high-pressure polymorph of chromite (>380 km deep). Silicate exsolutions in chromites are restricted in the nodular- and massive-type chromites, and disseminated-type chromites have no exsolutions. Petrographically, nodular-type chromites with abundant silicate-exsolutions are gradually modified into disseminated-type chromites in their morphology. The characteristic of the disseminated-type chromite, such as their interstitial distribution, euhedral to subhedral morphology and absence of silicate-exsolutions, suggest their formation under the low-pressure magmatic conditions.

We have measured the U?Pb age of zircon grains separated from podiform chromitites. Spot analyses with LA-ICPMS, assisted by CL images gave a wide age range, from the Cretaceous to the Late Archean (ca. 100-2700 Ma). Most of the ages are much older than those of the chromitite and ophiolite formation. Laser Raman analyses revealed that the zircons contain crustal mineral inclusions, such as quartz and K-feldspar, but lack mantle minerals (e.g., olivine, pyroxene, and chromite), suggesting that they had a crustal origin. From these results, we conclude that ancient crustal zircons in chromitites are xenocrysts that originated from continental materials that were brought into the upper mantle by ancient subduction processes, such as sediment subduction and subduction erosion.

We conclude that the podiform chromitites at the Luobusa retain evidence of their multi-stage development from ultrahigh-pressure environment to low-pressure magmatic processes, and tiny inclusions shielded by refractory minerals, such as chromite, diamond and zircon, record their prolonged history from the shallow crustal levels to the deep-mantle environments.

SMP10-04 Room:A05 Time:May 26 15:15-16:00

Research of UHP metamorphism and implication to Orogeny, Mantle dynamics, and thermal material evolution of Earth

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The most important research results of UHP metamorphism and belts are as follows; 1) Continental crust can subduct down to 100-200km depth at least, suggesting the concept that only density controls the survival of TTG crust on the surface through time forever is wrong, which is thought to be common sense geologically. Theory of continental crust subduction leads the three layers model of continents on the Earth (Kawai et al., 2008). 2) UHP-HP belts is a thin unit less than 2km which is sandwiched by a paired faults at the top and bottom, indicating the tectonic intrusion of regional metamorphic belt caused by wedge extrusion due to slab breakoff or ridge subduction. This led the orogenic model by continent-continent collision. 3) Barrovian metamorphism is not a progressive metamorphism but retrogressed hydration product during the exhumation to the surface at mid-crustal level. Role of water is to control the material circulation within the Earth from the surface to the bottom of upper mantle. 4) UHP-HP belts appear on the surface of the Earth only after 630Ma. It indicates rapid change of subduction geotherm at the onset of Phanerozoic, which initiated the return-flow of seawater into mantle. This was a trigger of emergence of huge landmass to deliver huge amount of nutrients to the continental margin and created the paradise on continental shelf for metazoans and sea plants because the sunlight was shining down to the bottom of continental shelf. 5) Specifically, the spatial limit of equilibrium domain contributed to understand the species and amounts of light elements in the core, and material circulation of the Earth's interior.

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SMP10-05 Room:A05 Time:May 26 16:15-16:45

Fluid control of deeply subducted continental materials and diamond formation by Intraslab UHP metasomatism

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Deep continental subductions are an input for material cycling from surface to deep mantle. UHPM rocks mean the part of the direct evidence of this process. The Kokchetav UHPM rocks are the best samples and evidence to understand chemical processes in the subducting materials in global material cycling. During subductions, volatiles are carried into deep mantle together with major components and control the chemical reactions in subducting materials. Transportation of H_2O and CO_2, is the most important role of the deep continental subduction. Silicate rocks are H_2O reservoirs as hydrate minerals and carbonate and calc-silicate rocks are CO_2 reservoirs during subduction. The timings of dehydration in silicate rocks and decarbonation in carbonate and calc-silicate rocks are different. Dehydrations precede decarbonations by different P-T-V relations of CO_2 and H_2O, and H_2O play as a trigger to occur decarbonations in carbonate and calc-silicate rocks. Decarbonations are a CO_2 extraction from carbonate and calc-silicate rocks and are difficult to occur under dry conditions in P-T range of UHP metamorphism. The amount of H_2O infiltrating in carbonate and calc-silicate rocks controls the amount of CO_2 carried into the mantle. Poor H_2O supply means abundant CO_2 transportation into the mantle.

H_2O-bearing fluid plays an important role for diamond formation during subduction of continental materials. Diamonds form and dissolve in subducting materials through H_2O fluid. In UHP dolomite marble, diamonds formed at two different stages and 2^{nd} stage growth was from H_2O fluid. The diamond at 2^{nd} stage growth has light carbon isotope compositions, -17 to -27 ‰, whereas 1st stage diamond has -8 to -15 ‰. The light carbon of 2^{nd} stage could be organic carbon in gneisses carried by fluid; dissolution of diamond in gneisses had occurred. H_2O fluid infiltration into dolomite marble caused the change of carbon solubility in fluid itself to precipitate abundant fine-grained (10-20 μm) diamonds quickly. Recently discovered sp^2 graphitic carbon inclusions in 2^{nd} stage diamond suggest the fluid participation in diamond growth from H_2O fluid. Very large cubic diamond (max. 200 μm) in garnet-clinopyroxene rocks could be different fluid conditions; low oversaturation degree of carbon in fluid and slow crystallization, and led to low abundance of diamond.

In deeply subducting carbonate rocks, the abundant carbonate remains after decarbonations and are carried to the mantle. H_2O is stored in NAMs, which become new water carriers to the mantle. The amount of H_2O in carbonate rocks carried to the mantle is smaller than calc-silicate rocks because of small modal compositions of silicate minerals. In the case of calc-silicate rocks, for example garnet-clinopyroxene rocks of the Kokchetav, the modal compositions of carbonate is small; therefore, even a small amount of H_2O can decompose all amount of carbonate to form garnet and clinopyroxene. These NAMs contain several hundreds to 1,000 ppm order of water (OH and H_2O) as new water reservoirs and carriers. The modal compositions of H_2O-bearing NAMs control the potential of water transportation. UHP metasomatism with skarn mineral formation brings the swapping of H_2O carrier from hydrate minerals in silicate rocks to NAMs in calc-silicate rocks to expand the life of H_2O transportation into mantle much longer.

We can regard deep continental subduction as the transportation mechanism of H_2O and CO_2. CO_2 transportation is controlled by H_2O behavior in deeply subducted materials and poor amount of H_2O expands the volume of CO_2 transportation into the deep mantle as carbonate. Summarizing these, *Intraslab UHP metasomatism* was proposed and will be available for volatile transportation into the mantle. All these ideas were occurred from the research on the Kokchetav UHPM rocks. The author thanks Prof. Shige Maruyama, who gave me a great opportunity to study exciting materials, Kokchetav UHPM rocks and diamonds.

Keywords: UHP metamorphism, Intraslab UHP metasomatism, metamorphic diamond, fluid, Kokchetav Massif, deep continental subduction

SMP10-06 Room:A05 Time:May 26 16:45-17:15

Maruyamaite, a new K-dominant tourmaline coexisting with diamond: Significance of tourmaline in UHP rocks

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Maruyamaite is a new end-member species of the tourmaline supergroup (IMA 2013-123, Lussier et al., 2014). The ideal chemical formula of maruyamaite is $K(MgAl_2)(Al_5Mg)(BO_3)_3(Si_6O_{18})(OH)_3O$, which is the K-analog of oxy-dravite. This new mineral was first reported as a K-dominant tourmaline coexisting with microdiamond inclusions from the Kokchetav Massif, Kazakhstan (Shimizu & Ogasawara, 2005) and named in honor of Professor Shigenori Maruyama (Earth-Life Science Institute, Tokyo Institute of Technology, Japan), who led the Japan-U.S.-Kazakhstan cooperative project on Kokchetav ultrahigh-pressure (UHP) metamorphism. The K content in maruyamaite is up to 0.576 apfu (2.76 wt% K_2O). Currently, the occurrence of maruyamaite has been reported exclusively from the type locality (the Kokchetav Massif) and maruyamaite is a unique K-dominant tourmaline species. Moreover, no K-rich dravitic tourmaline has been found from other UHP terranes (Marschall et al., 2009). The rarity of K-dominant tourmaline is probably due to the large ionic radius of K with respect to the X-site of magnesian tourmalines.

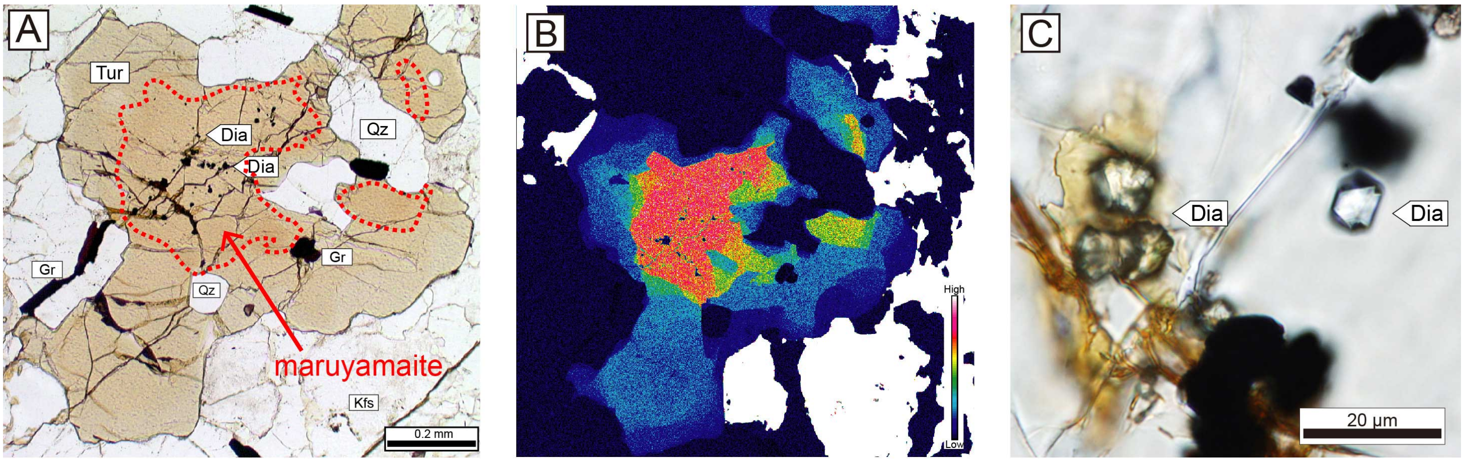
The systematic chemical analysis of various tourmalines including maruyamaite in diamond-bearing Kokchetav UHP rocks combined with detailed inclusion mineralogy demonstrated that K in tourmaline decrease with pressure (and temperature) decrease (Shimizu & Ogasawara, 2013). For instance, the figure shows that microdiamond occurs only in K-dominant core (maruyamaite) and the surrounding low-K parts (K-bearing dravite or oxy-dravite) contain low-pressure minerals such as graphite and quartz. Maruyamaite or ”K-dravite” component can form continuous solid solutions with other magnesian tourmalines up to ˜58% of K in the X-site, with a close relationship to pressure. In particular, the limited occurrence of microdiamond in maruyamaite strongly indicates that K-dominant tourmaline is a UHP phase. Ota et al. (2008) concluded that partial melting of gneisses under UHP condition had formed the maruyamaite-bearing tourmaline-rich quartzofeldspathic rock from the high δ^{11}B values of maruyamaite, which is quite unusual for high-grade metamorphic tourmaline.

There had been no experimental constraint on K-incorporation in tourmaline until fairly recently, however, K-dominant tourmaline (up to 0.71 K apfu) has been synthesized for the first time by Berryman et al. (2014). They showed that K-dominant tourmaline is stable at UHP conditions (2-4 GPa). It means that K-dominant tourmaline including maruyamaite can be a new UHP indicator. K in tourmaline also is a potential geobarometer once partition coefficient of K and Na between tourmaline and mica or feldspar is experimentally determined. Another important constraint is that K-incorporation in tourmaline structure requires not only high-pressure but also very high K/Na conditions (Berryman et al., 2014). A number of studies (e.g., Hwang et al., 2005) have shown that K-rich fluid had been present at the Kokchetav UHP stages and played an important role for the formation of metamorphic diamond and other UHP minerals such as K-rich clinopyroxene. The experimental results were consistent with the interpretation of the occurrence and chemical analyses of the natural maruyamaite-bearing rock.

Four generations of tourmaline from K-dominant maruyamaite to K-free low-grade tourmalines were recognized in the Kokchetav UHP gneisses based on their chemical compositions and inclusion contents. The tourmalines record the retrograde history from a diamond-grade partial melting to the latest greenschist facies overprint. This interpretation further emphasizes the feature of tourmaline for an excellent geochemical recorder of metamorphic events and a sink of light element such as boron in deeply subducted crustal materials.

Figure captions: (A) Photomicrograph of K-bearing tourmaline showing maruyamaite as domains rounded by red broken lines; (B) K zoning of tourmaline; and (C) Microdiamond inclusions in maruyamaite.

Keywords: maruyamaite, tourmaline, diamond, ultrahigh-pressure metamorphism, Kokchetav Massif, inclusion


A
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SMP10-07 Room:A05 Time:May 26 17:15-17:30

Water behavior in diamond-bearing and diamond-free garnet-clinopyroxene rocks from the Kokchetav Massif

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Garnet and clinopyroxene are important nominally anhydrous minerals (NAMs) in the ultrahigh-pressure (UHP) rocks because they contain significant amounts of water as OH in their structures. Diamond-free and diamond-bearing garnet-clinopyroxene rocks from the Kokchetav Massif are mainly composed of garnet and clinopyroxene. In the rocks, UHP evidences are recognized; supersilicic titanite in diamond-free rock and diamond with three morphologies: cubic form (up to 200 μm), ball-shaped form (covered with graphite) (up to 150 μm), and fine-grain (ca. 10 μm) which was discovered recently (Takabe et al., 2014). The mineral assemblages are similar to skarn and suggest a metasomatic product in the subducted slab at UHP conditions.

Water contents of garnet and clinopyroxene by micro-FTIR proved water-rich environment of the formation of garnet-clinopyroxene rocks and support the metasomatic origin at UHP condition (Sakamaki et al. 2014). Garnet contains significant amounts of structural OH and nonstructural molecular H_2O; 1727 ppm (wt. H_2O) of OH and 1592 ppm of H_2O at maximum in garnet of diamond-bearing, and 1655 ppm of OH and 1203 ppm of H_2O at maximum in garnet of diamond-free rock. In clinopyroxene, structural OH in exsolved phases and clinopyroxene host and nonstructural molecular H_2O were identified. Total water ($OH+H_2O$) contents in clinopyroxene are up to 8215 ppm in diamond-free rock and 4384 ppm in diamond-bearing rock, respectively.

Bulk water contents in garnet-clinopyroxene rocks reach into 3000 ppm which is much higher than that of diamond-facies eclogite from the Kokchetav Massif (e.g., 460 ppm by Katayama et al., 2006). Our analytical results suggest that formation of garnet-clinopyroxene rocks by metasomatism during deep continental subductions can be a trapping process of H_2O-rich metasomatic fluids and carrying into deep mantle. Such NAMs in UHP skarn means the birth of new water reservoirs and carriers into the mantle, as swapped for hydrous minerals in gneisses. This idea was based on ”Intraslab UHP metasomatism” model and its improvement.

In gneisses, which play as a main water reservoir at relatively early stage during the slab subduction, water is transported as OH in phengite to the mantle up to the stability limit of phengite. Phengite is gradually dehydrated and releases H_2O fluids during subduction. The dehydrated H_2O fluids from gneisses infiltrate into subducted materials themselves, such as carbonate and calc-silicate rocks, to occur decarbonations. As a result, the calc-silicate protoliths (silicate and carbonate mixtures) are transformed to skarn-like rocks, e.g., garnet-clinopyroxene rocks. Since garnet and clinopyroxene were formed by H_2O-mediated metasomatic processes at UHP condition, significant amounts of water were dissolved into NAMs, garnet and clinopyroxene. Such water-rich environments and UHP condition during ”Intraslab UHP metasomatism” are indispensable for water dissolution to NAMs.

Deep continental subduction has an aspect of the input of silicate rocks (e.g., gneisses) as ”wet” materials, and carbonate and calc-silicate rocks as ”dry” materials into the mantle. Dehydrations in gneisses are the extracting process of H_2O from ”wet” materials while decarbonations, which are the extracting process of CO_2 from ”dry” materials, were triggered off by water supply from dehydrations of gneisses. Water infiltration into carbonate and calc-silicate rocks has three aspects: 1) water transportation from wet materials to dry materials (”dry” materials are getting a little ”wet”, and ”wet” materials are getting ”dry”), 2) formation of UHP skarn by metasomatism, and 3) hydration of NAMs by metasomatic fluid (the birth of new water carrier). These processes in ”Intraslab UHP metasomatism” model are regarded as water transportation from ”wet” materials to ”dry” materials and expand the water input process into the mantle much deeper such as the mantle transition zone.

Keywords: the Kokchetav Massif, UHP metamorphism, diamond, supersilicic titanite, nominally anhydrous minerals, micro-FTIR spectroscopy

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SMP10-08 Room:A05 Time:May 26 17:30-17:45

Zircon U-Pb, Hf isotope and trace element geochemistry: source of the Himalayan UHP eclogites

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To understand the magmatic source and the metamorphic evolution of Himalayan ultrahigh-pressure rocks in the Kaghan Valley of Pakistan, we conducted an integrated study of U?Pb age-dating, Hf isotope and trace element geochemistry on zircons. Zircons Laser Ablation-Inductively Coupled Plasma-Mass Spectrometer (LA-ICP-MS) U?Pb age between 143 and 277Ma was obtained from zircons in High-pressure (Group I eclogites) with a concordant age of 255 ± 9 Ma (MSWD = 0.87, 95% conf., and probability = 0.56). Identical age values were obtained from the core portions of zircons in felsic gneisses. The rims of the oscillatory zoned zircons in felsic gneisses yielded 47 Ma. In contrast, zircons in ultrahigh-pressure (Group II) eclogites yielded U?Pb concordant age of 48 ± 4 Ma (MSWD = 1.4, 95% conf., and probability = 0.18).

LA-ICP-MS trace element compositions from the same spots on zircons analyzed for U?Pb age show two contrasting compositional groups. Zircons in felsic gneisses are trace-element enriched at the core domains and have higher Th/U ratios ($>$0.5) indicating their magmatic origin. Zircons in Group I eclogites are also trace element enriched and have higher Th/U ratios ($>$0.5) indicating typical magmatic protolith signatures. In contrast, zircons in Group II eclogites have significantly lower contents of trace elements, lower Th/U ratios ($<$0.5) and are typical of metamorphic origin. The identical age values and trace element compositions of zircons in felsic gneisses and eclogites suggest their crystallization from a same magma source which potentially produced both mafic and felsic rocks intermittently. The rim portions in zircons from felsic gneisses grew during the Himalayan UHP metamorphism. Zircons found in UHP eclogites, with no age data representing the protolith event, were recrystallized from the formerly formed zircons during the Himalayan UHP eclogite facies metamorphism. The Hf isotope data of zircons, obtained from the same age spots, support our interpretation. The relatively narrow range in the ?Hf, mostly positive, values (9.5 to -3.1 in zircons of Group I eclogites; +10.8 to -0.9 in zircons of Group II eclogites; and +15.6 to -2.6 in zircons of felsic gneisses), suggest their formation from a juvenile enriched mantle source.

Keywords: Himalaya, Zircon U-Pb age, Hf isotope, trace element, eclogites, Kaghan