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## Multiphase Solid Inclusions in Ultrahigh-Pressure Metamorphic Rocks: A Snapshot of Partial Melting during Continental Collision

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Multiphase solid (MS) inclusions were investigated for ultrahigh-pressure (UHP) metamorphic rocks in the Sulu orogen. They primarily consist of silicates, with minor but various contents of sulfides, chlorides, carbonates, sulfate, spinel and others. They can be hosted by a wide spectrum of metamorphic minerals (e.g., garnet, clinopyroxene, kyanite) in the UHP rocks of various bulk compositions. Texturally, the MS inclusions may exhibit negative crystal shapes, with possibly wedge-shaped offshoots filled by silicate minerals. The peak P-T conditions for UHP gneiss and eclogite from many continental subduction zones are possibly above the wet solidus of felsic rocks, yet the macroscale petrographic evidence for partial melting is scarcely found. This may be caused by the difficulty in recognizing the vestige of primary MS inclusions. As a record of former melt phases in metamorphic minerals, MS inclusions open new perspectives both for the microstructural approach to partially melted rocks and for the chemical characterization of natural crustal melts. However, the preservation of MS inclusions depends on the chemical and mechanical behavior of host mineral systems during continental collision.

The MS inclusions are small droplets of melt phases trapped in minerals, which were either quenched as glass or crystallized to polycrystalline aggregates. Usually, the average size of MS inclusion is  $<25 \,\mu$ m, but exceptionally large inclusions may reach up to  $\sim$ 300  $\mu$ m in metamorphic minerals (such as garnet, omphacite, kyanite). In hosted minerals, if MS inclusions are present, they often occupy central parts. In large host garnet crystals, inclusions concentrate in areas of irregular shape, spreading from central to outer zones of garnet. Most inclusions have polygonal to negative crystal shapes, and dimensions varying from less than 5  $\mu$ m to greater than 150  $\mu$ m. They typically contain a great and variable number of solids and lack a visible fluid phase. The former presence of a fluid phase may be assumed, because of the regular presence of

one or more deformed cavities (voids) within inclusions. Large inclusions are usually surrounded with radial cracks, similar to where garnet contains relict coesite. In addition, different phases in MS inclusions mostly occur in different forms. For micro-inclusions with palisade texture, Kfeldspar tends to be concentrated within the palisade or at the contact between the palisade and the core. Light grey large crystals occur as interstitials between K-feldspar (dark grey) grains, frequently resembling that of a holly leaf.

The MS inclusions commonly exhibit varying lithochemical compositions from felsic to mafic, but mainly felsic. Such a variation primarily depends on the bulk composition of host rocks, host minerals or reaction between the host mineral and the enclosed fluid/melt phase. Stockhert et al. (2001) found MS inclusions within garnet from diamond-bearing gneiss at Erzgebirge in Germany, which consist of phlogopite, paragonite, phengite and quartz with minor apatite, rutile and microdiamond. They were interpreted as representing the original inclusions of a dense C-O-H fluid rich in K, Na, and SiO<sub>2</sub>. Ferrando et al. (2005a, b) investigated MS inclusions in UHP quartzite and eclogite from the Sulu orogen in China and proposed that the silicate-carbonatesulfate inclusions represent precipitates from solute-rich aqueous fluids present at peak UHP conditions. Based on a study of MS inclusions in minerals from UHP garnet orthopyroxenite at Maowu in the Dabie orogen, Malaspina et al. (2006a) demonstrated that the metaultramafics were derived from garnet-harzburgite precursors that were metasomatized at peak UHP conditions by addition of a silica- and incompatible trace elements-rich fluid phase (hydrous melt), sourced from the associated crustal rocks. For MS inclusions in diamond-bearing calc-silicates at Kokchetav in Kazakhstan, Korsakov and Hermann (2006) found a distinction in trace element composition between inclusion and matrix carbonates, suggesting their crystallization from a trapped silicate-carbonate melt.

Zeng et al. (2013) observed unusual MS inclusions of

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K-feldspar + quartz + titanite + solid salt and K-feldspar + albite + quartz + epidote with textures similar to the other K-feldspar + quartz inclusions in omphacite grains of eclogite from the Sulu orogen. One of these inclusions contains square to round solid salt inclusions of KCl-NaCl composition. Such a mineral assemblage within Kfeldspar-bearing inclusions hosted by UHP metamorphic phases suggests the presence of potassium granitic melts rich in Cl components during UHP metamorphism or at the early stage of exhumation. Gao et al. (2012, 2013) observed various types of MS inclusions in garnet in UHP eclogite in the Dabie orogen, which consist of not only felsic minerals such as quartz, K-feldspar, albite and plagioclase, but also minor amounts of mafic minerals (epidote) and sulfate minerals (barite). An integrated study of petrology, mineralogy and geochemistry indicates that the MS inclusions represent products of partial melting in the UHP eclogite during the continental collision, with possible immiscibility between aqueous fluid and hydrous melt upon partial melting at UHP conditions in the continental subduction zone. Trace elements in the MS inclusions exhibit the enrichment of LILE, Sr and Pb but the depletion of HFSE in the primitive mantle-normalized spidergram. Such arc-like patterns of trace element distribution are common for continental crustal rocks. The melts have variably high K, Rb and Sr abundances, suggesting that the breakdown of phengite is a basic cause for partial melting of the UHP eclogite. These MS inclusions also exhibit consistently low HFSE and Y contents, suggesting partial melting of the eclogite in the stability fields of rutile and garnet. Consequently, the trace element composition of MS inclusions provides a proxy for that of hydrous silicate melts derived from dehydration melting of the UHP eclogite during the continental collision.

Metamorphic dehydration and partial melting are two common processes in continental subduction zones where crustal rocks suffered HP to UHP metamorphism (Zheng, 2012). This leads to different compositions of HP to UHP fluid/melt phases from different lithological systems. Available results from experimental petrology indicate that the hydrous melt has significantly different major element compositions from the aqueous fluid. The differences in the molar ratios of Si/Al and (Na+K)/Al provide a distinction between aqueous fluid and hydrous melt. While the Si/Al and (Na+K)/Al ratios for the hydrous melt are low with very limited ranges, those for the aqueous fluid are high with much larger ranges. Interestingly, the supercritical fluid is just distributed intermediately between the hydrous melt and the aqueous fluid. It is consistent with the assumption that the supercritical fluid is completely miscible fluid with a solute content varying continuously from aqueous fluid to hydrous melt.

While MS inclusions occur in various UHP metamorphic rocks, the interpretation of their origin is complicated and controversial. Diamond may occur as one phase in MS inclusions in calc-silicate rocks (e.g., Hwang et al., 2001; Stockhert et al., 2001; Korsakov and Hermann, 2006), indicating that the MS inclusions formed at UHP conditions. For the other MS inclusions that lack the index mineral for pressure, however, independent estimates of P-T conditions have to be taken with care (e. g., van Roermund et al., 2002; Ferrando et al., 2005a, 2005b; Malaspina et al., 2006a, 2006b, 2009). Inspection of published studies results in the following key issues for the interpretation of MS inclusions: (1) identification of primary phases (and step-daughter phases) and estimation of their volume ratios; (2) the effect of post-entrapment on the primary phases and chemical composition; (3) quantification of element composition in MS inclusions, which is a key to the composition of melt phases; (4) correct understanding of phase diagrams for hydrous silicate systems; (5) correct definition of the wet solidii for felsic and mafic UHP rocks.

The small size of MS inclusions represents an analytical challenge as it is near or below the limits of the spatial resolution of several conventional micro-analytical techniques. In addition, the primary difficulty for the analysis is sample preparation, as uncovering and polishing the MS inclusions for SEM, LA-ICPMS and EMP characterization is very difficult and often results in mechanical removal of the inclusion content. Usually, the MS inclusions are smaller than the typical size of laser spot used in the in situ LA-ICPMS analysis. The large size of laser spot does not allow just sampling a single MS inclusion in a host mineral, so that the analysis is made on varying proportions of the mixtures between the MS inclusion and the host mineral. Furthermore, MS inclusions are usually heterogeneous in composition, so that the laboratory melting of a single MS inclusion at appropriate P-T conditions inside the host mineral was used to solve the problem of compositional heterogeneity in the laser sampling (Halter et al., 2002; Heinrich et al., 2003). However, the experimental rehomogenisation of MS inclusions may lead to variable amounts of geochemical exchange between the host mineral and the MS inclusion during the laboratory melting, resulting in reequilibration of some trace elements between host and inclusion (Perchuk et al., 2008). In the case of mixture sampling, it requires an accurate estimate of the volume fraction of MS inclusions relative to the host mineral (Pettke et al., 2004). Therefore, a reasonable determination of major and trace element compositions in MS inclusions holds a key to the geochemical study of MS inclusions in metamorphic minerals.

Two approaches were used in the LA-ICPMS analysis of trace elements in MS inclusions by Gao et al (2013).

The first utilized different sizes of the laser spot that overlapped the bulk MS inclusions and sampled small volumes of the host mineral. The spot sizes vary between 24 and 160 µm, depending on the size of MS inclusions. The MS inclusions may occupy 75 to 95 vol. % of the total volumes, and the host garnet comprises the remaining volumes. To obtain the absolute abundances of trace elements in the MS inclusions within the garnet grains, a mass ratio (between the MS inclusions and their hosts) method was used in data reduction. The volume percentage of different minerals in the MS inclusions and the volume ratio of the MS inclusions to the host garnet were estimated by point counting using the high resolution BSE images, assuming the modal abundances of exposed materials represent those of the bulk MS inclusions. Based on these volume ratios and the compositions of the host garnet, the composition of individual MS inclusion was calculated. The second utilized a small laser spot (~24 µm), smaller than the MS inclusions. In this case, the analytical signal is completely from the MS inclusions. The rationale behind these analyses is that, if the two approaches yield consistent results, the trace element data are reliable within analytical uncertainties. The results from the two approaches exhibit generally similar patterns of trace element distribution. This suggests that the LA-ICPMS analyses have provided а first-order approximation to the trace element composition of MS inclusions.

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Key words: multiphase solid inclusion, continental collision, hydrous melt, aqueous fluid, supercritical fluid

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