NOTES

In-situ trace element analyses of zircons from Dabieshan Huangzhen eclogite: Trace element characteristics of eclogite-facies metamorphic zircon

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Abstract **The internal structures of zircons in eclogite from Huangzhen have been studied by cathodoluminescence (CL) microscopy. Two growth stages were distinguished: protolith magmatic cores and metamorphic overgrowth rims. These different domains were analyzed for trace elements using LAM-ICP-MS. The protolith and the overgrowth zircons have different trace elements characteristics. The trace element contents of protolith zircons are high and very variable. The overgrowth zircons show a typical trace element feature of equilibrium with garnet, e.g. low contents of HREE (132.2—197.6 μg/g) and small differential degree of HREE ($(Yb/Gd)_{CN}$=8.6—11.9). The contents of Nb, Ta and the ratio of Nb/Ta are lower in the metamorphic domains (0.5—1.4 μg/g, 0.7—1.5 μg/g, 0.3—1.3, respectively) than in the protolith domains (3.8—19.7 μg/g, 2.7—12.1 μg/g, 1.0—4.6, respectively). This is the first time to give the evidence that the metamorphic zircon equilibrates with the rutile, which formed during the peak metamorphic stage. The REEs and other trace elements data demonstrate that the metamorphic zircons overgrow in the eclogite-facies conditions. The trace element composition of zircon can therefore give new ways to constrain their formation conditions.**

Keywords: eclogite, zircon, trace elements, rutile.

Zircon is an accessory mineral occurring in different types of rocks. Because of U rich and low common Pb, it is the principal material used for U-Pb dating. But it is difficult to relate its U-Pb ages to geological events in complex metamorphic rocks. Recently, there are three approaches to link zircon ages to geological events: (1) internal structures and Th/U ratios[1—3]; (2) mineral inclusions in zircon[4,5]; and (3) rare earth elements (REEs) of zircon[6—9]. It is very easy to distinguish magmatic and metamorphic zircon domains by internal structures and Th/U ratios, but it is not feasible to relate metamorphic zircon with specific *P-T* conditions. Mineral inclusions in zircon can provide an effective way to constrain the zircon formation conditions. However, some factors, such as small volume of zircons and their inclusions, rare inclusions in some samples, limit its use. Moreover, the relationship between the inclusion and its host zircon sometimes is complex[4,10]. The REEs characteristics in zircons reflect not only the ability of REE entrying the zircon's lattice, but also the concurrent growth of minerals (such as garnet, feldspar, etc.). The presence or absence of these minerals can be indication of specific metamorphic conditions (i.e. eclogite, amphibolite, granulite facies). Moreover, the REEs analyses and U-Pb dating of zircon can be done in the same domain. It appears therefore possible that the characteristics of REEs in zircon can provide important constraints on its growth environment. At present, the studies of HP-UHP zircons REEs are concentrated in the eclogitic gneisses. There is neither study of the REEs for zircons in eclogite itself, nor study for other trace elements.

The present note studies the internal structures and trace elements for different domains of zircon in eclogite from Huangzhen by LAM-ICP-MS. The results show that the trace element characteristics are different in the magmatic and metamorphic domains, and the trace elements, such as Nb and Ta, characteristics can also be used to indicate the zircon growth conditions.

1 Samples and analytical methods

The sample (HZ01-1-10) in a 4—5 m eclogite lens south to the Taihu-Mamiao Road, from Zhujiachong in Huangzhen Town, Taihu Country, was chosen for this study. It is a kyanite-bearing eclogite, which contains assemblages of garnet + omphacite + amphibole + quartz + paragonite + rutile + epidote + kyanite. The eclogites in this area south to the UHP terrain, were often called cold eclogite zone, which could only experience the high pressure metamorphism[11,12]. The oxygen isotope showed disequilibrium among the eclogite-facies minerals, for amphibolite-facies retrogress[13]. Fifteen kilograms rock was processed using standard techniques (Wilfley table, methylene iodide, Frantz magnetic separator). Zircons were prepared as mineral separates, mounted in epoxy and polished down to expose the grain centers. The trace elements analyses were done on the basis of the CL images, which were carried out at the Nancy University, France.

Zircon trace elements analyses were performed on the Perkin-Elmer Sciex ELAN6000 ICP-MS coupled to a CETAC LSX-100 Laser Probe at Guangzhou Institute of Geochemistry, the Chinese Academy of Sciences. The analytical conditions of the LAM-ICP-MS are as follows: a frequency-quadrupled Nd-YAG UV laser system was operated at 266 nm; the ablation pits were (20—30) × (20—40) μm; the operating mode was Q-switched, with maximum energy of 3 mJ/pulse; the power of ICP was 1000 W; the mass resolution of the quadrupole mass analyzer was (0.7 ± 0.02)amu, AC rod offset voltage was 15.4 V; the produced aerosol was transported into the ICP-MS by an Ar gas stream; the mass discrimination factor was determined by analyzing glass NIST610 as an external standard, and selected Si as an internal standard for the content of SiO_2 in zircon equals 32.9. Precision of most trace elements is typically 5%—15% (RSD), but up to 20%—40% for a few trace elements with concentrations close to the limits of detection. The detailed analytical method has been reported by Li et al.[11] and Liang et al.[12]. The results are listed in table 1.

2 Results and discussion

(i) CL images of zircons. The morphologies of zircons from HZ01-1-10 are subhedral to anhedral, short prismatic to round. The clear core-rim structures are shown in CL images (fig. 1). The cores are low luminescent and black, the rims are high luminescent and white. These may reveal their difference in contents of trace element, especially the Th, U and REEs. In CL images the cores show oscillatory growth zoning arguing for a magmatic origin. The rims are homogeneous, indicating metamorphic origin. The boundaries between the rims and the cores are clear, the rims truncate the cores' oscillatory zones, and a few cores have resorption borders, all these suggest that the rims are formed by metamorphic overgrowth. The 1, 2, 6, 7 and 10 analyzed points are in the core domains, and the 3, 4, 8 and 9 are in the rims.

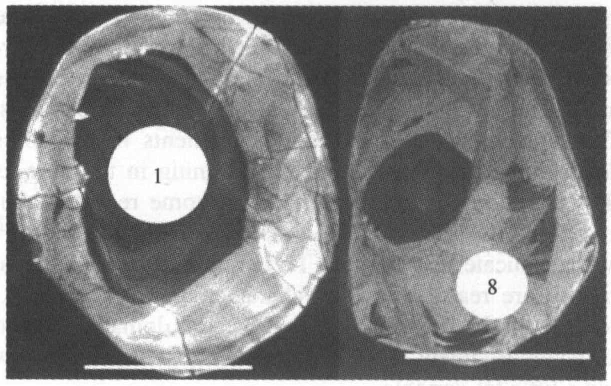

Fig. 1. CL images of zircons from Huangzhen eclogite and spot locations. Length bars: 50 μm.

(ii) Trace element characteristics

(1) Th and U. There is great difference of Th, U contents and Th/U ratios between the core and the rim domain. The contents of Th and U in the core domains are high and very variable (Th: 22.2—67.9 μg/g; U: 427.8—1180.7 μg/g), the Th/U ratios range from 0.04 to 0.05. The Th and U contents are low in the rim domains (7.4—10.7 μg/g and 333.1—453.0 μg/g, respectively), the ratios of Th/U are 0.02—0.03.

Table 1 Trace element analyses of zircons from Huangzhen eclogite[a)] (Hf, wt%; others, $\mu g \cdot g^{-1}$)

	Magmatic zircon					Metamorphic zircon			
	HZ-1	HZ-2	HZ-6	HZ-7	HZ-10	HZ-3	HZ-4	HZ-8	HZ-9
Ti	389.8	431.2	205.3	480.6	550.0	395.7	378.8	375.3	714.4
Rb	bd	0.1	3.2	bd	bd	bd	0.2	0.8	0.7
Sr	4.7	1.6	0.8	1.3	0.5	1.3	3.0	0.1	2.5
Y	426.5	877.5	597.8	696.1	365.6	298.1	249.0	385.5	387.9
Nb	6.1	19.7	12.5	9.5	3.8	0.5	1.4	1.0	0.9
La	0.6	0.4	2.8	bd	2.8	2.3	0.7	0.3	0.4
Ce	15.5	26.2	31.6	19.0	14.4	7.4	6.4	4.6	7.1
Pr	1.2	bd	1.8	bd	0.2	0.2	0.2	0.1	bd
Nd	4.1	0.0	11.0	1.0	3.0	0.3	0.5	0.8	0.9
Sm	bd	1.5	8.5	0.8	2.5	1.6	2.1	bd	1.6
Eu	0.8	0.8	2.2	0.5	0.9	0.6	0.4	0.7	0.4
Gd	2.0	8.4	16.5	10.4	15.5	5.4	7.0	8.3	8.7
Tb	2.3	2.8	5.7	3.7	3.3	3.4	2.2	3.1	2.4
Dy	26.4	52.8	53.1	43.7	35.3	22.7	28.2	40.4	32.8
Ho	14.6	21.3	17.4	19.0	12.9	8.0	8.1	12.3	11.4
Er	70.1	151.6	65.1	117.6	53.1	26.6	30.8	42.8	34.3
Tm	21.0	37.2	15.9	27.6	13.2	5.9	4.7	8.3	6.1
Yb	173.6	414.9	157.6	332.9	145.1	52.7	49.6	72.4	63.1
Lu	30.5	74.3	29.7	61.5	26.1	7.7	7.7	9.8	6.8
Hf	0.56	1.22	1.84	1.44	1.27	1.14	1.05	1.10	1.31
Ta	2.9	12.1	2.7	5.5	3.9	1.5	1.2	1.1	0.7
Pb	40.3	363.7	77.4	85.7	32.4	26.6	19.5	18.9	30.9
Th	22.2	67.9	46.1	61.5	29.1	8.8	7.4	10.7	10.0
U	427.8	1077.1	974.2	1180.7	737.2	376.3	333.1	423.0	453.0
Nb/Ta	2.1	1.6	4.6	1.7	1.0	0.3	1.2	0.9	1.3
Th/U	0.05	0.06	0.05	0.05	0.04	0.02	0.02	0.03	0.02
∑REE	362.8	792.1	418.9	637.6	328.2	144.6	148.6	204.0	175.9
∑HREE	340.6	763.2	361.0	616.4	304.5	132.2	138.5	197.6	158.7
$(Yb/Gd)_{CN}$	107.4	59.6	11.5	38.9	11.3	11.9	8.6	10.5	8.8

a) bd: below detection.

Although the Th/U ratios in the core domains are low (< 0.1), very similar to that of the metamorphic zircons, the high contents of Th, U and the oscillatory zones in CL images indicate that they are magmatic domains. The high variances of Th and U contents in the cores demonstrate that there is chemical zoning in the core as shown by the CL images. There are some reports about low Th/U ratios in magmatic zircons from basic rock[13], which indicate that the low Th/U ratios in our magmatic zircons are reasonable. The characteristics of Th and U contents in the rims indicate that the rim domains formed in the environment that the contents of Th and U are low and a little bit variable.

(2) Rare earth elements (REEs). There are some common features of REEs in the core and rim domains: all zircons are LREE-depleted, and HREE-increasing, clear Ce positive anomalies and variable negative Eu anomalies in the chondrite-normalized REE patterns (fig. 2). These are typical REE patterns of zircon, which are caused by the different abilities of REEs subsitituting into the Zr site within the zircon lattice[14].

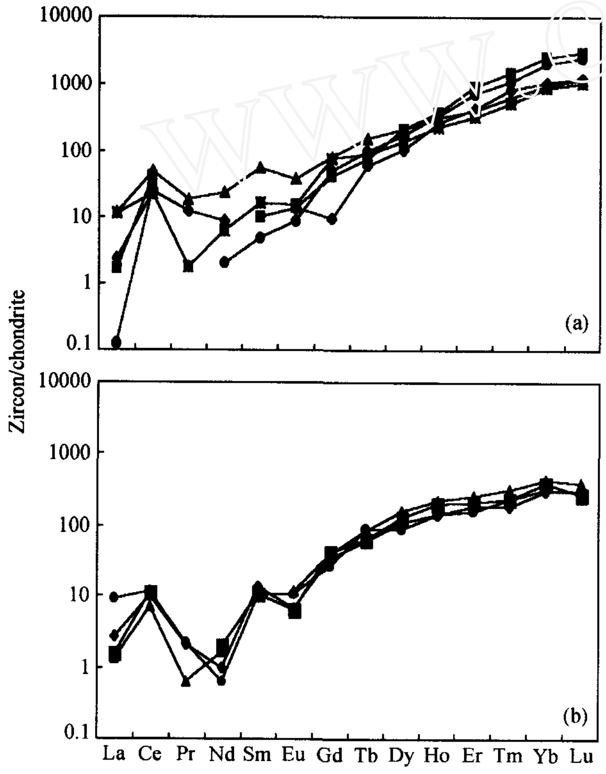

Fig. 2. Chondrite normalized REE patterns for different zircon domains of Huangzhen eclogite. (a) Protolith magmatic domains; (b) metamorphic overgrowth domains.

But there are some clear differences between the core and rim domains, shown in table 1 and fig. 2.

1) Total contents of REEs. The REEs contents of core domains are higher (328—792 μg/g) and more variable than those of the rims (145—204 μg/g).

2) Characteristics of HREEs. HREEs (Gd—Lu) contents are high in the core magmatic domains (304.5—763.2 μg/g), and large differential ($(Yb/Gd)_{CN}$= 11.3—107.4). The overgrowth domains have typical rare earth elements features of equilibrium with garnet, as low contents of HREEs (132.2—197.6 μg/g) and small differential degree of HREEs ($(Yb/Gd)_{CN}$ = 8.6—11.9)[7,8]. These indicate that the metamorphic rims overgrow at the eclogite-facies. Dating these areas can give the precise age of the eclogite metamorphism.

3) Ce and Eu anomalies. The core and the rim domains have similar positive Ce anomalies, but different negative En anomalies (fig. 2). The Eu anomalies in the cores are not clear, but they are clear in some rim domains. Rubatto and Williams[7] consider that the Eu anomalies are less clear in the eclogite-facies zircons than that of the protolith magmatic zircons. But Hermann et al.[8] find that the Eu anomalies in the UHP metamorpic zircons are clear and relative to the whole rocks composition from the Kokchetav terrain. Some zircon domains formed in eclogite-facies conditions show more clear Eu anomalies than those of the protolith zircons in our sample, which indicates that it is not an effective way to constrain the ecolgite-facies metamorphic conditions by the Eu anomalies.

Hoskin and Ireland[15] study the REEs of a variety of different metamorpic zircons, their result suggests that metamorphic processes do not affect the REEs of zircons. This conclusion is also sustained by Schaltegger's[9] investigating the metamorphic zircons' REEs of granulite samples. We cannot confirm if there are garnets in the sample which Hoskin and Ireland[15] studied. But the samples Schaltegger[9] studied have anatectic melt, and some metamorphic zircons crystallized from the melt, these zircons have REEs characteristics of typical magmatic zircons. But some zircons in their samples do show HREEs depleted characteristics, which indicate that they are equilibrated with garnets. It is attested by other researchs[6—8] and our data that the low REE contents and HREEs depleted of some metamorphic zircons can be used as evidence of equilibrated with garnets.

(3) Other trace elements. Large-ion lithophile elements are very low in different domains, and the contents of Rb and Sr do not exceed 5 μg/g. These are similar to the result of Li et al.[11]. These elements are very difficult to substitute into the Zr site.

There is clear difference of Nb and Ta in the cores and rims. The contents of Nb, Ta and the ratios of Nb/Ta are lower in the metamorphic domains (0.5—1.4 μg/g, 0.7—1.5 μg/g, 0.3—1.3, respectively) than in the protolith domains (3.8—19.7 μg/g, 2.7—12.1 μg/g, 1.0—4.6, respectively). The low values of Nb/Ta in zircons can be caused by Ta entering preferentially into the Zr site [11], but the low contents of Nb, Ta and low Nb/Ta ratios in the metamorphic rims require that these zircons equilibrate with a mineral which have a high Nb, Ta and Nb/Ta ratio. The rutile in eclogite is such a mineral[15]. It is rich of HFSE, especially Nb and Ta, and has high ratio of Nb/Ta[15]. It is the first time to demonstrate that the metamorphic zircons equilibrate with the rutiles, which formed during the peak metamorphic stage. This also indicates that the metamorphic domains grow in the eclogite-facies conditions. The ages obtained by SIMS also demonstrate that the metamorphic rims grow at ~235 Ma, the core domains grow at ~1900 Ma (Chen Daogong, unpublished data).

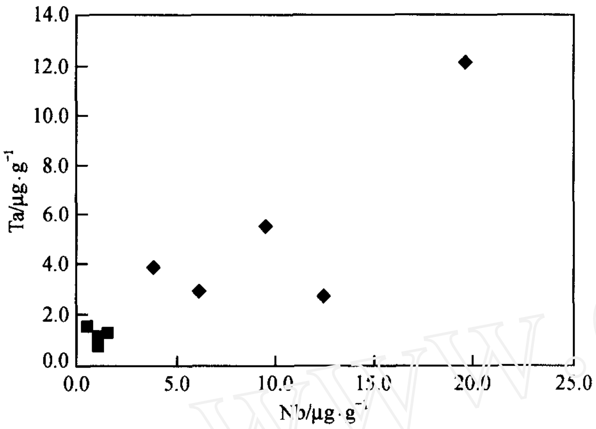

Fig. 3. Nb vs. Ta concentrations in zircons. Square, Metamorphic zircons; diamond, magmatic zircons.

3 Conclusions

The CL images reveal that the zircons of Huangzhen eclogite have core-rim structures. The core domains are protolith magmatic zircons, and the rim domains are metamorphic zircons.

Except for REEs, the contents of Nb, Ta and the ratios of Nb/Ta can also be used to constrain zircon formation conditions. The characteristics of REEs, Nb and Ta indicate that the metaorphic rims of Huangzhen eclogite overgrow in the eclogite-facies conditions, the cores are protolith magmatic zircons.

It is indicated by the trace elements that their contents are low in the eclogite metamorphic environment, because the zircons forming during the eclogite metamorphic conditions have low trace elements contents, such as Th, U, REEs, Nb, Ta, etc.

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