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Geochemistry and U–Pb Geochronology of Zircon in Garnet Amphibolites from Kamchatkskii Cape Peninsula, Eastern Kamchatka

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Abstract—The paper presents the first data on the geochemistry and U–Pb SHRIMP geochronology of zircon from garnet amphibolites whose fragments are hosted by the sole of the ophiolite complex of Kamchatskii Cape, eastern Kamchatka. The zircons compose a homogeneous sampling, have relatively small sizes, are unhedral, have no oscillatory zoning, and possess practically no inclusions. The chemistry and photoluminescent characteristics of the zircons testify to their metamorphic genesis. The U–Pb SHRIMP dates of the zircons (81.4 ± 9.6 Ma) indicate that the metamorphism of the amphibolite complex took place in Campanian time in the Late Cretaceous. These dates seem to correspond to the peak of the high-pressure metamorphism, which is thought to be related to the origin of an ophiolite complex of the suprasubduction type and its uplift within the Kronotskii Island arc.

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INTRODUCTION

One of the major problems arising when high-pressure metamorphic rocks are studied in the soles of ophiolite complexes of subduction and collision type (so-called complexes of metamorphic soles [1]) is the nature of the protoliths of the metamorphic rocks and their age relations with the host ophiolites. The solution of these problems is particularly important for eastern Kamchatka, because local metamorphic rocks of this type were traditionally thought to be either the rocks of the metamorphic (perhaps, Precambrian) basement of the peninsula [2–4] or those of Mesozoic volcanic complexes, which were dynamo-metamorphosed during the development of the accretion structure in this part of the peninsula [5–7 and others]. These problems should be elucidated to understand the evolutionary history of such large structural elements of the eastern Kamchatkan collisional–accretionary area as the Ganaly Range, Khavyven Highland, and Kamchatskii and Ozernyi capes, whose ophiolites are associated with allochthonous metabasite blocks, which were metamorphosed to the garnet amphibolite and granulite facies. Newly obtained dages of these rocks [8, 9, and others] significantly specified, extended, and, sometimes, even modified the understanding of the Mesozoic–Cenozoic evolutionary history of Kamchatka. Nevertheless, the age and nature of the metamorphic complexes in eastern Kamchatka are still largely uncertain, and their elucidation requires newly obtained data and new methodological approaches.

We attacked this problem using the example of the high-pressure metamorphic rocks in the sole of the heterochronous ophiolite complex in Kamchatskii Cape, eastern Kamchatka. The composition and genesis of the metamorphic rocks of the amphibolite complex were actively discussed elsewhere [10, 11, and others], but the disputable character of their genesis (first of all, their age and the nature of their protolith) is obvious enough. Our study was centered on the utilization of recently obtained data on the geochemistry and isotopic dating of zircons to provide insight into these aspects of the genesis of the metamorphic rocks in the context of their spatial relations with the Kamchatkskii Cape Peninsula ophiolite complex.

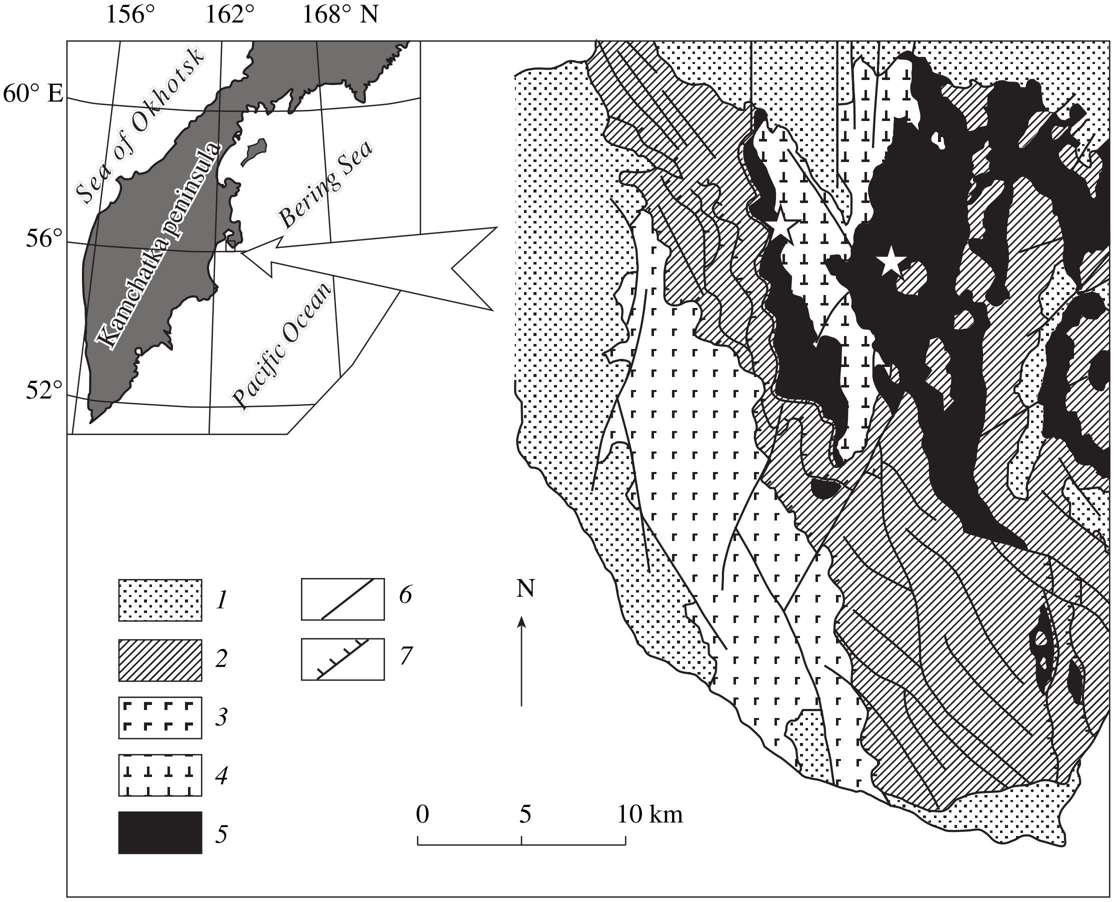

Fig. 1. Schematic geological map of the southwestern part of Kamchatkskii Cape Peninsula (modified after [5]). (*1*) Undifferentiated Neogene–Quaternary deposits; (*2*) volcanic–siliceous and terrigenous deposits of the Afrikanskaya Formation (K_{1-2}); (*3*) gabbroids of the Olenegorsk Massif; (*4*) ultramafic rocks of Mount Soldatskaya; (*5*) serpentine melange; (*6*) faults; (*7*) overthrusts. Asterisks show sampling sites of rocks of the amphibolite complex. The inset is the location map of the study area.

GEOLOGIC SETTING AND COMPOSITION OF AMPHIBOLITES

Inasmuch as most issues concerning the structural setting, geology, petrography, and chemistry of garnet amphibolite from Kamchatkskii Cape Peninsula were discussed in much detail in our previous publication [10], below we present only information directly pertaining to the problem discussed in this paper.

Garnet amphibolites occur in the southern part of Kamchatkskii Cape Peninsula, which has a complicated nappe-folded structure and is determined by the presence of a number of allochthonous nappe complexes (Fig. 1). The latter are dominated by siliceous–volcanic and terrigenous rocks of Late Cretaceous–Paleocene age. Individual spatially separated slices of the nappes consist of magmatic rocks, which compose an ophiolite association [5, 6]. It should be taken into account that the ophiolites do not compose a coherent rock succession but occur as disintegrated blocks, whose paleogeodynamic nature notably differs (they comprise complexes of both suprasubduction and oceanic types) [5, 6, 12–14, and others]. This brought about the viewpoint that the territory of the cape consists of two or more spatially combined heterochronous ophiolite complexes [6, 13, 14].

Amphibolites were found in the form of isolated tectonic blocks and boulders in the serpentine melange in the bottom of the Mount Soldatskaya peridotite massif in the central part of the cape. Based on the analysis of the general geology of the area and the microfaunistical age of the siliceous rocks, which overlie there the volcanic portion of the ophiolite complex, the rocks of the massif were traditionally dated at the Late Cretaceous [5, 6, 14]. A few Rb–Sr and Sm–Nd dates of whole-rock samples and minerals of the ultramafic rocks and gabbroids of the massif testify to a Late Cretaceous age (93–78 Ma) [15]. The most reliable dates for the rocks of the Mount Soldatskaya ophiolite complex are likely the Late Cretaceous (74 Ma) U–Pb SHRIMP ages on magmatic zircons from the plagiogranite [16]. The K–Ar dates on the basic rocks of the complex broadly vary [17] and most probably correspond not to the actual age of these rocks but to certain episodes of overprinted dynamo-thermal metamorphism, which was related to the detachment and displacement of the ophiolite nappes. The isotopic dates of other ophiolite complexes of the cape (for example, the Olenegorsk gabbroid massif) are also broadly scattered, up to the Precambrian [18], although these old dates are in conflict with geological observations (see, for example, [14]).

Individual blocks of the amphibolites usually do not exceed 10–20 m in size, and the blocks themselves group within stripes, which are sometimes traced for 500–600 m. The metamorphic rocks are mineralogically variable amphibolites and amphibole-bearing schists, whose maximum metamorphic grades correspond to the facies of garnet amphibolites. The zircons for our research were separated from the highest-grade metamorphic rocks of the complex: clinopyroxene–garnet–amphibole amphibolites. These rocks were determined to be the richest in Zr (80–120 ppm) [10]. The primary minerals of these rocks are dominated by high-Mg hornblende (50–85 vol %) of the tschermakite–pargasite series and also include lower amounts of garnet (5–25 vol %), which has relatively high concentrations of the almandine and grossular end members, and magnesian clinopyroxene (0–15 vol %), which contains practically no jadeite end member. The accessory minerals are, along with zircon, ilmenite, rutile, quartz, apatite (all of them occur as inclusions in primary minerals or as individual crystals and aggregates in the mesostasis), and titanite. The rocks abound in secondary minerals (chlorite, epidote, prehnite, pectolite, and others), which are contained in these rocks in variable amounts.

The geological setting and composition of the metamorphic rocks testify that they are typical components of a metamorphic sole, which are widespread in paleosubduction complexes [1].

ANALYTICAL TECHNIQUES

Representative samples of garnet amphibolites (~5–7 kg) were crushed to –350 μm (crushing by small portions for 15–20 s) at a Pulverizette-9 laboratory mill (working chamber 100 ml in volume), which ensured a high degree of preservation of the original shapes and morphologies of mineral grains in the crushed samples. The disintegration products were subdivided into narrow size fractions (<63, 63–125, 125–180, and 180–350 μm) on a RETSCH screener. Each fraction was then used to obtain "heavy" concentrates of accessory minerals (zircon, ilmenite, sulfides, etc.) on an HS-02 hydroseparator [19]. Zircon grains of the most typical morphology and color and devoid of cracks were handpicked under a binocular magnifier. Some of these grains were impregnated into plastic and used to prepare polished cemented thin sections.

The thin sections were examined on a CamScan-4DV scanning electron microscope equipped with a Link AN-10000 EDS analytical system at Mekhanobr (St. Petersburg, analyst A.N. Pilipyuk). The analyses were conducted at an accelerating voltage of 30 kV, sample current ~1 nA, and counting times from 50 to 120 s, with the use of conventional correction routines. The standards were pure metals and natural and synthetic minerals.

The photoluminescence of the zircons was examined in compliance with the method [20] (now under approval NSOMMI) on equipment based on a MSFU L-312 microscope–spectrophotometer and a LGI-505 gas laser (on molecular nitrogen) with $\lambda_{exc} = 337.1$ nm, which makes it possible to obtain spectral–kinetic characteristics of tiny objects as small as 20 μm within the range of 390–850 nm (Fedorovskii All-Russia Institute of Mineral Resources, Moscow, analyst V.A. Rassulov). The recording system consisted of blocks (CAMAC standard) that enabled measuring luminescence spectra without delay after laser pulses (time-integrated specters) and luminescence spectra 180 μs after a laser pulse (time-resolved spectra).

ZIRCON MORPHOLOGY AND GEOCHEMISTRY

In the heavy concentrates, zircon was found in size fractions <180 μm, with its maximum contents detected in the fractions 63–125 and <63 μm. The zircon grains were subdivided into four morphological types: (1) small (commonly no larger than 15–20 μm) rounded equant inclusions in primary minerals of the amphibolites (garnet, clinopyroxene, and amphibole) (Figs. 2e, 2f); (2) zircon grains <20 μm in aggregates with ilmenite in symplectitic ingrowths in secondary clinopyroxene; (3) relatively large (up to 100–120 μm) zircon grains in aggregates with amphibole (Fig. 2d) and chlorite (Fig. 2c); and (4) individual zircon grains from the matrix (Figs. 2a, 2b): rounded equant or, more rarely, elongated grains or, sometimes, euhedral crystals of pale violet and yellowish color. Individual zircon grains bear occasional inclusions of titanite (Fig. 2b).

Our microprobe data definitely indicate that the zircons of all of the aforementioned types have a relatively little varying chemical composition, regardless of the morphologies of the grains and the mineral assemblages (Table 1). Another important conclusion following from the results of our studies is the homogeneity of all of the analyzed grains and the absence of any traces of compositional zoning in them The admixtures detected in the zircons are P, Y, and REE (the overall concentrations of minor elements do not exceed 0.35 wt %). All of the analyzed minerals show relatively little varying Zr/Hf indicator ratios (53–64). Such values of this informative ratio make these minerals similar to zircons from kimberlites and eclogites [21]. At the same time, these values are much lower than those of zircons from

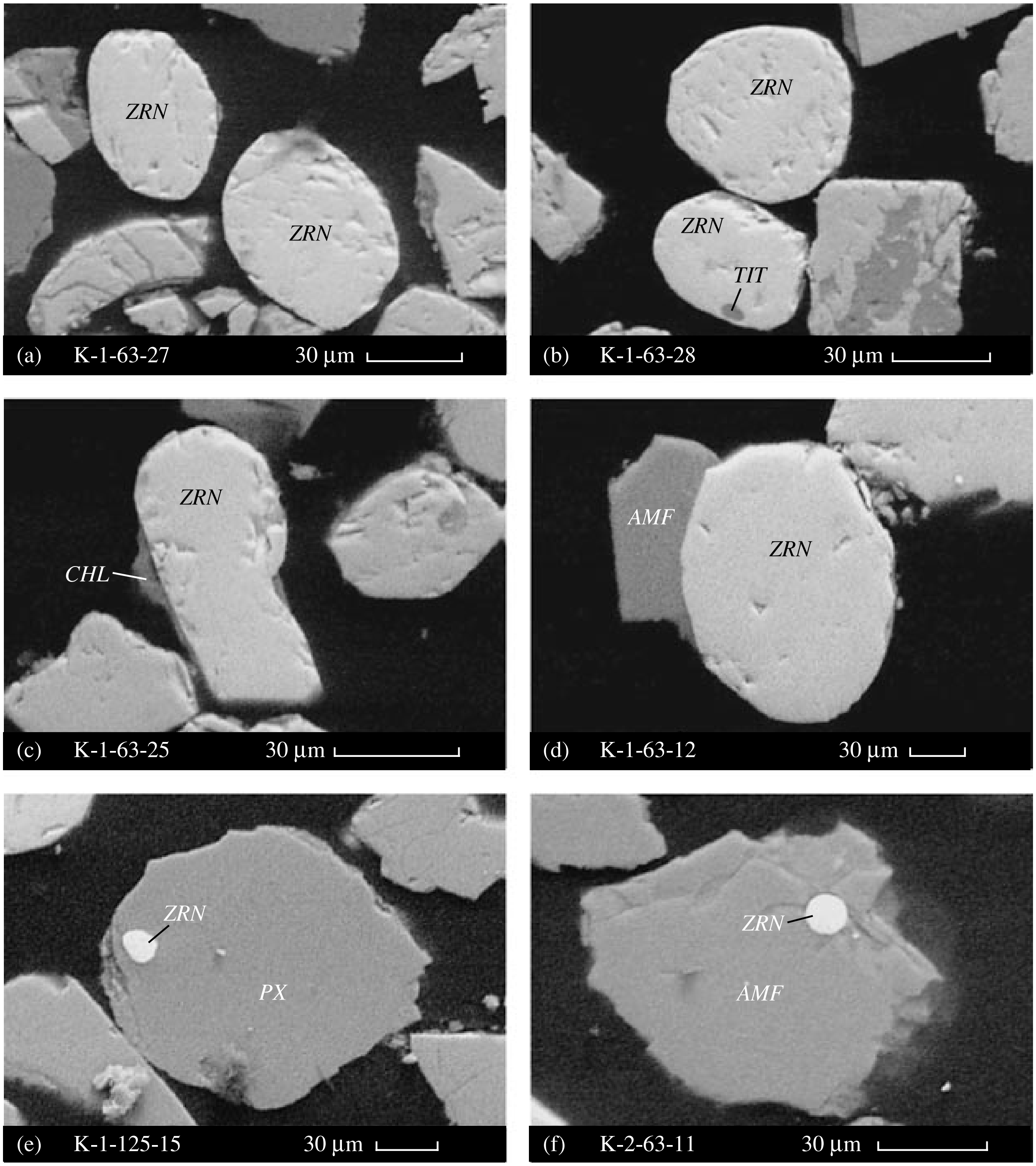

Fig. 2. Zircon grains from heavy concentrates obtained from amphibolites of Kamchatkskii Cape Peninsula. (a–b) Individual zircon grains from the matrix (b—with a titanite inclusion); (c) zircon in aggregate with chlorite; (d) zircon in aggregate with amphibole; (e, f) inclusions of rounded zircon grains in primary clinopyroxene and amphibole. Mineral symbols: *AMF*—amphibole; *CHL*—chlorite; *PX*—clinopyroxene; *TIT*—titanite; *ZRN*–zircon. BSE images were taken on a CamScan-4DV scanning electron microscope (Mekhanobr, St. Petersburg).

mantle ultramafic rocks and much greater than in zircons from granites and lamproites [22].

Modern studies demonstrate that indicator compositional parameters of zircon that provide information on the genesis of rocks hosting this mineral are the concentrations and distribution character of various REE, Y, and P [23, 24]; U and Th concentrations [24, 25]; and the presence of certain minor components (in particular, Ti and Fe^{3+}) [26].

We examined some of these indicative compositional characteristics of zircons by means of laser-induced luminescence, which is based on the visual

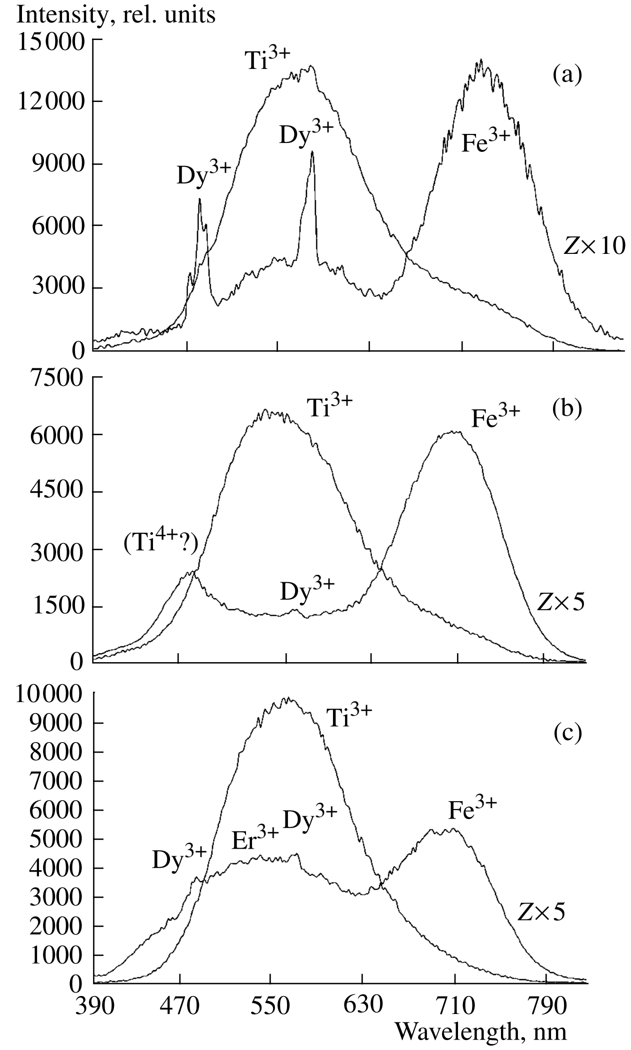

Fig. 3. Spectra of laser-excited luminescence of zircons from (a) amphibolites of Kamchatkskii Cape Peninsula, (b) Kumdy-Kol eclogites, Kokchetav Massif, and (c) Mir kimberlite pipe, Yakutia.

recording of light and the relative intensity of luminescence in measured time-resolved luminescence spectra of the Sm^{3+}, Dy^{3+}, Er^{3+}, Ti^{3+}, and Fe^{3+} active luminescence centers whose attenuation time is much longer than 10^{-6} s. The analysis of the luminescence spectra of a representative selection of zircon grains from the amphibolites (>20 grains) led us to the following conclusions concerning the character of petrogenetic processes accompanying the crystallization of zircons in the rocks:

(1) The luminescence characteristics of the zircons are very uniform and suggest their homogeneous composition, regardless of the grain sizes and morphologies.

(2) The REE spectra of the zircons (Fig. 3a) display only bands of Dy^{3+}, which suggests that the mineral crystallized in a relatively alkaline environment. This also seems to follow from the significant intensity of the luminescence of the Ti^{3+} center (560 nm), which also points to crystallization in an alkaline environment with the predominance of Na (isomorphism according to the scheme $Zr^{4+} + P^{5+} \longrightarrow Ti^{3+} + Na^{+}$) [27, 28].

(3) The significant intensity of the luminescence of the Fe^{3+} center (730 nm) most probably indicates that the zircons crystallized at relatively high temperatures (>700°C) and under reduced conditions [26].

This association of optically active centers is typical of zircons from eclogites (Fig. 3b) and kimberlites (Fig. 3c). We pointed out the geochemical similarities between these zircons above.

U–Pb SHRIMP DATING OF ZIRCONS

Zircon is now considered to be the main mineral geochronometer utilized in the U–Pb method. The main reasons for this are such characteristics of zircon as its elevate U and Th concentrations, relatively low concentrations of common Pb, and a high temperature at which its U–Pb isotopic system is closed. The chemical and morphological features of this mineral are quite strongly correlated with its composition and the genesis of its host rocks, thus making this mineral an informative petrogenetic indicator.

Zircons from the amphibolites were dated by the U–Pb method on a SIMS SHRIMP-II ion microprobe at TSII VSEGEI (St. Petersburg) [29]. The primary radiation source was negatively charged molecular oxygen ions O_2, whose flux was focused on the sample and produced a secondary ion radiation. The procedure of ion microanalysis generally corresponds to the method developed at the Australian National University for SHRIMP-II [30]. Our zircons were analyzed under the following conditions: diameter of the elliptical analytical spot was 10 × 14 or 25 × 27 μm, the ion current of the primary O_2 beam was 2.0–4.0 nA, the sensitivity was >20 imp/1 ppm of ^{206}Pb/1 nA; the mass resolution M/DM was 5300–5700. The mass spectrometer at the output of the SHRIMP-II microprobe is characterized by a resolution (>5000) sufficient for the practically complete separation of Pb and U isotopes from the interfering isobaric overlaps (of ZrO_2, HfO_2, and HfSi), which are characteristic of secondary-ion spectra emitted from a zircon target. The errors of the measured ^{206}Pb/^{238}U age for a homogeneous zircon population are no higher than 2% per analysis. If the number of analyses is seven or more, the average concordant age has an error of 1% (2σ). The precision of SHRIMP analyses of ^{238}U/^{206}Pb (which was estimated by the replicate analyses of the TEMORA and zircon 91500 standards) is approximately 0.5–2%. The results were processed by the SQUID 1.02 computer program [31]. The concordia plots were constructed by the ISOPLOT/EX [32]. The correction for common Pb was introduced based on the

Table 1. Representative chemical analyses (wt %) of zircons form amphibolites of Kamchatkskii Cape Peninsula

Component	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SiO_2	33.13	33.38	33.41	33.18	32.97	33.28	32.94	33.34	33.86	33.70	33.45	33.48	34.07	33.97	33.29	33.18
ZrO_2	64.08	64.57	64.04	65.00	63.8	64.08	64.09	64.00	64.58	64.97	65.01	65.83	64.45	64.87	64.73	65.36
HfO_2	1.05	1.06	1.04	0.94	1.08	1.07	1.12	1.09	0.94	0.95	0.97	1.12	0.99	1.01	0.99	0.98
Tb_2O_3	0.11	0.15	0.26	0.31	0.29	0.21	0.37	0.13	0.27	0.09	0.28	0.37	0.28	0.23	0.43	0.23
P_2O_5	0.11	0.08	0.03	0.07	0.09	0.00	0.10	0.10	0.02	0.11	0.01	0.02	0.09	0.05	0.09	0.04
Total	98.49	99.24	98.78	99.49	98.23	98.64	98.63	98.65	99.67	99.83	99.72	100.81	99.89	100.13	99.52	99.80

measured $^{204}Pb/^{206}Pb$ ratios, in compliance with the model [33].

The measured $^{207}Pb/^{206}Pb$ ratios were used to calculate the age value by extrapolating all measured points onto the concordia along the line connecting the composition of common model Pb [34] and the approximated age values of individual grains. In the Terra–Wasserburg concordia diagram, the dashed line corresponds to the tie line between common Pb (~0.84 [34]) and radiogenic Pb at the weighted mean age of the grains corrected for $^{207}Pb/^{235}U$–$^{206}Pb/^{238}U$. The scatter of the MSWD values is within the error of the method.

The SHRIMP dates of zircons from the amphibolites of Kamchatkskii Cape Peninsula are summarized in Table 2 and displayed in Fig. 4a. The analyzed zircons compose a homogeneous sampling, which is character-

Table 2. Results of U–Pb SHRIMP isotopic study of zircons from amphibolites of Kamchatkskii Cape Peninsula

No.	Sample	%, $^{206}Pb_c$	U (ppm)	Th (ppm)	$^{232}Th/^{238}U$	$^{206}Pb^*$ (ppm)	$^{207}Pb/^{206}Pb$ ± %		$^{238}U/^{206}Pb$ ± %		Age, Ma**
1	KAMCH 1.1	89.99	2	0	–	0.0294	0.279	15	53.4	9.9	85.0 ± 11.0
2	KAMCH 2.1	23.56	6	1	0.09	0.0732	0.131	12	68.6	6.1	83.5 ± 5.4
3	KAMCH 3.1	29.71	4	0	–	0.0392	0.221	13	81.3	7.8	61.6 ± 5.5
4	KAMCH 4.1	45.43	4	0	–	0.0460	0.215	12	67.5	7.7	74.8 ± 6.6
5	KAMCH 5.1	16.88	3	0	–	0.0377	0.216	14	73.0	7.2	70.2 ± 10.0
6	KAMCH 6.1	–	10	14	1.47	0.0690	0.094	11	77.8	7.4	77.5 ± 5.8
7	KAMCH 6.2	16.56	6	5	0.86	0.0698	0.082	16	74.1	9.0	82.6 ± 7.5
8	KAMCH 7.1	–	4	1	0.15	0.0551	0.131	19	61.4	7.1	93.4 ± 7.4
9	KAMCH 8.1	4.46	6	1	0.25	0.0745	0.122	11	70.0	5.8	82.9 ± 5.1
10	KAMCH 9.1	–	6	4	0.69	0.0596	0.124	14	80.1	6.5	72.4 ± 5.0
11	KAMCH 10.1	21.54	5	1	0.28	0.0638	0.05	10	73.7	8.0	86.6 ±7.6
12	KAMCH 11.1	–	4	1	0.27	0.0508	0.164	13	67.5	7.3	81.0 ± 6.4
13	KAMCH 12.1	55.64	5	1	0.12	0.0546	0.137	13	82.4	7.4	69.0 ± 5.4

Note: In sample KAMCH 6: 6.1—core of a zircon grain; 6.2—its margin. Errors: 1σ. Pb_c and Pb^* are common and radiogenic Pb, respectively. The error in the standard calibration is 0.87%.

** Common Pb is corrected with regard for the $^{207}Pb/^{235}U$–$^{208}Pb/^{238}Th$ concordant age.

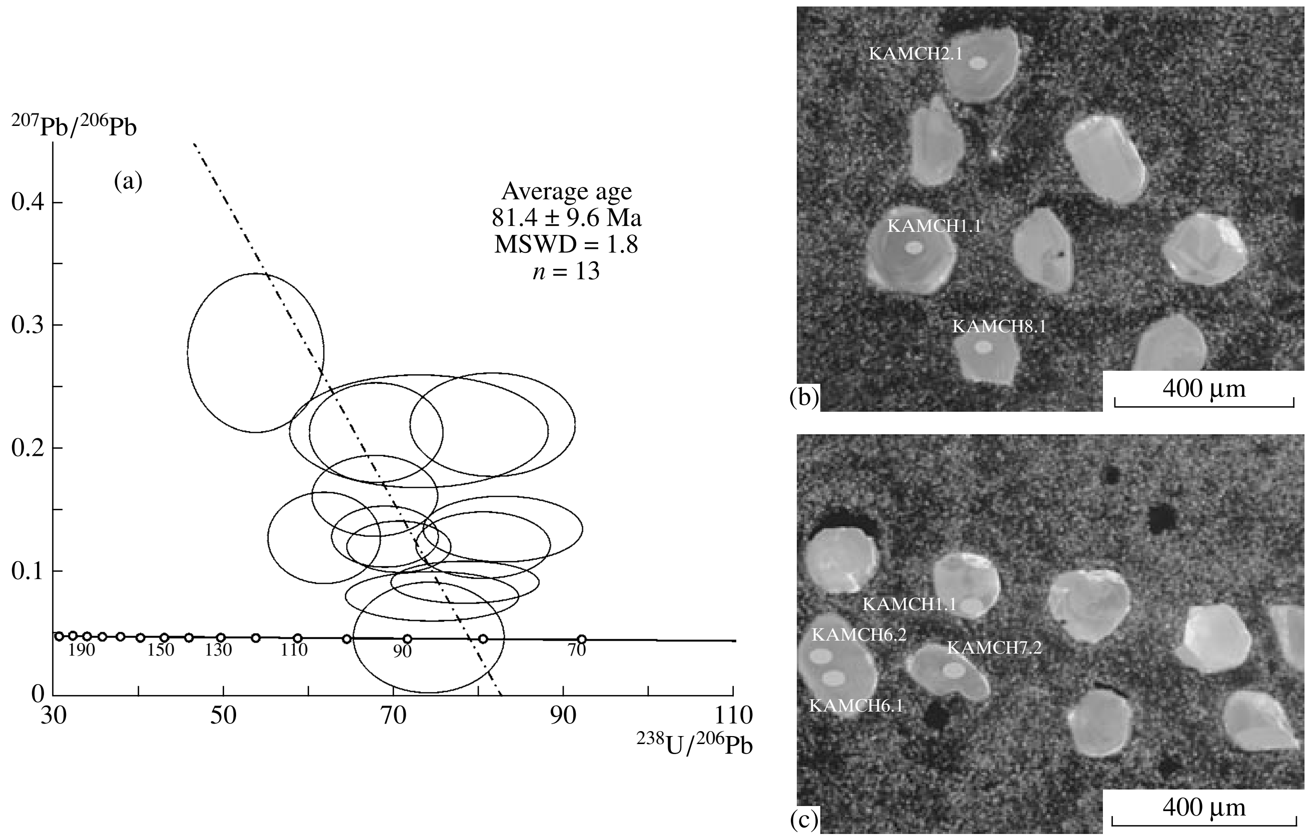

Fig. 4. (a) Terra–Wasserburg concordia diagram for U–Pb SHRIMP data on zircons from the amphibolite complex of Kamchatkskii Cape Peninsula. (b, c) Cathodoluminescence of zircon crystals. Labeled spots correspond to U–Pb SHRIMP dating spots.

ized by the aforementioned morphological features: the zircon grains are relatively small (60–100 μm), sub- to anhedral, exhibit absolutely no oscillatory zoning (Figs. 4b, 4c), and bear practically no inclusions. All minerals are characterized with very low concentrations of U and Th (2–10 ppm U and 0–4 ppm Th; Table 2). Considered together with the low Y, P, and REE concentrations (Table 1), this convincingly argues for the metamorphic genesis of the zircons [24]. They are also characterized by low U/Th ratios and concordant U–Pb ages (which show a good reproducibility). The isotopic analysis of core–margin pairs of a grain (Table 2, samples 6.1 and 6.2) does not yield a significant difference in the U–Pb dates. The obtained age characteristics can be interpreted as reflecting the primary metamorphic nature of the zircons, and the weighted mean age of the samples (81.4 ± 9.6 Ma, MSWD = 1.8; Fig. 4a) can be interpreted as the actual crystallization age of the zircons in the course of prograde metamorphism of the protolith during the metamorphic culmination. The upper discordia intercept is geologically meaningless.

There are known examples of SHRIMP isotopic dates of zircons with extremely low concentrations of U and Th in minerals from metamorphic rocks analogous to our rocks: eclogites [35, 36] and garnet amphibolites [37]. The genesis of those zircons with geochemical characteristics analogous to zircon from our rocks was also thought to be related to the culmination of high-pressure metamorphism.

CONCLUSIONS

Earlier geochemical studies gave rise to the hypothesis that the protolith of the amphibolites containing the zircons consisted of gabbroids of the N-MORB type [10], which underwent high-grade metamorphism associated with the following succession of geological processes: the subduction of the oceanic crust in Late Cretaceous–Paleocene time, the origin of an inverted thermal gradient in the upper part of the subducted nappe, the metamorphism of the basic rocks to the garnet amphibolite facies, and their subsequent exhumation coupled with the obduction of the suprasubduction ophiolites in the Eocene–Miocene. Although the minerals show typically metamorphic compositional features and cannot provide direct information on the nature of the protolith, they fairly reliably testify that the metamorphic rocks were produced at significant depths with the participation of an alkaline (Na-rich) fluid. This is consistent with some earlier ideas concerning the environments in which the metamorphic processes took place [10].

The U–Pb zircon dates indicate that the metamorphism of the rocks of the amphibolite complex took place in Campanian time in the Late Cretaceous (81.4 ± 9.6 Ma). With regard for earlier Late Cretaceous dates for rocks composing the magmatic succession of the Mount Soldatskaya ophiolite complex [15, 16], the U–Pb zircon dates for the amphibolites make it possible to reliably relate the metamorphism of these rocks to the origin of the ophiolite complex of the suprasubduction type [10] and its exhumation within the Kronotskii Island arc (KIA). Judging from available data, the Kronotskii Island arc (KIA) started to develop in pre-Campanian time. This, in turn, is consistent with the age of the principal tectonic restyling in the structures of the northwestern surroundings of the Pacific Ocean, a process that resulted in the reorganization of Pacific plates and changes in their movement vectors. This time also coincides with the folding and accretion phases of eastern Kasmchatkan terranes [5].

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