Ages of Zircons in Jadeitite and Jadeite-bearing Rocks of Japanese Islands

Yukiyasu Tsutsumi¹*, Kazumi Yokoyama¹, Ritsuro Miyawaki¹, Satoshi Matsubara¹ Kentaro Terada² and Hiroshi Hidaka²

¹Department of Geology and Paleontology, National Museum of Nature and Science, Shinjuku-ku, Tokyo 169–0073, Japan

²Department of Earth and Planetary Systems Science, Graduate School of Science, Hiroshima University,

Higashi-Hiroshima, Hiroshima, 739-8526, Japan

* Author for correspondence: ytsutsu@kahaku.go.jp

Abstract Radiometric ages of zircons in jadeitite and jadeite-bearing rocks from five areas in Japan were obtained from the ²³⁸U/²⁰⁶Pb ratio using a sensitive high resolution ion microprobe (SHRIMP II). The samples exist as blocks in serpentinite or greenstone mélange from Itoigawa (IT), Osayama (OS), Kochi (KC), Nishisonogi (NS) and Yorii (YR) areas. Coarse-grained zircon from IT yields ²⁰⁶Pb/²³⁸U mean age of 497±23 Ma and two zircons from the OS yield different mean ages; 496 ± 12 Ma and 532 ± 17 Ma, respectively. Fine-grained zircons in the jadeite rocks from KC, NS and YR yield mean ages; 501 ± 5 Ma, 136 ± 5 Ma and 159 ± 5 Ma, respectively. The protolith of the KC sample is considered to be a tectonic block which was a crustal material formed ~500 Ma and once subducted to certain depth of jadeite formation after tectonic erosion of the crust. The zircon age of the IT sample are consistent with previously reported values which is interpreted as an age of jadeitization. Age difference of two zircon grains from OS sample shows a possibility that zircons were not formed by a single event but multiple events. Zircons in the NS and YR samples are interpreted as protolith or hydrothermal origin. It is clear that the zircon ages of jadeite rocks are roughly bimodal; middle Mesozoic (NS and YR) and early Paleozoic (IT, OS and KC).

Key words : zircon, radiometric age, jadeite rock, origin

Introduction

Jadeitite and jadeite-bearing rocks are found at restricted number of localities in the world. Most of them exist as blocks in serpentinite mélange associated with high-P/T type metamorphic rocks, but there are some varieties of jadeite situation; "dyke" or pod in serpentinite, vein in high-P/T type schist (reviewed in Harlow and Sorensen, 2005). In Japan, although gem quality jadeitite is found only at the Itoigawa area, there are more than ten localities of jadeitite and jadeite-bearing rocks (Fig. 1). Jadeites at the Mikkabi and Yatsushiro areas occur as a vein cutting through metagabbro (Yokoyama and Samejima, 1982; Saito and Miyazaki, 2006). Jadeitebearing rock from the Shimonita area shows pillow texture and, therefore, is considered to be derived parentally from oceanic basalt (Tanabe *et al.*, 1982). Jadeite-bearing rock from Kamuikotan is a mafic rock consisting mostly of amphibole (Gouchi, 1983).

Jadeite rocks often contain zircon as accessory mineral and the zircon U–Pb ages are interpret as several mineralization stages; protolith or prejadeitization age, jadeitization age, or age of late stage hydrothermal process (e.g. Shi *et al.*, 2008). In this study, zircons were found in the jadeitite and jadeite-bearing rocks from the five areas which are tectonic blocks in serpentinite or greenstone mélange: Itoigawa, Osayama, Nishisonogi, Kochi and Yorii areas, and U–Pb ages of zircons from these five areas were obtained using an ion microprobe. Although zircon



Fig. 1. Tectonic division of geologic belts including jadeite rocks in Japan. I.S.T.L., Itoigawa–Shizuoka Tectonic Line; M.T.L., Median Tectonic Line. Round symbols indicate localities of jadeite found. Solid symbols among them indicate sample localities of this study.

ages of jadeite rocks dose not have direct relation to the timing of formation of mélange including the jadeite rocks, the ages would have some information about the framework of the Japanese Islands.

Geological Settings

Itoigawa area, Hida Mountains (IT)

This area is assigned to the Hida Gaien Belt which is a serpentinite mélange zone with various type of tectonic blocks; high-P/T type metamorphic rocks, weakly metamorphosed sedimentary rocks, amphibolites, metamorphosed mafic rocks. jadeitites. albitites and rodingites (Nakamizu et al., 1989). K-Ar, 40 Ar/39 Ar and Rb-Sr ages were obtained from high-P/T type metamorphic rocks of around 300 Ma (Shibata and Nozawa, 1968; Shibata et al., 1970; 1979) and eclogites of 340 Ma (Tsujimori et al., 2001). The weakly metamorphosed sedimentary rocks are Carboniferous to Permian from fossil evidence (Tazawa et al., 1984). Nishimura (1998) suggested the Hida Gaien Belt is a part of the Renge Belt. We selected a lavender color jadeitite from the stored specimen in National Museum of Nature and Science (hereafter NMNS) (register number: NSM-M-29604) which collected from Kotakigawa River (around N36°55′ E137°48′) as a boulder. The sample consists almost completely of jadeite, with small amounts of natrolite, zircon, titanite, tausonite and rengeite. Zircon in the sample is subhedral chasmy crystal with few millimeters in diameter. The ion microprobes U–Pb age of zircons in two types of jadeite rock from this area were reported as 519 ± 17 Ma and 512.3 ±6.9 Ma (Kunugiza *et al.*, 2002).

Osayama area, Chugoku Mountains (OS)

The Osayama area is a serpentinite mélange which contains small bodies of rodingite, albitite, jadeitite, and tectonic blocks of high-P/T type metamorphic rocks (Kobayashi et al., 1987; Tsujimori, 1997). Phengite K-Ar ages of the metamorphic rocks yield 289-327 Ma and they concentrated around 320 Ma which are comparable to the age of Renge Belt (Tsujimori and Itaya, 1999). U-Pb age of zircon in jadeitite from this area was reported as 472.0±8.5 Ma (Tsujimori et al., 2005). Two zircon grains were separated from jadeitite which is collected from the same outcrop as the jadeitite studied by Tsujimori, et al. (2005). They are a few millimeters in diameter and are subhedral clear crystals. The samples are the stored specimen in NMNS (register number: NSM-M-24785).

Kochi area (KC)

The Kochi area belongs to the Kurosegawa Belt which is a serpentinite mélange with various rock types of tectonic blocks; Silurian and Devonian sediments, granites, gneisses, amphibolites, basic schists and pelitic schists (e.g. Ichikawa et al., 1956). K-Ar ages of muscovite in jadeite-bearing schist were 208-240 Ma (Maruyama et al., 1978). The jadeite rock studied here is found as a boulder at Funakoshi, Hidaka Village, Kochi Prefecture (around N33°32'; E133°20'). The locality is 15 km WSW away from the famous locality of Engyoji area, eastward extension of serpentinite mélange of Kurosegawa Belt. The sample consists mainly of jadeite and quartz with a subordinate amount of glaucophane. The sample is the stored specimen in NMNS (register number: NSM-R-117953). Zircon in this sample is euhedral with length of 100 to 300 µm.

Nishisonogi area (NS)

The sample of the Nishisonogi area was collected as a boulder at Tone, Nishisonogi Peninsula (N32°53.5' E129°45.8') and jadeite rock of the area was reported by Shigeno et al. (2005). The area belongs to the Nagasaki Metamorphic Belt with K-Ar age of 60-90 Ma (Hattori and Shibata, 1982). The metamorphic belt consists mainly of pelitic, psammitic and basic schists with a small amount of serpentinite. The serpentinite occurs as a small pod or serpentinite mélange containing various types of tectonic blocks; metabasites, albitites, jadeitites, omphacite rocks, rodingites, zoisite rocks and epidote-garnet-crossite-barroisite rocks (Nishiyama et al., 1989). The major component of the jadeite rock is jadeite and albite; content of jadeite is 65-93%. Quartz is rarely observed as an inclusion in jadeite (Shigeno et al., 2005). The sample of jadeite rock is a stored specimen in NMNS (register number: NSM-M-28649). Zircon grains in this sample are subhedral with length of 100 to 300 microns.

Yorii area (YR)

The jadeite-bearing rock of the Yorii area is found as a huge block ca. 30 m in length associated with greenstone and serpentinite developed at the boundary between the Cretaceous Tochiya Formation and the Sanbagawa high-pressure type metamorphic belt (Hirajima, 1983). It consists mainly of jadeite, quartz and albite with a small amount of glaucophane. Jadeite is highly replaced by albite. Jadeite content is up to 50%. The Sanbagawa metamorphic rock has K-Ar age around 60-90 Ma (Miyashita and Itaya, 2002; Hirajima et al., 1992). No age datum was reported from the jadeite block. The sample is stored specimen in NMNS (register number: NSM-R-133439), which is collected from around N36°04.6' E139°11.9'. Zircons are fine-grained euhedral to subhedral crystals with length of 100 to 300 microns.

Analytical Methods and Results

Sample preparations

Zircon grains in the samples from KC, NS and YR were separated by standard crushing and heavy-liquid techniques and then handpicked to purify them. Zircon from IT was cut off from a thick polished section of the jadeitite sample. Two zircon grains of OS were picked up from a weathered jadeitite. The jadeitite chip including zircon (IT), half-cut large zircon grains (OS) and standard zircon (QGNG: ²³⁸U-²⁰⁶Pb* age of 1842.0±3.1 Ma; Black et al., 2003) were mounted in an epoxy resin and were polished. Finegrained zircon grains (KC, NS and YR) and OGNG were mounted in another epoxy resin and were polished till the surface was flattened with the center of the embedded grains exposed for SEM and SHRIMP analyses.

Texture and inclusion observations in zircon

Both backscattered electron (BSE) images and cathodoluminescence (CL) images were used to select the sites for SHRIMP analysis. Qualitative analysis of mineral inclusions in zircon was conducted by SEM-EDS, JEOL JSM5400 with Link QX2000 installed at NMNS.

Coarse-grained zircons from IT and OS show no clear compositional zoning on BSE images. However, the CL image of the zircon from IT sample shows a fragmentized texture, and zircons from OS have a clear zoning pattern (Fig. 3a and b). No inclusion in the zircons has yet been observed in this study. On the other hand, fine-grained zircons in the samples KC, NS and YR show oscillatory zoning on BSE and/or CL images (Fig. 3c-e) which are commonly observed not only in igneous zircons (e.g. Corfu et al., 2003) but also hydrothermal zircons (Dubińska et al., 2004; Tsujimori et al., 2005). Zircons have mineral inclusions. Especially, zircon in the sample KC is remarkable. The zircons in sample KC have quartz-feldspar-mica aggregate (Fig. 2a and b) and/or apatite as an inclusion. The aggregates are thought to be crystalline melt inclusions (e.g. Thomas et al., 2003) probably originated from felsic melt based on their mineral assemblage. The NS zircons have inclusions consisting mainly of Si, Na ad Al with subordinate amounts of Mg, Fe and K (Fig. 2c). YR zircons have inclusions consisting mainly of Si and Al with subordinate amounts of K, Mg and Fe (Fig. 2d) but inclusions in NS and YR zircons are too small to identify their minerals.

SHRIMP U-Pb dating of zircons

U-Pb dating of zircons from the samples was carried out using SHRIMP II installed at Hiroshima University, Japan. The experimental conditions and the procedures follow Sano et al. (2000) and references therein. The spot size of the primary ion beam was approximately $20 \,\mu m$. The ²⁰⁶Pb/²³⁸U ratios of the samples were calibrated using the empirical relationship described by Claoué-Long et al. (1995). The concentration of U in each analyzed spot was calibrated against an external standard SL13, which has a U content of 238 ppm (Claoué-Long et al., 1995). A correction for common Pb was made on the basis of the measured 206 Pb/ 208 Pb and 232 Th/ 238 U ratios and the two-stage model for common Pb compositions proposed by Stacey and Kramers (1975). Errors of all mean ages in this study are stated as



Fig. 2. a) and b) Transmission light (TL) and backscattered electron (BSE) images of zircons including melt inclusions (MI), and BSE images of MI in sample KC (KC19 and a unanalyzed grain). Mineral assemblages of the MIs are estimated quartz (Qtz), K-feldspar (K-f), plagioclase (Pl) and mica. c) BSE image of NS02 with a Na-rich inclusion (Inc) consists of Si, Na, Al, Mg, Fe and K d) BSE image of YR01 with albite and Na-free inclusions (Inc) consist of Si, Al, K, Mg and Fe.



Fig. 3. Cathodoluminescence images (CL) of typical zircon grains. Ellipses on the images point to analyzed spots by SHRIMP with the sub-numbers.

95% confidence interval.

Table 1 and 2 list zircon data in terms of U and Th concentrations, 204 Pb/ 206 Pb, 207 Pb/ 206 Pb, 208 Pb/ 206 Pb, 238 U/ 206 Pb, Th/U ratios, and 238 U/ 206 Pb* ages. All errors are 1 sigma level. Sub-numbers of labels such as KT1.01 to KT1.10 in the tables indicate different pits in a single grain. Figure 5 and 6 show Tera–Wasserberg concordia diagrams and 238 U/ 206 Pb* mean

ages for all analyzed spot, calculated by Isoplot 3/Ex (Ludwig, 2003).

In a zircon from IT, age data were scattered ranging from 525 to 427 Ma; the weighted mean of these ages yields 497 ± 23 Ma (Fig. 5a). Zircon age data for OS were scattered ranging from 540 to 487 Ma and two grains of OS1 (6 data) and OS2 (7 data) yield different mean ages; 496 ± 12 Ma and 532 ± 17 Ma, respectively (Fig. 5b and

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Table 1. SHRIMP U-Pb data and calculated ages of course zircons.

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Labels	²⁰⁴ Pb/ ²⁰⁶ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb	²³⁸ U/ ²⁰⁶ Pb	U (ppm)	Th (ppm)	Th/U	²³⁸ U- ²⁰⁶ Pb* age (Ma)	
Itoigawa	a area (IT)								
IT1.01	0.000697 ± 0.000089	0.0626 ± 0.0012	0.0422 ± 0.0020	11.94 ± 0.60	52	6	0.11	516.4 ± 25.1	
IT1.02	$0.000443 \!\pm\! 0.000091$	0.0601 ± 0.0009	0.0737 ± 0.0017	12.78 ± 1.01	91	20	0.22	484.0 ± 36.7	
IT1.03	0.000162 ± 0.000030	0.0586 ± 0.0026	0.0203 ± 0.0008	13.68 ± 1.95	215	11	0.05	454.0 ± 62.6	
IT1.04	0.002136 ± 0.001292	0.0761 ± 0.0032	0.0838 ± 0.0081	14.25 ± 1.39	22	3	0.11	427.3 ± 40.5	
IT1.05	0.001133 ± 0.000492	0.0600 ± 0.0014	0.0467 ± 0.0027	12.45 ± 0.84	29	3	0.11	495.0±32.0	
IT1.06	0.000429 ± 0.000069	0.0635 ± 0.0007	0.0363 ± 0.0027	11.68 ± 0.83	114	7	0.06	525.6 ± 36.1	
IT1.07	0.000915 ± 0.000168	0.0668 ± 0.0018	0.0513 ± 0.0029	12.35 ± 1.34	33	3	0.09	496.5 ± 52.0	
IT1.08	0.000746 ± 0.000298	0.0705 ± 0.0022	0.0818 ± 0.0038	12.95 ± 1.65	22	3	0.12	469.4 ± 57.6	
IT1.09	0.000216 ± 0.000062	0.0604 ± 0.0010	0.0740 ± 0.0022	11.76 ± 1.24	43	8	0.20	522.7 ± 52.8	
IT1.10	0.000698 ± 0.000212	0.0723 ± 0.0020	0.0802 ± 0.0056	12.05 ± 0.63	24	3	0.12	503.6 ± 25.2	
Osayama area (OS)									
OS1.02	0.000912 ± 0.000278	0.0624 ± 0.0018	0.1061 ± 0.0057	12.59 ± 0.45	55	15	0.28	488.1±16.9	
OS1.03	0.002747 ± 0.000544	0.0727 ± 0.0023	0.1684 ± 0.0082	12.61 ± 0.39	25	12	0.47	486.7 ± 14.8	
OS1.04	0.000497 ± 0.000117	0.0604 ± 0.0016	0.2444 ± 0.0056	12.53 ± 0.35	60	44	0.74	490.8±13.5	
OS1.05	0.000037 ± 0.000100	0.0650 ± 0.0017	0.1639 ± 0.0083	12.26 ± 0.33	32	15	0.46	500.2 ± 13.4	
OS1.06	0.000254 ± 0.000102	0.0607 ± 0.0014	0.1009 ± 0.0052	12.03 ± 0.34	43	12	0.28	511.3 ± 14.0	
OS1.08	0.000290 ± 0.000061	0.0636 ± 0.0015	0.1840 ± 0.0047	12.48 ± 0.49	63	36	0.57	495.0±19.0	
OS2.01	0.000021 ± 0.000054	0.0676 ± 0.0016	0.1482 ± 0.0068	11.31 ± 0.38	19	8	0.40	539.9±17.7	
OS2.02	0.000516 ± 0.000249	0.0695 ± 0.0023	0.1686 ± 0.0062	11.18 ± 0.54	16	6	0.40	539.9 ± 25.3	
OS2.03	0.000758 ± 0.000426	0.0712 ± 0.0019	0.1196 ± 0.0049	11.45 ± 0.52	15	4	0.26	529.8±23.2	
OS2.04	0.000247 ± 0.000190	0.0714 ± 0.0024	0.1166 ± 0.0075	11.76 ± 0.50	14	4	0.26	516.9±21.4	
OS2.05	0.000373 ± 0.000097	0.0792 ± 0.0029	0.1329 ± 0.0073	11.23 ± 0.44	16	4	0.24	534.6±20.3	
OS2.06	0.002237 ± 0.000493	0.0748 ± 0.0031	0.1175 ± 0.0072	11.55 ± 0.60	14	3	0.21	522.3 ± 26.3	
OS2.07	0.000684 ± 0.000373	0.0706 ± 0.0035	0.1306 ± 0.0072	11.14 ± 0.72	12	3	0.23	538.7±33.3	

 206 Pb* and 207 Pb* mean radiometric 206 Pb and 207 Pb, respectively. All errors are stated at 1 σ .

5c). Most of their U and Th concentrations are remarkably low (Fig. 4). Zircon ages of KC were scattered ranging from 520 to 451 Ma and weighted mean of these ages is 501 ± 5 Ma (Fig. 6a). NS and YR zircons yield younger mean ages, 136 ± 5 Ma and 159 ± 5 Ma, respectively (Fig. 6b and 6c).

Discussion

Multi-stage formation of zircons in jadeite rocks from Itoigawa (IT) and Osayama area (OS)

Zircons in jadeite rocks sometimes have inclusions indicating high-pressure condition (e.g. Tsujimori *et al.*, 2005; Bröcker and Keasling, 2006), but it is not always for all jadeite rock (e.g. Shi *et al.*, 2008). In this study, we couldn't find inclusions in zircons from IT and OS. Kunugiza *et al.* (2002) concluded that zircons in jadeitite from Itoigawa area were formed coincidentally with jadeite because of their euhedral shape, presence in zeolite matrix which also contains euhedral jadeite and absence of negative Eu anomaly in zircon. Tsujimori et al. (2005) reported jadeite inclusion in zircon in jadeitite from Osayama area. According to these report, it is probable that the coarse-grained zircons in this study also formed coincidentally with jadeite. The age of each spot in the zircon from IT yields a mean age of 497 ± 23 Ma, in agreement with previously reported values (519±17 Ma and 512.3±6.9 Ma; Kunugiza et al., 2002). But two zircons from sample OS (OS1 and OS2) yield different mean ages, 496±12 Ma and 532±17 Ma. Individual zircon spot ages of OS scattered from 540 to 487 Ma, and zircon age data from four zircon grains of Tsujimori et al. (2005) also scattered from 527 to 447 Ma. Although Tsujimori et al. (2005) concluded that the mean age of

Table 2. SHRIMP U-Pb data and calculated ages of fine zircons.

Labels	²⁰⁴ Pb/ ²⁰⁶ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb	²³⁸ U/ ²⁰⁶ Pb	U (ppm)	Th (ppm)	Th/U	²³⁸ U- ²⁰⁶ Pb*
								age (Ma)
Kochi area (KC)								
KC01.01	0.001217 ± 0.000693	0.0706 ± 0.0029	0.0963 ± 0.0072	11.97 ± 0.37	54	10	0.19	508.2 ± 15.3
KC02.01	0.000063 ± 0.000249	0.0630 ± 0.0013	0.1165 ± 0.0053	12.22 ± 0.23	109	31	0.29	500.4 ± 9.3
KC03.01	0.000027 ± 0.000087	0.0657 ± 0.0024	0.1044 ± 0.0067	11.90 ± 0.22	78	18	0.24	512.5 ± 9.2
KC04.01	0.000019 ± 0.000008	0.0566 ± 0.0008	0.1771 ± 0.0042	12.47 ± 0.19	339	190	0.56	496.4 ± 7.6
KC05.01	0.000005 ± 0.000090	0.0626 ± 0.0020	0.1194 ± 0.0034	11.86 ± 0.26	88	30	0.34	518.0 ± 11.1
KC05.02	< 0.000001	0.0662 ± 0.0019	0.0946 ± 0.0053	11.98 ± 0.25	48	10	0.20	508.9 ± 10.4
KC06.01	0.000441 ± 0.000294	0.0746 ± 0.0044	0.1285 ± 0.0081	11.82 ± 0.37	47	13	0.28	513.3 ± 15.5
KC06.02	0.000106 ± 0.000311	0.0658 ± 0.0020	0.0919 ± 0.0077	12.27 ± 0.37	66	12	0.18	496.8±14.6
KC07.01	0.000045 ± 0.000584	0.0695 ± 0.0026	0.1114 ± 0.0087	11.60 ± 0.50	55	11	0.20	520.5 ± 21.8
KC08.01	< 0.000001	0.0735 ± 0.0042	0.1053 ± 0.0076	12.24 ± 0.39	59	11	0.19	495.4±15.4
KC08.02	0.000044 ± 0.000085	0.0632 ± 0.0019	0.0646 ± 0.0043	12.38 ± 0.47	135	21	0.15	496.8 ± 18.2
KC09.01	< 0.000001	0.0682 ± 0.0024	0.0822 ± 0.0043	12.11 ± 0.28	86	14	0.17	504.2 ± 11.2
KC10.01	< 0.000001	0.0572 ± 0.0028	0.1351 ± 0.0054	12.37 ± 0.91	243	95	0.39	497.7±35.6
KC10.02	0.000076 ± 0.000035	0.0594 ± 0.0012	0.0683 ± 0.0022	12.82 ± 0.26	199	37	0.19	481.7 ± 9.5
KC11.01	< 0.000001	0.0600 ± 0.0011	0.1420 ± 0.0041	12.63 ± 0.23	261	115	0.44	489.8 ± 8.6
KC12.01	0.000315 ± 0.000972	0.0932 ± 0.0079	0.1619 ± 0.0086	12.05 ± 0.49	41	11	0.26	494.0±19.5
KC13.01	< 0.000001	0.0675 ± 0.0026	0.1413 ± 0.0108	12.49 ± 0.39	93	32	0.35	488.8 ± 15.0
KC14.01	< 0.000001	0.0669 ± 0.0028	0.1039 ± 0.0045	12.35 ± 0.42	105	26	0.25	495.4±16.4
KC14.02	0.000296 ± 0.000297	0.0873 ± 0.0067	0.1468 ± 0.0152	12.24 ± 0.34	55	12	0.22	487.6±13.6
KC15.01	< 0.000001	0.0852 ± 0.0064	0.1129 ± 0.0079	11.73 ± 0.57	30	5	0.16	511.8 ± 23.8
KC16.01	< 0.000001	0.0699 ± 0.0021	0.1111 ± 0.0091	11.67 ± 0.46	54	10	0.18	516.3 ± 19.8
KC17.01	0.000056 ± 0.000259	0.0719 ± 0.0031	0.0954 ± 0.0064	11.94 ± 0.23	88	16	0.18	509.2 ± 9.7
KC18.01	0.001390 ± 0.000563	0.0774 ± 0.0031	0.1110 ± 0.0070	11.82 ± 0.25	81	14	0.18	510.0 ± 10.6
KC19.01	0.000065 ± 0.000085	0.0585 ± 0.0008	0.1879 ± 0.0046	13.67 ± 0.70	558	312	0.56	451.8±22.9
KC19.02	0.000011 ± 0.000102	0.0577 ± 0.0021	0.1700 ± 0.0047	12.57 ± 0.67	421	211	0.50	490.0±25.9
KC20.01	0.000364 ± 0.000767	0.0895 ± 0.0045	0.1359 ± 0.0126	11.74 ± 0.39	43	8	0.18	507.1 ± 16.6
Nishisonogi area (NS)								
NS01.01	0.000208±0.000092	0.0609 ± 0.0044	0.2099 ± 0.0076	45.92 ± 1.22	154	84	0.55	136.0 ± 3.6
NS01.02	0.000632 ± 0.000275	0.0610 ± 0.0029	0.0320 ± 0.0028	74.78 ± 1.94	857	14	0.02	84.6±2.2
NS02.01	< 0.000001	0.0508 ± 0.0021	0.0325 ± 0.0017	45.65 ± 1.73	1079	77	0.07	139.0 ± 5.2
NS03.01	< 0.000001	0.0757 ± 0.0092	0.3541 ± 0.0252	46.37 ± 2.37	208	179	0.86	131.1 ± 7.1
NS03.02	0.000307 ± 0.002354	0.1135 ± 0.0120	0.2528 ± 0.0287	40.53 ± 1.38	79	32	0.41	147.2 ± 5.5
NS03.03	0.001142 ± 0.000560	0.0707 ± 0.0047	0.2693 ± 0.0118	47.59 ± 1.54	143	98	0.68	130.1±4.3
NS04.01	< 0.000001	0.1271 ± 0.0242	0.3232 ± 0.0514	44.26 ± 6.37	30	14	0.46	130.9 ± 19.3
NS05.01	< 0.000001	0.0921 ± 0.0078	0.2894 ± 0.0163	42.42 ± 1.19	43	23	0.52	140.5 ± 4.1
NS05.02	0.000316 ± 0.001116	0.0996 ± 0.0107	0.2884 ± 0.0231	45.22 ± 1.44	83	41	0.50	131.5 ± 4.5
Yorii area (YR)								
YR01.01	0.000070 ± 0.000057	0.0506 ± 0.0008	0.2663 ± 0.0061	39.76±2.79	1061	908	0.86	160.0 ± 11.7
YR02.01	$0.000025 \!\pm\! 0.000064$	$0.0537 {\pm} 0.0016$	0.1490 ± 0.0089	40.97 ± 2.61	519	230	0.44	154.5 ± 9.9
YR03.01	$0.000022 \!\pm\! 0.000035$	$0.0514 {\pm} 0.0010$	0.2933 ± 0.0066	39.99 ± 0.93	906	814	0.90	157.9 ± 3.8
YR04.01	0.000113 ± 0.000063	$0.0500 \!\pm\! 0.0008$	0.4189 ± 0.0076	40.47 ± 0.96	1841	2418	1.31	156.2 ± 4.4
YR04.02	$0.000231 \!\pm\! 0.000129$	0.0549 ± 0.0012	0.4318 ± 0.0071	37.62 ± 1.50	1850	2489	1.35	167.6±7.9
YR05.01	$0.000036 {\pm} 0.000023$	$0.0527 {\pm} 0.0016$	0.2476 ± 0.0071	38.77 ± 2.36	862	676	0.78	163.7 ± 10.3

 206 Pb* and 207 Pb* mean radiometric 206 Pb and 207 Pb, respectively. All errors are stated at 1 σ .

 472 ± 8.5 Ma indicate age of jadeitization, we propose a possibility that jadeitization or zircon formation process in Osayama area is not a single event but multiple events from about 540 to 450 Ma. Actually, Fu *et al.* (2010) reported two types of zircons are recognized in jadeitite from

Osayama area by observation of cathodoluminescence image and measurement of oxygen isotopes. On the other hand, three zircon ages are recognized in Myanmar jadeitite; Shi *et al.* (2005) interpreted the ages as inherited, jadeitite formation and thermal event.



Fig. 4. U–Th relations of all analyzed spots. The lines indicate Th/U ratios for reference.

Although it is difficult to conclude the origin of zircons in the Renge Belt, it is important that the approx. 500 Ma age has been recorded in the rocks from the Renge Belt.

Jadeite rock from Kochi area (KC)

The protolith of the KC sample is considered to be felsic igneous rock which age is 501 ± 5 Ma because some zircons have felsic melt inclusions (Fig. 2a and b) and zircon ages concentrate enough to interpret the mean age to igneous age of the protolith (Fig. 6a). Th/U ratios (Hoskin and Black, 2000) and inner structure of oscillatory zonings (Corfu et al., 2003) also support this idea. Formation of jadeite requires high-pressure condition (reviewed in e.g. Harlow and Sorensen, 2005) while felsic igneous rock was formed in island arc or continental crust. Therefore, the KC sample is interpreted as parentally a crustal material and once subducted (e.g. Clift and Vannucchi, 2004) to certain depth of jadeite formation. The K-Ar age of a jadeite-bearing schist from the Kurosegawa Belt is around 208-240 Ma (Maruyama et al., 1978), far younger than the zircon age of 501 ± 5 Ma. The former age will be corresponding to metamorphic stage, i.e. jadeitiszation, whereas the latter to the protolith igneous stage.

On the Japanese Islands, now, around 500 Ma igneous rocks are scarce; the Daiouin granitoid (Hitachi area, Ibaraki Pref.) and Hikawa granitoid (Higo Belt, Kumamoto Pref.) which ages are 490.8 ± 6.1 Ma; 502.5 ± 9.6 Ma, respectively (Sakashima *et al.*, 2003). It is probable that these 500 Ma igneous rocks and associated rocks (Higo belt and Hitachi metamorphic rocks) were residues of missing crusts. Yokoyama *et al.* (2009) reported that detrital monazite age distribution of the Maizuru Belt (Permian to Triassic) have distinct peaks of 504–511 Ma. Although it is difficult to compare zircon age with monazite age, it is evident that 500 Ma crust existed extensively at least until Triassic in time. In spite of similar ages of zircons in the jadeitite from the Renge Belt and jadeite-bearing rocks from the Kurosegawa Belt, their origins would be different each other.

Mesozoic zircon ages of jadeite rocks in Nishisonogi (NS) and Yorii (YR) areas

Zircons in NS and YR samples show oscillatory zoning on BSE and/or CL images (Fig. 3d and e) which are commonly observed not only in igneous zircons (Corfu et al., 2003) but also in hydrothermal zircons (e.g. Dubińska et al., 2005; Tsujimori et al., 2005). Hoskin and Black (2000) suggested that higher Th/U ratio (>0.1) of zircon is igneous in origin (e.g., Hoskin and Black, 2000). However, hydrothermal zircon also yield higher Th/U ratio (e.g. Tsujimori et al., 2005). Origins of zircons in the NS and YR samples are interpreted to be protolith or hydrothermal reaction. The zircons in the NS sample have mineral inclusions which compositions are relatively Narich, consisting of Si, Na, Al, Mg, Fe and K, whereas zircon inclusions in the YR sample consist of Si, Al, K, Mg and Fe. Although they are too small to identify the minerals, it is important whether the inclusions are Na-rich or not because it has been considered that there is strong relation between formation of jadeite rocks and Na-Al-Si rich fluid (Harlow and Sorensen, 2005; Tsujimori et al., 2005).

Associated metamorphic rocks have muscovite K–Ar ages of about 60–90 Ma for NS (Hattori and Shibata, 1982) and YR (Miyashita and Itaya, 2002; Hirajima *et al.*, 1992). The zircons in the NS and YR are 136 ± 5 Ma and 159 ± 5 Ma, re-



Fig. 5. Tera-Wasserberg U–Pb concordia diagrams of zircons and ²³⁸ U–²⁰⁶ Pb age distribution plot of the course zircon samples IT, OS1 and OS2. ²⁰⁷ Pb* and ²⁰⁶ Pb* indicate radiometric ²⁰⁷ Pb and ²⁰⁶ Pb, respectively. Solid curve indicates concordia curve. All error bars and ellipses are stated at 2 σ.

spectively, far younger that the zircons as mentioned above. Metamorphic conditions of the jadeite rocks are within a stability field of jadeite-quartz assemblage, and are different from those of the associated metamorphic rocks in NS and YR. The latter conditions are within a stability field of albite. Although it is difficult to discuss the origin of zircons of NS and YR samples, it is important that the zircon ages of jadeite rocks of NS and YR are far younger than jadeite rocks of the Renge Belt and the Kurosegawa Belt.

Conclusions

The protolith of the KC sample is thought to be a \sim 500 Ma felsic igneous rock and is interpreted as a continental material which once subducted to certain depth of jadeite formation. The zircon ages of IT are concentrated and yield a mean age of 497±23 Ma, in agreement with pre-



Fig. 6. Tera-Wasserberg U–Pb concordia diagrams of zircons and ²³⁸U–²⁰⁶Pb age distribution plot of the fine zircon samples KC, NS and YR. ²⁰⁷Pb* and ²⁰⁶Pb* indicate radiometric ²⁰⁷Pb and ²⁰⁶Pb, respectively. Solid curve indicates concordia curve. All error bars and ellipses are stated at 2*σ*.

viously reported values. But two zircons from sample OS (OS1 and OS2) yield different mean ages, 496 ± 12 Ma and 532 ± 17 Ma, respectively. Although individual zircon spot ages of OS were scattered from 540 to 487 Ma as well as the previous report from 527 to 447 Ma, it is difficult whether they show igneous stage or metamorphic stage. Zircons from NS and YR are far younger, 136 ± 5 Ma (NS) and 159 ± 5 Ma (YR), than those from the Renge Belt and the Kurosegawa Belt. It is probable that these young ages show igneous ages because of existence of felsic melt inclusions and concentrated zircon ages.

All the ages obtained are not corresponding to the K–Ar ages of the associated metamorphic rocks. As the fine-grained zircons from three localities show apparently igneous zoning, it is probable that the ages are of the igneous stage different from the jadeitization stage of the parental rocks. Ages around 500 Ma have been scarcely described from the Japanese Islands. Referring to the age data of the East Asia, the zircons with 500 Ma had belonged probably to the Jiamusi and Khanka blocks with ages around 500 Ma. The zircons with 136 Ma and 159 Ma from Kochi and Yorii, respectively, are enigmatic because of absence of the age in the Japanese Islands and Korean Peninsula. Further study will be necessary to discuss the origin of these zircons.

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References

- Black, L. P., Kamo, S. L., Williams, I. S., Mundil, R., Davis, D. W., Korsch, R. J. and Foudoulis, C. (2003) The application of SHRIMP to Phanerozoic geochronology; a critical appraisal of four zircon standards. *Chemical Geology*, **200**, 171–188.
- Bröcker, M. and Keasling, A. (2006) Ionprobe U-Pb zircon ages from the high-pressure/low-temperature mélange of Syros, Greece: age diversity and the importance of pre-Eocene subduction. *Journal of Metamorphic Geology*, 24, 615–631.
- Claoué-Long, J. C., Compston, W., Roberts, J. and Fanning, C. M. (1995) Two Carboniferous ages: a comparison of SHRIMP zircon dating with conventional zircon ages and ⁴⁰ Ar/³⁹ Ar analysis. In Geochronology, time scales and global stratigraphic correlation (Berggren W.A., Kent D.V., Aubry M.P. and Hardenbol J. Ed.). Society of Economic Paleontologists and Mineralogists (Society for Sedimentary Geology) Special Publication, 54, 3–21.
- Clift, P. and Vannucchi, P. (2004) Controls on tectonic accretion versus erosion in subduction zones: implications for the origin and recycling of the continental crust. *Review of Geophysics*, 42, RG2001.
- Corfu, F., Hancher, J. M., Hoskin, P. W. O. and Kinny, P. (2003) An atlas of zircon textures. In Zircon (Hancheer,

J. M. and Hoskin, P. W. O. Eds.). pp. 500, Reviews in Mineralogy and Geochemistry 53, Mineralogical Society of America, Washington, D. C., 278–286.

- Dubińska, E., Bylina, P., Kozłowski, A., Dörr, W., Nejebert, K., Schastock, J. and Kulichi, C. (2004) U–Pb dating of serpentinization: hydrothermal zircon from a metasomatic rodingite shell (Sudetic ophiolite, SW Poland). *Chemical Geology*, 203, 183–203.
- Fu, B., Valley, J. W., Kita, N., Spicuzza, M. J., Paton, C., Tsujimori, T., Bröcker, M. and Hallow, G.E. (2010) Multiple origin of zircon in jadeitite. *Contributions to Mineralogy and Petrology*, **159**, 769–780.
- Gouchi, N. (1983) Kamuikotan metamorphic rocks in the Kamuikotan gorge area, west of Asahikawa, Hokkaido. Journal of the Japanese Association of Mineralogists, Petrologists and Economic Geologists, 78, 383–393.
- Harlow, G. E. and Sorensen, S. S. (2005) Jade (nephrite and jadeitite) and serpentinite: metasomatic connections. *International Geology Review*, 47, 113–146.
- Hattori, H. and Shibata, K. (1982) Radiometric dating of Pre-Neogene granitic and metamorphic rocks in northwest Kyushu, Japan—with emphasis on geotectonic of the Nishisonogi zone. *Bulletin of the Geological Survey* of Japan, **33**, 57–84.
- Hirajima, T., (1983) Jageite+quartz rock from the Kanto Mountains. Journal of Association of Mineralogist, Petrologist and Economic Geologist, 78, 77–83.
- Hirajima, T., Isono, T. and Itaya, T. (1992) K-Ar age and chemistry of white mica in the Sanbagawa metamorphic rocks in the Kanto Mountains, central Japan. *Journal of Geological Society of Japan*, **98**, 445–455 (in Japanese with English abstract).
- Hoskin, P. W. and Black, L. P. (2000) Metamorphic zircon formation by solid-state recrystallization of protolith igneous zircon. *Journal of Metamorphic Geology*, 18, 423–439.
- Ichikawa, K., Ishii, K., Nakagawa, C., Suyari, K. and Yamashita, N. (1956) Die Kurosegawa zone. *Journal of the Geological Society of Japan*, **62**, 82–103 (in Japanese with German abstract).
- Kobayashi, S., Miyake, H. and Shoji, T. (1987) A jadeite rock from Oosa-cho, Okayaman Prefecture, southwestern Japan. *Mineralogical Journal*, **13**, 314–327.
- Kunugiza, K., Nakamura, E., Miyajima, H., Goto, A. and Kobayashi, K. (2002) Formation of Jadeite–Natrolite rocks in the Itoigawa–Ohmi area of the Hida marginal belt inferred from U-Pb zircon dating. Abstracts of annual meeting of the Japanese Association of Mineralogists, Petrologists and Economic Geologists in 2002, GP20 (in Japanese)
- Ludwig, K. R., (2003) Isoplot 3. Berkeley, CA, Berkeley Geochronology Center, Special Publication, no. 4.
- Maruyama, S., Ueda, Y. and Banno, S. (1978) 208–240 m.y. old jadeite-graucophane schists in the Kurosegawa

Tectonic Zone, near Kochi City, Shikoku. *Journal of* Association of Mineralogists, Petrologists and Economic Geologists, **73**, 300–310.

- Miyashita, A. and Itaya, T. (2002) K–Ar Age and Chemistry of Phengite from the Sanbagawa Schists in the Kanto Mountains, Central Japan, and their Implication for Exhumation Tectonics. *Gondwana Research*, **5**, 837–848.
- Nakamizu, M., Okada, M., Yamazaki, T. and Komatsu, M. (1989) Metamorphic rocks in the Omi-Renge serpentinite mélange, Hida Marginal Tectonic Belt, Central Japan. *Memoirs of Geological Society of Japan*, 33, 21–35 (in Japanese with English abstract).
- Nishimura, Y. (1998) Geotectonic subdivision and areal extent of the Sangun belt, Inner Zone of Southwest Japan. *Journal of Metamorphic Geology*, **16**, 129–140.
- Nishiyama, T. (1989) Petrological study of the Nagasaki metamorphic rocks in the Nishisonogi Peninsula —with special reference to greenrock complex and the reaction-enhanced ductility—. *Memoirs of the Geological Society of Japan*, 33, 237–257 (in Japanese with English abstract).
- Saito, M. and Miyazaki, K. (2006) Jadeite-bearing metagabbro in serpentinite melange of the "Kurosegawa Belt" in Izumi Town, Yatsushiro City, Kumamoto Prefecture, central Kyushu. *Bulletin of Geological Survey of Japan*, 57, 169–176 (in Japanese with English abstract).
- Sakashima, T., Terada, K., Takeshita, T. and Sano, Y. (2003) Large-scale displacement along Median Tectonic Line, Japan: evidence from SHRIMP zircon U-Pb dating of granites and gneiss from the South Kitakami and paleo-Ryoke belt. *Journal of Asian Earth Science*, 21, 10199–1039.
- Sano, Y., Hidaka, H., Terada, K., Shimizu, H. and Suzuki, M. (2000) Ion microprobe U-Pb zircon geochronology of the Hida gneiss: Finding of the oldest minerals in Japan. *Geochemical Journal*, **34**, 135–153.
- Shi, G., Cui, W., Cao, S., Jiang, N., Jian, P., Liu, D., Miao, L. and Chu, B. (2008) Ion microprobe zircon U-Pb age and geochemistry of the Myanmar jadeitite. *Journal of the Geological Society, London*, **165**, 221–234.
- Shibata, K. and Nozawa, T. (1968) K-Ar age of Omi schist, Hida Mountains, Japan. Bulletin of Geological Survey of Japan, 19, 243–246.
- Shibata, K., Nozawa, T. and Wanless, R. K. (1970) Rb–Sr geochronology of the Hida metamorphic belt, Japan. *Canadian Journal of Earth Science*, 7, 1383–1401.
- Shibata, K., Uchiumi, S. and Nakagawa, T. (1979) K–Ar age resulr-1. *Bulletin of Geological Survey of Japan*, 30, 675–686 (in Japanese with English abstract).

- Shigeno, M., Mori, Y. and Nishiyama, T. (2005) Reaction microtextures in jadeitites from the Nishisonogi metamorphic rocks, Kyushu, Japan. *Journal of Mineralogical and Petrological Sciences*, **100**, 237–246.
- Stacey, J. S. and Kramers, J. D. (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth and Planetary Science Letters*, 26, 207–221.
- Tanabe, K., Tomioka, N. and Kanehira, K. (1982) Jadeite– Aragonite-Bearing Rocks from the Sanbagawa Metamorphic Terrane in the Kanto Mountains. *Proceedings* of the Japan Academy. Ser. B, 58, 199–203.
- Tazawa, J., Aita, Y., Yuki, T. and Otsuki, K. (1984) Discovery of Permian radiolarians from the "non-calcareous Paleozoic strata" of Omi, central Japan. *Earth Science (Chikyu Kagaku)*, 38, 264–267 (in Japanese).
- Thomas, J. B., Bodnar, R. J., Shimizu, N. and Chesner, C.A. (2003) Melt inclusions in zircon. In Reviews in Mineralogy and Geochemistry 53, Zircon (Hancheer, J.M. and Hoskin, P.W.O Ed.). pp. 500, Mineralogical Society of America, 63–87.
- Tsujimori, T. (1997) Omphacite-diopside vein in an omphacitite block from the Osayama serpentinite melange, Sangun-Renge metamorphic belt, southwestern Japan. *Mineralogical Magazine*, **61**, 845–852.
- Tsujimori, T. and Itaya, T. (1999) Blueschist-facies metamorphism during Paleozoic orogeny in southwestern Japan: Phengite K–Ar ages of blueschist-facies tectonic blocks in a serpentinite melange beneath early Paleozoic Oeyama ophiolite. *Island Arc*, 8, 190–205.
- Tsujimori, T., Hyoudo, H., and Itaya, T. (2001) ⁴⁰Ar/³⁹Ar phengite age constrains on the exhumation of the eclogite facies rocks in the Renghe metamorphic belt, SW Japan. Abstracts 2001 Japan Earth and Planetary Science Joint Meeting, Tokyo, Japan, Gr-P007.
- Tsujimori, T., Liou, J. G., Wooden, J. and Miyamoto, T. (2005) U-Pb Dating of Large Zircons in Low-Temperature Jadeitite from the Osayama Serpentinite Mélange, Southwest Japan: Insights into the Timing of Serpentinization. *International Geology Review*, **47**, 1048– 1057.
- Williams, I. S. (1998) U–Th–Pb Geochronology by Ion Microprobe. *Reviews in Economic Geology*, 7, 1–35.
- Yokoyama, K. and Samejima, T. (1982) Miscibility gap between jadeite and omphacite. *Mineralogical Journal*, 11, 53–61.
- Yokoyama, K., Shigeta, Y. and Tsutsumi, Y. (2009) Age distribution of detrital monazites in the sandstones. In The Lower Triassic system in the Abrek Bay area, south Primorye, Russia (Shigeta, Y., Zakharov, Y. D. and Popov, A. M. Eds). *National Museum of Nature* and Science Monographs, **38**, 34–36.