Research Paper

High-reliability zircon separation for hunting the oldest material on Earth: An automatic zircon separator with image-processing/microtweezers-manipulating system and double-step dating

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ABSTRACT

Despite the recent development in radiometric dating of numerous zircons by LA-ICPMS, mineral separation still remains a major obstacle, particularly in the search for the oldest material on Earth. To improve the efficiency in zircon separation by an order of magnitude, we have designed/developed a new machine — an automatic zircon separator (AZS). This is designed particularly for automatic pick-up of 100 μm-sized zircon grains out of a heavy mineral fraction after conventional separation procedures. The AZS operates in three modes: (1) image processing to choose targeted individual zircon grains out of all heavy minerals spread on a tray, (2) automatic capturing of the individual zircon grains with micro-tweezers, and (3) placing them one-by-one in a coordinated alignment on a receiving tray. The automatic capturing was designed/created for continuous mineral selecting without human presence for many hours. This software also enables the registration of each separated zircon grain for dating, by recording digital photo-image, optical (color) indices, and coordinates on a receiving tray. We developed two new approaches for the dating; i.e. (1) direct dating of zircons selected by LA-ICPMS without conventional resin-mounting/polishing, (2) high speed U-Pb dating, combined with conventional sample preparation procedures using the new equipment with multiple-ion counting detectors (LA-MIC-ICPMS). With the first approach, Pb-Pb ages obtained from the surface of a mineral were crosschecked with the interior of the same grain after resin-mounting/polishing. With the second approach, the amount of time required for dating one zircon grain is ca. 20 s, and a sample throughput of >150 grains per hour can be achieved with sufficient precision (ca. 0.5%).

We tested the practical efficiency of the AZS, by analyzing an Archean Jack Hills conglomerate in Western Australia with the known oldest (>4.3 Ga) zircon on Earth. Preliminary results are positive; we were able to obtain more than 194 zircons that are over 4.0 Ga out of ca. 3800 checked grains, and 9 grains were over 4300 Ma with the oldest at 4371 ± 7 Ma. This separation system by AZS, combined with the new approaches, guarantees much higher yield in the hunt for old zircons.

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1. Introduction

Zircon geochronology is a tremendous addition to the panoply of research techniques in the investigation of igneous, sedimentary and metamorphic rocks. In addition to the latest highly-tuned Nano secondary ion mass spectrometer (Nano-SIMS) and sensitive high-resolution ion-microprobe (SHRIMP) instruments, well-developed laser ablation inductively-coupled plasma mass spectrometry (LA-ICPMS) has dramatically enhanced the determination of mineral/rock ages, and the ability to handle numerous mineral grains (e.g., Iizuka and Hirata, 2004); these new techniques have changed the style of research in geosciences in the last decade. Despite such improvements in dating techniques *per se*, mineral separation still remains a major obstacle because it requires enormous amounts of time and human effort. Crushing rocks, sieving, panning, and heavy liquid/magnetic treatments are the conventional procedures for mineral separation, and the hardest part is the final hand-picking of individual grains under the microscope. When we look for rare material, such as the oldest zircon on Earth, efficient and accurate separation of mineral grains is essential but may be difficult, even for well-trained researchers who may misidentify minerals and overlook small-sized targets.

In order to enhance the efficiency in mineral separation by an order of magnitude, and to emancipate many researchers from painstaking, time-consuming work, we have designed and developed a new separation system specifically customized for zircons, i.e. an automatic zircon separator (AZS). This AZS machine is designed for the automatic separation of 100 μm-sized individual zircon grains from a condensed mineral fraction after conventional separation procedures. We have modified a micromanipulator machine originally designed for picking up microscopic objects and relevant image-processing software, and thus have assembled a proto-type AZS (Fig. 1A) to test its practical efficiency.

The preliminary results are positive, as we have been able to reliably separate particular target minerals with this new machine. For a preliminary test, we analyzed the heavy mineral fraction of the well-known 3.0 Ga conglomerate from the Narryer gneiss complex in Western Australia, which contains the oldest zircons (>4.3 Ga) ever reported on Earth (Wilde et al., 2001). Still under progress, this machine likely provides a promising new tool for all zircon seekers. This article briefly reports the results of our first attempt. More detailed descriptions and geological implications of our new Hadean zircons will be reported in a sister article elsewhere by S. Yamamoto and others.
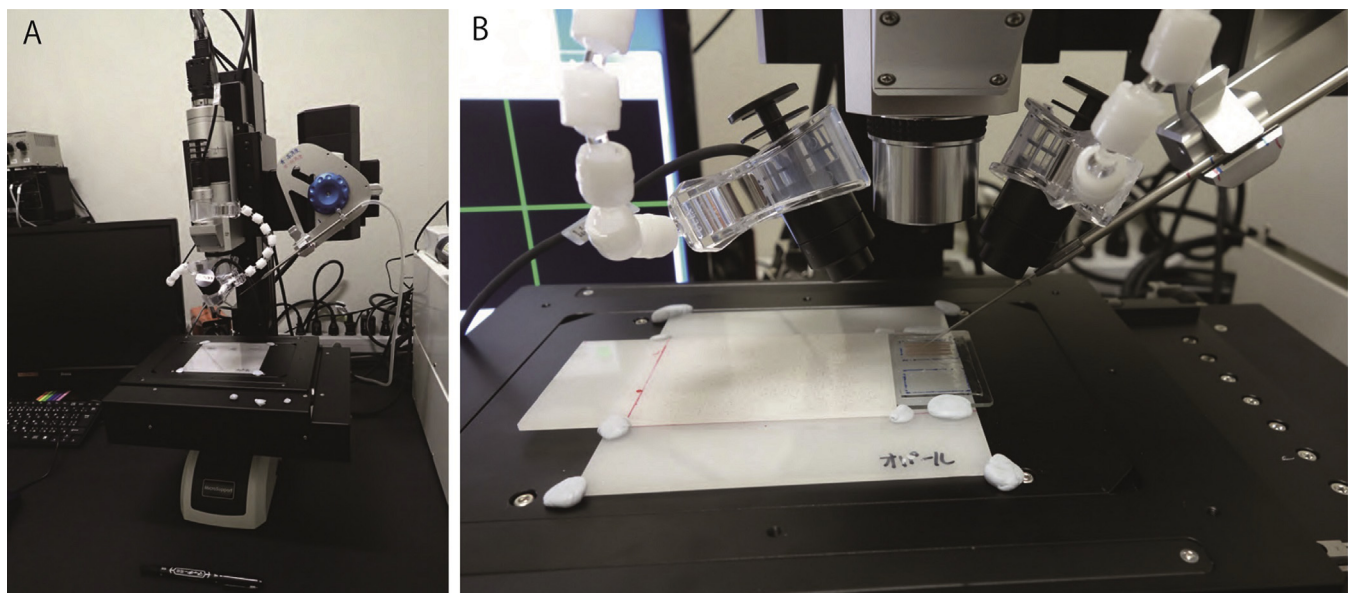
2. Automatic zircon separator (AZS)

2.1. Basic concept

The new zircon separation system (AZS; Fig. 1A) operates in three functions: i.e. (1) optical recognition of targeted mineral grains on a tray with randomly scattered heavy minerals, (2) mechanical capturing of individual grains one by one, and (3) placing and aligning the captured grains on a receiving tray with registered coordinates. The first function is an application of pre-existing image-processing software, which we have further customized it for a particular mineral (e.g. zircon) by adding more specific constraints on optical characteristics (color, transparency, reflectance etc.) and the external morphology of mineral grains on the basis of our empirical knowledge of hand-picking procedures. The second and third functions also come from the modification of the micromanipulator, which is designed for capturing microscopic small-objects with a built-in digital microscope connected to a monitor screen of a desktop computer and with a mechanical micro-tweezer (vacuum-driven fine tube) (Fig. 1B). For the mechanical motion of the AZS machine and its procedure, readers may find a good analogy in the so-called "crane game machine" for capturing reward bunny-dolls in amusement parks, although obviously the size is larger.

2.2. Specification

The basic framework of the AZS machine is a micromanipulator system (Axis Pro™, MicroSupport Co.), which was primarily designed for picking up small objects grain-by-grain with a semi-manual control on a monitor screen. Users can manipulate the tip of the tweezers in enlarged images on the monitor screen. For capturing/releasing grains, a vacuum tweezer is used as an interlocking device (Fig. 1B). To complement these mechanical

Figure 1. The automatic zircon separator (AZS). (A) The main body of the machine with an arm of microtweezers, (B) enlarged image of the microtweesers.

operations, a software for optical recognition/image processing is already available (Contami-Analyzer™, Mitani Corporation). We have customized the micromanipulator together with this software into a more zircon-specific version. By adding discrimination criteria for the empirically known common characteristics of zircons, such as color, reflectance, surface texture, shape, roundness/aspect ratio etc., the image-processing software is capable of identifying zircon-like objects. The final identification by the software has proven to be highly reliable; however, the final capturing rate has not yet reached 100%, mainly due to grain irregularities, such as crystal breakage, color heterogeneity, and surface smoothness with respect to lighting angles etc. Nonetheless, the high reliability of the system is getting closer to the level of human eye-recognition.

A mineral separating procedure with this system is performed as follows. First, we scatter randomly mineral grains from a condensed heavy mineral fraction on an acrylic plate (50 mm × 100 mm), avoiding any grain overlaps.

The area on the plate with mineral grains is separated into multiple grids on the monitor screen (Fig. 2), and for each grid, the system will check a photo image of each individual grain one by one with respect to the reference values of the optical characteristics of registered zircons. Grains identified as zircons by this image screening are registered first for each grid and illustrated individually in a thumbnail photo with an ID number on the monitor (Fig. 3). After this first-round screening, we can easily evaluate the validity of the image-selected grains by observing their thumbnail images on the monitor. At this stage, wrongly selected grains are screened out, if necessary.

When the selection of grains is fixed for one sample, we can move onto the mechanical picking of zircons with the microtweezer (Fig. 1B). The movement of a microtweezer *per se* is two-fold; a vertical motion from the rest position to the horizon of the targeted grain for the pick-up and *vice versa*, and a small-scale horizontal motion for actual capturing/releasing of grains over short distances. For carrying the captured grain, the horizontal

stage of the microscope itself moves horizontally between the tray with randomly scattered grains and the receiving tray with only the selected/aligned zircon grains. The receiving tray will catch the transported grains with adhesive tape on surface.

The big advantage of the new separation system is the continuous automated pick up or placing of numerous grains without much human involvement. Nonetheless, we emphasize that the best part of this machine is in the resulting organized alignment of captured grains with equal spacing on a receiving tray with a registered number and photo image of each grain (Fig. 4).

3. Preliminary attempt

3.1. Material

For the preliminary test of the reliability of the AZS system, we examined the ca. 3.0 Ga Jack Hills meta-conglomerate of the Narryer gneiss complex in the Yilgarn craton, Western Australia, which is well known for the occurrence of the oldest (ca. 4.40 Ga) zircons on Earth (Wilde et al., 2001). Sample EH19 was collected from an outcrop on Eranondoo Hill, near the discovery site of the oldest zircon (W74; Holden et al., 2009) in the Jack Hills supracrustal belt. About 5 kg of meta-conglomerate was processed by conventional mineral separation techniques, i.e., crushing, sieving, panning, heavy liquid- and magnetic-separation, in the laboratory of the University of Tokyo at Komaba. For the present pilot study, we used a heavy mineral fraction that was put through a sieving cloth with a 150 μm opening. The heavy mineral fractions usually include not only zircons but other heavy minerals with similar physical properties. The AZS machine collected zircons and zircon-like minerals from the condensed fraction of heavy mineral grains, mostly of 50−100 μm size.

In the heavy mineral fraction from the pilot sample (EH19), zircons occupied merely 60% of the captured grains (Fig. 2). For identifying/sorting out non-zircon minerals contained in the
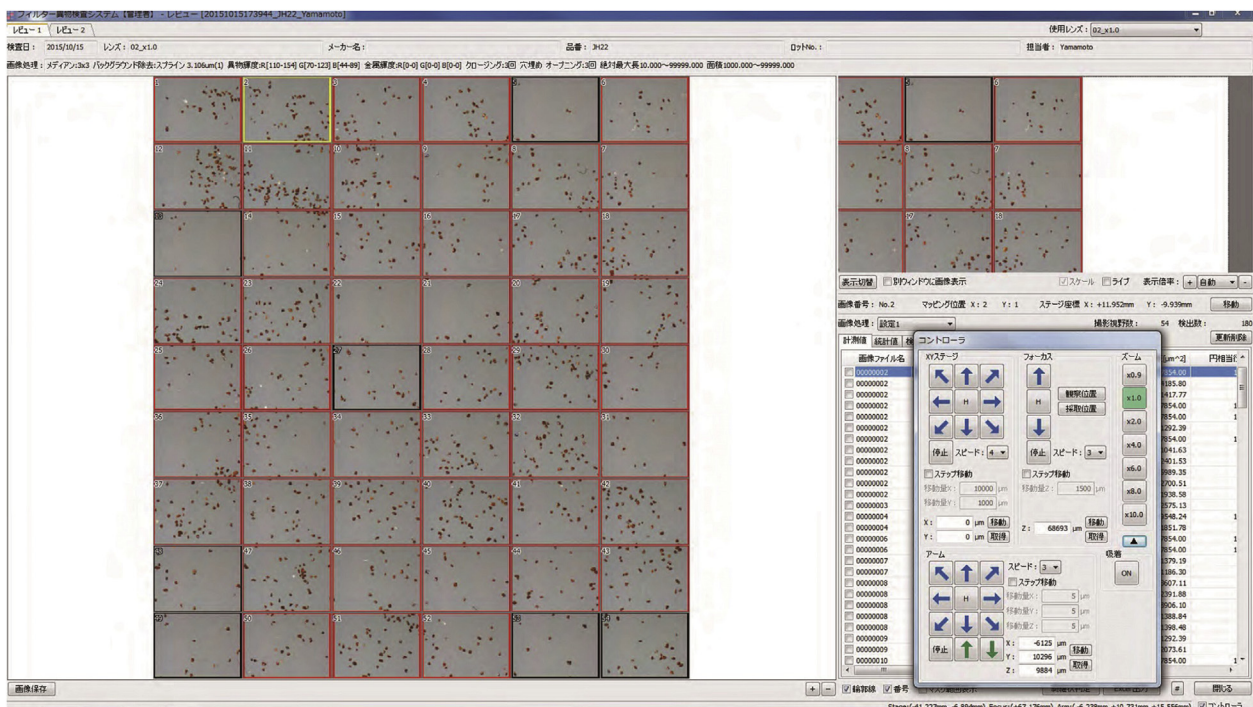
Figure 2. Image processing of target zircons by the AZS system on the monitor screen of the AZS machine. Heavy mineral grains including target zircons are randomly scattered on a target tray (made of acryl), which are scanned by the image processer to identify zircon grains. Samples are all from 3.0 Ga Jack Hills meta-conglomerate from Western Australia.

Figure 3. Thumbnail photo images of identified/registered zircon grains appearing on a monitor screen of the AZS machine. These images are recorded before the pick-up of zircon grains and the relocation from a target tray to capture tray.
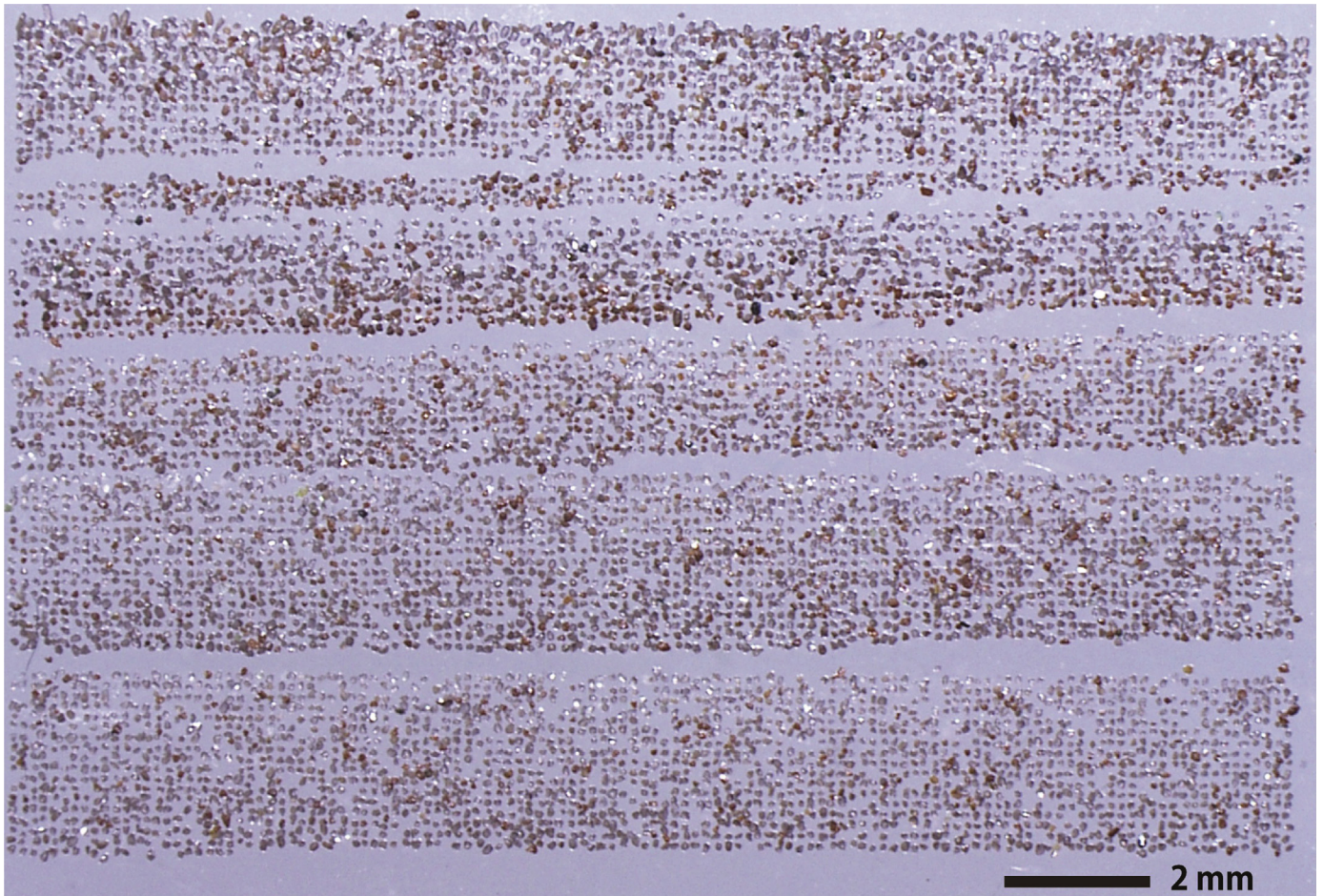

Figure 4. Organized alignment of selected zircon-like grains on a capture tray after transferring from a target tray. This image shows nearly 10,000 zircon grains systematically aligned on a target tray.

fraction, the next step was to use the signal intensity of Si, P, Ti, Fe, Y, and Zr of individual grains briefly monitored by LA-ICPMS. This analysis of the above elements, except for the Pb isotope ratio, is highly simplified and cannot be quantitatively accurate; nonetheless, the measured intensity is useful for knowing which elements are the major constituents of the measured grains. Consequently, this analysis is able to identify zircons and discriminate between other heavy minerals, such as rutile, monazite, and baddelyite in the heavy mineral fraction, as will be mentioned below.

3.2. Double-step dating: pre-dating and main dating

To identify zircons under the microscope, we empirically focus on color, reflectance and/or the shape of individual crystal grains. Through numerous pick-up processes, we have learnt that deep violet grains commonly yield relatively old, early Archean to Hadean radiometric ages. This color tendency is probably the result of accumulated fissions made by the decay of radiogenic uranium and thorium. Nonetheless, these criteria are often imperfect, owing to the various irregularities of the mineral grains. In fact, some Hadean grains are almost colorless; and some external features (crystal breakage, aspect ratio, surface smoothness etc.) vary considerably. In spite of the conventional manual pick-up, the newly designed separator cannot completely overcome these obstacles. Thus, even for the selected zircon fraction after the machine pick-up, we need to purify older grains by screening out younger ones as far as possible.

In order to preferentially collect older zircons, we introduced a new approach; that is direct Pb-Pb dating of the zircon surface by LA-ICPMS without any conventional preparation, e.g., mounting in resin and surface polishing, for observing internal textures (within-crystal core-rim relations and oscillatory zoning) using cathodoluminescence (CL). This measurement can obtain just the crude Pb isotope ratios in the surface area of zircons with a low degree of accuracy; however, using a quick scan by LA-ICPMS of multiple grains from the machine-selected zircon fraction, we can get guide signals particularly of potentially old zircons with higher $^{207}Pb/^{206}Pb$ ratios. After this quick selection, we can measure more precisely the Pb-Pb ages just of the identified promising zircons with a more sophisticated procedure we normally use for dating.

Zircon grains used for the analysis were attached on adhesive tape to a pyrex glass through the machine specification process. Then, the isotopic composition of Pb near the surface area of each grain was measured by LA-ICP-MS. There are both advantages and disadvantages of this approach, compared with normal *in-situ* U-Pb dating using a LA-ICP-MS. By skipping the mounting and polishing procedures, it is possible to shorten the total time required for the sample preparation. More importantly, the loss of material caused by surface polishing can be avoided with this method. On the other hand, deciding the analytical area with the guide by the observation with an optical microscope and CL image is almost impossible. In addition, it is difficult to measure the U-Pb age correctly and the precision of $^{207}Pb/^{206}Pb$ age could be worse than the normal method. However, for detecting Hadean zircons, the minimum age of the sample can be estimated by Pb-Pb dating with an adequate common Pb correction, even if the sample has experienced a certain degree of Pb loss. For the search of old materials, therefore, information about the minimum age of the sample is very helpful, and an increase in efficiency of the analyses would be advantageous in the search for old zircons.

In this study, we evaluated the efficiency of direct $^{207}Pb/^{206}Pb$ dating of unpolished zircons, and checked its reliability by re-analyzing the same sample with conventional sample preparation methods (i.e. mounting in resin, polishing with diamond paste and

observing its internal structure using a CL image) after the Pb-Pb dating of unpolished zircons.

3.3. High speed dating by multiple-ion counting ICP-MS

While double-step dating can shorten the time required for sample preparation, fast analytical technique for U-Pb isotope measurement is also important for hunting old zircons. Recently, a short time dating technique was reported using a LA-ICPMS equipped with multiple ion counting detectors (LA-MIC-ICPMS; Hattori et al., 2017; Obayashi et al., 2017). The multiple-ion counting detection system achieves both a high duty cycle (>70%) and a quick response time to a transient signal, and these capabilities allow a short analytical time for a single ablation pit (<1 s) and an applied analytical precision (<3%, Hattori et al., 2017). Hence, we employed a fast U-Pb isotope analysis of >2000 zircons, which were tweezed and lined up by the AZS machine, and then mounted in resin and polished.

3.4. Analytical method

The isotopic analysis of Pb of unpolished zircons was carried out using an Agilent 8800 quadruple ICP-MS (Agilent Technology) coupled to a NWR213 Nd:YAG laser ablation system (ESI) at Gakushuin University, Japan. To discriminate minerals other than zircons and to correct the isobaric interference on 204 amu from Hg, the counts of ^{29}Si, ^{31}P, ^{49}Ti, ^{57}Fe, ^{89}Y, ^{91}Zr, ^{202}Hg, ^{232}Th and ^{238}U were monitored, in addition to those of ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. From the monitoring of these elements, non-target minerals were effectively identified and excluded. The actual procedure for laser ablation and measurement by ICP-MS was as follows: gas blank counts were monitored for 5 s at first, and then laser ablation during 8 s was employed. In laser ablation, we waited for the first 3 s and the next signals for 5 s were integrated for further calculation. For the interval time of each analytical spot, we waited for 7 s because the 1/1000 washout time of the present LA-ICP-MS system is about 5 s. The total analytical time consumed for one grain is about 20 s and the capability of sample throughput is 180 grains per hour. For each 200−300 samples, NIST SRM610 was measured 3 times in order to calibrate the mass bias of Pb. In this experiment, 1321 zircon grains were dated. Subsequently, 52 zircon grains of those dated above were picked up and mounted in epoxy resin, and then polished using diamond paste with a diameter of 1 μm. After that, CL images were obtained using an INCA X-Sight 7582 (OXFORD Instruments) equipped with SEM (JEOL-JSM6060LV) at the University of Tokyo, Komaba. The resulting CL images were used for the determination of the analytical area by LA-ICP-MS.

In-situ U-Pb dating of polished surface was employed using a Nu Plasma II multiple collector ICP-MS (Nu Instruments) coupled to a NWR193 ArF excimer laser ablation system (ESI) at Kyoto University, Japan. The instrumental set up and operational conditions are similar to those previously studied (Hattori et al., 2017). We used two operational settings for the polished zircons in double-step dating and high speed dating. The total analytical times consumed for one grain in the case of double-step and high speed dating were 90 and 20 s, respectively. In high speed dating, 2378 zircons were completely analyzed, and grains that showed discordant U-Pb isotopic features (>5%) were excluded. Hence, 1926 concordant grains were used for further discussion.

In all datings in this study, ^{202}Hg was monitored and isobaric interference on ^{204}Pb from ^{204}Hg was subtracted assuming $^{204}Hg/^{202}Hg = 0.223$ (Blum and Bergquist, 2007). Common Pb correction was based on the ^{204}Pb-based method (Williams, 1998). The isotopic composition of common Pb was estimated assuming terrestrial Pb isotope evolution by a two-stage model (Stacey and

Kramers, 1975), through a five step iterative process. The age spectrum of resulting data was made with ISOPLOT 4.15 (Ludwig, 2003). Details of the analytical method are summarized in Supplementary file 1.

4. Results

4.1. High gain in capturing zircon

In order to complete one cycle of picking up one grain from the sample tray and placing it on the capture tray, it took ca. 1 min, thus the AZS machine can collect ca. 60 zircons and zircon-like grains in 1 h, or 600 grains in 10 h on average. For the heavy mineral fraction from the Jack Hills meta-conglomerate, one continuous operation for ca. 20 h collected 1496 grains (Fig. 3). After the present attempt, we needed to expand further the size range of zircons for capturing at more or less the same rate.

Checking the signal intensity of Si, P, Ti, Fe, Y, and Zr of individual grain surfaces was also successful after the AZS operation. We were able to collect 1321 zircon grains out of 1496 grains picked by the AZS machine, and the remaining 175 non-zircon grains were identified as rutile (113 grains), baddeleyite (8 grains), ferrioxide (6 grains, e.g. magnetite), phosphate (6 grains, e.g. monazite, apatite), quartz (5 grains), and unknown minerals (37 grains). After repeating a similar process with the AZS machine, we obtained a fair zircon capturing rate of nearly 90%.

### 4.2. Accuracy of the Pb-Pb age of unpolished zircons

Newly obtained ^{207}Pb/^{206}Pb ages of 52 zircon grains dated by the two methods (unpolished and polished) are shown in Fig. 5 and

detailed isotopic data are summarized in Supplementary file 2. For the direct dating of unpolished grains, ^{207}Pb/^{206}Pb ages were solely considered because it is difficult to calibrate the Pb/U fractionation correctly without surface polishing. In Fig. 5, Δm (%) is defined as follows: $\Delta m = ((Age)_{polished}/(Age)_{unpolished} - 1) \times 100$. Here, $(Age)_{polished}$ and $(Age)_{unpolished}$ represent ^{207}Pb/^{206}Pb age after common Pb correction for polished and unpolished zircons, respectively. From comparison, more than 90% of the values of Δm are distributed in the range from −10% to +10%. This indicates that the direct Pb-Pb dating method for the unpolished zircon has roughly 10% uncertainty at 90% confidence. As for the data with huge Δm values, these large deviations can be explained by the difference in the area actually analyzed by the two methods, or they can be related to the possible measurement of other tiny grains attached to the surface of the targeted zircons.

In our preliminary runs, out of the 1321 unpolished zircons with Pb-Pb ages by the direct analysis, we arbitrarily selected 22 grains with apparent Hadean ages. Out of these 22 grains, we confirmed a further 17 grains with Hadean ages by more reliable measurement after resin-mounting and polishing. Although still not achieving 100%, our approach was easily able to eliminate almost 98% of the post-Hadean zircons.

4.3. Results of direct and high speed dating

Through several runs by the AZS machine, we were so far able to detect nearly 42 grains of Hadean age including 4 grains with ages greater than 4.3 Ga, which correspond to the oldest age of the Earth's material (Fig. 6) by direct analysis of 1321 unpolished zircons. For these 4 grains, the resulting ages of unpolished and polished surface are as follows: 4373 ± 74 and 3600 ± 5 Ma (JH22-small mount-351), 4347 ± 91 and 4315 ± 7 Ma (JH22-2-437-1), 4353 ± 47 and
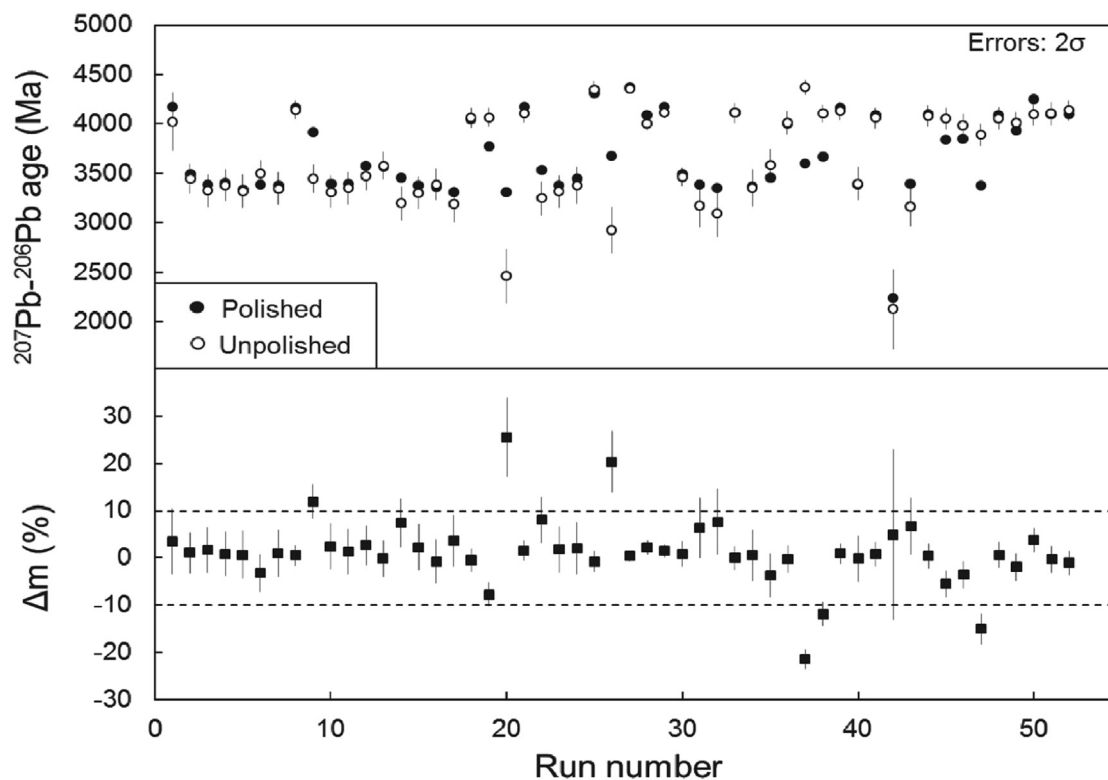

Figure 5. Comparison between the crude Pb-Pb dating for non-polished grains and more sophisticated U-Pb dating for the same but polished grains. Note that most grains have similar ages regardless of polishing in resin before dating. Solid square: deviation of Pb-Pb age between polished and unpolished zircon defined as: $\Delta m = ((Age)_{polished}/(Age)_{unpolished} - 1) \times 100$.
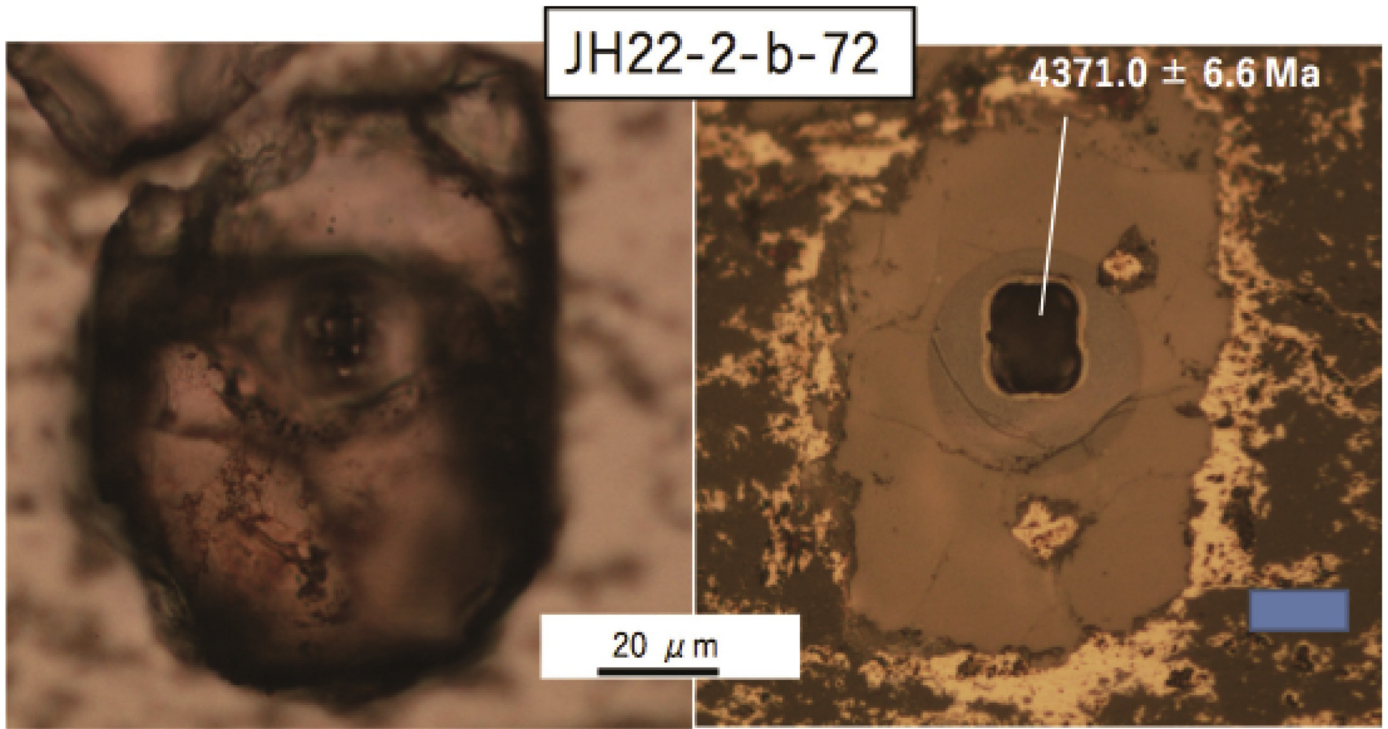
Figure 6. Photo images of the oldest zircons of over 4300 Ma from the mid-Archean (ca. 3.0 Ga) Jack Hills meta-conglomerate in the Yilgarn craton, Western Australia.
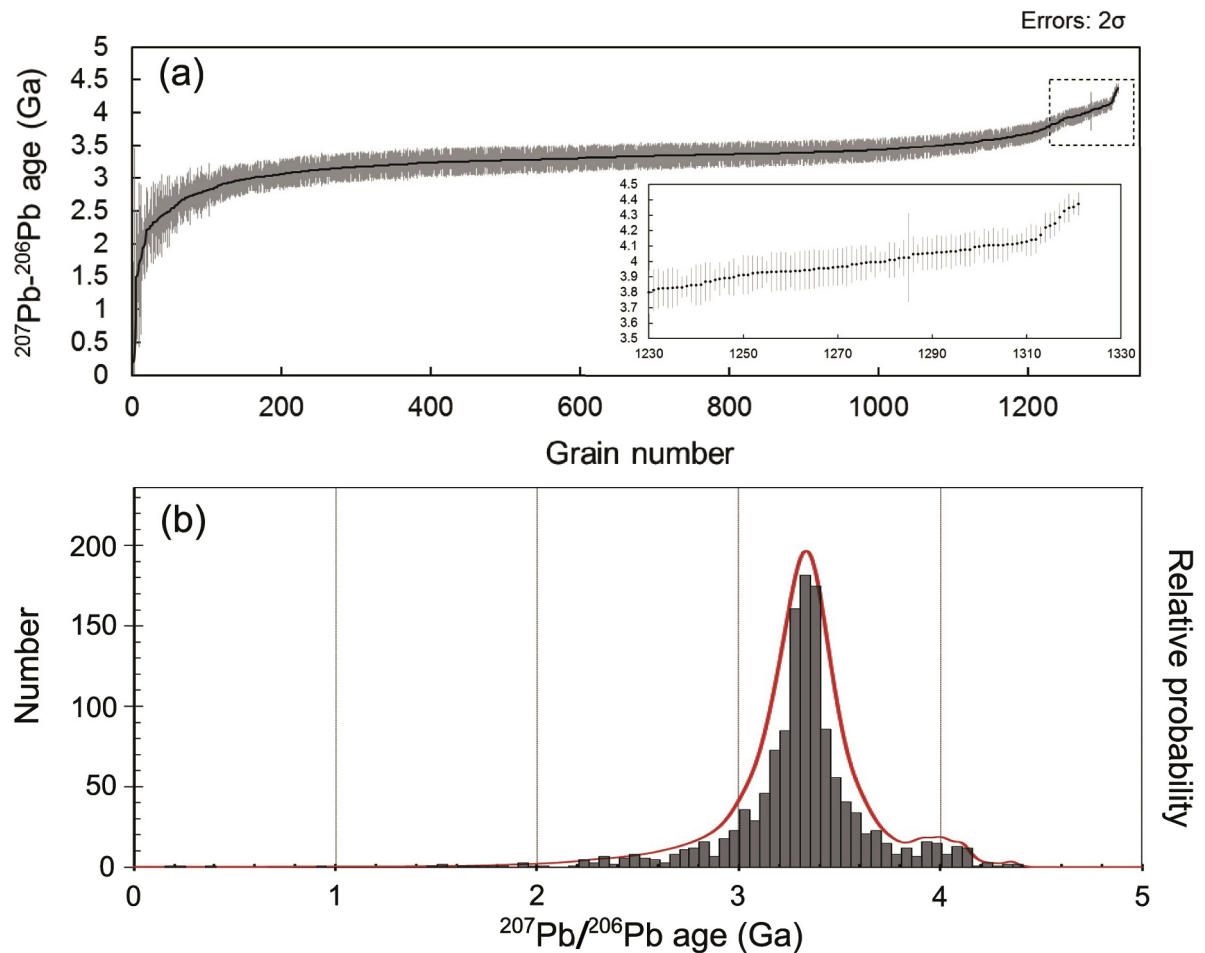
Figure 7. Age spectrum of the Hadean zircon grains separated from the Jack Hills meta-conglomerate by direct analysis of unpolished zircons. Out of ca. 1400 separated grains by the AZS machine, more than 42 Hadean zircons were obtained. Note that 4 zircon grains with the oldest ages over 4300 Ma were captured.
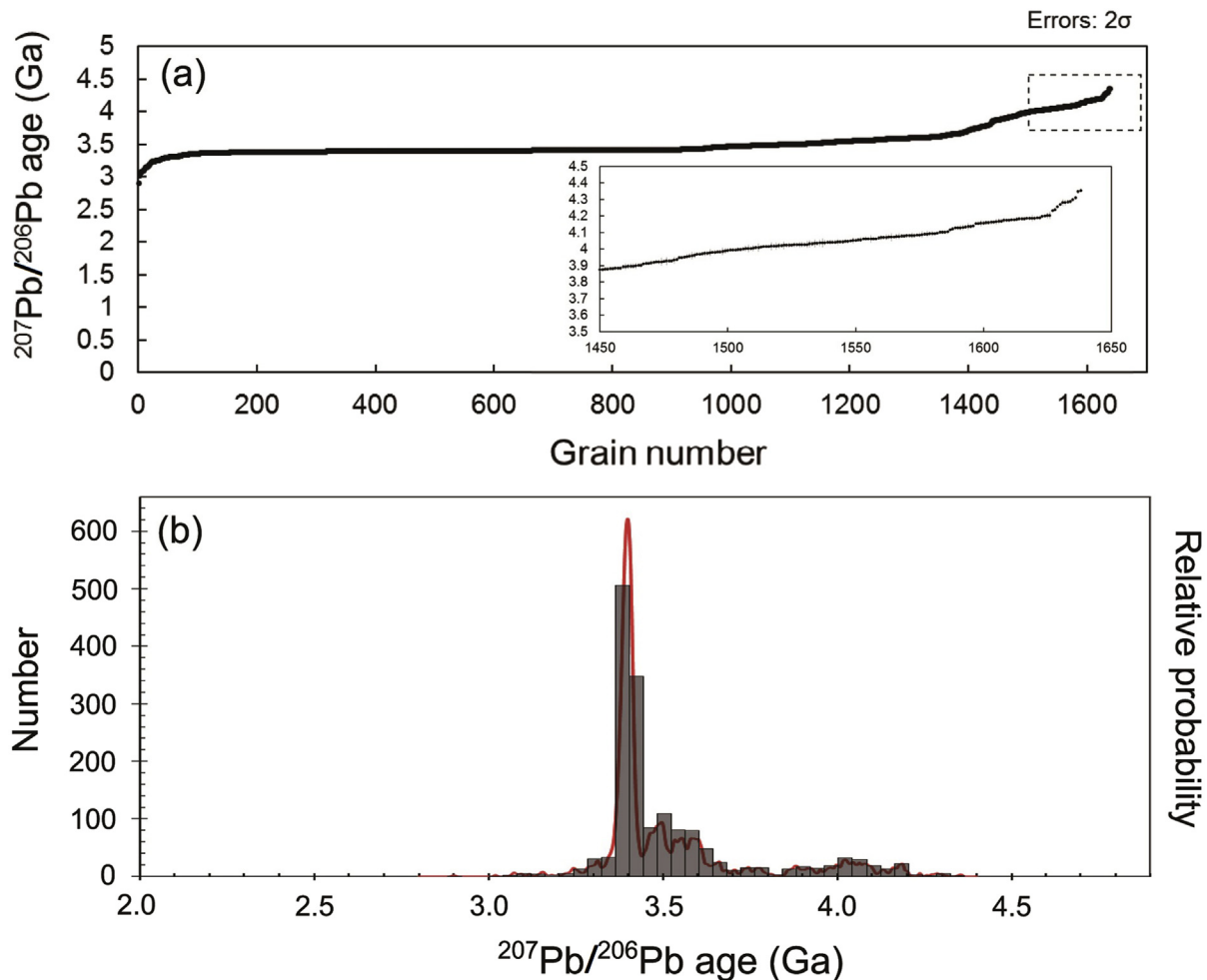
Figure 8. (a) Age spectrum of the Hadean zircon grains separated from the Jack Hills meta-conglomerate by the high speed analysis of polished zircons using LA-MIC-ICP-MS. (b) Out of ca. 3800 separated grains by the AZS machine, more than 152 Hadean zircons were obtained. Note that 5 zircon grains with the oldest ages over 4300 Ma were captured.

4371 $\pm$ 7 Ma (JH22-2-b-72), and 4329 $\pm$ 76 (JH22-small mount-16, unpolished data only), respectively (Supplementary files 2 and 3).

On the other hand, we obtained 152 Hadean zircons out of 1926 concordant grains, including 5 grains with ages greater than 4.3 Ga by the high speed dating method (Supplementary file 4). The oldest Pb-Pb age of these 5 grains is 4355 $\pm$ 9 Ma (JH-22-2-g-667). The resulting ages from direct dating and the high speed dating method are given in Figs. 7 and 8, respectively. The average error (2σ) of ^{207}Pb/^{206}Pb age is ca. 0.5%. This precision is enough to distinguish the difference of ca. 20 Ma among Hadean zircons. In total, 192 Hadean zircons out of the ca. 3800 Jack Hills zircons were detected in this study.

4.4. Hadean zircons collected

In this study the oldest zircon that we found has an age of 4371 $\pm$ 7 Ma (JH22-2-b-72). It shows nearly concordant analyses in the U-Pb isotope system; i.e., concordance is 100.8% and the ^{238}U/^{206}Pb age is slightly older than the ^{235}U/^{206}Pb age; it should be noted that the analytical uncertainty of the U-Pb age is about 0.4% (2σ). As seen from the above, the U-Pb age of this grain is reversely discordant to a slight degree (<1%), and this phenomena has been occasionally reported in Archean zircons, which have a high U content (>1000 µg/g) using an ion microprobe (Williams et al., 1984; Williams and Hergt, 2000; White and Ireland, 2012; Kusiak et al., 2013). One possible explanation for

this reverse-discordance is by the secondary mobilization of radiogenic Pb caused by high-temperature metamorphism (Kusiak et al., 2013). Nonetheless, in this study, the degree of reverse-discordance is relatively small and the influence on the ^{207}Pb/^{206}Pb age from the Pb mobilization is not so large (at least less than 15 Myr).

The oldest ^{207}Pb/^{206}Pb age that we obtained shows excellent agreement with the oldest age (4372 $\pm$ 6 Ma) previously reported by Holden et al. (2009) through the analysis of over 100,000 zircons from the Jack Hills conglomerate using an ion microprobe. Moreover, the resulting age spectrum shows a bimodal distribution with peaks close to ca. 3.3–3.4 Ga and ca. 3.8–4.2 Ga (Figs. 7 and 8). This unique age spectrum is consistent with those reported by many previous studies about the U-Pb dating of the Jack Hills zircons (Compston and Pidgeon, 1986; Maas et al., 1992; Amelin, 1998; Amelin et al., 1999; Mojzsis et al., 2001; Cavosie et al., 2004; Trail et al., 2007; Holden et al., 2009).

5. Discussion

5.1. Reliability of mineral separation by AZS

Our preliminary attempt to collect old zircons by the AZS machine produced positive results, as shown above. Through continuous operation for 20 h without a break, the machine could pick up

nearly 1500 zircon and zircon-like grains. This crude result roughly corresponds to a 2 day-long intense work by one well-trained person (e.g., S. Yamamoto) in collecting more or less the same number of grains from the same heavy mineral fraction. With further continuous tests with daily intermittent sample changes, the AZS system could collect nearly 10,000 zircon grains systematically aligned on a target tray in one week (Fig. 4). Judging from these results, the AZS machine has no doubt proved its high performance/capability compared to those of human labor by hand-picking.

For the next step after the mechanical pick-up by the AZS machine, a rapid check was made with a LA-ICPMS to detect non-zircon heavy minerals. The elimination of noise (non-zircon) grains, which are up to 10% in number, can upgrade considerably the reliable selection of targeted zircon grains. This 2-stepped dating approach without measuring unpromising zircons enhanced the efficiency of collecting Hadean zircons. We were able to separate 42 Hadean grains out of ca. 1400 zircons from the Jack Hills sample by direct analysis, and 152 grains out of ca. 2400 by the high-speed analysis, with an average percentage of gain at nearly 3 and 6%, respectively. This is comparable to or slightly greater than that of manual pick-up (ca. 2%), and the age spectra of AZS-picked zircons are more or less the same as those previously reported. After all, our preliminary test showed that the AZS system performed efficiently in selecting target zircons, with almost the same quality as human effort by hand-picking.

The remaining current practical problems of the prototype AZS machine include the stacking in a microtweezer; namely the interlocking of smaller plural grains within a fine-tube glass that prevents smooth capture/release of target grains. In order to avoid this, further modification to the microtweezer is needed.

5.2. Post-4.37 Ga continuous age spectrum of the Hadean zircons

Among the 194 Hadean zircons, 9 grains are older than 4300 Ma, with the oldest a 4371.1 ± 6.7 Ma zircon. These zircon ages are fully consistent with previously reported ages, with the oldest at 4372 ± 6 Ma, from the same geologic unit in Western Australia (Cavosie et al., 2004; Holden et al., 2009). Not necessarily the oldest, but a preferential collection of >4.0 Ga zircon is valuable in research on the early Earth.

The present capturing of 194 4.3–4.0 Ga zircons confirms that Hadean crust has been exposed to some extent and/or recycled on the surface at least until 3.0 Ga in the Yilgarn craton, as previously suggested. Besides the classical regions, such as the Slave province in northern Canada, the Yilgarn block in Western Australia, and the Anshan area in North China (e.g., Bowring and Williams, 1999; Wilde et al., 2001; Harrison, 2009), more occurrences of Hadean zircons have recently been reported from elsewhere, e.g. Brazil, Argentina, Antarctica, and South China (Paquette et al., 2015; Roberts and Spencer, 2015; Xing et al., 2015; Li et al., 2016). These examples support the idea that the active formation, probably of felsic crust, occurred during the Hadean on a global scale, and that some parts have remained and/or been recycled into Archean units.

This study also demonstrated that active magmatism and resultant formation of zircon-bearing crust had already occurred in the second half of the Hadean after 4.3 Ga. In general, zircons occur abundantly in felsic plutonic rocks such as granitoids in the modern Earth, in particular, along active continental margins with arc magmatism, whereas they are rare in mafic rocks (komatiite/basalt), and extremely rare in ultramafic rocks (peridotite).

The time of onset of plate tectonics has long been debated (e.g. Roberts and Spencer, 2015), and many researchers agree that the plate tectonic regime had already existed by the Mesoarchean (e.g., Hoffman, 1989; Card, 1990; Dirks and Jelsma, 1998; Korsch et al., 2011). Furthermore, some Japanese geologists promised that plate

subduction had started much earlier probably in Eoarchean time or even before that on the basis of the occurrence of 3.8–3.9 Ga accretionary complexes in Greenland and Labrador (Maruyama et al., 1991; Komiya et al., 1999, 2015; Maruyama and Komiya, 2011). The robust geological lines of evidence are in identifying ocean plate stratigraphy (OPS) and layer-parallel horizontal-shortening duplex structure, just like Phanerozoic examples (Isozaki et al., 1990; Matsuda and Isoaki, 1991; Isozaki, 2014).

Nonetheless, most Precambrian researchers are still conservative enough to assume that non-plate tectonic komatiitic/basalatic magmatism dominated during the Hadean–Eoarchean (e.g., Kramers, 2007; Altermann et al., 2012; Kamber, 2015; Roberts and Spencer, 2015) with regard to the much higher temperature gradients of the young planet compared with today. On the basis of Hf isotope, for example, Nebel et al. (2014) speculated that the first crust was mafic in composition; Kenny et al. (2016) even proposed a contribution of meteorite impacts in forming Hadean zircons.

On the other hand, oxygen isotope signatures and zircon thermometer of >4.0 Ga grains suggest that most Hadean zircons crystallized in a felsic magma at a relatively low temperature under water (Mojzsis et al., 2001; Watson and Harrison, 2005; Harrison et al., 2008). Igneous zircon crystallizes at ca. 700 °C under wet conditions, but at ca. 1400 °C under dry conditions. The Hadean zircons from the Jack Hills conglomerate show an almost continuous age spectrum from 4.3 Ga to 4.0 Ga with an increasing trend of dominance with time (Figs. 7 and 8), and this condition likely continued into Eoarchean times. These observations suggest the continuous production of zircon-bearing granitoids during the second half of the Hadean and in Eoarchean time. Clearly after the 4.5 Ga magma ocean stage on the ocean-bearing planet's surface, felsic igneous rocks similar to modern granitoids probably formed in primitive subduction zones in an arc-trench setting. Relatively steady-state subduction-related arc magmatism/crust formation probably continued during that time but all the putative volcanic arcs were small in size, not larger than modern intra-oceanic island arcs.

5.3. Hadean inselbergs in provenance

Regarding Archean tectonics, all the emergent land masses were probably composite blocks composed of plural collided island arcs (e.g., Hoffman, 1989; de Wit and Hart, 1993). Accordingly, we speculate that the provenances of Archean sedimentary basins, not only in Yilgarn but also in the rest of Archean cratons in the world, were such small land masses composed of amalgamated island arcs, which once featured Hadean granitic crusts to a large extent, or at least they hosted frequent recycling of Hadean crustal material, such as zircon, until the mid-Archean time.

For providing Hadean zircon in Archean terrigenous clastics, there is an alternative mechanism related to the heavy bombardment of extraterrestrial objects during the Hadean/Eoarchean (Marchi et al., 2014). As observed in a lunar regolith, material recycling from the primordial crust is possible (Borg et al., 2015; Hopkins and Mojzsis, 2015), and repeated bombardment of extraterrestrial objects may have excavated buried primordial Hadean crusts with zircons to be provided as recycled material afterwards, as long as the impact was not one big one, but multiple small ones for a longer duration.

After all, we must admit that Hadean material existed to some extent until mid-Archean time on the surface throughout most of the Archean cratons. Most Hadean zircons were not directly from solid rock exposures on the ground but were recycled from older sedimentary rocks; nonetheless we cannot rule out the possibility of direct exposure of Hadean rocks in inselbergs (small island-like monadnock hills) within extensive Archean crustal rocks.

5.4. A limit for the oldest zircons on Earth?

Except for the whole-rock Nd-Sm model age of 4280 Ma reported from the Nuvvuavittuq gneiss in NE Canada (O'Neil et al., 2008), rocks with precise mineral ages older than 4000 Ma have never been reported. With our present results, we confirm that the oldest mineral age of 4370 Ma for the Earth's crustal material is recorded in the detrital zircon grains from the Jack Hills meta-conglomerate. It is important to recognize another 9 ca. 4370 Ma zircons, in addition to the previously reported 3 coeval grains (Cavosie et al., 2004; Holden et al., 2009). At present, all the documented age spectra of detrital zircons from the Jack Hills meta-conglomerate appear to be consistent, and may suggest that the Earth's oldest zircons had an apparent age limit of around 4370 Ma.

In contrast, lunar rock samples brought back by the Apollo 12, 14, 15 and 17 missions yielded much older zircons up to 4440 Ma (Borg et al., 2015; Hopkins and Mojzsis, 2015); nonetheless, numerous dated zircons demonstrated a significant age cluster around 4345 Ma (e.g., Meyer et al., 1996; Pidgeon et al., 2007; Grange et al., 2009; Nemchin et al., 2009; Taylor, 2009; Liu et al., 2012). Considering the evolution of lunar crust after the initial magma ocean stage, possible scenarios for explaining this ca. 4.3 Ga zircon event have been proposed, e.g. the resurfacing/restructuring of primary crust by later asteroid bombardment etc. (e.g., McLeod et al., 2016).

The present results positively suggest an apparent coincidence in age between the oldest group of Earth's zircons and the significant peak in lunar zircons, therefore, a certain ubiquitous episode occurred in the near-Sun environment of the young solar system during the planetary formation of the Earth, Moon, and possibly other terrestrial planets (Mercury, Venus, and Mars). The apparent difference between the terrestrial and lunar zircons exists in the height of their age peaks; however, this can be blamed on the multiple episodes of impact on the moon and associated material recycling into the regolith, of which records were not preserved on the Earth.

In this regard, a recent proposed two-stepped formation scenario of the Earth (ABEL model by Maruyama and Ebisuzaki, 2017) appears promising; i.e. the initial formation of a dry planet solely from accumulated enstatitic chondrites at 4.55 Ga and the secondary addition of volatile elements by icy planetesimals after 4.37 Ga to start the change of a dry planet into a water-lain one. Our preliminary study has identified tiny inclusions of apatite, $Ca_5(PO_4)_3(F,Cl,OH)_2$ in composition, within 2 grains of the 4.3 Ga zircons (will be reported elsewhere by S. Yamamoto et al.). This confirms that the 4.3 Ga Earth had already acquired liquid water on its surface that enabled the crystallization of hydrous minerals, such as apatite, through magmatism in shallower parts of the crust. In order to prove or disprove this scenario or to propose other options, we need to obtain more solid lines of evidence in particular, from more Hadean zircons, and to determine their ages and characteristics.

6. Conclusions

In order to find and collect the oldest material of the Earth, we recently developed a new machine, i.e. an automatic zircon separator (AZS), which is designed for improving the efficiency of mineral separation compared with conventional procedures by an order of magnitude. The proto-type of the AZS machine was tested for its practical efficiency. We used Pb-Pb dating of unpolished zircons to select relatively older zircons before we undertook the high-resolution U-Pb dating after polishing. Fast U-Pb isotope analysis using LA-MIC-ICPMS is helpful for such a Hadean investigation. Our preliminary results from the well-known Archean conglomerate of Jack Hills in Western Australia are positive; we were able to detect at least 2 grains of the Earth's oldest (over 4350 Ma) zircons out of about ca. 3800 checked grains. Still under progress, this machine provides a hopeful message for all zircon seekers whatever their perspectives.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.gsf.2017.04.010.

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