In-Situ U–Pb Dating of Apatite by Hiroshima-SHRIMP: Contributions to Earth and Planetary Science

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The Sensitive High Resolution Ion MicroProbe (SHRIMP) is the first ion microprobe dedicated to geological isotopic analyses, especially in-situ analyses related to the geochronology of zircon. Such a sophisticated ion probe, which can attain a high sensitivity at a high mass resolution, based on a double focusing high mass-resolution spectrometer, designed by Matsuda (1974), was constructed at the Australian National University. In 1996, such an instrument was installed at Hiroshima University and was the first SHRIMP to be installed in Japan. Since its installation, our focus has been on the in-situ U–Pb dating of the mineral apatite, as well as zircon, which is a more common U-bearing mineral. This provides the possibility for extending the use of in-situ U–Pb dating from determining the age of formation of volcanic, granitic, sedimentary and metamorphic minerals to the direct determination of the diagenetic age of various meteorites, which can provide new insights into the thermal history on the Earth and/or the Solar System. In this paper, we review the methodology associated with in-situ apatite dating and our contribution to Earth and Planetary Science over the past 16 years.

Keywords: in-situ analyses, U–Pb dating, SIMS, ion microprobe, chronology

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INTRODUCTION

The U–Pb system is a useful chronometer for understanding the formation and/or the evolution of the Solar System including the Earth, Moon, Mars and asteroids. Since the monumental studies reported in 1955, an enormous amount of work related to the Pb–Pb dating of meteorites has been reported via the use of TIMS (Thermal Ionization Mass Spectrometry). These studies showed that the ages for the formation of chondrites, Earth and Moon are effectively equal to the age of the Solar System (ca. 4.6 billion years ago. Hereafter, referred to as "Ga").

After the pioneering studies involving ion microprobe U–Pb dating in the 1970s, Sensitive High Resolution Ion MicroProbes (SHRIMP) were developed to examine individual minerals and/or the internal texture of single grains in order to obtain relevant isotopic and geochronological data. The design of SHRIMP I, a proto type of SHRIMP, was based on an ion optical description developed by Matsuda for a double focusing high mass-resolution spectrometer. In order to reduce second-order aberrations, an electrostatic quadrupole lens was located between the ESA (ElectroStatic Analyzer) and the magnet, the radii of which are 1.272 m and 1.000 m, respectively. After a re-evaluation of the design, the commercial version of SHRIMP (SHRIMP II) manufactured by Australian Scientific Instruments Pty Ltd. was made commercially available (Fig. 1).

The most common application of SHRIMPs has been the U–Pb dating of the mineral zircon (ZrSiO4), the findings of

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Fig. 1. Schematic diagram of the SHRIMP II instrument (upper panel; quote from ref. 11) and a photograph of the Hiroshima-SHRIMP (lower panel).
which placed significant constraints on the evolution of the Earth; e.g. (1) evidence from detrital zircon for the existence of a continental crust and oceans on the Earth at 4.4 Ga,
(2) Oxygen-isotope evidence from ancient zircons for the presence of liquid water on the Earth’s surface at 4.3 Ga,
(3) evidence for life on Earth prior to 3.85 Ga,
(4) the presence of a geomagnetic field strength at 3.4 Ga, as recorded in single silicate crystals,
(5) Iron deposits at 1.88 Ga as a consequence of rapid crustal growth,
(6) Early Cambrian ocean anoxia in the South China area,
(7) Oxygen-isotope evidence from ancient zircons for the existence of a continental crust and oceans on the Earth at 4.4 Ga,
(8) Iron deposits at 1.88 Ga as a consequence of rapid crustal growth,
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(10) evidence from detrital zircon for the existence of a continental crust and oceans on the Earth at 4.4 Ga,
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(16) Oxygen-isotope evidence from ancient zircons for the existence of a continental crust and oceans on the Earth at 4.4 Ga,
(17) Iron deposits at 1.88 Ga as a consequence of rapid crustal growth,
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(20) Oxygen-isotope evidence from ancient zircons for the presence of liquid water on the Earth’s surface at 4.3 Ga,
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(22) the presence of a geomagnetic field strength at 3.4 Ga, as recorded in single silicate crystals,
(23) Iron deposits at 1.88 Ga as a consequence of rapid crustal growth,
(24) Early Cambrian ocean anoxia in the South China area,
(25) evidence from detrital zircon for the existence of a continental crust and oceans on the Earth at 4.4 Ga,
(26) Oxygen-isotope evidence from ancient zircons for the presence of liquid water on the Earth’s surface at 4.3 Ga,
(27) evidence for life on Earth prior to 3.85 Ga,
(28) the presence of a geomagnetic field strength at 3.4 Ga, as recorded in single silicate crystals,
(29) Iron deposits at 1.88 Ga as a consequence of rapid crustal growth,
(30) Early Cambrian ocean anoxia in the South China area.

In 1996, the first SHRIMP instrument in Japan was installed at Hiroshima University (Fig. 1). Since then, research has focused on the in-situ U–Pb dating of apatite minerals as well as zircon, which is also a possible host phase for U and has a higher closure temperature of 500–600°C. Since mineral apatite occurs more widely than zircon, this development provides the possibility for extending the use of SHRIMP from determining the age of formation of volcanic glass to the direct determination of the diagenetic age of fossils. In this paper, we provide an overview of analytical methods for in-situ apatite dating, and some highlights of our recent results.

**ANALYTICAL CONDITIONS**

The sample surface is polished using 1/4μm diamond paste and observed by EPMA (Electron Probe MicroAnalyzer) and/or SEM-EDS (Scanning Electron Microscopy-Energy Dispersive Spectroscopy). After this, following cleaning with ethanol, to minimize surface contaminating Pb, the thin section was gold-coated to prevent a charge from developing on the sample surface during SHRIMP analyses. In order to further reduce the very small Pb interference on the ‘Pb’ peaks, the thin-section was evacuated in a “pre-load chamber” overnight (“Vacuum lock” shown in Fig. 1). An important final step before the actual analysis, involves rastering the primary ion beam over the entire sample surface for 3 min in order to remove any remaining possible contaminants.

A few nA O_{2}^{−} primary beams with an acceleration voltage of 10kV was focused to sputter an area ~10μm in diameter on the phosphates. The positive secondary ions were thereby extracted and detected on a single electron multiplier by peak switching. For the U–Pb dating of apatites, the mass resolution was set to ~5800 at 208Pb for U–Pb analyses. The magnet was cyclically peak-stepped from mass 159 u to mass 254 u as follows: 40Ca, 238U+/, 202Hg, 204Pb, 206Pb, 208Pb, 238U, 232ThO, and 230UO. For example, the mass peak for 182Tb (158.925 u) is clearly separated from that of the matrix peak of 40Ca, 238U+/, (158.884 u), and that of 206Pb (205.977 u) is clearly separated from that of 182Tb (205.928 u) at a mass resolution of 5800 and no significant isobaric interference in this mass range for the apatite was detected, except for interference by Hg on 204u and 206Pb on 204u. Although their effects would be negligible in most cases, it is necessary to monitor the 202Hg and 204Pb counts to apply appropriate corrections.

**U–Pb CALIBRATION METHODS**

It is well known that observed Pb/U ratios vary with UO/U ratios even in the homogeneous zircon standards, in which the elemental ratios of Pb/U should be identical, as predicted by the Local Thermodynamic Equilibrium model and this can be used to calibrate Pb/U in geochemistry. The relationship between Pb/U and UO/U can be determined empirically as being dominated by a near-quadratic component as follows

\[
\frac{182\text{Pb}}{238\text{U}}_{\text{sample}} = A \times \frac{182\text{Pb}}{238\text{U}}_{\text{std}} ^{31P16O3} = 0.002717 \pm 0.000002
\]

where \(A\), \(\alpha\) and \((182\text{Pb}/238\text{U})_{\text{std}}\) are constants, and \((182\text{Pb}/238\text{U})_{\text{sample}}\) and \((182\text{Pb}/238\text{U})_{\text{sample}}\) are the observed ion ratios of the sample. The constant \(A\) and \(\alpha\) can be obtained by repeated measurements of a standard mineral and, experimentally, \(\alpha\) should be nearly 2.11,12 This experimental law also can be applied to U–Pb systematics in apatites (Fig. 2). A similar equation also describes the U–Pb secondary ion emission data from other minerals such as monazite, titanite, baddeleyite, rutile. Therefore, Williams13 proposed that the correlation between secondary ion relative sensitivity factors and molecular speciation would be controlled by a fundamental physical process that does not depend on mineral species and instruments.

**TOTAL U/Pb ISOCHRON METHODS FOR Apatite U–Pb DATING**

In the case of ion microprobe U–Pb zircon dating, the expected initial lead based on the U–Pb evolution model is subtracted from the observed lead signals. Since the initial lead content in zircon is extremely low (typically, \(206\text{Pb}_{\text{initial}}/206\text{Pb}_{\text{total}}\) is less than 0.01, mostly 0.005), calibrated ages are not so sensitive to the models used, i.e., the “single stage model” and/or the “two stage model”13. This calibration method can be used to obtain information on age from an individual zircon grain. On the other hand, apatite mineral contains low levels of initial lead (typically, \(206\text{Pb}_{\text{initial}}/206\text{Pb}_{\text{total}}\) in the ranges from 0.01 to 0.5). Therefore, isochron age where both age and initial lead composition are free parameters would be superior to the conventional zircon method, because the obtained ages are sensitive to the U–Pb evolution model used and require the assumption of \(\mu\)-values (208U/204Pb). For example, since the \(\mu\)-values of the Moon have been highly debatable (from 10–100; for a review, see ref. 60), the age calibration of apatite from the Moon is a subject that must be addressed. Moreover, it should be noted that it would be a demerit where only one (or two in some cases) age information data sets from a number of apatite grains are obtained by an isochron

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method in comparison with the conventional calibration for zircon.

For an improved age calibration from an obtained U–Pb data set, we adopt a more advanced "Total Pb/U isochron method" in the 238U/206Pb–207Pb/206Pb–204Pb/206Pb 3-D space, pioneered by Levchenkov and Shukolyukov61) (for details, see refs. 62–64). Cogenetic samples with an undistributed U–Pb system that share the same common-Pb isotopic composition must define a line in 238U/206Pb–207Pb/206Pb–204Pb/206Pb space, whose intersection with the 238U/206Pb–207Pb/206Pb plane must fall precisely on the U–Pb Concordia curve, and whose intersection with 207Pb/206Pb–204Pb/206Pb is the isotopic composition of commonly occurring Pb. The crucial advantages of this method are that it is not necessary to know the isotopic composition of common Pb in contrast to the conventional Concordia diagram, and that both 238U and 235U decay schemes are used simultaneously, yielding a smaller justifiable age uncertainty for the case of U–Pb systematics.64) For the concordia case, the observed data are expressed by LINEAR regression in 3-D space (Fig. 3 left). On the other hand, for the discordia case, the plotted data in 3-D space are expressed by PLANAR regression (Fig. 3 right). In general, the PLANAR regression for U–Pb discordia data in the 238U/206Pb–207Pb/206Pb–204Pb/206Pb 3-D space can be interpreted by two kinds of geological cases.66 One is the combination of a linear discordia on the 238U/206Pb–207Pb/206Pb plane and one point of the common Pb component on the 207Pb/206Pb–204Pb/206Pb plane (case I). In this case, both the upper and lower intercept ages are geologically valid, corresponding to a formation age and an alteration age, respectively. Another case is the combination of one concordant age on the 238U/206Pb–207Pb/206Pb plane and a mixing line on the 207Pb/206Pb–204Pb/206Pb plane (case II). Although the upper intercept age is not a geological age in case II, the lower intercept ages are geochronologically valid in both cases I and II. In following chapters, we overview our research findings obtained using these methods.

DIRECT U–Pb DATING OF BIOLOGICAL MATERIALS

In the past few decades, the direct dating of sedimentary rocks has enjoyed only limited success with Pb isotopic analyses of metamorphic carbonates.65,66) This is partly due to complex post-depositional histories such as diagenesis with U expulsion and/or Pb incorporation or exchange under the influence of pore fluids in sediments.67) Based on Oxygen isotopic records, Karhu and Epstein68) suggested that apatite may be more stable and more resistant to post-depositional alteration than calcite. Cherniak32) and Cherniak et al.69) pointed out that the diffusion of Pb in apatite was significantly smaller than that in calcite, suggesting a higher
closure temperature and resistance to various thermal effects. If the direct U–Pb dating of a fossil itself is possible, the method could have a great impact on the origin and evolution of life. For the first step of this research project, Sano et al.37) directly investigated apatite from sediment sequences from Akilia island, in southwest Greenland, that are more than 3.85 Ga in age. SHRIMP isochron data suggested an age of about 1.5 Ga, these apatites in Akilia island experienced a metamorphic event of about 600°C that might have disturbed the carbon isotope system.37)

Sano and Terada70) also found that the abundance of 238U in small areas (about 250 μm × 250 μm) of a fossil tooth from a Permian shark also varied significantly from 10 ppm to 100 ppm and its distribution indicates an apparent coincidence with radiogenic 206Pb, suggesting that the success of the ion microprobe dating depends on the heterogeneity of diagenetically incorporated U on a scale of a few hundred μm and the consequent variations in Pb isotopic distributions using a high-spatial resolution of the ion micro probe (typically, 10–30 μm). Since the direct dating of fossilized teeth was first successfully completed70) using the ion microprobe 238U–206Pb isochron method, this technique was subsequently extended to a Carboniferous conodont via the total Pb/U isochron method,38) Silurian conodonts via the 238U/206Pb–207Pb/206Pb–204Pb/206Pb 3-D isochron method.40) These results have convincingly shown that the U–Th–Pb isotopic systems of fossil apatite can yield credible age data with a reasonable degree of precision.

THERMAL HISTORY OF LUNAR MARE BASALT

In the chronology of planetary science, an “absolute age” based on U–Pb systematics is crucial to understanding the onset and evolution of the solar system,1–9) because “relative ages” such as for Al–Mg, Mn–Cr systems are only available for the early solar system (within tens of millions of years from the beginning). Moreover, except for lunar highland rock71) and some eucrites,72,73) the occurrence of zircon is very rare in extraterrestrial materials. Because phosphates like apatite are often the main host phase of U in extraterrestrial materials, in-situ U–Pb apatite dating has the potential to provide us with new insights into the evolution of the Solar System. Since we established in-situ apatite dating,25) we have been successfully applied the approach to the chronology of the solar system.41–53) The most remarkable impetus is to decipher the thermal history recorded in lunar meteorites, because chronological studies of lunar meteorites are typically difficult because of the complexity of the texture of polymict breccias, and in some cases, their radiometric “clocks” typically have been disturbed by subsequent impact events.

Figure 4 shows a comparison of the total isochron diagram of a launch-paired lunar meteorite of EET 87521 (left top and bottom) and EET96008 (right top and bottom). The U–Pb systematics of EET 87521 is concordant and the plotted data in 3-D space are in good agreement with linear regression data, giving an apatite formation age of 3.53 ± 0.11 Ga.48) On the other hand, that of EET 96008 is discordant (scattered in the 207Pb/206Pb–204Pb/206Pb plane), and the plotted data in 3-D space are well expressed by planar regression, giving a formation age of 3.57 ± 0.10 Ga and an alteration age of 0.10 ± 0.13 Ga.47) It should be noted that the formation age of these meteorites are quite consistent with each other.

Fig. 4. Comparison of the launch-paired lunar meteorite of EET 87521 (left top and bottom) and EET96008 (right top and bottom). The U–Pb systematics of EET 87521 is concordant and the plotted data in 3-D space are well expressed by linear regression, giving an apatite formation age of 3.53 ± 0.11 Ga.48) On the other hand, that of EET 96008 is discordant (scattered in the 207Pb/206Pb–204Pb/206Pb plane), and the plotted data in 3-D space are well expressed PLANAR regression, giving a formation age of 3.57 ± 0.10 Ga and an alteration age of 0.10 ± 0.13 Ga.47) It should be noted that the formation age of these meteorites are quite consistent with each other.
discordant (scattered in $^{207}\text{Pb}/^{206}\text{Pb}$–$^{204}\text{Pb}/^{206}\text{Pb}$ plane; see the right-upper panel in Fig. 4), and the plotted data in 3-D space are a well expressed PLANAR regression, giving a formation age of 3.57 ± 0.10 Ga and an alteration age of 0.10 ± 0.13 Ga. It should be noted that the formation age of these meteorites are quite consistent with each other and for the case of EET 96008, the alteration age possibly due to the impact age are also obtained. Thus, these results successfully demonstrate that U–Pb systematics of apatite grains has the potential to provide, only formation age but also alteration age by assessing the two U decay series.

Figure 5 illustrates the distribution of formation ages of basaltic lunar meteorites coupled with data determined by conventional methods, which have been reported in previous studies. Here, the red and blue data were obtained by Hiroshima-SHRIMP and conventional methods, respectively. In comparison, the age distribution of samples collected by Apollo missions and Luna Missions are shown. In general, the high-Ti (HT) basalts from the Apollo 11 and Apollo 17 sites are relatively old; commonly ranging in age from 3.5 to 3.9 Ga. In contrast, low-Ti (LT) mare basalts samples are generally younger; ranging in age from 3.1 to 3.4 Ga, although some exceptions exist (Apollo 14 mare-basalts have ages from 3.9 to 4.2 Ga). Based on the available data for Very-low Ti (VLT) basalts, Nyquist et al. suggested that the formation ages of VLT mare-basalts for Luna 24 are younger at 3.2–3.3 Ga. On the other hand, the age distribution of lunar meteorites that are possibly derived from unexplored regions of the Moon, show magmatic activity, spanning a billion year from 3.9 to 2.8 Ga, consistent with those of the Apollo and Lunar collection. However, our new findings suggest that each trend for the age distribution of LT and VLT basalts are different from those of collected samples. Especially for the VLT basalt magmatism, our results clearly demonstrate that the thermal activities recorded
in VLT basaltic meteorites are quite different from those from regions of the Moon explored by the Luna mission (3.2–3.3 Ga), and indicate protracted VLT basalt volcanism on the Moon, which appears to have spanned from 4.35 Ga to 2.9 Ga ago. It should be noted that the ancient age of 4.35±0.15 Ga for Kalahari 009 suggests that the basaltic volcanism on the Moon started relatively soon after its formation and differentiation.\(^8\)

**REMARKS**

As remarks, Fig. 6 illustrates the empirical relationship between age uncertainties and the absolute ages of various terrestrial/extraterrestrial samples that we have obtained over the past 16 years. Here, it should be noted that these analytical conditions are different (e.g. primary beam size from about 5 to 30 micron, accumulation time from 20 to 120 min). The uncertainties associated with the determined age depends on not only the counting statistics of Pb (corresponding to, age of the sample and/or U content) but also the heterogeneity of U–Pb ratios in the sample because of the isochron method used. Although about a 10% uncertainty is too large in comparison with those of other conventional methods, such as TIMS (about a 0.01‰ uncertainty at around 4.6 Ga\(^6\)), deciphering the thermal history of polymict breccia meteorites (mineral aggregation consisting of individual grains of which the origin and onset are different) and/or the collected fine particles from the Itokawa asteroid remains a crucial issue.\(^8\)

In summary, we established in-situ U–Pb dating methods using Hiroshima-SHRIMP. In general, the in-situ analysis of apatites can be very useful, because it is a more common accessory mineral that includes U. In actual fact, however, it is NOT ALWAYS powerful in comparison with the conventional TIMS method and/or zircon individual dating, because of a quasi-destructive analysis, common lead and low U contents can have an effect on the analysis. Therefore, the availability and feasibility of this technique strongly depend on the characteristics of the samples being considered and scientific issues (for a mineral aggregation sample without any zircon, with different origins). For future prospects, the robust estimation of the initial lead composition, the developments of multi-collector systems and/or post-ionization methods using high-intensity pulsed-lasers would be desirable.

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