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Report

In-situ U–Pb age determination of titanite by LA-ICP-MS

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Abstract: U–Pb dating of titanite could constrain the timing of its crystallization and cooling associated with thermal processes such as magmatic and metamorphic events, owing to high U and Pb contents in titanite. In this study, we performed *in-situ* U–Pb dating of titanite standard (MKED1: ca. 1518 Ma) by using a 193-nm ArF Excimer laser with a single-collector ICP-MS, and inspected the matrix effects caused by difference of external standard materials (titanite, zircon, and synthetic glass). The $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ ages of MKED1 corrected by the combination of BLR-1 titanite and NIST SRM 612 glass were almost consistent with the reference ages. On the other hand, those ages by the combination of 91500 zircon and NIST SRM 612 were ~12 % younger than the reference values. Our results indicate that fractionation of U/Pb ratios is significantly different between titanite and zircon during LA-ICP-MS U–Pb age analysis, and same-matrix minerals should be used as the external standards for fractionation corrections during *in-situ* LA-ICP-MS titanite U–Pb analysis.

I. Introduction

Isotopic geochronology could unravel the time-scale information of complex geological processes. In particular, U–Pb dating of accessory minerals have become a common geochronological method since 2000 due to recent advance in *in-situ* microanalyses such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and secondary-ion mass spectrometry (SIMS). Titanite ($CaTiSiO_5$) is one of suitable minerals for U–Pb isotopic dating because of high U contents from 10 to 100 ppm (e.g., Frost et al. 2000) and a ubiquitous appearance in various igneous and metamorphic rocks. Moreover, as its closure temperature of U–Pb system has been estimated to be from 650 to 700 °C (Cherniak 1993, Frost et al. 2000, Spencer et al. 2013, Stearns et al. 2015), it is used as an indicator of thermochronometer for the temporal and spacial evolution of not only the host rocks but also the whole of geological bodies. Therefore, the titanite U–Pb isotopic dating has become widely popular in earth science and material science fields (e.g., Aleinikoff et al. 2007, Sun et al. 2012, Spandler et al. 2016).

Many studies suggest that the matrix effect of the LA-ICP-MS significantly influences the fractionation of U/Pb ratio between different matrix materials during LA-ICP-MS U–Pb dating (e.g., Black et al. 2004, Storey et al. 2006, 2007, Sun et al. 2012). Therefore, it is possible that different-matrix minerals are not used as external standards for fractionation correction for LA-ICP-MS titanite U–Pb age determination. In this study, to verify whether precise *in-situ* titanite U–Pb age can be obtained by using LA-ICP-MS in Okayama University of Science (OUS), we analyzed the MKED1 titanite standard by using variable external standards (zircon, titanite, and glass), and inspected the matrix effect of different minerals as U–Pb fractionation corrections.

II. Descriptions and preparations of titanite standards

We prepared two titanite standards of BLR-1 and MKED-1. The former mineral was used as an external standard for the latter. Also, 91500 zircon and NIST SRM 612 were analyzed as external standards, and their information has already been described in the previous study by Aoki et al. (2019). Those titanite standards were mounted on a 12-mm acrylic disc and polished before the analysis.

BLR-1 titanite is a metamorphic megacryst collected in Bear Lake Diggings locality, Ontario, Canada. The U–Pb dating by ID-TIMS yields the weighted-mean $^{207}Pb/^{206}Pb$, $^{206}Pb/^{238}U$, and $^{207}Pb/^{235}U$ ages with 2σ uncertainties are 1049.9 ± 1.3 Ma (MSWD = 2.9), 1047.1 ± 0.4 Ma (MSWD = 0.56) and 1048.0 ± 0.7 Ma (MSWD = 2.8) (Aleinikoff et al. 2007).

MKED1 titanite was collected in the Flaine Dorothy Cu-Au-REE prospect of the Mount Isa Inlier, Queensland, Australia (Page 1983, Oliver et al. 1999, Spandler et al. 2016). Its occurrence is associated with coarse pink calcite

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and minor diopside in a vein that cuts banded diopside-K-feldspar-scapolite skarn rocks in the prospect (Spandler et al. 2016). MKED1 titanite contains low level of common Pb (< 0.5 ppm). The U–Pb dating by ID-TIMS shows that the weighted-mean $^{207}Pb/^{206}Pb$, $^{206}Pb/^{238}U$, and $^{207}Pb/^{235}U$ ages with 2σ uncertainties are 1521.02 ± 0.55 Ma (MSWD = 1.2), 1517.32 ± 0.32 Ma (MSWD = 0.55) and 1518.87 ± 0.31 Ma (MSWD = 0.25) (Spandler et al. 2016).

III. Analytical method

In this study, we conducted *in-situ* U–Pb measurements in this study using iCAP-RQ single-collector quadrupole ICP-MS (Thermo Fisher Scientific, Waltham, USA) coupled to Analyte G2 laser ablation (LA) system that utilizes a 193-nm ArF excimer laser (Teledyne Cetac Technologies, Omaha, USA) in OUS. To check whether different minerals can be used as external standards for fractionation correction of *in-situ* titanite U–Pb measurements, the U/Pb ratios of MKED-1 were corrected by analyzing the combination of BLR-1 titanite and NIST SRM 612 glass, or that of 91500 zircon and NIST SRM 612 glass. Also, we tested whether the calculated ages of the MKED1 corrected by above external standards could match with the reference $^{238}U/^{206}Pb$, $^{235}U/^{207}Pb$ and $^{207}Pb/^{206}Pb$ ages by Spandler et al. (2016).

The standard materials were set in a two-volume HelEx2 sample cell of the LA system. The areas free of cracks and inclusions in them were chosen for the analysis with a LA camera using transmitted and reflected light. In addition, the analyzed spots were ablated by a pulse of laser of 85-μm diameter for removing potential contaminants on their surfaces prior to the analysis.

The laser fluence was set to 5 J/cm^2 at the sample surfaces with laser repetition rate and laser diameter set to 10 Hz and 65 μm, respectively. After laser shooting with shutter closed for 30 s (laser warming up), the analytical areas were ablated for 30 s. At the ablation, He carrier gas was introduced into the HelEx2 sample cell (MFC1) and its arm part (MFC2). The flow rates into MFC1 and MFC2 were set to 0.5 L/min and 0.3 L/min, respectively. The ablated materials of the samples in He carrier gas were passed through the signal-smoothing device “squid” and mixed with Ar gas before the ionization at the ICP-MS.

The ICP-MS was optimized using continuous ablation of a NIST SRM 612 standard to provide maximum sensitivities of ^{206}Pb and ^{238}U while maintaining low oxide formation ($^{232}Th^{16}O/^{232}Th$ < 1%). On the ICP-MS, 5 nuclides (^{202}Hg, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{238}U) were analyzed. The background and ablation data for each analysis were collected for 15 s of the laser warming-up time and 20 s of the ablation time, respectively. Those data were acquired for multiple analyses of MKED1 titanite bracketed by trio of analyses of BLR1 titanite and NIST SRM 612 or those of 91500 zircon and NIST SRM 612. BLR1 titanite and 91500 zircon were analyzed as external standards for correction of the Pb/U ratio of MKED1 titanite. On the other hand, NIST SRM 612 glass was analyzed for correction of its $^{207}Pb/^{206}Pb$ ratio. As normalization value of 91500 zircon, apparent $^{206}Pb/^{238}U$ without common Pb correction was used (Sakata et al. 2017, i.e. $^{206}Pb/^{238}U$ = 0.17928 ± 0.00018). The instrumental mass bias of $^{207}Pb/^{206}Pb$ ratios was corrected by normalizing to compiled values of NIST SRM 612 glass standard by Jochum et al. (2005). On the other hand, the radiogenic $^{206}Pb/^{238}U$ ratio of BLR-1 titanite was used for the correction by calculation based on the assumption that its common Pb isotopic ratio is equal to the terrestrial Pb isotopic ratio of 1049.9 ± 1.3 Ma by Stacey & Kramers (1975).

The background intensities collected at the laser warming-up time were subtracted from following signals at the ablations. The intensity of ^{202}Hg of all analyses was used to correct the isobaric interference of ^{204}Hg on ^{204}Pb. Corrected ^{204}Pb intensities of the analyzed spots of MKED1 titanite were too low to correct U–Pb ages for common Pb contamination with sufficient precision based on ^{204}Pb (Stern 1997). Thus, common Pb correction of the analyzed values of MKED1 titanite was not performed in this study.

All uncertainties were quoted at 2-sigma level to which repeatability of each of the six measurements of external standard data of BLR-1 titanite and NIST SRM 612 glass, or 91500 zircon and NIST SRM 612 glass bracketing analyses of the MKED1 was propagated. Elemental fractionation of U/Pb ratio and mass fractionation of $^{207}Pb/^{206}Pb$ ratio were linearly interpolated by the measured data of each of the six analyses of BLR-1 titanite and NIST SRM 612 glass, or 91500 zircon and NIST SRM 612 glass, respectively. ^{235}U intensities were calculated from ^{238}U using a $^{238}U/^{235}U$ ratio of 137.88 (Jaffey et al. 1971).

IV. Results and Discussion

Table 1 lists the $^{238}U/^{206}Pb$, $^{235}U/^{207}Pb$ and $^{207}Pb/^{206}Pb$ ratios of MKED1 titanite with their ages corrected by the combination of BLR-1 titanite and NIST SRM 612 glass, and Table 2 lists that of 91500 zircon and NIST SRM 612 glass. Their Tera-Wasserburg concordia diagrams are shown in Figures 1 and 2, respectively.

The weighted-mean $^{238}U/^{206}Pb$ and $^{235}U/^{207}Pb$ ages of MKED1 titanite corrected by BLR-1

Table 1. Summary of the isotopic and age data of MKED1 corrected by the external-standard combination of BLR-1 titanite and NIST SRM 612 glass.

	Isotopic Ratio						Age (Ma)					
Spot no.	207Pb/235U	2σ	206Pb/238U	2σ	207Pb/206Pb	2σ	235U-207Pb	2σ	238U-206Pb	2σ	207Pb-206Pb	2σ
MKED1-1	3.5806	0.1466	0.2695	0.01053	0.09637	0.001178	1545.23	32.49	1538.08	53.46	1555.03	22.95
MKED1-2	3.3685	0.1379	0.2564	0.01002	0.09530	0.001166	1497.11	32.06	1471.18	51.39	1534.01	23.03
MKED1-3	3.5595	0.1457	0.2708	0.01058	0.09533	0.001165	1540.55	32.45	1544.84	53.67	1534.66	23.01
MKED1-4	3.5001	0.1433	0.2636	0.01030	0.09629	0.001177	1527.24	32.33	1508.41	52.55	1553.43	22.95
MKED1-5	3.5011	0.1433	0.2686	0.01050	0.09452	0.001155	1527.46	32.33	1533.90	53.33	1518.55	23.05
MKED1-6	3.5505	0.1453	0.2710	0.01059	0.09502	0.001161	1538.54	32.43	1545.84	53.70	1528.52	23.01
MKED1-7	3.5630	0.1459	0.2724	0.01064	0.09488	0.00116	1541.32	32.46	1552.76	53.91	1525.67	23.03
MKED1-8	3.5637	0.1459	0.2707	0.01057	0.09550	0.001167	1541.50	32.46	1544.14	53.65	1537.88	22.99
MKED1-9	3.5346	0.1447	0.2681	0.01047	0.09563	0.001169	1534.99	32.40	1531.04	53.25	1540.44	22.99
MKED1-11	3.6190	0.1482	0.2771	0.01083	0.09473	0.001157	1553.72	32.57	1576.62	54.65	1522.71	23.03
MKED1-12	3.5591	0.1457	0.2675	0.01045	0.09648	0.001179	1540.46	32.45	1528.32	53.16	1557.16	22.93
MKED1-13	3.5545	0.1455	0.2691	0.01051	0.09580	0.001171	1539.43	32.44	1536.27	53.41	1543.77	22.97
MKED1-14	3.5974	0.1473	0.2737	0.01069	0.09534	0.001165	1548.95	32.53	1559.40	54.12	1534.72	22.99
MKED1-15	3.6519	0.1495	0.2769	0.01082	0.09565	0.001169	1560.92	32.63	1575.80	54.62	1540.85	22.98

Table 2. Summary of the isotopic and age data of MKED1 corrected by the external-standard combination of 91500 zircon and NIST SRM 612 glass.

	Isotopic Ratio						Age (Ma)					
Spot no.	207Pb/235U	2σ	206Pb/238U	2σ	207Pb/206Pb	2σ	235U-207Pb	2σ	238U-206Pb	2σ	207Pb-206Pb	2σ
MKED-1-16	2.8715	0.0847	0.2197	0.00579	0.09479	0.001258	1374.46	22.21	1280.36	30.59	1523.85	25.02
MKED-1-17	3.0162	0.0890	0.2246	0.00592	0.09741	0.001292	1411.72	22.49	1305.96	31.14	1575.14	24.84
MKED-1-18	3.0074	0.0887	0.2306	0.00607	0.09460	0.001255	1409.50	22.48	1337.50	31.82	1520.11	25.02
MKED-1-19	3.0201	0.0891	0.2305	0.00607	0.09501	0.001262	1412.70	22.50	1337.33	31.81	1528.27	25.02
MKED-1-20	3.1119	0.0918	0.2325	0.00612	0.09708	0.001289	1435.64	22.67	1347.49	32.03	1568.80	24.88
MKED-1-21	2.9838	0.0880	0.2282	0.00601	0.09484	0.00126	1403.51	22.44	1324.94	31.55	1524.94	25.03
MKED-1-22	3.0476	0.0899	0.2299	0.00606	0.09616	0.001277	1419.64	22.55	1333.81	31.74	1550.85	24.94
MKED-1-23	3.0765	0.0908	0.2331	0.00614	0.09571	0.001271	1426.86	22.61	1350.87	32.10	1542.11	24.97
MKED-1-24	3.0615	0.0903	0.2331	0.00614	0.09524	0.001264	1423.12	22.58	1350.89	32.10	1532.90	24.99
MKED-1-25	3.1223	0.0921	0.2364	0.00623	0.09578	0.001271	1438.21	22.68	1368.15	32.47	1543.40	24.95

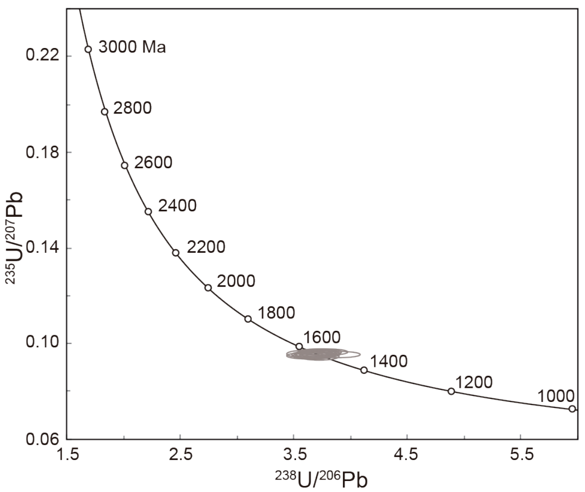

Fig. 1. Tera-Wasserburg plot of MKED1 corrected by the external-standard combination of BLR-1 titanite and NIST SRM 612 glass.

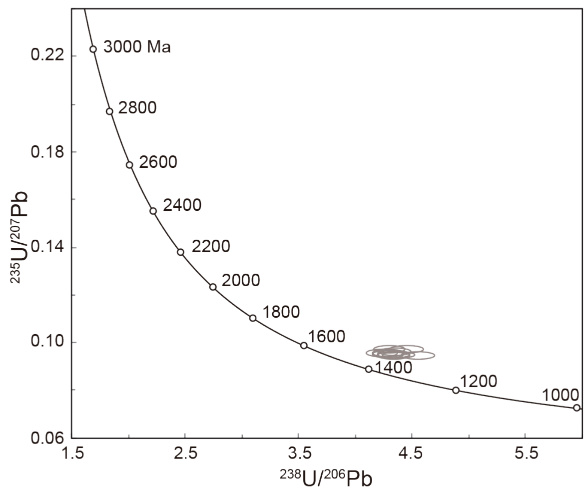

Fig. 2. Tera-Wasserburg plot of MKED1 corrected by the external-standard combination of 91500 zircon and NIST SRM 612 glass.

titanite and NIST SRM 612 glass show 1538 ± 14.0 Ma (N = 14, MSWD = 1.02) and 1538 ± 8.5 Ma (N = 14, MSWD = 0.85), respectively (Fig. 3). Those ages are close to the ID-TIMS weighted-mean $^{238}U/^{206}Pb$ and $^{235}U/^{207}Pb$ ages of 1517.32 ± 0.32 Ma and 1518.87 ± 0.31 Ma by Spandler et al. (2016). Moreover, these data are plotted on the Tera-Wasserburg concordia curve (Fig. 1).

On the other hand, the weighted-mean $^{238}U/^{206}Pb$ and $^{235}U/^{207}Pb$ ages of 1333 ± 18 Ma (N = 10, MSWD = 2.6) and 1415 ± 13 Ma (N = 10, MSWD = 2.7) corrected by 91500 zircon and NIST SRM 612 glass are significantly younger than the $^{238}U/^{206}Pb$ and $^{235}U/^{207}Pb$ ages by Spandler et al. (2016) (Fig. 4). In addition, these data are not plotted on the Tera-Wasserburg concordia curve (Fig. 2). The same results are reported by Sun et al. (2012). The age discrepancy between the calculated U–Pb values and the reference U–Pb ones is possibly due to the fractionation of U and

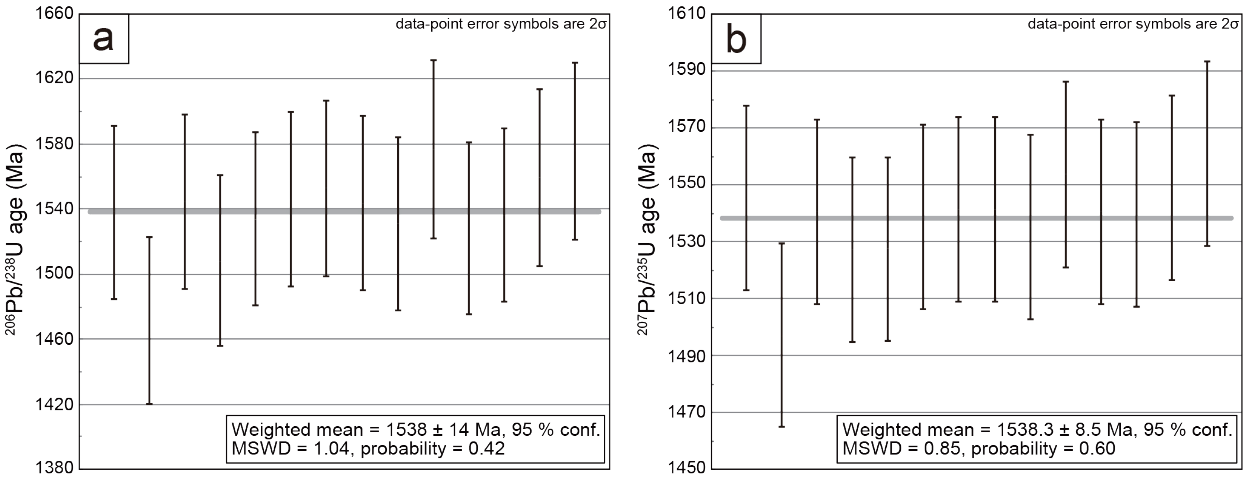

Fig. 3. Weighted mean of (a) $^{238}U/^{206}Pb$ ages and (b) $^{235}U/^{207}Pb$ ages of MKED1 corrected by the external-standard combination of BLR-1 titanite and NIST SRM 612 glass.

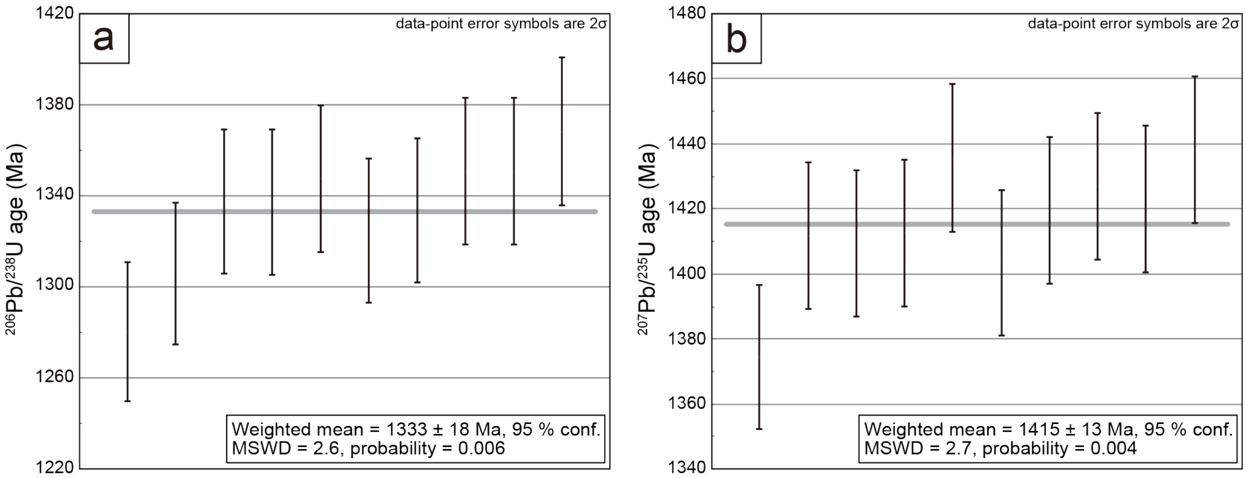

Fig. 4. Weighted mean of (a) $^{238}U/^{206}Pb$ ages and (b) $^{235}U/^{207}Pb$ ages of MKED1 corrected by the external-standard combination of 91500 zircon and NIST SRM 612 glass.

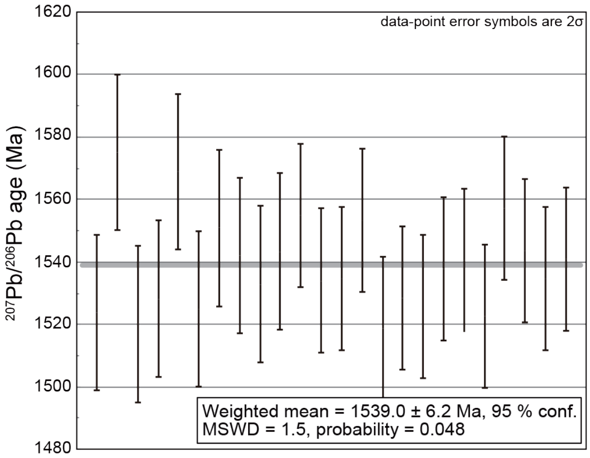

Fig. 5. Weighted mean of $^{207}Pb/^{206}Pb$ ages of MKED1 corrected by the external standard of NIST SRM 612 glass.

Pb at the ablation of the different matrix minerals.

In conclusion, we would like to emphasize that the titanite standard has to be analyzed as an external standard material correcting the fractionation of U/Pb ratios at the ablation of the unknown titanite minerals for reducing the influence of the fractionation on the $^{238}U/^{206}Pb$ and $^{235}U/^{207}Pb$ ages.

On the other hand, the weighted-mean $^{207}Pb/^{206}Pb$ age of MKED1 corrected by NIST SRM 612 glass throughout this study shows 1539 ± 6.2 Ma (N = 24, MSWD = 1.5) (Fig. 5). This age is close to the ID-TIMS weighted-mean $^{207}Pb/^{206}Pb$ age of 1521.02 ± 0.55 Ma by Spandler et al. (2016). Thus, with no significant matrix effect, NIST SRM 612 glass can be used as an external standard in the case of titanite $^{207}Pb/^{206}Pb$ age dating as well as that of zircon $^{207}Pb/^{206}Pb$ age determination.

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青木翔吾・青木一勝：LA-ICP-MSによるチタナイトの局所U–Pb年代測定

要約

チタナイトは様々な火成岩や変成岩に含まれており，そのU–Pb年代値はマグマからの結晶化年代や，熱変成イベント時の冷却年代を制約することに使える．本論では, レーザーアブレーション誘導結合プラズマ質量分析法を用いて，年代既知のMKED1チタナイトのU–Pb年代測定を行い，そのU/Pb比の外部補正試料としてスフェーンとジルコンを，^{207}Pb/^{206}Pb比の外部補正試料として合成ガラス(NIST SRM 612)を使いマトリックス効果の影響を調べた．その結果，NIST SRM 612の分析値で補正したMKED1チタナイトの^{207}Pb/^{206}Pb年代値は，参照値と一致あるいは近い年代値が得られた．^{206}Pb/^{238}Uおよび^{207}Pb/^{235}U年代値については，BLR-1チタナイトとNIST SRM 612を組み合わせて外部補正試料に用いた場合は，参照値とほぼ一致する年代値が得られた．しかし，91500ジルコンとNIST SRM 612を用いた場合は，参照値よりも明らかに若い年代が得られた．このことから，^{206}Pb/^{238}Uおよび^{207}Pb/^{235}U年代値については，アブレーション時のマトリックスの違いによるU/Pb比の分別の影響が大きいことが確かめられた．

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