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High precision titanium isotope measurements on geological samples by high resolution MC-ICPMS

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Abstract

A method has been developed for the precise and reproducible measurement of Ti isotopes in natural materials using high resolution MC-ICPMS. Instrumental mass fractionation is internally corrected using ^{49}Ti/^{47}Ti. Replicate measurements of synthetic standard solutions, terrestrial rocks, and the carbonaceous chondrite Allende yield a long-term reproducibility (2σ) of 0.28ε, 0.34ε, and 0.28ε for ^{50}Ti/^{47}Ti, ^{48}Ti/^{47}Ti, and ^{46}Ti/^{47}Ti, respectively. Isobaric interferences from ^{46,48}Ca$^+$, ^{50}V$^+$, ^{50}Cr$^+$, and doubly charged Zr can be corrected for reliably in separated Ti solutions with $\mathrm{Ca/Ti} < 5$, $\mathrm{V/Ti} < 0.3$, $\mathrm{Cr/Ti} < 0.2$, and $\mathrm{Zr/Ti} < 1$, respectively. Such elemental ratios are achieved easily in most samples using the anion-exchange procedure presented. Single and double charged polyatomic ions can either be resolved, e.g., ^{14}N^{36}Ar$^+$, or do not compromise the measurements. The method has been successfully applied to terrestrial rocks, meteorites, and various mineral separates. Terrestrial samples and standards agree within analytical uncertainties but are consistently different from the recommended values of Niederer et al. [F.R. Niederer, D.A. Papanastassiou, G.J. Wasserburg, Geochim. Cosmochim. Acta 45 (1981) 1017] with the largest effect on ^{50}Ti/^{47}Ti. The new results provide evidence that the recommended terrestrial ^{50}Ti/^{47}Ti is not well constrained; our data are higher by $\sim 13\varepsilon$ than the recommended value. Better agreement is found with the values recommended by Heydegger et al. [H.R. Heydegger, J.J. Foster, W. Compston, Earth Planet. Sci. Lett. 58 (1982) 406]. Our best estimate for the isotopic composition of terrestrial Ti (relative to $^{49}\mathrm{Ti}/^{47}\mathrm{Ti} = 0.749766$) is: $^{50}\mathrm{Ti}/^{47}\mathrm{Ti} = 0.73010$, $^{48}\mathrm{Ti}/^{47}\mathrm{Ti} = 10.06884$, and $^{46}\mathrm{Ti}/^{47}\mathrm{Ti} = 1.09325$. This corresponds to an atomic weight of 47.877, significantly different from the value of 47.867 recommended by IUPAC. A ^{50}Ti/^{47}Ti anomaly for bulk Allende of $3.37 \pm 0.51\varepsilon$ is found, while for ^{48}Ti/^{47}Ti and ^{46}Ti/^{47}Ti the data are identical to the terrestrial value within the uncertainties. This is consistent with other recently reported differences between the bulk Earth and chondrites in neutron-rich nuclides.

Keywords: Early solar system; Titanium isotopes; Allende; Isotopic anomalies

1. Introduction

Isotopic anomalies in solar system objects provide powerful constraints on the origin and evolution of the early solar system. The solar system is relatively homogeneous isotopically, indicating efficient mixing of the material that formed the solar system out of its precursor molecular cloud. Isotopic anomalies due to *in situ* effects such as radioactive decay and particle irradiation are well known. Nucleosynthetic isotope anomalies in bulk chondrites have been identified for a variety of elements, including, e.g., oxygen [1], sulfur [2,3], titanium [4], chromium [5–7], molybednum [8,9], and ruthenium [10,11], although some of these observations have not been reproduced and need confirmation. Such isotopic anomalies indicate incomplete homogenization of the precursor material and are of great importance for understanding the processes and their timing in the early solar system. The isotopic composition of titanium is of special interest for various reasons.

First, titanium isotopes in refractory inclusions from primitive meteorites are important indicators of stellar nucle-

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osynthetic processes contributing to iron group elements. Iron group elements have nuclear binding energies close to the maximum and therefore provide particular clues for understanding hydrostatic and/or explosive burning phases in stellar interiors. Titanium is of special interest because it has been shown to exhibit striking isotopic anomalies [14–20]. Second, titanium has a low ionization potential compared to other iron group elements and is abundant in refractory inclusions making it ideal for mass spectrometric studies. Titanium isotopes can also serve as an indicator of possible irradiation processes in the early solar system. For example, assuming that some of the relatively short-lived radionuclides alive in the early solar system have been produced by particle irradiation [12], a collateral shift in ^{48}Ti/^{47}Ti of a few epsilon (ε) would be expected, where ε is the deviation in parts per 10^4 from the terrestrial standard, i.e.,:

$$\varepsilon\left(\frac{^{i}\mathrm{Ti}}{^{47}\mathrm{Ti}}\right)=\left[\frac{(^{i}\mathrm{Ti}/^{47}\mathrm{Ti})_{\mathrm{sample}}}{(^{i}\mathrm{Ti}/^{47}\mathrm{Ti})_{\mathrm{standard}}}-1\right]\times 10,000$$

Note that both applications benefit from the fact that titanium forms one of the most refractory oxides and therefore is concentrated in refractory inclusions either by condensation or evaporation processes [13].

Variations in Ti isotope compositions in refractory inclusions from the CV3 chondrite Allende were first reported in 1977 by Heydegger et al. [14] using thermal ionization mass spectrometry (TIMS), the major effect being an enhancement in ^{50}Ti. This effect has subsequently been confirmed by two other groups using TIMS [4–10], whereas anomalies for the other titanium isotopic ratios could not be well characterized. For example, Niederer et al. [17] published positive and negative anomalies for ^{47}Ti, ^{49}Ti, and ^{50}Ti, while Niemeyer and Lugmair [18–20] confirmed the anomalies for ^{50}Ti, but reported only negative anomalies for ^{47}Ti. Nevertheless, all three groups agreed that virtually every Ca–Al-rich refractory inclusion from Allende contains anomalous titanium. Confusion also plagues the data from other meteorite constituents. Whereas Heydegger et al. [14] found no anomalies for Allende pyroxene chondrules, Niemeyer and Lugmair [21] reported anomalous titanium in a bulk sample of the Cl chondrite Ivuna and in matrix separates from C2 chondrites Murchison and Murray. The latter authors also found hints of unusual Ti in chondrules from unequilibrated chondrites. In a later study of chondrules from carbonaceous chondrites Niemeyer [4] detected anomalies only for ^{50}Ti. Although all three studies used different isotopic ratios for normalization, which makes a direct comparison of the data difficult, they all agreed that at least three isotopically distinct titanium components are necessary to explain the measured data. Note that two of the groups used TiO^{+} beams [4,17–21], possibly suffering from isobaric interferences from $^{A-1}$Ti^{17}O^{+} and $^{A-2}$Ti^{18}O^{+} on ^{A}Ti^{16}O^{+} and unknown oxygen fractionation effects [22].

In a recent study by Zhu et al. [23] and Makashima et al. [24] a method was developed for the measurement of the Ti isotopes in natural samples using multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS). Since the analyses were performed on a low mass-resolution MC-ICPMS, a very sophisticated purification procedure consisting of a three-column ion exchange chromatography was necessary to remove isobaric interferences on Ti isotopes. Despite this effort, some plasma specific interferences, e.g., argides, which could not be resolved compromised their data. For example, the authors demonstrated that their measured Ti isotope ratios depend strongly on the Ti concentration. However, using a sample–standard bracketing technique most such effects cancelled out and long-term reproducibilities of 0.4ε, 0.6ε, 0.7ε, and 0.8ε (2σ) for ^{47}Ti/^{46}Ti, ^{48}Ti/^{46}Ti, ^{49}Ti/^{46}Ti, and ^{50}Ti/^{46}Ti, respectively, were obtained. By comparing the titanium isotope composition of mantle xenoliths, basalts, and loess samples with data from the eucrite Camel Donga mass dependent fractionation effects of more than 12ε were reported [23]. Apart from these studies little work has been done characterizing titanium isotope compositions of various solar system materials and in recent years most studies of titanium are based on presolar material using secondary or resonance ionization, e.g., [25–27].

A primary purpose of this study was to develop a new analytical procedure for high precision Ti isotope measurements using high resolution MC-ICPMS that overcomes the previous limitations of TIMS measurements (e.g., TiO interferences), and low resolution MC-ICPMS measurements (e.g., argide interferences). The presented procedure allows the precise and accurate determination of Ti isotopes in various geologic materials. We will apply the procedure to a large range of samples from various solar system objects and determine their Ti isotope composition. In addition, we will search for ^{48}Ti/^{47}Ti anomalies in early refractory condensates to prove or reject the hypothesis that some of the relatively short-lived radionuclides have been produced by particle irradiation in the early solar system.

2. Sample preparation and ion exchange chromatography

Sample preparation and chemical separation follows the procedure described by Schönbächler et al. [28]. A brief summary is given in the following. Whole rock samples of stony meteorites and terrestrial basalts are crushed in a boron carbide mortar. A mixture of 3 ml concentrated HF and 700 µl concentrated HNO$_3$ is used to dissolve sample powders of up to 150 mg. Digestion is accomplished over 4.5 days at a temperature of 180 °C in 16 ml Savillex® vials placed inside a 125 ml Parr® bomb. Subsequently, the samples are dried down and are completely re-dissolved in 6 ml 6 M HCl, whereas aqua regia is used instead for samples containing carbonaceous material. Finally, traces of HF are added to keep Ti in solution.

Titanium is separated via a two-stage anion exchange chromatography using Bio-Rad AG1-X8 resin (200–400 mesh, chloride form). The digested samples are dried down and 2 ml 4 M HF is added. After letting the sample solution stand for at least 2 h, the samples are centrifuged and decanted. Subsequently, they are treated twice with 1.5 ml 4 M HF such that a total of 5 ml acid is collected. The first column, which consists of 0.7 ml of resin, is preconditioned with 6 ml 4 M HF. After loading the sample the matrix is eluted with 8 ml 4 M HF, while Ti, Zr, Hf, Mo, Te, and W remain on the column. Stripping Ti (together with Zr and Hf) is achieved using 2 ml 6 M HCl–1 M

HF. Following the first column the Ti fraction is dried down and taken up in 1.5 ml of (freshly prepared) 0.25 M H_2SO_4–1% H_2O_2. This solution is loaded onto the second column, which contains 0.7 ml resin and which has been preconditioned with 6 ml of 0.25 M H_2SO_4–1% H_2O_2. Titanium is stripped from the column using 8 ml 0.25 M H_2SO_4–1% H_2O_2. For further details of the sample preparation and chemical separation procedures see Schönbächler et al. [28]. Total procedural chemistry blanks typically are <200 pg. However, if Teflon bombs are used for digestion the sample blank can reach ∼2 ng. The blank is negligible for the data obtained in this study because all analyzed samples contain more than a few tens of nanograms of titanium and some samples even contain a few milligrams of titanium.

3. Mass spectrometry

3.1. Instrumentation and data collection protocols

Measurements of isotopic ratios are performed with the high resolution MC-ICPMS (Nu 1700) at ETH Zürich. The Nu 1700 (Nu Instruments, Wrexham, North Wales, United Kingdom) is a large-geometry double focusing mass spectrometer. To focus the ion beam with the high energy dispersion inherited from the plasma source, a 70° sector electrostatic analyzer (ESA) with a radius of 943 mm is placed before a 70° laminated magnet with a radius of 750 mm. Two electrostatic lenses located after the magnet enable the dispersion of the ion beams to vary, making a range of different multidetector measurements possible. Ion signals can be simultaneously measured with an array of 16 Faraday collectors, 10 fixed and 6 mechanically adjustable (three on either side). Moreover, three discrete-dynode electron multipliers, operating in counting mode, are interspersed. An electrostatic quadrupole lens between the ESA and the magnet enables the fine tuning of double-focussing. A manually adjustable source slit and computer controlled adjustable detector slits at all 19 detectors permit a variable resolution of the system (from ∼400 to ∼10,000).

Standards and samples are analyzed in 0.1 M HNO_3–0.01 M HF. The solutions are aspirated using a low-uptake Teflon nebuliser (20–50 μl/min, Elemental Scientific, USA). Titanium standard solutions with a concentration of 300 ppb usually yield total titanium ion beams of $\sim 10^{-12}$ A. One complete measurement usually consumes 2–3 ng of titanium. Before analyzing samples, the performance of the mass spectrometer is checked with several runs of titanium standard solutions. Between the analyses, the sample introduction system is cleaned with 0.1 M HNO_3–0.01 M HF for about 5 min. A sample measurement includes two different data collection protocols performed on Nu 1700. Both protocols comprise two blocks of 20 measurements with 15 s integration time. On-peak baselines are measured for 30 s before each block by deflecting the ion beam with the ESA. Typically each sample is measured at least four times.

The two data collection protocols are necessary because the detector array of the Nu 1700 does not allow the simultaneous measurement of all titanium isotopes including some selected Ca-, V-, and Cr-isotopes. The latter are needed to correct for isobaric interferences. During the first cycle, the masses 44–49 are measured. The second cycle includes the masses 47–53. In both cases, the mass resolution is about 2000. This allows interferences on mass 50 from, for example, $^{14}N^{36}Ar^+$, to be fully resolved. Interfering Ca-, V-, and Cr-isotopes require a much higher mass resolution and were corrected as discussed below. An aliquot of each sample is measured on a quadrupole mass spectrometer to determine the Zr/Ti and Mo/Ti ratios. These ratios are used to monitor and correct for interferences from doubly charged Zr and Mo, respectively.

3.2. Data reduction and interference correction

Instrumental mass fractionation is internally corrected via $^{49}Ti/^{47}Ti = 0.749766$ [17] using the exponential law. The variability of mass fractionation effects throughout one session, i.e., within one day, is <0.5%. Therefore, the measured data, once corrected for instrumental mass fractionation and normalized to synthetic standard solutions, show no (or only very minor) dependence on the type of fractionation law used (linear, exponential, power-law). The overall mass fractionation is 4–5% per mass unit (u), which is slightly higher than the approximately 3% u^{-1} observed by Zhu et al. [23]. We chose $^{49}Ti/^{47}Ti$ for normalization because this ratio is not (or barely) compromised by isobaric interferences and can be measured with high accuracy and reproducibility. Important interferences on titanium isotopes are discussed in the following and are summarized in Table 1.

Isobaric interferences of Ti isotopes from single charged atomic ions are possible from $^{46}Ca^+$ (0.004% relative abundance) and ^{48}Ca (0.187%), ^{50}V (0.2497%), and ^{50}Cr (4.3452%). Such interferences were corrected using signals on mass 44 (^{44}Ca, 2.086%), mass 51 (^{51}V, 99.7503%), and mass 53 (^{53}Cr, 9.5006%), respectively. The ion currents of the corresponding isotopes were measured simultaneously. The reliability of the corrections was investigated by means of synthetic standard solutions with variable i/Ti ratios (i = Ca, V, and Cr). The corrections on $^{48}Ti/^{47}Ti$ and $^{46}Ti/^{47}Ti$ from ^{46}Ca and ^{48}Ca are reliable up to 60ε and 30ε, respectively. For the standard solutions the corrections are always below 0.5ε and for most samples the corrections are below 1ε and seldom reach 3ε. For some samples, however, corrections are as high as 500ε and 100ε for $^{48}Ti/^{47}Ti$ and $^{46}Ti/^{47}Ti$, respectively. Such samples need further purification through ion exchange chemistry and they will therefore not be discussed any further. Correcting V-interferences is reliable up to about 1.6% (mass 50). For the majority of the samples the corrections are always below 1ε. Some lunar samples, however, require corrections in the range of 1%. The corrections from ^{50}Cr on ^{50}Ti, which are checked to be reliable up to about 16%, are usually below 5ε and 20ε for standards and samples, respectively. Some sample solutions, however, contain significantly larger Cr amounts that can require corrections up to about 20%. Such samples need further chemical purification and will therefore not be discussed any further. Note, measurements of ^{44}Ca, which are used to correct for Ca interferences, are very sensitive to baseline variations caused by the large ^{40}Ar beam. This is probably the reason for the rather low range (compared to the other single charged atomic interferences) where corrections are reliable. Moreover, the isobaric interferences on ^{50}Ti

Table 1
Important interferences on titanium isotopes for MC-ICPMS measurements

Isotope	^{46}Ti	^{47}Ti	^{48}Ti	^{49}Ti	^{50}Ti	Correction[a]
Interference						
Single charged atomic	$^{46}Ca^+$		$^{48}Ca^+$			Ca/Ti ∼ 5
					$^{50}V^+$	V/Ti ∼ 0.3
					$^{50}Cr^+$	Cr/Ti ∼ 0.2
Double charged atomic	$^{92}Zr^{2+}$	$^{94}Zr^{2+}$	$^{96}Zr^{2+}$			Zr/Ti ∼ 1
Polyatomic ions[b] (single charged)	$^{34}S^{12}C$, $^{33}S^{13}C$, $^{32}S^{14}N$, $^{31}P^{15}N$, $^{30}Si^{16}O$, $^{29}Si^{17}O$, $^{28}Si^{18}O$, ...	$^{34}S^{13}C$, $^{33}S^{14}N$, $^{32}S^{15}N$, $^{31}P^{16}O$, $^{29}Si^{18}O$, $^{36}S^{11}B$, $^{30}Si^{16}O^{1}H$, ...	$^{36}S^{12}C$, $^{34}S^{14}N$, $^{33}S^{15}N$, $^{32}S^{16}O$, $^{31}P^{17}O$, $^{30}Si^{18}O$, $^{31}P^{16}O^{1}H$, ...	$^{36}S^{13}C$, $^{34}S^{15}N$, $^{33}S^{16}O$, $^{32}S^{17}O$, $^{31}P^{18}O$, $^{32}S^{16}O^{1}H$, $^{31}P^{17}O^{1}H$, ...	$^{36}S^{14}N$, $^{33}S^{15}H^{1}H$, $^{34}S^{16}O$, $^{32}S^{17}O^{1}H$, $^{33}S^{17}O$, $^{32}S^{18}O$, $^{33}S^{16}O^{1}H$, ...	
Argides[b]	$^{6}Li^{40}Ar$, $^{10}B^{40}Ar$, ...	$^{11}B^{36}Ar$, $^{9}Be^{38}Ar$, $^{7}Li^{40}Ar$, ...	$^{10}B^{38}Ar$, $^{12}C^{36}Ar$, ...	$^{11}B^{38}Ar$, $^{9}Be^{40}Ar$, ...	$^{14}N^{36}Ar$, $^{12}C^{38}Ar$, ...	

[a] The values indicate the maximum elemental ratios that are permissible for an accurate correction. Higher ratios can lead to erroneous Ti isotopic data.

[b] Only a few examples of possible interfering polyatomic ions and particularly argides are given. Most of these species can either be resolved by the mass resolution used or do not occur in our measurements, which is clearly indicated by various dilution series.

by Cr was corrected using ^{53}Cr because ^{52}Cr measurements are themselves compromised by interferences of $^{40}Ar^{12}C$. Since interferences of $^{40}Ar^{13}C$ on ^{53}Cr are about two orders of magnitude smaller than those of $^{40}Ar^{12}C$ on ^{52}Cr, correcting ^{50}Ti via ^{53}Cr is considerably more reliable.

Interferences of doubly charged Zr are corrected using the Zr/Ti ratios obtained from solution aliquots by ICPMS and experimentally determined Zr^{2+}/Ti^{+} ratios. The corrections are reliable up to 0.3%, but they never exceeded 1ε due to the good separation of Ti from Zr during the ion exchange chemistry. The Zr/Ti ratios are usually below 0.008. Systematic tests with solutions having variable Mo/Ti ratios show that Mo^{2+} is not formed at a level that could disturb the Ti analyses and therefore no corrections are necessary. This is probably due to the higher second ionization potential of Mo (1560 kJ mol^{-1}) compared to that of Zr (1270 kJ mol^{-1}).

A few examples of possible interfering polyatomic ions are summarized in Table 1. However, such interferences are either resolved by the mass resolution used or do not occur in the measurements as it is clearly demonstrated by various dilution series.

4. Results and discussion

4.1. The titanium isotope composition of standard solutions

The Ti standard solution used in this study was obtained from Alfa-Aesar (AAS standard, not really an isotope standard). The grand average for all standard solutions measured over more than 2.5 years, internally normalized for instrumental mass fractionation to $^{49}Ti/^{47}Ti = 0.749766$ [17], is $\varepsilon(^{50}Ti/^{47}Ti) = 12.71 \pm 0.14$, $\varepsilon(^{48}Ti/^{47}Ti) = 0.22 \pm 0.14$, and $\varepsilon(^{46}Ti/^{47}Ti) = 2.29 \pm 0.98$, respectively, relative to the values recommended in [17]. The uncertainty is the 2σ standard deviation of the weighted mean. Our data for $^{50}Ti/^{47}Ti$ are therefore about 13ε-units higher than the reference value of 0.729175 [17]. Similar discrepancies have been observed previously. In an interlaboratory comparison of terrestrial titanium isotopic ratios Heydegger et al. [22] also noted (after renormalization) that the $^{46}Ti/^{49}Ti$ results for all groups agree within 1σ but those for $^{48}Ti/^{49}Ti$ and $^{50}Ti/^{49}Ti$ are not in agreement even at the 2σ level. The range observed for $^{50}Ti/^{49}Ti$ between the different studies was about 15ε-units.

Given that the discrepancies between our data and the ratios given by Niederer et al. [17] are largest for ^{50}Ti, we now investigate whether the offset of 13ε might be due to analytical artifacts from our side. The following checks on the quality of our data have been performed. First, the observed offset does not depend on the Ti concentration of the analyzed solutions. Fig. 1 shows $^{50}Ti/^{47}Ti$ ratios as a function of $^{49}Ti/^{47}Ti$ ratios for more than 250 measurements of standard solutions with Ti concentrations of 100, 200, and 300 ppb, respectively. The data shown are not corrected for instrumental mass fractionation, interferences or blank contributions. Error bars smaller than symbol sizes are suppressed. All data fall on a mass dependent fractionation line with slope 1.5 (mdf). The total mass fractionation is 4–5% u^{-1}.

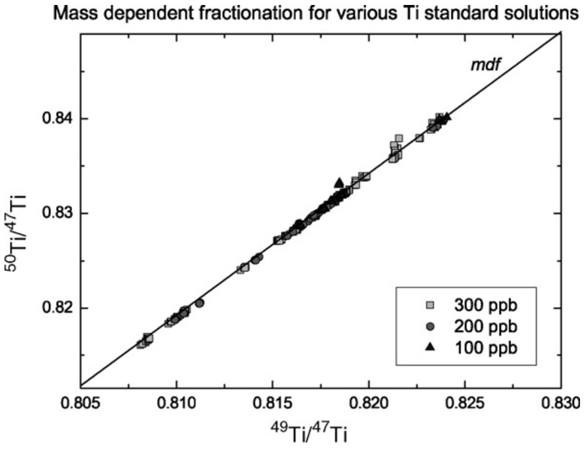

Fig. 1. $^{50}Ti/^{47}Ti$ as a function of $^{49}Ti/^{47}Ti$ for Ti standard solutions of 100, 200, and 300 ppb. The data shown are not corrected for instrumental mass fractionation, interferences or blank contributions. Error bars smaller than symbol sizes are suppressed. All data fall on the mass dependent fractionation line with slope 1.5 (mdf), indicating no or only minor effects due to (constant) interferences. The total mass fractionation is 4–5% u^{-1}.

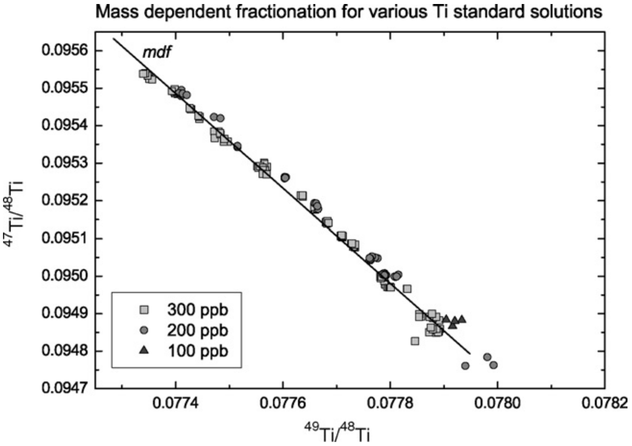

Fig. 2. $^{47}Ti/^{48}Ti$ as a function of $^{49}Ti/^{48}Ti$ for Ti standard solutions of 100, 200, and 300 ppb. The data shown are not corrected for instrumental mass fractionation, interferences or blank contributions. Error bars smaller than symbol sizes are suppressed. All data fall on the mass dependent fractionation line with slope −1 (mdf), indicating no or only minor effects due to (constant) interferences. The total mass fractionation is 4–5% u^{-1}.

Since any interferences from the spectrometer are expected to be rather constant, such interferences would have bigger effects on solutions with low Ti concentrations. Consequently, the data clearly indicate that such interferences have no or only very little effect. A similar result is obtained by plotting $^{47}Ti/^{48}Ti$ as a function of $^{49}Ti/^{48}Ti$ for standard solutions with Ti concentrations of 100, 200, and 300 ppb, respectively (Fig. 2). Again, the data shown are not corrected for instrumental mass fractionation, interferences, or blank contributions and error bars smaller than symbol sizes are suppressed. Again, all data fall on a mass dependent fractionation line with slope −1 indicating no or only very minor contributions from interferences. The trend observed for $^{46}Ti/^{48}Ti$ versus $^{49}Ti/^{48}Ti$ (not shown) is very similar; all data fall on a mass dependent fractionation line with slope −2. Second, we measured various dilution series with solutions having variable Ca/Ti, V/Ti, Cr/Ti, Mo/Ti, and Zr/Ti ratios. Fig. 3 shows $\varepsilon(^{50}Ti/^{47}Ti)$ as a function of the elemental ratios i/Ti, with i = Zr, Mo, Cr, or V. All dilution series clearly demonstrate that $\varepsilon(^{50}Ti/^{47}Ti)$ shows no dependence on the elemental ratios. All results display $\varepsilon(^{50}Ti/^{47}Ti) \sim 13$. Note that the slight offsets between the different dilution series are due to fact that the measurements were performed on separate days and with slightly different instrument settings. However, the offsets do not compromise the important results, namely that interferences from Zr, Mo, Cr, and V can reliably be corrected for and that matrix effects from any of these elements can be excluded. Third, the mass resolution of about 2000 used in this study is sufficient to resolve plasma specific interferences on mass 50 from, e.g., $^{14}N^{36}Ar$. This is further confirmed by the observation that the results for standards taken up either in 0.1 M HNO_3–0.01 M HF or in 0.1 M HCl–0.01 M HF always agree within their uncertainties (see inset in Fig. 3). Finally, we also checked whether the $^{50}Ti/^{47}Ti$ ratio is affected by the cup configuration used for measurement, i.e., if the apparent high ratio is caused by an offset or gain error of the Faraday cups used. However, changing the cup configuration had no influence on the observed offset.

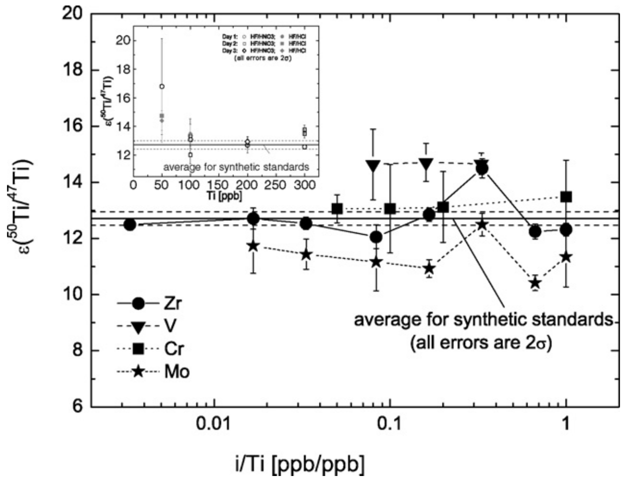

Fig. 3. $\varepsilon(^{50}Ti/^{47}Ti)$ as a function of i/Ti, with i = V, Cr, Zr, and Mo. The data shown are internally normalized for instrumental mass fraction to $^{49}Ti/^{47}Ti = 0.749766$ [17]. The data clearly indicate that interferences from V, Cr, Zr, and Mo can reliable be corrected for and that matrix effect from any of these elements can be excluded. The slight offsets between the different dilution series are due to the fact that the measurements were performed on different days and with slightly different instrument setting. However, the offsets do not compromise the major results. The solid line shows the average value obtained for synthetic standard solutions over about 2.5 years. All uncertainties are 2σ. Inset: $\varepsilon(^{50}Ti/^{47}Ti)$ as a function of Ti concentration [ppb] for standards taken up either in 0.01 M HF + 0.1 M HNO_3 (open symbols) or 0.01 M HF + 0.1 M HCl (solid symbols). The data are distinguished according to the day of measurement. The results indicate that plasma specific interferences on mass 50 from, e.g., $^{14}N^{36}Ar$ can reliably be corrected.

After having carefully checked our data we conclude that the observed offset in $\varepsilon(^{50}Ti/^{47}Ti)$ is not due to an experimental artefact and therefore normalized the $^{50}Ti/^{47}Ti$, $^{48}Ti/^{47}Ti$, and $^{46}Ti/^{47}Ti$ ratios measured for the samples and corrected for mdf via $^{49}Ti/^{47}Ti = 0.749766$ [17] relative to the ratios obtained for pure standard solutions on the same day (also corrected for mdf via $^{50}Ti/^{47}Ti = 0.749766$). For further explanations see Table 2. However, the true reason for the offset of about 13ε relative to the values of Niederer et al. [17] remains currently unexplained.

Considering the offsets in $^{50}Ti/^{47}Ti$, $^{48}Ti/^{47}Ti$, and $^{46}Ti/^{47}Ti$ of 12.71ε, 0.22ε, and 2.29ε, respectively, relative to the values given by Niederer et al. [17] it is important to empha-

Table 2
Average values, internal errors, and reproducibilities for synthetic standard solutions (Alfa-Aesar)

Isotopic ratios	Average value[a]	Internal error[b] (2σ)	External reproducibility[c] (2σ)
$\varepsilon(^{50}Ti/^{47}Ti)$	12.71	0.10	0.14
$\varepsilon(^{48}Ti/^{47}Ti)$	0.22	0.02	0.14
$\varepsilon(^{46}Ti/^{47}Ti)$	2.29	0.12	0.98

All values are given in ε relative to the ratios reported by Niederer et al. [17]. The standard solutions were measured over more than 2.5 years and are internally normalized for instrumental mass fractionation to $^{49}Ti/^{47}Ti = 0.749766$ [17].

[a] The average values are weighted means using the standard deviation as a weighting factor.

[b] The internal error s is calculated via $s = \sqrt{1/\sum_i 1/S_i}$ with S_i as the variance of the individual measurement.

[c] The external reproducibility is the standard deviation of the weighted mean.

size that the isotopic composition of titanium is relatively poorly known [29]. For example, using $^{49}\mathrm{Ti}/^{47}\mathrm{Ti} = 0.7279970$ published recently by Shima and Torigoye [29] the discrepancies increase further, i.e., the grand average values for $^{50}\mathrm{Ti}/^{47}\mathrm{Ti}$, $^{48}\mathrm{Ti}/^{47}\mathrm{Ti}$, and $^{46}\mathrm{Ti}/^{47}\mathrm{Ti}$ are 8.70ε, 2.79ε, and 11.37ε, respectively. However, using instead the ratios preferred by Heydegger et al. [22] for normalization yields grand average values for $^{50}\mathrm{Ti}/^{47}\mathrm{Ti}$, $^{48}\mathrm{Ti}/^{47}\mathrm{Ti}$, and $^{46}\mathrm{Ti}/^{47}\mathrm{Ti}$ of about 2.5ε, -1.4ε, and -0.7ε, i.e., in very good agreement. Turning the argument around and taking our data at face value the titanium isotopic composition which would fit our data best is (relative to $^{49}\mathrm{Ti}/^{47}\mathrm{Ti} = 0.749766$): $^{50}\mathrm{Ti}/^{47}\mathrm{Ti} = 0.73010$, $^{48}\mathrm{Ti}/^{47}\mathrm{Ti} = 10.06884$, and $^{46}\mathrm{Ti}/^{47}\mathrm{Ti} = 1.09325$. This corresponds to an atomic weight of 47.877, i.e., significantly different from the value of 47.867 recommended by IUPAC.

To summarize, from our data alone we cannot prove that the terrestrial $^{50}\mathrm{Ti}/^{47}\mathrm{Ti}$ ratio used recently is incorrect by 13ε, but the excess observed by us is most probably not due to an experimental artefact. Interferences which scale with the Ti concentration of the standard solutions, cannot completely be excluded but we expect such interferences to be very unlikely in pure standards. Furthermore, they would need to be of a molecular or doubly charged nature and unresolvable using our measurement technique.

4.2. *Precision, accuracy, and reproducibility for terrestrial rock samples*

Since synthetic standard solutions typically do not exactly match the samples in terms of matrices, we expect a slightly worse reproducibility for sample measurements compared to the synthetic standards. We therefore determined the external reproducibilities also by repeated measurements of the Icelandic basalts BIR and BTHO, and the rhyolite ATHO, which are widely used as basaltic standard materials. Since the titanium concentrations of these samples are rather high ($\mathrm{TiO_2}$: 0.96% for BIR, 0.27% for ATHO, and 0.93% for BTHO) significant dilution after chemical separation was possible. This enabled us to measure the same solutions (after chemical separation) up to eight times in different runs over a time span of 3 years. The results for $^{50}\mathrm{Ti}/^{47}\mathrm{Ti}$, $^{48}\mathrm{Ti}/^{47}\mathrm{Ti}$, and $^{46}\mathrm{Ti}/^{47}\mathrm{Ti}$ are summarized in Table 3 and shown in Fig. 4.

Table 3
Titanium isotopic ratios for Icelandic basalts BIR and BTHO, and the rhyolite ATHO

Sample	$\varepsilon(^{50}\mathrm{Ti}/^{47}\mathrm{Ti})$			$\varepsilon(^{48}\mathrm{Ti}/^{47}\mathrm{Ti})$			$\varepsilon(^{46}\mathrm{Ti}/^{47}\mathrm{Ti})$		
	Sample[a]	Standard[b]	Final[c]	Sample[a]	Standard[b]	Final[c]	Sample[a]	Standard[b]	Final[c]
BIR	13.75 ± 0.22	13.13 ± 0.25	0.62 ± 0.94	0.12 ± 0.10	0.41 ± 0.05	−0.29 ± 0.30	1.22 ± 0.28	1.61 ± 0.13	−0.39 ± 0.82
	12.85 ± 0.16	12.67 ± 0.16	0.18 ± 0.64	0.71 ± 0.09	0.69 ± 0.14	0.02 ± 0.46	2.52 ± 0.21	2.24 ± 0.17	0.28 ± 0.56
	11.16 ± 0.21	10.91 ± 0.12	0.25 ± 0.66	−1.12 ± 0.08	−1.19 ± 0.05	0.07 ± 0.26	1.47 ± 0.43	0.37 ± 0.13	1.10 ± 1.12
	15.19 ± 0.17	13.40 ± 0.13	1.79 ± 0.60	−0.63 ± 0.04	−1.07 ± 0.07	0.44 ± 0.22	3.91 ± 0.13	3.27 ± 0.12	0.64 ± 0.50
	13.99 ± 0.43	15.09 ± 0.19	−1.10 ± 1.24	0.80 ± 0.09	1.14 ± 0.11	−0.34 ± 0.40	1.91 ± 1.03	2.41 ± 0.27	−0.50 ± 2.60
	13.30 ± 0.41	13.30 ± 0.12	0.00 ± 1.06	0.39 ± 0.06	0.65 ± 0.06	−0.26 ± 0.24	1.28 ± 0.77	1.28 ± 0.11	0.00 ± 1.76
	12.99 ± 0.38	12.92 ± 0.17	0.07 ± 1.10						
Mean			0.55 ± 0.30[d]			0.00 ± 0.13[d]			0.37 ± 0.32[d]
ATHO	13.16 ± 0.56	13.13 ± 0.25	0.03 ± 1.62	−0.06 ± 0.13	0.41 ± 0.05	−0.47 ± 0.36	0.84 ± 0.36	1.61 ± 0.13	−0.77 ± 0.98
	12.88 ± 0.28	12.67 ± 0.16	0.21 ± 0.88	0.43 ± 0.10	0.78 ± 0.27	−0.35 ± 0.74	1.68 ± 1.00	1.03 ± 0.16	0.65 ± 2.32
	11.86 ± 0.82	11.57 ± 0.42	0.29 ± 2.48	−1.37 ± 0.13	−1.70 ± 0.06	0.33 ± 0.38	0.35 ± 0.38	−0.22 ± 0.29	0.57 ± 1.34
	11.67 ± 0.49	12.02 ± 0.16	−0.35 ± 1.30	0.70 ± 0.14	0.65 ± 0.06	0.05 ± 0.40	1.98 ± 1.86	1.28 ± 0.11	0.70 ± 3.94
	13.78 ± 0.22	13.40 ± 0.13	0.38 ± 0.70						
	14.68 ± 0.61	14.52 ± 0.19	0.16 ± 1.60						
	12.25 ± 0.70	12.54 ± 0.17	−0.26 ± 1.74						
Mean			0.17 ± 0.44[d]			−0.07 ± 0.21[d]			−0.17 ± 0.74[d]
BTHO	13.38 ± 0.32	12.80 ± 0.27	0.58 ± 1.18	−3.12 ± 0.14	0.09 ± 0.10	−3.21 ± 0.48	1.25 ± 0.43	1.82 ± 0.24	−0.57 ± 1.34
	12.39 ± 0.29	13.09 ± 0.24	−0.70 ± 1.06	0.80 ± 0.14	0.78 ± 0.27	0.02 ± 0.82	1.24 ± 0.61	1.03 ± 0.16	0.21 ± 1.54
	12.42 ± 0.51	12.54 ± 0.17	−0.12 ± 1.36	0.21 ± 0.11	1.44 ± 0.14	−1.23 ± 0.50	3.56 ± 0.62	4.27 ± 0.50	−0.71 ± 2.24
	12.60 ± 0.06	12.28 ± 0.14	0.32 ± 0.40	1.39 ± 0.15	1.71 ± 0.11	−0.32 ± 0.52	1.12 ± 0.58	0.75 ± 0.21	0.37 ± 1.58
				0.68 ± 0.13	0.38 ± 0.20	0.30 ± 0.66	0.40 ± 0.55	−0.21 ± 0.48	0.61 ± 2.06
				−2.33 ± 1.30	0.95 ± 0.35	−3.28 ± 3.30	−0.65 ± 1.28	−2.27 ± 0.17	−1.62 ± 2.90
Mean			0.21 ± 0.35[d]			−1.23 ± 0.54[d]			−0.14 ± 0.72[d]

All values are given in ε-units. All data are corrected for blanks, interferences, and corrected for instrumental mass fractionation via $^{49}\mathrm{Ti}/^{47}\mathrm{Ti} = 0.749766$ [17].

[a] Each data point is an average of at least four individual measurements. The given uncertainties are the 1σ standard deviations of the mean.

[b] The data for the standards are obtained from AAS standard solutions (Alfa-Aesar, see Section 4.1) measured on the same day. Each data point is an average of at least four individual measurements. The given uncertainties are the 1σ standard deviations of the mean.

[c] The final data are determined by subtracting the data for the standards (column 1) from the data for the sample (column 2). The final uncertainties are obtained by adding the two individual uncertainties. The given uncertainties are the 2σ standard deviations.

[d] The uncertainties given for the mean values are 2σ and are either internal errors (see footnote of Table 2) or standard deviations of the weighted mean, whatever is larger.

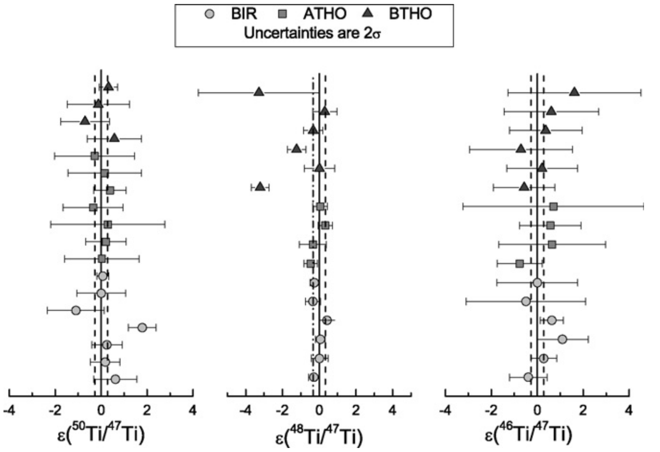

Fig. 4. $\varepsilon(^{50}Ti/^{47}Ti)$, $\varepsilon(^{48}Ti/^{47}Ti)$, and $\varepsilon(^{46}Ti/^{47}Ti)$ for Icelandic basalts BIR and BTHO and rhyolite ATHO, respectively. The error bars shown are 2σ. For $^{50}Ti/^{47}Ti$ all data, except one, are zero within the 2σ uncertainty. For $^{48}Ti/^{47}Ti$ 16 out of the 18 data are normal within the 2σ uncertainty. The large discrepancy observed for one BTHO sample is possibly due to the large Ca background of the nebulizer. For $^{46}Ti/^{47}Ti$ all data are normal within the 2σ uncertainties. From the data we obtain a 2σ-external reproducibility for $^{50}Ti/^{47}Ti$, $^{48}Ti/^{47}Ti$, and $^{46}Ti/^{47}Ti$ of 0.28ε, 0.34ε, and 0.28ε, respectively.

Table 4
Titanium isotopic ratios for the carbonaceous chondrite Allende (CV3)

Sample	$\varepsilon(^{50}Ti/^{47}Ti)$	ε(48Ti/47Ti)	$\varepsilon(^{46}Ti/^{47}Ti)$
Allende-1	4.30 ± 0.90	−0.51 ± 0.76	0.26 ± 2.08
Allende-2	2.51 ± 1.20	−0.27 ± 0.24	0.57 ± 1.56
Allende-3	n.d.	−0.74 ± 1.06	0.67 ± 2.22
Allende-4	3.45 ± 1.02	−1.19 ± 0.36	−0.51 ± 1.62
Allende-5	2.61 ± 1.04	0.23 ± 0.24	0.75 ± 1.54
Mean	3.37 ± 0.74[a]	0.25 ± 0.44[a]	0.33 ± 0.78[a]

All values are given in ε. The data are corrected for blanks, interferences, and for instrumental mass fractionation via $^{49}Ti/^{47}Ti = 0.749766$ [17]. The data are normalized to Alfar-Aesar standard solutions measured on the same day. The given uncertainties are the 2σ external reproducibilites.

[a] The uncertainties given for the mean values are 2σ and are either internal errors (see footnote of Table 2) or standard deviations of the weighted mean, whatever is larger.

For $^{50}Ti/^{47}Ti$ all 18 data, except one, are zero within the 2σ uncertainty. One sample (BIR) deviates from zero by about 6σ, i.e., by 1.79ε. The reason for the observed discrepancy is not yet clear. However, interference corrections and/or blank contributions can be excluded and the other samples and standards measured at the same day show a normal behavior. Considering all data results in a grand average of $0.35 \pm 0.40\varepsilon$. The external reproducibility is 0.28ε. Neglecting the discrepant BIR analysis results in a grand average of $0.17 \pm 0.42\varepsilon$ and an external reproducibility of 0.16ε.

For $^{48}Ti/^{47}Ti$ 16 out of the 18 data are normal within the 2σ uncertainty. For BTHO two of the five studied samples show significant scatter. For one sample the deviation is 5σ (1.23ε) and one sample is off by more than 13σ (3.21ε). The latter discrepancy is possibly due to the large Ca background of the nebulizer on the day of the measurement, which was close to the range were corrections are no longer reliable. Considering all data results in a grand average of $-0.20 \pm 0.20\varepsilon$ with an external reproducibility of 0.34ε. Neglecting the 13σ-outlier results in a grand average of $0.08 \pm 0.20\varepsilon$ and an external reproducibility of 0.20ε. The large uncertainty for one of the BTHO samples is due to the large nebulizer background on this day.

For $^{46}Ti/^{47}Ti$ all data are normal within the 2σ-uncertainty. The grand average is $0.15 \pm 0.62\varepsilon$ with an external reproducibility of 0.28ε. Neglecting the BTHO sample with the 13σ-deviation in $^{48}Ti/^{47}Ti$ results in a grand average value of $0.19 \pm 0.64\varepsilon$ and an external reproducibility of 0.26ε, i.e., indistinguishable from the original data set.

All uncertainties given above are 2σ uncertainties. The uncertainties given for the mean values are the internal errors (for a definition see Table 2). The external reproducibilities are the standard deviations of the weighted means. To summarize, for the terrestrial rock samples we obtain a 2σ-external reproducibility for $^{50}Ti/^{47}Ti$, $^{48}Ti/^{47}Ti$, and $^{46}Ti/^{47}Ti$ of 0.28ε, 0.34ε, and 0.28ε, respectively.

Note, the Ti isotope composition of the Earth is expected to be homogeneous. Therefore, the uniformity of our results (Table 3) clearly demonstrates that the chemical separation procedure is adequate and that the analytical method does not suffer from matrix effects and/or spectral interferences. Moreover, the results further substantiate the reproducibility of our Ti determinations including the 13ε offset relative to the data from previous studies [17].

4.3. *The titanium isotope composition of the Allende meteorite—accuracy and reproducibility*

The external reproducibilities for meteorite samples were determined from five analyses of bulk material of the carbonaceous chondrite Allende (CV3). The results are given in Table 4 and are shown in Fig. 5. Most of the Allende data are for separate dissolutions of a homogeneous sample powder. For $^{46}Ti/^{47}Ti$ all data are normal within the 2σ uncertainties. The grand average value is $0.33 \pm 0.78\varepsilon$ and the external reproducibility is 0.44ε. For $^{48}Ti/^{47}Ti$ all data, except one, are normal within the 2σ uncertainty. The grand average value is $-0.25 \pm 0.16\varepsilon$ and the reproducibility is 0.44ε. The reason for the observed discrepancy for one sample is not yet clear. All other samples measured the same day were normal and blank and interference corrections are only very minor. For $^{50}Ti/^{47}Ti$ all data agree within the uncertainties. The grand average value is $3.37 \pm 0.52\varepsilon$ with an external reproducibility of 0.74ε. The uncertainties for the average values are the 2σ internal errors (see footnote Table 2). The reproducibilities are 2σ. Note that these reproducibilities include the total uncertainty introduced through sample digestion, ion exchange chemistry, and mass spectrometry.

By comparing the statistical data (internal error and standard deviation of the mean) for Allende samples and terrestrial rocks it can be seen that the uncertainty of the data differ very little. If we consider that the data for the terrestrial rocks were obtained from repeated measurements of only three solutions (one for ATHO, one for BTHO, and one for BIR) and that for

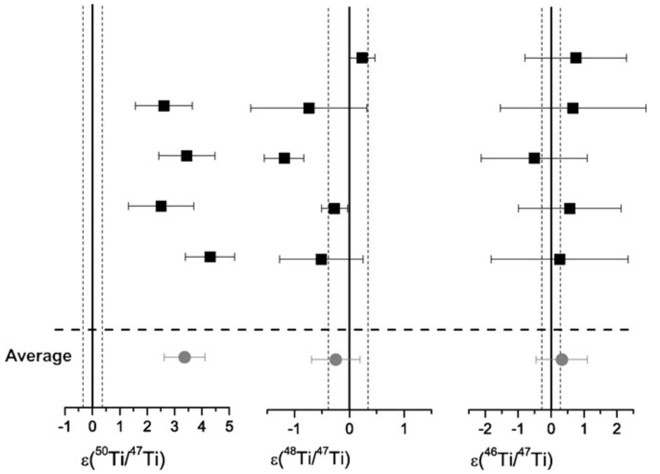

Fig. 5. $\varepsilon(^{50}\mathrm{Ti}/^{47}\mathrm{Ti})$, $\varepsilon(^{48}\mathrm{Ti}/^{47}\mathrm{Ti})$, and $\varepsilon(^{46}\mathrm{Ti}/^{47}\mathrm{Ti})$ for whole rock samples from the carbonaceous chondrite Allende. For $^{46}\mathrm{Ti}/^{47}\mathrm{Ti}$ all data are normal within the 2σ uncertainty. For $^{48}\mathrm{Ti}/^{47}\mathrm{Ti}$ all data, except one, are normal within the 2σ uncertainty. The reason for the observed discrepancy is not yet clear. However, interferences and/or blank corrections cannot serve as an explanation. For $^{50}\mathrm{Ti}/^{47}\mathrm{Ti}$ all data agree within the uncertainties. The grand average value is $3.37 \pm 0.51\varepsilon$ with an external reproducibility of 0.74ε. The data provides strong evidence for anomalous titanium in bulk material from the carbonaceous chondrite Allende. Also shown are the average values for $\varepsilon(^{50}\mathrm{Ti}/^{47}\mathrm{Ti})$, $\varepsilon(^{48}\mathrm{Ti}/^{47}\mathrm{Ti})$, and $\varepsilon(^{46}\mathrm{Ti}/^{47}\mathrm{Ti})$.

each Allende sample the total chemical separation procedure was performed, this finding clearly indicates that the major part of the uncertainties is introduced by the ICP measurements. The chemical separation adds only a minor part to the total uncertainties. However, one exception is the $^{50}\mathrm{Ti}/^{47}\mathrm{Ti}$ ratio, for which the reproducibility for Allende samples is about a factor of two worse compared to terrestrial rocks. We interpret this finding as due to the fact that the processed Allende samples had rather variable Cr/Ti and V/Ti ratios, although the chemical separation procedure was the same for all samples. Consequently, the magnitude of the interference corrections significantly vary between the individual samples. For example, the corrections for chromium range between 5ε and 35ε; for vanadium the corrections are between 1ε and 19ε. Such variable corrections influence the reproducibility of the measurements and slightly increase the uncertainties. Note that the uncertainties on the corrections are propagated through the reported uncertainties on the corrected ratios.

Our data clearly demonstrate the presence of anomalous $^{50}\mathrm{Ti}$ ($\varepsilon(^{50}\mathrm{Ti}/^{47}\mathrm{Ti}) = 3.37 \pm 0.74$) in bulk material from Allende. The measured excess is at the 10σ level. This observation is in contrast to an earlier study, in which no anomalies for Allende whole rock samples or matrix separates have been found [14,22]. However, our data are more precise and the 3ε excess observed by us would not have been detected in the earlier study because the authors reported 2σ errors of about 5ε. Moreover, in a later study, Niemeyer and Lugmair found anomalous titanium in bulk material from the CI1 chondrite Ivuna and in matrix separates of the CM2 chondrites Murchison and Murray [21]. Furthermore, the finding of anomalous titanium is in good agreement with the recent reports of anomalous S, Cr, Mo, and Ru in bulk carbonaceous chondrites [2–10].

5. Concluding remarks

We present a new method for the determination of titanium isotope compositions in geologic samples. After sample digestion, titanium is separated by ion exchange chromatography and the isotopic composition is measured by high resolution MC-ICPMS. The external reproducibilities are 0.28ε, 0.34ε, and 0.28ε for $^{50}\mathrm{Ti}/^{47}\mathrm{Ti}$, $^{48}\mathrm{Ti}/^{47}\mathrm{Ti}$, and $^{46}\mathrm{Ti}/^{47}\mathrm{Ti}$, respectively. The method has been successfully applied to terrestrial samples, lunar rocks, bulk meteorites, various mineral separates, and etch leachates [30]. Our data indicate that the terrestrial titanium isotopic composition is not well constrained. We also demonstrate that bulk material from the carbonaceous chondrite Allende (CV3) has anomalous titanium, i.e., a $^{50}\mathrm{Ti}/^{47}\mathrm{Ti}$ excess of $3.37 \pm 0.74\varepsilon$ relative to synthetic standards and terrestrial rocks. The latter finding is in contrast to earlier less precise measurements for Allende [14] but is in agreement with the observation of anomalous titanium in bulk material from the CI1 condrite Ivuna in and matrix separates from the CM2 chondrites Murchison and Murray [21].

Clearly the measurement of titanium isotopes via MC-ICPMS is not straightforward. For a precise analysis of a sample one needs three independent measurements, two with a mass resolution of at least 2000 (one for $^{53}\mathrm{Cr}$, $^{51}\mathrm{V}$, $^{50}\mathrm{Ti}$, $^{49}\mathrm{Ti}$, $^{48}\mathrm{Ti}$, and $^{47}\mathrm{Ti}$ and one for $^{49}\mathrm{Ti}$, $^{48}\mathrm{Ti}$, $^{47}\mathrm{Ti}$, $^{46}\mathrm{Ti}$, and $^{44}\mathrm{Ca}$) and one measurement for the Zr/Ti elemental ratios. In addition, the measurement of $^{44}\mathrm{Ca}$ is very sensitive to baseline variations caused by the large $^{40}\mathrm{Ar}$ beam. However, despite such difficulties, our data are more precise than earlier measurements performed by TIMS [14–22]. The TIMS studies usually suffered from higher blanks, i.e., about 10 ng compared to less than 200 pg. In addition, the uncertainties of between 1ε and 3ε given for the TIMS studies are slightly higher than the uncertainties obtained by us. Consequently, the MC-ICPMS data are very precise and reproducible and should provide better constraints on the titanium isotopic compositions of early solar system objects.

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