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International Journal of Mass Spectrometry 220 (2002) 21–29

International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

High precision measurement of titanium isotope ratios by plasma source mass spectrometry

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Received 4 March 2002; accepted 21 June 2002

Abstract

A method using multiple-collector inductively coupled plasma source mass spectrometry for the precise measurement of Ti isotope composition in natural materials has been developed. Instrumental mass discrimination is corrected using a "standard-sample bracketing" approach by expressing the isotope ratios of samples relative to those of the bracketing standard. Variations in ^{47}Ti/^{46}Ti, ^{48}Ti/^{46}Ti, ^{49}Ti/^{46}Ti and ^{50}Ti/^{46}Ti ratios of samples are expressed in ε units which are deviations in parts per 10^4 from the same isotope ratios of the reference material. The long-term repeatability at the 2 standard deviation level is 0.4, 0.6, 0.7 and 0.8 ε units in terms of ^{47}Ti/^{46}Ti, ^{48}Ti/^{46}Ti, ^{49}Ti/^{46}Ti and ^{50}Ti/^{46}Ti ratio measurements, respectively. The technique reported here makes it possible for the first time that both mass-dependent fractionation and isotope anomalies of Ti isotopes in natural materials can be measured to high precision. (Int J Mass Spectrom 220 (2002) 21–29)

Keywords: Titanium isotopes; Plasma source mass spectrometry; Stable isotopes; Matrix effects; Transition metal

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1. Introduction

Ti is an element of considerable geochemical and cosmochemical importance. In geochemical context, it is an important element in the study of petrogenesis, and its isotope composition may offer a means of tracing the geochemical cycling of Ti in terrestrial environments. Moreover, Ti is an element which is not biologically utilised. Thus, its isotope compositions might be used as a reference in distinguishing between biologically and non-biologically induced mass fractionations of transition metal isotopes. In cosmochemical context, Ti is a refractory element and it is abundant in many early solar system solids [1]. This, combined with its immobility during most later asteroidal processes, makes it possible for Ti isotopes to preserve information about nebular processes during early solar system evolution. Furthermore, Ti has five naturally occurring stable isotopes, namely ^{46}Ti, ^{47}Ti, ^{48}Ti, ^{49}Ti and ^{50}Ti with relative abundances of 8.25, 7.44, 73.72, 5.41 and 5.18%, respectively. Variations of the relative abundances of multiple isotopes of an element can in principle be used to determine if the initial reservoir of solar system material

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PII S1387-3806(02)00767-4

was a homogeneous mixture or if it contained several distinct sources of precursor material. This kind of information is crucial in understanding early solar system evolution [2,3].

In previous studies Ti isotope ratio measurements were performed using thermal ionisation mass spectrometry [4] or secondary ion mass spectrometry (SIMS) [5], where the measured Ti isotope ratios are internally normalised. Those approaches are however only of limited value, because they eliminate all information about mass-dependent fractionation. Following the successful development of high precision isotope ratio measurements of transition metals such as Fe, Cu and Zn using plasma source mass spectrometry [3,6–9], here we present techniques for the abundance measurement of five Ti isotopes in both terrestrial and extraterrestrial materials. The new technique is applicable to studies of both Ti isotope mass-dependent fractionation and mass-independent variations—the so-called "isotope anomalies."

2. Analytical method

2.1. Sample preparation and introduction

For precise and accurate Ti isotope analysis, chemical purification of natural materials is necessary. This is because natural materials usually contain a wide spectrum of elements, which may result in isobaric interferences for Ti isotope signals (Table 1) and/or matrix effects. A new ion exchange chromatographic method has been developed for Ti purification, which uses three columns: the first and the third columns using AG 1X8 resin, and the second using U/TEVA resin. A high-level of purification of Ti from other elements is achieved using this procedure, with the exception of W which is only partially removed. Details of the procedure have been described elsewhere [10].

All Ti standards as well as Ti separated from samples were introduced into the plasma in 0.1 M HF through a modified Cetac MCN 6000 desolvation nebuliser. This device minimises the introduction of H_2O, O_2, CO_2 and N_2 into the plasma and thus the production of interfering molecular species. Runs of sample and standard were separated by washes using 0.1 M HF for 5 min.

2.2. Mass spectrometry

Ti isotope ratios were measured using a Nu Instruments plasma source mass spectrometer, which is a double focusing magnetic sector instrument with variable dispersion ion optics and a fixed array of 12 Faraday collectors [11]. The signals of five isotopes of Ti are simultaneously collected in a static mode, with $^{46}\text{Ti}^+$ and $^{50}\text{Ti}^+$ in the extreme collectors on the low and high mass sides, respectively. $^{48}\text{Ti}^+$, which is the most abundant isotope, is collected in the axial Faraday cup equipped with a $10^{10}\ \Omega$ resistor, whereas $^{46}\text{Ti}^+$, $^{47}\text{Ti}^+$, $^{49}\text{Ti}^+$ and $^{50}\text{Ti}^+$ are collected in Faraday cups using $10^{11}\ \Omega$ resistors. Data were acquired in blocks of 15 ratios with 10 s integration times, and background measurements were taken prior to each data block.

Instrumental mass discrimination in the Ti mass region is approximately 3% amu^{-1} under the working conditions. This is estimated from repeated measurements of an Fe isotope reference material IRMM-14, as there is no isotopically characterised Ti reference materials available. In principle the instrumental mass

Table 1
Some potential interfering molecules on Ti isotopes

Isotope	Interfering signal
$^{46}\text{Ti}^+$	$[^{23}\text{Na}_2]^+$; $[^{6}\text{Li}^{40}\text{Ar}]^+$; $[^{34}\text{S}^{12}\text{C}]^+$; $[^{32}\text{S}^{14}\text{N}]^+$; $[^{28}\text{Si}^{18}\text{O}]^+$; $[^{31}\text{P}^{15}\text{N}]^+$; $[^{27}\text{Al}^{19}\text{F}]^+$; $^{92}\text{Mo}^{2+}$; $^{92}\text{Zr}^{2+}$
$^{47}\text{Ti}^+$	$[^{23}\text{Na}^{24}\text{Mg}]^+$; $[^{7}\text{Li}^{40}\text{Ar}]^+$; $[^{31}\text{P}^{16}\text{O}]^+$; $[^{11}\text{B}^{36}\text{Cl}]^+$; $[^{28}\text{Si}^{19}\text{F}]^+$; $^{94}\text{Mo}^{2+}$; $^{94}\text{Zr}^{2+}$
$^{48}\text{Ti}^+$	$^{48}\text{Ca}^+$; $[^{24}\text{Mg}_2]^+$; $[^{12}\text{C}^{36}\text{Ar}]^+$; $[^{12}\text{C}^{26}\text{Ar}]^+$; $[^{34}\text{S}^{14}\text{N}]^+$; $^{96}\text{Mo}^{2+}$; $^{96}\text{Zr}^{2+}$; $^{96}\text{Ru}^{2+}$
$^{49}\text{Ti}^+$	$[^{9}\text{Be}^{40}\text{Ar}]^+$; $[^{24}\text{Mg}^{25}\text{Mg}]$; $[^{18}\text{O}^{31}\text{P}]^+$; $^{98}\text{Mo}^{2+}$; $^{98}\text{Ru}^{2+}$
$^{50}\text{Ti}^+$	$^{50}\text{Cr}^+$; $^{50}\text{V}^+$; $[^{14}\text{N}^{36}\text{Ar}]^+$; $^{100}\text{Mo}^{2+}$; $[^{23}\text{Na}^{27}\text{Al}]^+$; $[^{19}\text{F}^{31}\text{P}]^+$

discrimination for isotope ratio measurement using MC-ICPMS may be corrected using a doping method [7,11–13], or a standard-sample bracketing procedure [6–9], or a double-spike technique [14]. Following experience with other transition metal isotope measurements such as those of Fe, Cu and Zn [3,6–9], the standard-sample bracketing method is adopted for correction of instrumental mass discrimination of Ti isotopes. For this approach, samples and standard are analysed alternatively. By expressing the isotope results of samples relative to those of the bracketing standard, the instrumental mass fractionation is cancelled out.

3. Results and discussion

The Ti isotope ratios of samples are expressed as deviations from those of the reference standard as follows:

$$\varepsilon^{x}\mathrm{Ti} = \left(\frac{{}^{x}R_{\mathrm{sample}}}{{}^{x}R_{\mathrm{standard}}} - 1\right) \times 10,000$$

where ${}^{x}R_{\mathrm{sample}}$ and ${}^{x}R_{\mathrm{standard}}$ are measured ratios of ${}^{x}\mathrm{Ti}/{}^{46}\mathrm{Ti}$ for the unknown sample and the standard, respectively, and x denotes 47, 48, 49 or 50. The material used as Ti isotope standard is NIST 3162a (lot no. 992801).

3.1. Assessment of isobaric interferences

All elements which might produce molecular interferences on Ti isotope signals (Table 1) have been reduced to negligible levels from natural samples through a three-column procedure separation process [10]. However, to ensure the contributions from ${}^{50}\mathrm{V}^{+}$ and ${}^{50}\mathrm{Cr}^{+}$ to the measured ${}^{50}\mathrm{Ti}^{+}$ signal are negligible, the major isotope signals of these elements, ${}^{51}\mathrm{V}^{+}$ (99.76%) and ${}^{52}\mathrm{Cr}^{+}$ (83.45%), are routinely monitored during Ti concentration measurements. It has been found that in all cases for both natural samples and Ti standard solutions the ${}^{51}\mathrm{V}^{+}/{}^{50}\mathrm{Ti}^{+}$ and ${}^{52}\mathrm{Cr}^{+}/{}^{50}\mathrm{Ti}^{+}$ ratios are smaller than 10^{-3} and 10^{-4}, respectively. This implies that both the contributions of ${}^{50}\mathrm{V}^{+}$ and ${}^{50}\mathrm{Cr}^{+}$ to the measured ${}^{50}\mathrm{Ti}^{+}$ are $<10^{-5}$, which are negligible relative to the precision achieved. Thus, no correction for the measured ${}^{50}\mathrm{Ti}^{+}$ signal is required.

Under optimised working conditions, the signal intensity for ${}^{46}\mathrm{Ti}^{+}$ is typically about 4×10^{-11} A. The background signals are estimated to be below 10^{-16} A at masses 46, 47, 48 and 49. This has been observed by measuring Ti-free 0.1 M HF solution after long washing of the sample introduction system. At mass 50, however, a small interfering signal at ca. 10^{-15} A persists. The intensity of this signal is fairly constant under optimised working conditions regardless of the strength of acid being used, but varies with the flow rates of Ar and $\mathrm{N_2}$ used in the Cetac-6000 nebuliser, which suggests that this isobaric interference signal is most likely $[{}^{36}\mathrm{Ar}{}^{14}\mathrm{N}]^{+}$.

As ${}^{50}\mathrm{Ti}$ is the most likely Ti isotope to be anomalous in extraterrestrial materials [4,5], the accurate and precise measurement of its relative abundance is of special importance in cosmochemical studies. Thus, the contribution of $[{}^{36}\mathrm{Ar}{}^{14}\mathrm{N}]^{+}$ at mass 50 in Ti-bearing solutions is examined further (Fig. 1). The anticipated effect of this interference at mass 50 on $\varepsilon^{50}\mathrm{Ti}$ has been calculated as a function of parameters C' and f. C' is the ratio of the Ti concentration in a sample solution over that in the standard solution, whereas f is the fractional contribution of the interfering ion at mass 50 for a fixed concentration of Ti in the standard solution. The modelling is simplified by assuming that both sample and standard have identical real $\varepsilon^{50}\mathrm{Ti}$ values. Thus, in Fig. 1a, $\varepsilon^{50}\mathrm{Ti} = 0$ when the effect of the interfering signal at mass 50 is zero, or is equal between sample and standard. The modelling results shown in Fig. 1a demonstrate that: (1) the true $\varepsilon^{50}\mathrm{Ti}$ value can be obtained when the Ti concentrations in both sample and standard solutions are identical, no matter how large is the interfering signal at mass 50; (2) even where the interfering signal at mass 50 is very small, its effect on $\varepsilon^{50}\mathrm{Ti}$ may be significant particularly where C' is much less than 1.0; (3) the extent to which the Ti concentration of a sample may be varied relative to that of the standard depends upon the relative intensity of the interfering signal (parameter f)

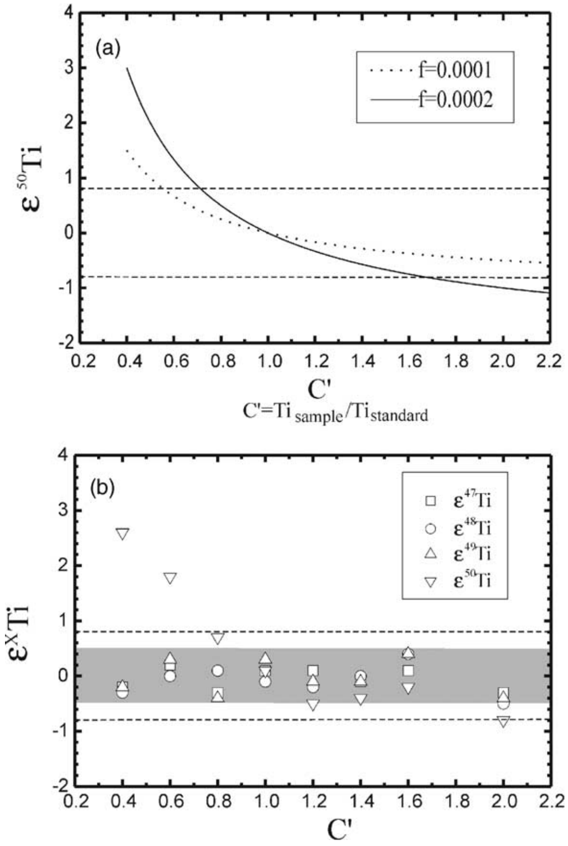

Fig. 1. Assessment of the effects of interfering signals on measured ^{50}Ti/^{46}Ti ratio. (a) Calculation of the effect of an interfering signal (such as ^{36}Ar^{14}N^{+}) at mass 50 on the measured ε^{50}Ti of a sample. Model calculations have been performed at different values of $f = 1 \times 10^{-4}$ and $f = 2 \times 10^{-4}$, where f is the fractional contribution of the interfering signal at mass 50 to the ^{50}Ti ion beam intensity at a given concentration of the standard. C' is the ratio of Ti concentration in "sample" relative to that in the "standard." Both "sample" and "standard" are assumed to have identical true ε^{50}Ti values. Therefore, the deviation in ε^{50}Ti value as a function of f and C' are due solely to the interfering signal at mass 50. (b) Measurement of ε^{x}Ti values in NIST 3162a "sample" Ti solutions with concentration ranging from 2 to 10 ppm, relative to NIST 3162a "standard" Ti solution at 5 ppm. The two dashed horizontal lines bracket the measurement repeatability of ε^{50}Ti at 2 S.D. level, whereas the width of the grey band represents the repeatability of ε^{47}Ti at 2 S.D. level, as defined in Fig. 4.

and the analytical precision. Fig. 1b shows the results of a series of measurements of ε^{47}Ti, ε^{48}Ti, ε^{49}Ti and ε^{50}Ti in NIST "sample" solutions with different Ti concentrations, relative to NIST 3162a "standard" Ti solution at 5 ppm. The Ti concentration in the NIST 3162a Ti "sample" solutions used vary from 2 to 10 ppm, which is equivalent to C' values ranging from 0.4 to 2. The dependence of ε^{50}Ti on Ti concentration observed from these measurements (Fig. 1b) is very similar to the predicted dependence shown in Fig. 1a. The similarity between the predicted and the actual measured values validates the assumptions adopted for the simple model, and shows that the interfering signal at mass 50 is indeed very small during analysis for the working conditions used. Also, the results presented in Fig. 1b demonstrate further that the effects of interfering signals on masses 46, 47, 48 and 49 are indeed negligible, and that Ti concentration has little effect on instrumental mass discrimination under the working conditions used. From Fig. 1b it is deduced that the concentrations of Ti in sample and standard solutions may differ by ca. ±230% with a negligible introduction of error into the ε^{50}Ti value relative to the measurement repeatability achieved (see Section 3.4).

The above discussion is based on the assumption that both sample and standard have identical Ti isotope composition. In the case where the Ti isotope composition is different from that of standard, the concentration matching between sample and standard, in strict sense, should be performed in terms of ^{50}Ti. However, as the variations of transition metal isotopes in natural materials are expected to be much smaller than the extent to which the Ti concentration of a samples is allowed to be varied relative to that of the standard [3,7–9], the concentration matching between sample and standard can in practice be made in terms of either the bulk Ti element or any of its isotopes.

3.2. *Effects of Ti concentration*

An alternative approach to minimise the interference signal of $[^{36}\mathrm{Ar}^{14}\mathrm{N}]^{+}$ on $^{50}\mathrm{Ti}^{+}$ is to desolvate samples running the MCN 6000 nebuliser with no N_2 flow, which has been a method successfully adopted to reduced the isobaric interference of $[^{40}\mathrm{Ar}^{14}\mathrm{N}]^{+}$ on $^{54}\mathrm{Fe}^{+}$ for Fe isotope measurement using plasma

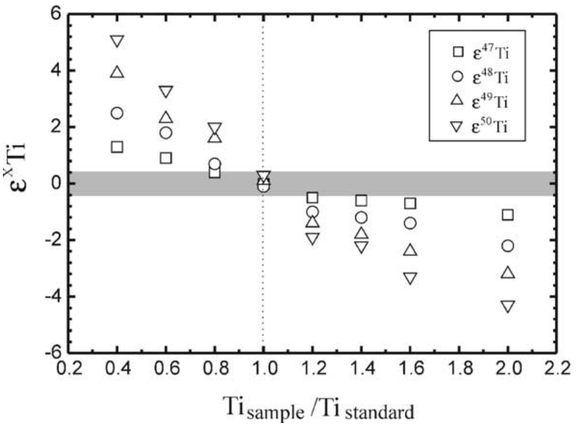

Fig. 2. A plot showing the effect of varying Ti concentration on the measured Ti isotope ratios. Unlike the interference effects shown in Fig. 1b, the variances of the measured Ti isotope ratios follow a mass-dependent manner. These results were obtained with the desolvating nebuliser running without N_2 gas. The width of the grey band represents the long-term repeatability of ε^{47}Ti at the 2 standard deviation level, as defined in Fig. 4. The dotted line represents the position where the Ti concentration of "sample" solution is the same as that of the standard. The Ti concentration of solution used as the standard in these experiments is 5 ppm.

source mass spectrometry [6,9]. To investigate the feasibility of this approach, a series of measurements have been carried out using NIST 3162a Ti solutions with Ti concentrations varying from 2 to 10 ppm vs. the same Ti solution at a fixed concentration of 5 ppm. The obtained ε values of the measured Ti isotope ratios of the "sample" vary significantly with Ti concentration in a mass-dependent manner (Fig. 2). These variations cannot be explained by molecular interferences, but must result from instrumental mass fractionation. This implies that the instrumental fractionation of Ti isotopes varies according to the Ti concentration introduced into the mass spectrometer, at least for the given set of working conditions. This phenomenon may be regarded as a special case of matrix effects (see next section).

Ti ionisation efficiency is reduced by ca. 30% when the desolvating nebuliser is employed without N_2 gas, which is presumably due to the decrease of the plasma temperatures relative to when both Ar and N_2 are used. The observation of variance of instrumental mass fractionation resulting from concentration differences of the element analysed highlights the potential challenges for high-precision isotope ratio measurement using "cold" plasma approaches.

3.3. Matrix effects

The term matrix effects used here refers to the phenomenon that mass fractionation during plasma source mass spectrometry varies with changes in composition of sample solutions under a given set of working conditions, which is analogous to the usage of the term in SIMS (e.g., [15,16]). A solution to this potential problem is chemical purification. Investigations are focused only on the elements where complete separation is not achieved after chemical processing [10]. They are Al, W and P.

3.3.1. Effects of aluminium

The effects of Al on the measured Ti isotope ratios has been examined for nine synthetic mixtures with Al:Ti weight ratios varying from 0.002 to 2. A NIST 3162a Ti solution of 5 ppm concentration is used as both standard and samples. As plotted in Fig. 3a, the results show that under the working conditions the effects of Al concentration in the final solution on the measured Ti isotope ratios is minimal for Al/Ti weight ratio of up to 0.04. However, the measured Ti isotope ratios show clear dependency on Al contents where Al/Ti weigh ratios $\geq$0.1.

The above observations imply that, under the working conditions used in this study, precise and accurate Ti isotope ratio measurement can be made only if Al content in the final solution is no more than a few percent of the Ti content. For most terrestrial and extraterrestrial materials, this degree of sample purity can be readily achieved through chemical processing using a three-column procedure, which reduces Al by more than 5 orders of magnitude relative to its original content [10].

3.3.2. Effects of tungsten

Investigation of the effects of W content in the final solution on the measured Ti isotope ratios is

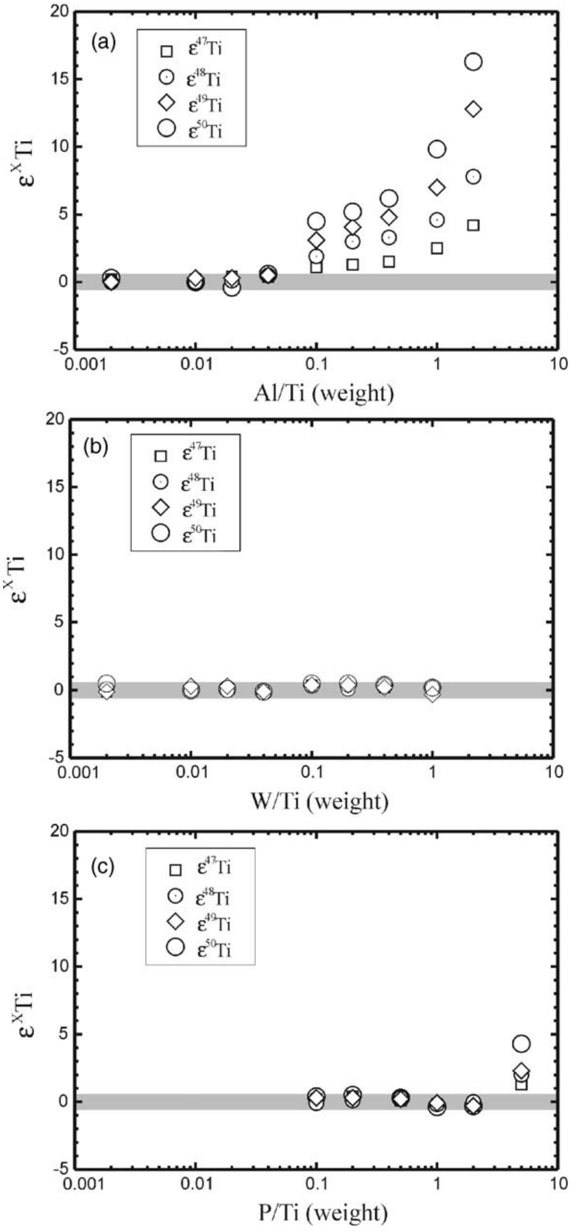

Fig. 3. Plots showing the effects of matrix chemistry on measured Ti isotope results. (a) Al; (b) W; (c) P. The external precision at 2σ level is represented by the sizes of data points. The width of the grey line approximates the long-term repeatability of ε^{48}Ti measurement at 2 standard deviation level (see Fig. 4).

performed on eight synthetic mixtures with W:Ti weight ratio varying from 2×10^{-3} to 1. Ti contents in the standard and "sample" solutions are 5 ppm. Results of these analyses are plotted in Fig. 3b. There is no observable dependency of Ti isotope ratio on W/Ti ratio, and the obtained ε values vary within the instrumental repeatability (see Section 3.4).

Although only a fraction of W in samples is removed using the three-column procedure [10], the abundance of W in both terrestrial and extraterrestrial materials is normally 2 or 3 orders of magnitude lower than Ti [17,18]. Thus, under the given working conditions, W exerts no significant effect on the Ti isotope ratio measurements for the majority of nature geological and meteoritic materials.

3.3.3. *Effects of phosphorus*

Although P in samples is effectively removed after the first column, some P is re-introduced into samples from the U/TEVA resins used in the second column, which may not be completely eliminated through processing of the third column [10]. Thus, it is necessary to investigate whether the presence of P in the final solutions affects Ti isotope ratio measurements.

Assessment of the presence of P on the measured Ti isotope ratios has been performed on six synthetic mixtures with P/Ti weight ratios ranging from 0.1 to 5. NIST 3162a Ti has been used as both samples and standard, with a concentration of 5 ppm. Results of these analyses are presented in Fig. 3c. It is observed that under the working conditions the effect of P in the final solution on the measured Ti isotope ratios is minimal for P/Ti weight ratio up to 2. However, a significant effect on the measured Ti isotope ratios is observed when P/Ti ratios increase to 5.

The P/Ti ratio of samples after chemical purification is generally smaller than 0.1. Repeated tests on synthetic mixtures following chemical processing show that the amount of P left in the final solutions exerts no detectable effect on Ti isotope ratio measurements [10]. This conclusion is further reinforced by the results of duplications of natural samples (Table 2).

Table 2
Ti isotope results of terrestrial and extraterrestrial samples relative to NIST 3162a

Sample	Description	ε^{47}Ti[a]	ε^{48}Ti[a]	ε^{49}Ti[a]	ε^{50}Ti[a]
BD3855	Amphibole, Tanzanian mantle xenolith	−2.3	−4.9	−6.9	−9.3
Basalt 243	Icelandic basalt	−5.8	−11.5	−16.9	−22.7
Basalt 244	Icelandic basalt	−5.6	−11.2	−16.4	−22.4
Basalt 266	Icelandic basalt	−5.5	−11.1	−16.4	−22.5
Basalt 267	Icelandic basalt	−5.6	−10.7	−16.1	−22.0
YH-5	Lamproite, China	−4.8	−9.9	−14.6	−19.5
YH-5	Duplicate[b]	−4.9	−9.6	−14.4	−19.4
XF97S1	Chinese loess, Xifeng	−4.5	−9.2	−13.6	−18.5
XF97L1	Chinese loess, Xifeng	−4.5	−9.1	−13.6	−18.7
XF97S3	Chinese loess, Xifeng	−4.6	−9.3	−13.6	−18.7
XF97L3	Chinese loess, Xifeng	−4.6	−9.2	−13.9	−18.0
Camel Donga	Eucrite	−5.3	−10.7	−15.9	−22.3
Camel Donga	Duplicate[b]	−5.4	−10.3	−16.1	−22.4

[a] Errors are better than 0.4, 0.6, 0.7 and 0.8 ε units for ε^{47}Ti, ε^{48}Ti, ε^{49}Ti, ε^{50}Ti, respectively, at 2σ level, which are estimated from the long-term repeatability at 2 S.D. level (Fig. 3).

[b] The duplication includes sample digestion, column separation and mass spectrometry.

3.4. Standard repeatability and analytical precision

The performance of the instrument for Ti isotope analysis has been assessed by repeated measurement of standard solutions Aldrich Ti against NIST Ti. Results obtained over a period of 11 months are presented in Fig. 4. The average Ti isotope values obtained for Aldrich Ti are $\varepsilon^{47}\mathrm{Ti} = -5.0 \pm 0.4$ (2 S.D.), $\varepsilon^{48}\mathrm{Ti} = -10.0 \pm 0.6$ (2 S.D.), $\varepsilon^{49}\mathrm{Ti} = -15.0 \pm 0.7$ (2 S.D.)

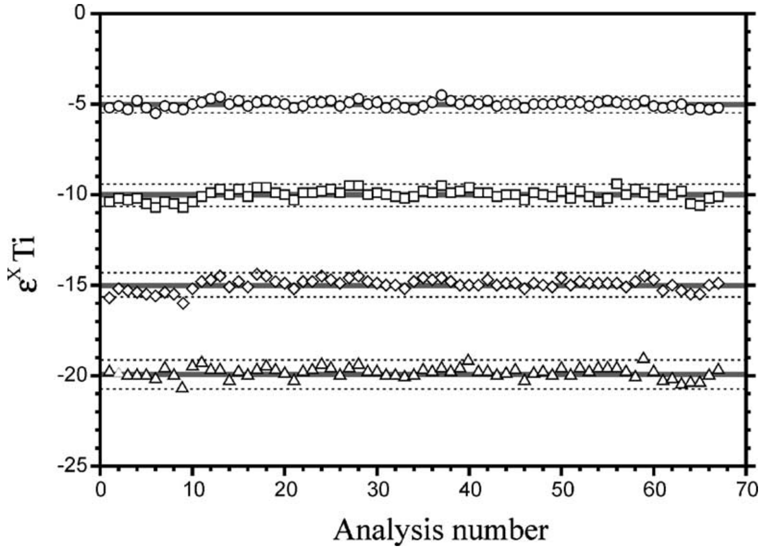

Fig. 4. Repeatability of Ti isotope ratio measurements. The average isotope values for Aldrich Ti relative to the NIST 3162a Ti obtained over a period of 11 months are $\varepsilon^{47}\mathrm{Ti} = -5.0 \pm 0.4$ (2 S.D.), $\varepsilon^{48}\mathrm{Ti} = -10.0 \pm 0.6$ (2 S.D.), $\varepsilon^{49}\mathrm{Ti} = -15.0 \pm 0.7$ (2 S.D.) and $\varepsilon^{50}\mathrm{Ti} = -19.8 \pm 0.8$ (2 S.D.). The long-term repeatability obtained in this study defines an external precision of 0.4, 0.6, 0.7 and 0.8 ε units for ^{47}Ti/^{46}Ti, ^{48}Ti/^{46}Ti, ^{49}Ti/^{46}Ti and ^{50}Ti/^{46}Ti ratio measurements, respectively, at 95% confidence (2σ) level. Open circle—ε^{47}Ti; open square—ε^{48}Ti; open diamond—ε^{50}Ti; open triangle—ε^{50}Ti.

and ε^{50}Ti $= -19.8 \pm 0.8$ (2 S.D.). The long-term repeatability obtained in this study defines an external precision of 0.4, 0.6, 0.7 and 0.8 ε units for ^{47}Ti/^{46}Ti, ^{48}Ti/^{46}Ti, ^{49}Ti/^{46}Ti and ^{50}Ti/^{46}Ti ratio measurements, respectively, at 95% confidence (2σ) level.

Variations in Ti isotope ε values of natural samples and synthetic mixtures after replicated column processing are all within the precision stated above (Table 2 and [10]). Therefore, the long-term repeatability obtained above is regarded as an overall analytical precision.

3.5. Mass-dependent fractionation and isotope anomalies

3.5.1. Ti isotope composition of terrestrial materials

A number of natural samples have been analysed using the procedures described above, following complete digestion and chemical purification [10]. These include terrestrial materials of mantle xenolith, basalt and loess samples. They are expected to provide some basic information about Ti isotope compositions in the continental crust and the Earth's upper mantle. In addition, an extraterrestrial sample eucrite has also been measured. These samples exhibit variations ranging from 3.3 ε units in terms of ^{47}Ti/^{46}Ti ratio to 12.4 ε-units in terms of ^{50}Ti/^{46}Ti ratio (Table 2), which show unequivocally that natural variation in Ti isotope composition exists. These preliminary results therefore demonstrate that potential exist in using Ti isotopes to address some important geological and cosmochemical processes related to Ti mobilisation, redistribution and mass fractionation.

3.5.2. Mass-dependent fractionation curves and isotope anomalies

Variations in the isotope composition of Ti in solar system materials arise ultimately through two sources: (1) mass-dependent fractionation resulting from various physical and chemical processes, such as volatilisation and condensation, and chemical speciation; (2) stellar nucleosynthesis.

Physical and chemical processes operating on an initially isotopically uniform reservoir induce Ti isotope variations following a mass-dependent fractionation pattern [19,20]. The Ti isotope results of natural samples (Table 2) and an Aldrich Ti standard are presented in Fig. 5 in a manner analogous to a three-isotope plot, together with the isotope variations resulting from instrumental fractionation. As shown in the diagram, Ti isotope results of the measured natural materials are plotted on the same lines with those resulting from instrument mass fractionation, including the data from Ti concentration effects (Fig. 2) and from Al effects (Fig. 3a). The correlation between ε^{48}Ti/^{46}Ti and ε^{47}Ti/^{46}Ti, ε^{49}Ti/^{46}Ti and ε^{47}Ti/^{46}Ti, and ε^{50}Ti/^{46}Ti and ε^{47}Ti/^{46}Ti of all the results defines three lines with the following relationship: $\varepsilon^{48}\mathrm{Ti} = (1.987 \pm 0.014) \times \varepsilon^{47}\mathrm{Ti} - (0.08 \pm 0.05)$, $\varepsilon^{49}\mathrm{Ti} = (2.960 \pm 0.020) \times \varepsilon^{47}\mathrm{Ti} - (0.05 \pm 0.08)$ and $\varepsilon^{50}\mathrm{Ti} = (4.003 \pm 0.028) \times \varepsilon^{47}\mathrm{Ti} - (0.13 \pm 0.10)$. The correlation coefficients R^2 for these three regression lines are 0.9988, 0.9988 and 0.9987, respectively. The observed correlation between these isotopes is broadly

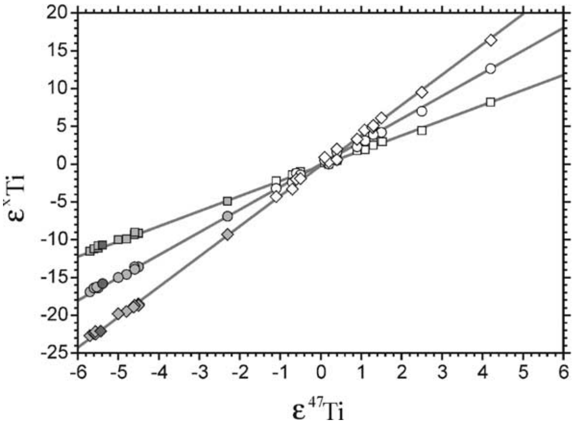

Fig. 5. Multiple-isotope presentation showing the ε^{x}Ti values of terrestrial (light grey symbols) and extraterrestrial (dark grey symbols) materials plotted on the same lines together with those resulting from instrumental mass fractionation caused by concentration and matrix effects (open symbols). The correlation between ε^{48}Ti/^{46}Ti and ε^{47}Ti/^{46}Ti, ε^{49}Ti/^{46}Ti and ε^{47}Ti/^{46}Ti, and ε^{50}Ti/^{46}Ti and ε^{47}Ti/^{46}Ti of all results defines three lines which obey the following equations: $\varepsilon^{48}\mathrm{Ti} = (1.987 \pm 0.014) \times \varepsilon^{47}\mathrm{Ti} - (0.08 \pm 0.05)$, $\varepsilon^{49}\mathrm{Ti} = (2.960 \pm 0.020) \times \varepsilon^{47}\mathrm{Ti} - (0.05 \pm 0.08)$ and $\varepsilon^{50}\mathrm{Ti} = (4.003 \pm 0.028) \times \varepsilon^{47}\mathrm{Ti} - (0.13 \pm 0.10)$. The correlation coefficients R^2 for these three regression lines are 0.9988, 0.9988 and 0.9987, respectively.

consistent with theoretical expectations [20,21], if the Ti isotope compositions of the analysed materials evolved from a single isotopically uniform reservoir in a mass-dependent manner. These correlation lines between the Ti isotopes are therefore the terrestrial mass-dependent fractionation lines. Any materials, originating from the same isotopically uniform source of terrestrial materials, will possess Ti isotope variations on these mass fractionation lines.

Conversely, Ti isotopes produced in different stars have distinctive signatures. The mixing between these isotopically distinct reservoirs will result in Ti isotope variations that do not necessarily follow mass-dependent fractionation, which give rise to the so-called "isotope anomalies." Previous studies have shown that Ti isotope anomalies exist in some extraterrestrial materials [3–5]. For the approach developed in this study, deviations of Ti isotope ratios from any of the mass-dependant fractionation lines (Fig. 5) will be referred to as isotope anomalies. The size of any anomalies can be readily calculated using the equations above with their ε^{47}Ti values as reference points.

4. Conclusions

The new technique reported here makes it possible for the first time to measure both mass-dependent fractionation and anomalies of Ti isotopes to high precision. This new capability for Ti isotope measurement is expected to have a major impact in the study of Galactic and solar nebular evolution. It is also anticipated that this new technique offers the potential for using Ti isotopes to trace the geochemical cycling of Ti in terrestrial environments. The technique is both sensitive and rapid. Sample sizes as small as 2×10^{-6} g Ti may be readily analysed at high precision.

Acknowledgements

This research was supported by grants from The Leverhulme Trust and the NERC, UK.

References

[1] L. Grossman, Geochim. Cosmochim. Acta 36 (1972) 597.
[2] R.N. Clayton, Annu. Rev. Earth Planet. Sci. 21 (1993) 115.
[3] X.K. Zhu, R.K. O'Nions, Y. Guo, E.D. Young, R.D. Ash, Nature 412 (2001) 311.
[4] S. Niemeyer, G.W. Lugmair, Earth Planet. Sci. Lett. 53 (1981) 211.
[5] T.R. Ireland, W. Compston, H.R. Heyegger, Geochim. Cosmochim. Acta 49 (1985) 1989.
[6] N.S. Belshaw, X.K. Zhu, Y. Guo, R.K. O'Nions, Int. J. Mass Spectrom. 197 (2000) 191.
[7] X.K. Zhu, R.K. O'Nions, Y. Guo, N.S. Belshaw, D. Rickard, Chem. Geol. 163 (2000) 139.
[8] X.K. Zhu, R.K. O'Nions, Y. Guo, B.C. Reynolds, Science 287 (2000) 2000.
[9] X.K. Zhu, Y. Guo, R.J.P. Williams, R.K. O'Nions, A. Matthews, N.S. Belshaw, G.W. Canters, E.C. de Waal, U. Weser, B.K. Burgess, B. Salvato, Earth Planet. Sci. Lett. 200 (2002) 47.
[10] A. Makishima, X.K. Zhu, N.S. Belshaw, R.K. O'Nions. J. Anal. Atom. Spectrom., in press.
[11] N.S. Belshaw, P.A. Freedman, R.K. O'Nions, M. Frank, Y. Guo, Int. J. Mass Spectrom. Ion Process. 181 (1998) 51.
[12] C.N. Maréchal, P. Télouk, F. Albarède, Chem. Geol. 156 (1999) 251.
[13] A.D. Anbar, K.A. Knab, J. Barling, Anal. Chem. 73 (2001) 1425.
[14] C. Siebert, T.F. Nägler, J.D. Kramers, Geochem. Geophys. Geosys. 2 (2001) 2000GC000124.
[15] J.M. Eiler, C. Graham, J.W. Valley, Chem. Geol. 138 (1997) 221.
[16] X.K. Zhu, R.K. O'Nions, A.J. Gibb, Chem. Geol. 144 (1998) 305.
[17] W.F. McDonough, S.S. Sun, Chem. Geol. 120 (1995) 223.
[18] J.T. Wasson, G.W. Kallemeyn, Phil. Trans. R. Soc. A325 (1988) 535.
[19] H.C. Urey, J. Chem. Soc. (1947) 562.
[20] R.E. Criss, Principles of Stable Isotope Distribution, Oxford University Press, New York, 1999, p. 254.
[21] E.D. Young, A. Galy, H. Nagahara, Geochim. Cosmochim. Acta 66 (2002) 1095.