

The isotope abundances and the atomic weight of cadmium by a metrological approach

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Received 3 July 2006; received in revised form 27 July 2006; accepted 28 July 2006

Available online 7 September 2006

Abstract

Gravimetric synthetic mixtures of seven enriched, purified cadmium isotope materials were used to determine the correction factors for mass fractionation (MC-TIMS) and mass discrimination (MC-ICP-MS). The isotope abundance ratios determined for various natural cadmium materials represents the isotope composition for natural cadmium materials. Correction of the isotope abundance ratios observed yielded isotope abundances of ^{106}Cd 0.012450(8), ^{108}Cd 0.008884(4), ^{110}Cd 0.124846(16), ^{111}Cd 0.127955(14), ^{112}Cd 0.241110(38), ^{113}Cd 0.122254(22), ^{114}Cd 0.287439(60) and ^{116}Cd 0.075183(32). The newly determined atomic weight of natural cadmium based on SI-traceable evaluation of the isotope abundance ratios is 112.41384(18). The cadmium material designated in the paper as Cd-2211 can be used as an isotope reference material with a $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ -value of 0‰. The results obtained show that the uncertainties for the isotope abundances and the atomic weight given as IUPAC values for cadmium are overestimated.

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Keywords: Atomic weight; Isotope abundance; Isotopic composition; Cadmium

1. Introduction

The interest in the isotopic composition of cadmium (Cd) occurring in natural/geological materials has increased significantly in recent years. The Cd isotope abundance variations of $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ observed range from -13.4‰ up to 24.8‰ [1–10]. In terrestrial samples the observed isotope abundance variation for $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ amounts from -3.6‰ to 3.4‰ . The determination of the δ values requires a standard material that can be used as a reference for all measurements. Ideally, an isotope reference material should be used that is well characterised in terms of its isotope abundance.

The IUPAC values of isotope abundances and the atomic weights of the elements and their uncertainties are subjected to isotope dilution mass spectrometry (IDMS). In many cases, the uncertainty contributions determined by these IUPAC values are the main part of a calculated uncertainty budget for an IDMS result.

Thanks to improved measurement techniques, today even smaller differences can be observed in the isotopic composition of elements. If the IUPAC values and their uncertainties are considered, the observed variations in isotope abundance do not differ significantly. That would mean that the materials show no deviation in isotopic composition; which, of course, cannot be correct. The observed isotope abundance variations in several elements today raise the question as to which values should be used as the IUPAC values and which uncertainty should correspondingly be attributed to it.

In the IUPAC table from 2003 [11], for instance, a value of $6s$ (s : standard deviation) is given as the “best measure” for uncertainty of the Cd isotope abundance.

For these reasons the atomic weight of Cd should be redetermined and a Cd δ material (isotopic reference material) certified.

In order to determine the atomic weight of Cd, the isotope abundances in natural Cd material must be determined. Mass spectrometrical measurements provide observed isotope abundance ratios, which are biased by mass fractionation (TIMS) or mass discrimination (ICP-MS), respectively. In order to calculate the necessary correction factors, synthetic mixtures

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Nomenclature

h_{ij}	isotope abundance, i , isotope (^iCd); j , enriched isotope material (Cd- j); t , corrected value
K_i	correction factor for each isotope abundance ratio originating from mass spectrometric measurements
$m_{12\text{C}}$	atomic mass of isotope ^{12}C (kg)
m_i	atomic mass of ^iCd (kg)
M_i	atomic mass of ^iCd (kg mol^{-1})
M_{Ij}	atomic mass of ^iCd (atomic mass ratio number)
M_j	atomic weight of Cd- j (kg mol^{-1})
N_A	Avogadro constant (mol^{-1})
N_{ij}	number of ^iCd atoms in Cd- j
R_{oij}	isotope abundance ratio in Cd- j ; o , observed value
R_{tij}	isotope abundance ratio ($^i\text{Cd}/^b\text{Cd}$), b , basic isotope; t , corrected value
R_{mi}	isotope abundance ratio in the mixture; t , corrected value
w_{Ej}	mass of Cd- j in mixture (g)
w_j	mass content of Cd- j (g kg^{-1})

of isotopically enriched, purified Cd materials were prepared gravimetrically. The intention was to use enriched Cd isotope materials as highly as possible with one particular isotope. For the synthetic mixtures, theoretical isotope abundance ratios can be calculated using the isotope abundances of the Cd isotope materials. However, because these isotope abundances are not known precisely, they had to be determined also by means of mass spectrometry. Since both the isotope abundance values for the natural Cd material and those of the Cd isotope materials had to be corrected, a problem emerged that could only be resolved through an iteration cycle, or optimised by least squares.

Mass fractionation or mass discrimination in mass spectrometers generally can be described by means of a model equation, from which a factor ε , characterising the mass discrimination per mass unit, can be calculated for the correction (see Section 2.4 calculations). Yet this correction factor ε , which is the same for all isotope abundance ratios, can only be determined with an uncertainty greater than the correction factors K_{ij} ($K(^i\text{Cd}/^j\text{Cd})$), which are specific to each isotope abundance ratio R_{ij} ($R(^i\text{Cd}/^j\text{Cd})$).

Seven purified Cd isotope materials were used to prepare the synthetic mixtures. The purification of the Cd isotope materials from undesired trace elements was performed in a vacuum sublimation apparatus. From these metal materials stock solutions were prepared gravimetrically, which served as base material for six different mixtures. Two mixtures with four Cd isotope materials each (Mix 1: Cd-106, Cd-110, Cd-111, Cd-112; Mix 2: Cd-111, Cd-113, Cd-114, Cd-116), which yielded isotope abundance ratios R_{ij} ($R(^i\text{Cd}/^{111}\text{Cd})$) each approximating 1, were carefully prepared to calculate the K_{ij} values. Four further mixtures with four Cd isotope materials each (Mix 3 through Mix 6: Cd-110, Cd-111, Cd-114, Cd-116), which yielded isotope abundance ratios R_{ij} ($R(^i\text{Cd}/^{111}\text{Cd})$) approximating 0.01–100, were

used to confirm the linearity of the K_{ij} values ($K_{ij} = f(R_{ij})$). The correction factors K_{ij} ($K(^i\text{Cd}/^{111}\text{Cd})$) were calculated using the programmes KFAKT [12], which uses an iteration cycle, and MINUIT [13], which performs a least squares optimisation.

The natural isotopic composition of the Cd in six different materials was determined and compared with the IUPAC values.

All mass spectrometric measurements were performed using a TIMS (MC-TIMS, Sector 54, GV Instruments) and an ICP-MS (MC-ICP-MS, IsoProbe, GV Instruments), equipped with a multicollector (nine Faraday cups).

Lately atomic weights have been determined by MC-TIMS (multicollector thermal ionisation mass spectrometer) and MC-ICP-MS (multicollector inductively coupled plasma mass spectrometer). De Laeter and Bukilic used the TIMS for the determination of ytterbium atomic weight [14] and Lanthanum atomic weight [15]. Zhao et al. used both spectrometers for the determination of neodymium atomic weight [16].

Remarks on the designations “atomic weight” and “atomic mass”: neither term is correct in the context used here. They are atomic mass ratio numbers, since they are scaled according to the atomic mass of ^{12}C . They are relative atomic masses and therefore they are often given without the unit u. Ideally these numbers should be used as molar mass with the unit g mol^{-1} . The conversion of atomic mass in kg into molar mass in g mol^{-1} is defined by the use of the Avogadro constant (IUPAC table, page 700 [11]). These conversions do not change the numerical value, but the uncertainty of the atomic mass increases by a factor of approximately 10. By no means can the atomic mass and the uncertainty from the literature [17] be used and the unit of measure g mol^{-1} be appended.

In this report the numerical values and their uncertainty given in the IUPAC tables [11,17,18] are used by means of comparison.

2. Experimental

2.1. Purification of Cd isotope materials

The seven Cd isotope materials (Cd-106, Cd-110, Cd-111, Cd-112, Cd-113, Cd-114, Cd-116), which had a 95–99% degree of enrichment, were purified by sublimation in a vacuum vessel at a pressure of approximately 10^{-5} mbar to 10^{-7} mbar. These enriched Cd isotope materials (metal) were purchased from Urenco (Cd-106, Cd-113), Chemgas (Cd-110, Cd-112, Cd-116) and STB Isotope (Cd-111, Cd-114). During the purification process, non-metallic and metallic trace elements, and above all, gaseous traces were removed from the Cd. The theoretical background of this method of purification is based on the different vapour pressures of the individual elements. The sublimation in a vacuum took place in a specially formed tantalum crucible by means of increasing the DC-current step by step that flew through the crucible which acted at the same time as a resistor and thus raised its temperature gradually. In this manner a quantitative outgassing of the Cd material is achieved. The sublimated Cd is condensed at a water-cooled collector, whereby with increasing duration a Cd pearl grows in the interior of the crucible. The geometry of the crucible ensures that the sublimated Cd is not contaminated with the crucible material. The sublimation for Cd takes place at

Table 1
Isotope abundance of enriched Cd isotope materials

Material	Isotope abundance							
	¹⁰⁶ Cd	¹⁰⁸ Cd	¹¹⁰ Cd	¹¹¹ Cd	¹¹² Cd	¹¹³ Cd	¹¹⁴ Cd	¹¹⁶ Cd
Cd-106	0.964439(24)	0.020558(6)	0.001497(6)	0.000257(2)	0.002662(22)	0.008398(4)	0.002167(8)	0.000022(4)
Cd-110	0.000040(6)	0.004422(14)	0.960867(32)	0.006071(10)	0.009051(10)	0.012051(18)	0.006215(18)	0.001283(4)
Cd-111	0.000111(10)	0.000088(14)	0.003506(20)	0.960755(40)	0.020350(16)	0.004985(22)	0.009031(20)	0.001174(8)
Cd-112	0.000019(12)	0.000017(12)	0.000095(6)	0.006656(2)	0.986985(26)	0.005395(12)	0.000574(14)	0.000259(2)
Cd-113	0.000071(18)	0.000225(16)	0.001028(12)	0.001455(4)	0.011999(8)	0.961197(40)	0.022179(10)	0.001846(30)
Cd-114	0.000066(14)	0.000048(6)	0.000824(2)	0.000955(4)	0.002827(32)	0.002548(2)	0.990464(36)	0.002268(6)
Cd-116	0.000011(10)	0.000005(8)	0.000010(16)	0.000003(8)	0.000083(6)	0.002146(8)	0.007272(8)	0.990470(24)

The expanded uncertainties U are given in parentheses; $U = k \cdot u_c$ with $k = 2$, u_c is the combined standard uncertainty.

a temperature of 350–400 °C and a pressure of 5×10^{-7} mbar. The surface temperature of the crucible was measured on a spot of 2 mm² by means of a calibrated laser pyrometer through a special quartz window of the vacuum vessel. The temperature resolution was about 1 °C. The bottom part of the crucible was always hotter by about 10–20 °C degrees than the crucible top. The rate of sublimation was around 5–10 mg min⁻¹. A maximum of 0.5 g Cd can be processed in each sublimation process. The product was a polycrystalline metal material, which also contained larger monocrystalline areas. In some cases the growth of facets can also be observed, indicating single crystal quality.

The amount of Cd material collected mostly after several sublimations was between 166 mg and 199 mg. The isotope abundance and the number of sublimations are summarised in Tables 1 and 2.

The sublimated Cd isotope materials were monitored for trace elements by means of a HR-ICP-MS (Finnigan ELEMENT, Thermo Electron GmbH). The total contamination in the solid material amounted to approximately 100 µg g⁻¹, which was taken into consideration in the calculations.

2.2. Preparation of the Cd solutions

The gravimetric preparation of the stock solutions, dilutions and mixtures took place under defined climatic conditions, which were measured and recorded constantly. From these climate data (air temperature, air pressure, relative air humidity) was calculated the air density and used for the air buoyancy correction of the weighing values, which ultimately were used to determine the masses. The climatic values were measured by

appropriate sensors with a Klimet A30 calibrated measurement device (Meteolabor, Wetzikon, Switzerland).

2.2.1. Preparation of the stock solutions and the dilutions

The Cd isotope materials sublimated in a vacuum were filled into vessels under a protective dry argon gas and then weighed on the UMT5 balance (Mettler Toledo). The weighed materials were then filled into bottles (FEP material, 125 ml volume), which were previously weighed on the AT201 balance (Mettler Toledo) and then filled with argon gas.

In order to produce the Cd stock solutions, the bottles with the Cd isotope materials were weighed on the AT201 balance. Before this weighing procedure the argon was pressed out of the bottle. To dissolve the Cd isotope material in the bottle, 1 ml of water (Milli-Q Element, Millipore) and 1 ml nitric acid (sub-boiled HNO₃) were added. Then a defined amount of 0.5 M HNO₃ was added to the bottle, which was placed on the SR64001 balance (Mettler Toledo) for approximate check of the weight. The liquid was weighed on the tared AT201 balance. As a final step, the bottle with the dissolved Cd isotope material and the 0.5 M HNO₃ was weighed on the AT201 balance.

The stock solution necessary for the dilution was charged into a purified dry syringe (2 ml syringe with a cap to reduce evaporation losses) and weighed on the AT201 balance. Then the AT201 balance was tared with the syringe (syringe with stock solution). The calculated amount of the stock solution for dilution was then poured into the bottle, which was placed on the PR2003 DR balance (Mettler Toledo) for control. Next the syringe was weighed on the AT201 balance again. The bottle was filled with 0.5 M HNO₃ up to 125 g on the PR2003 DR balance.

Table 2
Masses of solid metallic Cd isotope materials after vacuum sublimation

Material	Mass (mg)	Solid density (kg m ⁻³)	Clean runs	Liquid total mass (g)	Liquid density (g cm ⁻³)
Cd-106	166.3911(72)	8143(30)	5	127.7801(1)	1.0139(1)
Cd-110	198.7042(68)	8450(30)	1	126.0252(2)	1.0141(1)
Cd-111	191.9179(49)	8527(30)	3	124.6259(2)	1.0131(1)
Cd-112	182.3553(84)	8604(30)	1	127.1645(2)	1.0141(1)
Cd-113	185.3456(69)	8681(30)	6	129.9344(1)	1.0140(1)
Cd-114	192.4547(88)	8758(30)	3	129.4797(1)	1.0141(1)
Cd-116	191.6394(82)	8912(30)	4	126.6656(2)	1.0141(1)

The expanded uncertainties U are given in parentheses; $U = k \cdot u_c$ with $k = 1$.

Table 3
Mass values of stock solutions for the mixture 1 and 2

Material	Mass of solution (mg)	
	Mix-1	Mix-2
Cd-106, stock	4635.6612(81)	
Cd-110, stock	3949.128(10)	
Cd-111, stock	4132.844(25)	4078.6141(71)
Cd-112, stock	4203.9601(81)	
Cd-113, stock		4347.5896(61)
Cd-114, stock		3910.0590(80)
Cd-116, stock		4193.5513(81)
Density (g cm ⁻³)	1.0095(1)	1.0093(1)

The expanded uncertainties U are given in parentheses; $U = k \cdot u_c$ with $k = 1$.

2.2.2. Preparation of the synthetic isotopic mixtures

The stock solution necessary for the mixture was charged into a purified dry syringe (2 ml, 10 ml, 20 ml syringe) and weighed on the AT201 balance. Then the AT201 balance was tared with the syringe (syringe with the stock solution). The amount of stock solution calculated for the mixture was then poured into the bottle, which was placed on the PR2003 DR balance for control. Then the syringe was weighed on the AT201 balance again. The bottle was filled with 0.5 M HNO₃ up to 125 g on the PR2003 DR balance.

The amounts and mass contents of the Cd solutions used for the six mixtures are given in Tables 3–5.

The density of the stock solutions, the dilutions and mixtures were measured with a calibrated thermostated densitometer (DMA-45, Anton Paar GmbH).

2.3. Mass spectrometric measurements

For the TIMS measurements various techniques were tested ($I_F = \text{const.}$, $T_F = \text{const.}$, $I_I = \text{const.}$), in which the filament current I_F , filament temperature T_F or ion current I_I was held constant during measurement. The technique and the evaporation parameters with the best reproducibility of the R_{ij} values were used. The temperature of the Re-band could not be measured with the desired reproducibility. Since baked-out (clean) Re-bands were used, the technique with constant fila-

Table 5
Mass content of solution

Material	Mass content of solution (μg g ⁻¹)		Density (g cm ⁻³)
	Stock solution	Dilution	Dilution
Cd-106	1300.474(56)		
Cd-110	1574.221(54)	12.74556(47)	1.0090(1)
Cd-111	1537.584(39)	12.50362(40)	1.0089(1)
Cd-112	1431.957(70)		
Cd-113	1424.423(53)	12.11294(56)	1.0090(1)
Cd-114	1484.164(68)	12.35626(56)	1.0090(1)
Cd-116	1510.670(65)		

The expanded uncertainties U are given in parentheses; $U = k \cdot u_c$ with $k = 1$.

ment current was not suitable either, as the Re-bands could have various thicknesses. In addition, Re-bands and Re-boats were tested, whereby the Re-bands and the evaporation technique with a constant ion current ($I_I = \text{const.}$) supplied the best results. The Re-bands were prepared using the silica gel technique. More information and a introduction on ion formation processes is given by Platzner [19]. A total of five different silica gel suspensions were tested. With the silica gel suspensions TIMS measurements without Cd samples were performed, in order to check them for Cd contaminations and isobar interferences and also to determine the optimum evaporation parameters. The TIMS measurements were monitored over the entire measurement period using the Cd material Cd-I012 as the measurement standard. The Cd-I012 solution was prepared as isotopic reference material with natural isotopic composition and a $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ not equal 0‰ by BAM. This Cd material (shot, 6N) was purchased from Alfa Aesar, Johnson Matthey Company.

For the TIMS measurements 50 ng Cd was used for each measurement and 300 measurement values were recorded. For the MC-ICP-MS measurements the sample consumption per measurement was 330 ng Cd (mass concentration of the solutions: 190 pg μl⁻¹; sample consumption rate: 220 μl min⁻¹; measurement time for one sample (30 measurement values): 8 min). The sum of the ion currents for all Cd isotopes was 2×10^{-11} A (2 V) for the TIMS measurements and 3×10^{-11} A (3 V) for the

Table 4
Mass values of stock solutions for the mixture 3–6

Material	Mass of stock solution and diluted stock (mg)			
	Mix-3	Mix-4	Mix-5	Mix-6
Cd-110, stock	7074.4789(81)	1924.8195(80)		
Cd-110, dilution			20324.773(20)	136.376(23)
Cd-111, stock			1844.3739(40)	2001.013(20)
Cd-111, dilution	2617.132(23)	23594.594(22)		
Cd-114, stock	7210.373(10)	1991.782(11)		
Cd-114, dilution			21409.995(24)	533.6522(50)
Cd-116, stock			1896.3354(11)	2063.3311(50)
Cd-116, dilution	5919.400(18)	24012.150(23)		
Density (g cm ⁻³)	1.0095(1)	1.0090(1)	1.0090(1)	1.0088(1)

The expanded uncertainties U are given in parentheses; $U = k \cdot u_c$ with $k = 1$.

Table 6
Observed isotope abundance ratios of the mixtures by MC-TIMS measurement

Isotope abundance ratio	Mixture					
	Mix-1	Mix-2	Mix-3	Mix-4	Mix-5	Mix-6
$R(^{106}\text{Cd}/^{111}\text{Cd})$	0.99866(56)	0.000278(30)	0.009791(59)	0.001201(260)	0.000109(10)	0.000101(23)
$R(^{108}\text{Cd}/^{111}\text{Cd})$	0.025775(27)	0.000355(14)	0.46281(200)	0.045375(130)	0.000531(14)	0.000084(14)
$R(^{110}\text{Cd}/^{111}\text{Cd})$	0.98260(16)	0.005460(12)	98.809(199)	9.6669(7)	0.096027(21)	0.004236(22)
$R(^{112}\text{Cd}/^{111}\text{Cd})$	0.98265(11)	0.035870(38)	1.1990(27)	0.136747(38)	0.022316(7)	0.021226(4)
$R(^{113}\text{Cd}/^{111}\text{Cd})$	0.030944(38)	0.97233(21)	1.4714(14)	0.15063(22)	0.008672(10)	0.007329(19)
$R(^{114}\text{Cd}/^{111}\text{Cd})$	0.018238(25)	0.95798(36)	94.123(110)	9.3492(23)	0.106455(72)	0.018661(23)
$R(^{116}\text{Cd}/^{111}\text{Cd})$	0.002740(24)	0.98627(60)	0.95178(290)	0.92422(75)	0.98489(110)	0.98771(26)

The standard deviations of the means (1s) are given in parentheses.

MC-ICP-MS measurements. The possible parameter drifts in the ICP-MS measurements were controlled for and corrected by alternating the measurement of sample and measurement standard (Cd-I012).

Argon was used as collision gas in the hexapole collision cell. Additional hydrogen increased the Cd^+ ion current considerably, but because CdH^+ interferences were generated at the same time, no hydrogen was used.

The control of molecular ion interferences in the MC-ICP-MS was achieved with a higher mass resolution (approximately 2400). The natural Cd solutions were monitored for trace elements by HR-ICP-MS (high resolution inductively coupled plasma mass spectrometer with double focusing sector field) which have isobaric interferences with Cd. The concentration of Sn, In and Pd in the natural Cd solutions were too low so that no Sn, In and Pd intensities could be observed in the Faraday cup during MC-ICP-MS measurement.

With TIMS and MC-ICP-MS, six mixtures (Mix 1 through Mix 6) and six Cd materials with a natural isotopic composition were measured. The seven Cd isotope materials were measured only with the TIMS.

The isotope abundance ratios observed in the mixtures R_{omi} are summarised in Table 6. The R_{omi} values used for the calculations are printed in bold type in Table 6.

2.4. Calculations

The starting point for additional calculations are the observed isotope abundance ratios R_{oij} of the seven Cd isotope materials, whereby the base isotope varies. In each case the Cd isotope with the highest isotope abundance in the Cd isotope material was used as the base isotope. These R_{oij} values are given in Table 7. For the transformation to other base isotopes, all individual values were transformed and subsequently the mean values were

Table 7
Observed isotope abundance ratios of the isotope materials by MC-TIMS measurement

Isotope abundance ratio	Cd isotope material			
	Cd-106	Cd-110	Cd-111	Cd-112
$R(^{106}\text{Cd}/\text{Cd})$	1	0.0000425(35)	0.0001071(48)	0.0000192(63)
$R(^{108}\text{Cd}/\text{Cd})$	0.0211863(34)	0.0046294(76)	0.0000926(74)	0.0000176(57)
$R(^{110}\text{Cd}/\text{Cd})$	0.0015340(26)	1	0.0036597(99)	0.0000967(31)
$R(^{111}\text{Cd}/\text{Cd})$	0.0002628(6)	0.0062997(48)	1	0.0067627(9)
$R(^{112}\text{Cd}/\text{Cd})$	0.002712(11)	0.0093652(51)	0.0211213(81)	0.0054479(61)
$R(^{113}\text{Cd}/\text{Cd})$	0.0085264(22)	0.0124278(94)	0.0051569(110)	1
$R(^{114}\text{Cd}/\text{Cd})$	0.0021951(45)	0.0063940(83)	0.0093196(100)	0.0005778(57)
$R(^{116}\text{Cd}/\text{Cd})$	0.0000223(23)	0.0013129(18)	0.0012051(36)	0.0002600(6)

Isotope abundance ratio	Cd isotope material			Natural Cd
	Cd-113	Cd-114	Cd-116	Cd-I012
$R(^{106}\text{Cd}/\text{Cd})$	0.0000751(97)	0.0000686(74)	0.0000109(50)	0.098976(158)
$R(^{108}\text{Cd}/\text{Cd})$	0.0002376(80)	0.0000497(26)	0.0000055(40)	0.070130(73)
$R(^{110}\text{Cd}/\text{Cd})$	0.0010789(60)	0.0008418(5)	0.0000099(79)	0.97797(21)
$R(^{111}\text{Cd}/\text{Cd})$	0.0015235(25)	0.0009725(15)	0.0000026(38)	1
$R(^{112}\text{Cd}/\text{Cd})$	0.0125246(41)	0.0028706(160)	0.0000850(26)	1.87822(54)
$R(^{113}\text{Cd}/\text{Cd})$	1	0.0025790(13)	0.0021838(36)	0.94897(37)
$R(^{114}\text{Cd}/\text{Cd})$	0.0230184(48)	1	0.0073833(72)	2.22458(143)
$R(^{116}\text{Cd}/\text{Cd})$	0.001906(15)	0.0022773(25)	1	0.57775(65)

^jCd : the basic isotope changes with the Cd isotope material (Cd-106: $j = 106$ and so on). The standard deviations of the means (1s) are given in parentheses. Natural Cd (Cd-I012): basic isotope is ^{111}Cd .

calculated, because it is true that

$$\frac{\overline{R}_o(i\text{Cd}/^{111}\text{Cd})}{\overline{R}_o(j\text{Cd}/^{111}\text{Cd})} = \frac{\sum_{n=1}^m R_{on}(i\text{Cd}/^{111}\text{Cd})}{\sum_{n=1}^m R_{on}(j\text{Cd}/^{111}\text{Cd})} \quad (1)$$

but not that

$$\frac{\overline{R}_o(i\text{Cd}/^{111}\text{Cd})}{\overline{R}_o(j\text{Cd}/^{111}\text{Cd})} \neq \sum_{n=1}^m \left(\frac{R_{on}(i\text{Cd}/^{111}\text{Cd})}{R_{on}(j\text{Cd}/^{111}\text{Cd})} \right). \quad (2)$$

This mathematical relationship becomes especially clear for extreme R_{oij} values. For the Cd-116 isotope material, whose minimal isotope abundance of ^{111}Cd makes it unsuitable as a base isotope because it yields high uncertainties for all $R_o(i\text{Cd}/^{111}\text{Cd})$ values, the $R_o(i\text{Cd}/^{111}\text{Cd})$ values have to be calculated from the isotope abundance $h_o(i\text{Cd})$ of the Cd-116 isotope material. The $h_o(i\text{Cd})$ values were calculated beforehand from the $R_o(i\text{Cd}/^{116}\text{Cd})$ values.

Mathematical models (equations) are used to adequately describe the mass fractionation in the TIMS measurements and the mass discrimination in the ICP-MS measurements. Various approaches are found in the literature [20–25]. The following equations are used frequently:

linear function

$$R_{ii} = (\varepsilon \cdot \Delta m_i + 1) \cdot R_{oi}; \quad \varepsilon = \frac{(R_{ii}/R_{oi}) - 1}{\Delta m_i} \quad (3)$$

power law function

$$R_{ii} = (\varepsilon + 1)^{\Delta m_i} \cdot R_{oi}; \quad \varepsilon = \left(\frac{R_{ii}}{R_{oi}} \right)^{(1/\Delta m_i)} - 1 \quad (4)$$

exponential function

$$R_{ii} = \exp(\varepsilon \cdot \Delta m_i) \cdot R_{oi}; \quad \varepsilon = \ln \frac{R_{ii}/R_{oi}}{\Delta m_i} \quad (5)$$

exponential law

$$R_{ii} = R_{oi} \cdot \left(\frac{m_i}{m_b} \right)^\varepsilon; \quad \varepsilon = \frac{\ln(R_{ii}/R_{oi})}{\ln(m_i/m_b)} \quad (6)$$

If it is considered that

$$(\varepsilon + 1)^{\Delta m_i} = \exp(\beta \cdot \Delta m_i), \quad \text{with } \beta = \ln(\varepsilon + 1)$$

then one receives

$$R_{ii} = \exp(\beta \cdot \Delta m_i) \cdot R_{oi}. \quad (7)$$

Thus Eq. (5) does not yield any new findings as compared with Eq. (4).

R_{ii} represents the corrected isotope abundance ratios and R_{oi} the observed isotope abundance ratios, $\Delta m_i = m_i - m_b$ is the mass differences of the isotopes, ε is the mass fractionation factor (per mass unit), or the mass discrimination factor (per mass unit), respectively.

Table 8

Atomic masses of the Cd isotopes

Cd-isotope	Atomic mass
^{106}Cd	105.906459(6)
^{108}Cd	107.904184(6)
^{110}Cd	109.9030021(29)
^{111}Cd	110.9041781(29)
^{112}Cd	111.9027578(29)
^{113}Cd	112.9044017(29)
^{114}Cd	113.9033585(29)
^{116}Cd	115.904756(3)

The “standard deviation errors” are given in parentheses, Audi et al. [17].

If only the mass fractionation or mass discrimination are corrected, respectively, the better approach is to use the correction factor K_i for each isotope abundance ratio observed.

$$K_i = \frac{R_{ii}}{R_{oi}} \quad (8)$$

If the ε -values and the K_i values for several datasets are calculated, it becomes clear that the ε -values are clearly more highly scattered and have a higher uncertainty than the K_i values. The scatter of the ε -values amounts to several percent.

For this reason the observed isotope abundance ratios R_{oij} and R_{omi} are corrected using the K_i values. The correction factor $K(^{108}\text{Cd}/^{111}\text{Cd})$ had to be calculated using the mass discrimination factor, because no isotope material for ^{108}Cd was available with the required isotopic purity.

The isotope abundance ratios of the mixtures R_{imi} were calculated according to the following equation (see Appendix A):

$$R_{imi} = \left[K_i \cdot \frac{\sum_{j=1}^m w_j \cdot w_{Ej} \cdot R_{oij}}{\sum_{i=1}^n M_{ii} \cdot K_i \cdot R_{oij}} \right] \cdot \left[K_4 \cdot \frac{\sum_{j=1}^m w_j \cdot w_{Ej} \cdot R_{o4j}}{\sum_{i=1}^n M_{ii} \cdot K_i \cdot R_{oij}} \right]^{-1} \quad (9)$$

The index i (with $n = 8$) stands for the isotope abundance ratio $R(i\text{Cd}/^{111}\text{Cd})$ and the index j (with $m = 7$) for the isotope material Cd- j . The value w stands for the mass content of the solution and w_E for the mass of the solution. The atomic mass of the Cd isotope, which is given in Table 8, is designated by M_i , and the observed isotope abundance ratio of the isotope material by R_o . The data listed in Table 8 are the values of Audi et al. [17]. In their paper they give the uncertainty as the “standard deviation error”.

The correction factor for each isotope abundance ratio is calculated with the observed isotope abundance ratios of the mixtures (Mix 1 and Mix 2).

$$K_i = \frac{R_{imi}}{R_{omi}} \quad (10)$$

Table 9
Calculated $K(^i\text{Cd}/^{111}\text{Cd})$ factors by the programs MINUIT and KFAKT

K-factor	Program		Δ	Mean value of K factor
	MINUIT	KFAKT		
$K(^{106}\text{Cd}/^{111}\text{Cd})$	0.985192	0.985180	12×10^{-6}	0.985186(40)
$K(^{108}\text{Cd}/^{111}\text{Cd})$	0.991209	0.991198	11×10^{-6}	0.991204(40)
$K(^{110}\text{Cd}/^{111}\text{Cd})$	0.996997	0.997001	-4×10^{-6}	0.996999(20)
$K(^{111}\text{Cd}/^{111}\text{Cd})$	1	1	–	1
$K(^{112}\text{Cd}/^{111}\text{Cd})$	1.002820	1.002822	-2×10^{-6}	1.002821(60)
$K(^{113}\text{Cd}/^{111}\text{Cd})$	1.006150	1.006126	24×10^{-6}	1.006138(30)
$K(^{114}\text{Cd}/^{111}\text{Cd})$	1.008600	1.008595	5×10^{-6}	1.008598(40)
$K(^{116}\text{Cd}/^{111}\text{Cd})$	1.013980	1.013980	$<1 \times 10^{-6}$	1.013980(20)

The expanded uncertainties U are given in parentheses; $U = k \cdot u_c$ with $k = 1$.

2.4.1. Calculation of the K_i factors

The correction factors were calculated using iteration cycles and least squares fitting. For these calculations the programs KFAKT [12], which works with iteration cycles, and MINUIT [13], which performs a least squares refinement, were used. The programs were tested with a theoretical data set. Realistic, observed R_{omi} values were calculated with mass fractionation ($\varepsilon = 0.00219$) for this purpose. The values were refined starting with $K_i = 1$ and converged to the previously calculated K_i values.

The calculated K_i values, which were calculated for the synthetic isotope mixtures Mix 1 and Mix 2, are summarised in Table 9. The two programs yield values that are in good agreement with each other. The maximum difference is $\Delta = 24 \times 10^{-6}$.

One criterion for the usability of the Eqs. (3)–(6) is the demand that the reciprocal values of the $K(^i\text{Cd}/^{111}\text{Cd})$ values must also fulfil the equation.

The $K(^i\text{Cd}/^{111}\text{Cd})$ values can be transformed mathematically to the other $K(^i\text{Cd}/^b\text{Cd})$ values with the base isotope ^bCd .

$$K\left(\frac{^i\text{Cd}}{^b\text{Cd}}\right) = \frac{K(^i\text{Cd}/^{111}\text{Cd})}{K(^b\text{Cd}/^{111}\text{Cd})} \quad (11)$$

Eq. (6) was used to calculate $K(^{108}\text{Cd}/^{111}\text{Cd})$. However, no mean ε -value was calculated with the other K_i values; rather, the function $K_i = C \cdot (m_i/m_b)^\varepsilon$ was fitted to the K_i values.

The coefficient of determination for fit to the K_i values from the KFAKT program was $r^2 = 0.9996$ ($C = 0.99997$, $\varepsilon = 0.32158$). For fit with the K_i values from the MINUIT program, the values $r^2 = 0.9995$ ($C = 0.99998$, $\varepsilon = 0.32154$) are obtained. The $K(^{108}\text{Cd}/^{111}\text{Cd})$ results calculated with the two ε -values are given in Table 9.

The linearity of the K_i factor, a function of the numerical value of the isotope abundance ratio, is represented in Fig. 1. The figure shows that $K(^{110}\text{Cd}/^{111}\text{Cd})$ is constant in the range of 1×10^4 ($R(^{110}\text{Cd}/^{111}\text{Cd})$: from 0.01 to 100). The greater uncertainties, especially for the R value of Mix 3 and Mix 6, result from the small ion currents that had to be measured to obtain these R values.

All uncertainty budgets were calculated using the GUM Workbench [26] program. The individual parameters and their contributions to the uncertainty budget of the results are to be discussed in a separate article.

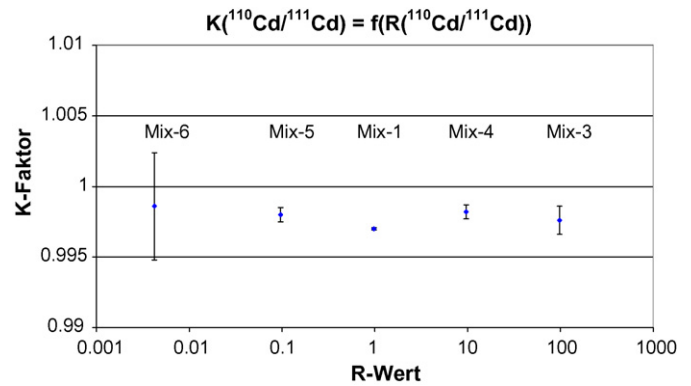


Fig. 1. $K(^{110}\text{Cd}/^{111}\text{Cd})$ factor as function of $R(^{110}\text{Cd}/^{111}\text{Cd})$ values shows the good linearity.

2.5. The isotopic composition of cadmium in nature

Rosman and de Laeter [1–5], Rosman et al. [6,7], Sands et al. [8], Wombacher et al. [9] and Cloquet et al. [10] reported on Cd isotope abundance variations in terrestrial and extraterrestrial material.

Rosman and de Laeter [2] found isotope abundance variations of $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ from $-3.6(3)\%$ to $+3.4(3)\%$ in terrestrial minerals (cadmium-bearing minerals). Both an enrichment of the light isotopes ($-\delta(^{114}\text{Cd}/^{110}\text{Cd})$) and an enrichment of the heavy ($+\delta(^{114}\text{Cd}/^{110}\text{Cd})$) isotopes were observed. In meteorites (chondrite), Rosman and de Laeter [5] found isotope abundance variations of $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ from $-3.4(5.1)\%$ to $+14.4(2.8)\%$. Sands et al. [8] found isotope abundance variations of $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ from $-5.0(2.4)\%$ to $+24.8(2.6)\%$ in lunar soils.

These δ -values, which were calculated according to Eq. (12), and their uncertainties, which are given in parentheses, were calculated from the R values and the values of the standard deviations given in the papers. The δ -values were referenced to a laboratory standard (Cd solution), which also is given in the papers.

Wombacher et al. [9] reported on Cd isotope abundance variations in terrestrial rock and minerals and in meteorites (chondrite). In the terrestrial samples Cd isotope abundance variations of $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ from -0.68% to $+3.04\%$ were found, and in the chondrite samples $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ from -7.80% to $+14.80\%$. A commercial ICP standard solution (Alfa Aesar, Johnson Matthey Company) was used as the Cd standard solution, designated as Cd-JMC solution. As an additional standard, a fractionated Cd solution (VTA-3 Cd) was used, in which an isotope abundance variation of $\delta(^{114}\text{Cd}/^{110}\text{Cd}) = 3.88(24)\%$ was observed. The Cd VTA-3 (Vacuum Technology Aalen) was produced by sublimation (Wombacher et al. [27]).

The δ -values were calculated from the ε -values used by Wombacher et al. [9] to describe the isotope abundance variation. The authors did not give the uncertainties for all values.

Cloquet et al. [10] reported on Cd isotope abundance variations in geological reference materials and anthropogenic samples. Isotope abundance variations of $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ from $-0.38(19)\%$ to $+0.51(2)\%$ were found in the ref-

Table 10

Observed isotope abundance ratios of natural terrestrial Cd materials by MC-ICP-MS measurement

Isotope abundance ratio	Material					
	Cd-2211	Cd-2212	Cd-2213	Cd-2214	Cd-JMC	Cd-I012
$R(^{106}\text{Cd}/^{111}\text{Cd})$	0.087493(20)	0.087481(1)	0.087471(21)	0.087496(7)	0.087509(16)	0.087677(9)
$R(^{108}\text{Cd}/^{111}\text{Cd})$	0.065007(10)	0.065007(19)	0.065015(10)	0.065016(7)	0.065018(6)	0.065087(7)
$R(^{110}\text{Cd}/^{111}\text{Cd})$	0.949501(32)	0.949507(20)	0.949481(14)	0.949508(28)	0.949507(32)	0.949930(20)
$R(^{112}\text{Cd}/^{111}\text{Cd})$	1.907531(45)	1.907539(66)	1.907563(26)	1.907547(25)	1.907462(46)	1.906701(38)
$R(^{113}\text{Cd}/^{111}\text{Cd})$	0.985327(49)	0.985328(23)	0.985356(16)	0.985321(39)	0.985301(64)	0.984484(42)
$R(^{114}\text{Cd}/^{111}\text{Cd})$	2.37265(11)	2.372640(59)	2.37282(20)	2.372692(88)	2.37264(19)	2.36979(19)
$R(^{116}\text{Cd}/^{111}\text{Cd})$	0.638454(46)	0.638435(40)	0.638505(55)	0.638409(72)	0.637965(93)	0.636551(48)

The standard deviation of the means (1s) are given in parentheses.

reference materials, and of $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ from $-0.64(19)\%$ to $+0.36(19)\%$ in the anthropogenic samples. The δ -values referred to a Cd solution (Spex). Cloquet et al. [10] used three further Cd solutions: Cd solution (Prolabo), Cd-JMC solution (Alfa Aesar, Johnson Matthey Company), Cd VTA-3 solution (Wombacher et al. [27]). In three Cd solutions: Spex: $\delta(^{114}\text{Cd}/^{110}\text{Cd}) = 0.00(7)\%$, Prolabo: $\delta(^{114}\text{Cd}/^{110}\text{Cd}) = 0.00(8)\%$, JMC: $\delta(^{114}\text{Cd}/^{110}\text{Cd}) = 0.03(10)\%$ no significant isotope abundance variations were observed. In the VTA-3 Cd solution a value of $\delta(^{114}\text{Cd}/^{110}\text{Cd}) = 3.35(3)\%$ was found.

In this report six different natural Cd materials were investigated. These Cd metals were purchased from Alfa Aesar, Johnson Matthey Company (AA-JMC) and Bleiberger Bergwerkunion (BBU), respectively: Cd-2211 (Cd rod, 6N, AA-JMC), Cd-2212 (Cd shot, 6N, AA-JMC), Cd-2213 (Cd bar, 4N+, AA-JMC), Cd-2214 (Cd rod, 3N5, BBU), Cd-I012 (Cd shot, 6N, AA-JMC), Cd-JMC (Cd ICP standard solution, AA-JMC). The materials are Cd metals of high purity.

The standard deviations (single value) of the isotope abundance ratios observed were 10 times higher in the TIMS measurements than in the MC-ICP-MS measurements given in Table 10. For $R(^{106}\text{Cd}/^{111}\text{Cd})$ and $R(^{108}\text{Cd}/^{111}\text{Cd})$ the standard deviations are between 0.01 and 0.02%, and for the other $R(^i\text{Cd}/^{111}\text{Cd})$ values they are less than 0.01%.

The R_{oi} values of Cd-I012 show significant differences from the four other Cd materials (Cd-2211 through 2214), which did not differ significantly. The Cd-JMC shows a significant difference only in the $R_o(^{116}\text{Cd}/^{111}\text{Cd})$ value. All six Cd materials were analysed with the HR-ICP-MS in terms of the trace

elements Sn, In and Pd. The Sn contents, which could cause interference of the mass 116, amounted to approx. 10 pg g^{-1} in the Cd-JMC solution and is a factor of 100 greater than in the 4 other Cd solutions. This content would cause an ion current of approximately $1 \times 10^{-16} \text{ A}$ for ^{116}Sn , but this current would be located in the background noise during measurement with the Faraday cups. The Sn content in the Cd-I012 solution is a factor of 2 smaller than in the Cd-JMC solution. This means that the difference of the $R_o(^{116}\text{Cd}/^{111}\text{Cd})$ in the Cd-JMC solution cannot be due to Sn interference. In the works of Wombacher et al. [9] and Cloquet et al. [10], who also used Cd-JMC, no R_{oi} values or δ -values were given with ^{116}Cd .

The $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ values are given with Cd-2211 as standard in Table 11 and with Cd-JMC as standard in Table 12. For the Cd-I012 material, $\delta(^{114}\text{Cd}/^{110}\text{Cd}) = -2.44(18)\%$ was observed with Cd-2211 as the standard. This value is less than the values found in terrestrial minerals by Rosman and de Laeter [2].

From Table 11 it can be recognised that the Cd materials Cd-2212 through Cd-2214 show no significant differences when Cd-2211 is used as standard. Only for $\delta(^{114}\text{Cd}/^{116}\text{Cd})$ does Cd-JMC show a significant difference. The δ -values of Cd-I012 are all significantly different from the other Cd materials. Table 12, with Cd-JMC as standard, shows that all Cd materials have a significant difference in the $\delta(^{114}\text{Cd}/^{116}\text{Cd})$ value. The cause for this is the deviant $R_o(^{116}\text{Cd}/^{111}\text{Cd})$ value (see above).

3. Discussion

As mentioned above, the standard deviations in the MC-ICP-MS measurements were clearly smaller than those in the TIMS

Table 11

 $\delta(^{114}\text{Cd}/^i\text{Cd})$ values of natural terrestrial Cd materials with R_{oi} -values of Cd-2211 as standard

Delta (‰)	Material				
	Cd-2212	Cd-2213	Cd-2214	Cd-JMC	Cd-I012
$\delta(^{114}\text{Cd}/^{106}\text{Cd})$	0.13(27)	0.33(37)	-0.02(27)	-0.19(73)	-3.30(31)
$\delta(^{114}\text{Cd}/^{108}\text{Cd})$	0.00(29)	-0.05(21)	-0.13(15)	-0.17(31)	-2.44(18)
$\delta(^{114}\text{Cd}/^{110}\text{Cd})$	-0.01(8)	0.09(11)	0.01(10)	-0.01(25)	-1.66(11)
$\delta(^{114}\text{Cd}/^{111}\text{Cd})$	0.00(6)	0.07(9)	0.02(7)	0.00(17)	-1.21(9)
$\delta(^{114}\text{Cd}/^{112}\text{Cd})$	-0.01(4)	0.06(8)	0.01(6)	0.03(12)	-0.77(8)
$\delta(^{114}\text{Cd}/^{113}\text{Cd})$	0.00(1)	0.04(7)	0.02(4)	0.03(5)	-0.35(7)
$\delta(^{114}\text{Cd}/^{116}\text{Cd})$	0.03(5)	-0.01(10)	0.09(9)	0.76(19)	1.78(8)

The expanded uncertainties U are given in parentheses; $U = k \cdot u_c$ with $k = 1$.

Table 12
 $\delta(^{114}\text{Cd}/^i\text{Cd})$ values of natural terrestrial Cd materials with R_{oi} -values of Cd-JMC as standard

Delta (‰)	Material				
	Cd-2211	Cd-2212	Cd-2213	Cd-2214	Cd-I012
$\delta(^{114}\text{Cd}/^{106}\text{Cd})$	0.19(37)	0.32(25)	0.52(36)	0.17(25)	−3.11(29)
$\delta(^{114}\text{Cd}/^{108}\text{Cd})$	0.17(15)	0.17(27)	0.13(19)	0.05(12)	−2.26(16)
$\delta(^{114}\text{Cd}/^{110}\text{Cd})$	0.01(12)	0.00(10)	0.10(12)	0.02(12)	−1.65(13)
$\delta(^{114}\text{Cd}/^{111}\text{Cd})$	0.00(9)	0.00(7)	0.08(10)	0.02(9)	−1.20(10)
$\delta(^{114}\text{Cd}/^{112}\text{Cd})$	−0.03(6)	−0.04(5)	0.02(8)	−0.02(6)	−0.80(8)
$\delta(^{114}\text{Cd}/^{113}\text{Cd})$	−0.03(2)	−0.03(2)	0.02(7)	0.00(4)	−0.37(7)
$\delta(^{114}\text{Cd}/^{116}\text{Cd})$	−0.76(9)	−0.74(9)	−0.77(13)	−0.67(12)	1.02(11)

The expanded uncertainties U are given in parentheses, $U = k \cdot u_c$ with $k = 1$.

measurements, because mass discrimination is not a function of time. Despite good preparation of the bands and the use of the same measurement parameters, it was not possible to avoid minor fluctuations in the mass fractionation $R_{oi} = f(t)$ during the TIMS measurements, so that greater standard deviations are received than in the MC-ICP-MS measurements. The advantage for TIMS measurement is the minimal risk of interferences. In the MC-ICP-MS measurements molecule interferences must always be expected and the sample checked for possible contaminations.

Table 13 shows the isotope abundance values of the “best measurement” (Rosman et al. [7]) and of three Cd materials. The isotope abundance values for Cd-2211 and Cd-I012 are significantly different except for the $h(^{113}\text{Cd})$ value. The comparison of Cd-2211 with Cd-JMC shows that only the $h(^{116}\text{Cd})$ value is significantly different and the other values agree within the given range of uncertainty. The uncertainties (2s) of the “best measurement” values are a factor of 18–38 times greater than for the Cd-2211 values. As a consequence, all isotope abundance values for Cd-2211, Cd-I012 and Cd-JMC correspond very well to the “best measurement” values.

The isotope abundance values in Table 13 were calculated using the observed isotope abundance ratios from Table 10. The mass discrimination was corrected by the calculated mass fractionation factors K_i and the device factors K_{Gi} that were determined from the observed isotope abundance ratios

of the Cd material Cd-I012 during TIMS and MC-ICP-MS measurement.

$$\begin{aligned} K_{Di} &= K_i \cdot K_{Gi}; & R_{ii} &= K_i \cdot R_{oi,TI}; & R_{oi,TI} &= K_{Gi} \cdot R_{oi,IC}; \\ R_{ii} &= K_i \cdot K_{Gi} \cdot R_{oi,IC}; \\ R_{ii} &= K_{Di} \cdot R_{oi,IC}; \end{aligned}$$

The index TI stands for TIMS measurements and IC for MC-ICP-MS measurements. K_{Di} values are the correction factors for mass discrimination.

The comparison of the isotope abundance variations in Cd is complicated by the facts that these are given in different formats, and that no globally accepted standard material is used. IRMS (isotope ratio mass spectrometry) users use the δ -values for the isotope abundance variations (for hydrogen to chlorine). The Eq. (12) includes: R_{ST} observed isotope abundance ratio of the standard material, R_S observed isotope abundance ratio of the sample, and j is by definition the isotope with the highest isotope abundance.

$$\delta = \left(\frac{R_S(i/j)}{R_{ST}(i/j)} - 1 \right) \cdot 10^3, \quad \text{in } \text{‰} \quad (12)$$

The papers by Wombacher and Rehkämper [28] and Carignan [29] discuss the notation of the isotope abundance variations of Cd and related reference materials.

The form in which the isotope abundance variations are given is not very important, but these values should be transparent. It should be possible to recognise which R values were used to

Table 13
 Isotope abundance and atomic weight of natural terrestrial Cd

Isotope abundance	IUPAC values	Best measurement	Cd-2211	Cd-I012	Cd-JMC
$h(^{106}\text{Cd})$	0.0125(6)	0.0125(2)	0.012450(8)	0.012485(8)	0.012453(8)
$h(^{108}\text{Cd})$	0.0089(3)	0.0089(1)	0.008884(4)	0.008901(4)	0.008886(4)
$h(^{110}\text{Cd})$	0.1249(18)	0.1249(6)	0.124704(16)	0.124846(16)	0.124713(18)
$h(^{111}\text{Cd})$	0.1280(12)	0.1280(4)	0.127955(14)	0.128043(12)	0.127963(14)
$h(^{112}\text{Cd})$	0.2413(21)	0.2413(7)	0.241110(38)	0.241170(38)	0.241117(42)
$h(^{113}\text{Cd})$	0.1222(12)	0.1222(4)	0.122275(22)	0.122254(22)	0.122280(68)
$h(^{114}\text{Cd})$	0.2873(42)	0.2873(14)	0.287439(60)	0.287290(58)	0.287457(66)
$h(^{116}\text{Cd})$	0.0749(18)	0.0749(6)	0.075183(32)	0.075011(32)	0.075131(34)
Atomic weight	#1	#2	#3	#3	#3
$A_r(\text{Cd})$	112.411(8)	112.4116(36)	112.41384(18)	112.41218(18)	112.41362(20)

The expanded uncertainties U are given in parentheses. IUPAC values: $U = 6s$ of “best measurement” values; best measurement (Rosman et al. [7]): $U = 2s$; Cd-2211, Cd-I012 and Cd-JMC: $U = k \cdot u_c$ with $k = 2$. #1: Standard atomic weight [11,30]; #2: atomic weight calculated with the values of isotope abundances (see text); #3: atomic weight calculated with the isotope abundance ratios.

calculate these values. It would be ideal, of course, if uniform notation were used, as it is for IRMS.

The uncertainties for the Cd isotope abundances given in the IUPAC table [11] (see Table 13) are overestimated. The observed variations in isotope abundance in terrestrial samples allow for a lower estimate of uncertainty. The Cd material Cd-2211 constitutes a material with a $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ value of 0‰. Taking into consideration the isotope abundance variations of $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ from -3.6% to $+3.4\%$ in terrestrial samples, Eqs. (12) and (6) yield the minimum and maximum values for isotope abundances. The isotope abundances of Cd should be within the following orders of magnitude ($\sum_i h_i = 1$):

$$\begin{aligned} h(^{106}\text{Cd}) &: 0.01245(8); \quad h(^{108}\text{Cd}) : 0.00889(4); \\ h(^{110}\text{Cd}) &: 0.12471(28); \quad h(^{111}\text{Cd}) : 0.12796(17); \\ h(^{112}\text{Cd}) &: 0.24111(11); \quad h(^{113}\text{Cd}) : 0.12227(6); \\ h(^{114}\text{Cd}) &: 0.28743(38); \quad h(^{116}\text{Cd}) : 0.07518(23). \end{aligned}$$

It is apparent that, even taking the isotope abundance variations into account, the uncertainties of the IUPAC values are overestimated by a factor of 10.

For the isotope abundances in the IUPAC table [11], the study by Rosman et al. [7] was cited under “best measurement”. However, this paper explicitly avoids giving any isotope abundances and atomic weights. The isotope abundances were probably calculated afterwards from the observed isotope abundance ratios of a sample. By correcting these values with Eq. (4) and a factor of $\varepsilon = 0.002125$ for the mass fractionation, it is possible to obtain the isotope abundances given in the IUPAC table.

For the uncertainty evaluation of the atomic weight it is essential to know how the atomic weight was calculated. Using the IUPAC values of isotope abundances and their uncertainties (assumption: $U = k \cdot u_c$ with $k = 2$), first the isotope abundance ratios were calculated and then these values were used to calculate the atomic weight $A_r(\text{Cd}) = 112.412(11)$, ($U = k \cdot u_c$ with $k = 2$). The values given under “best measurement” yield an atomic weight of $A_r(\text{Cd}) = 112.4116(36)$, ($U = k \cdot u_c$ with $k = 2$).

The atomic weights of the four natural Cd materials that exhibit no significant differences in isotope abundance ratios (Table 13) have the following values: $A_r(\text{Cd-2211}) = 112.41384(18)$, $A_r(\text{Cd-2212}) = 112.41384(18)$, $A_r(\text{Cd-2213}) = 112.41391(18)$, $A_r(\text{Cd-2214}) = 112.41382(24)$, (all with $U = k \cdot u_c$ with $k = 2$).

Taking into account the isotope abundance variations in terrestrial samples, as listed above, yields an atomic weight of $A_r(\text{Cd}) = 112.4138(14)$, ($U = k \cdot u_c$ with $k = 2$). This means that the uncertainty of the given standard atomic weight (see Table 13) could be reduced by at least a factor of 6.

4. Conclusions

By using seven enriched and purified Cd isotope materials out of which synthetic isotope mixtures have been prepared gravimetrically, it was possible to calculate the correction factor for mass fractionation for every isotope abundance ratio. The iso-

tope abundances and the atomic weights of different natural Cd materials were determined using TIMS and MC-ICP-MS. It was possible to demonstrate that the isotope abundances of four different natural Cd materials do not differ significantly and to provide $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ -values that are not significantly different from zero.

The uncertainties of the isotope abundances in the IUPAC values [11] are a factor of 54–112 greater, and those of Rosman et al. [7], which were given in the IUPAC table [11] under “best measurement”, are a factor of 18–38 greater, than the isotope abundances calculated in this report. Considering the isotope abundance variations $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ for terrestrial samples that range from -3.6% to $+3.4\%$ as given in the literature, the uncertainties of the IUPAC values are overestimated by a factor of 10.

The atomic weight of $A_r(\text{Cd}) = 112.41384(18)$ calculated using the isotope abundance ratios of Cd-2211 accords with the atomic weight of $A_r(\text{Cd}) = 112.4116(36)$ from Rosman et al. [7], which was calculated with the isotope abundances from the IUPAC table [11] listed under “best measurement”. The uncertainty of the atomic weight in this study is a factor of 20 smaller than those of Rosman et al. [6,7], and a factor of 44 smaller than the standard atomic weight of IUPAC. In consideration of the Cd isotope abundance variations in terrestrial samples, the uncertainty of the atomic weight is overestimated by a factor of 6.

The Cd materials Cd-2211 and Cd-I012 can be used as isotope materials, whereby Cd-2211 has a $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ equal 0‰ and Cd-I012 a $\delta(^{114}\text{Cd}/^{110}\text{Cd})$ equal -1.66% with reference to Cd-2211.

Acknowledgements

The authors thank M. Czerwensky for assistance of the HR-ICP-MS measurements, and M. Sachwitz for providing the CERN Program Library and helpful discussions.

Appendix A

Deriving Eq. (9) for the isotope abundance ratio of mixture.

The isotope abundance ratio can be expressed by number of atoms.

$$R_{ij} = \frac{N_{ij}}{N_{bj}} \quad (\text{A.1})$$

$$N_{ij} = \left(\sum_{i=1}^n N_{ij} \right) \cdot h_{ij} \quad (\text{A.2})$$

with (A.2) in (A.1) follows:

$$R_{ij} = \frac{h_{ij}}{h_{tbj}} \quad (\text{A.3})$$

with (A.4) follows (A.5).

$$\sum_{i=1}^n h_{ij} = 1 \quad (\text{A.4})$$

$$\sum_{i=1}^n R_{ij} = \frac{1}{h_{tbj}} \quad (\text{A.5})$$

The isotope abundance can be expressed by the isotope abundance ratios (inserting (A.5) in (A.3)).

$$h_{ij} = \frac{R_{ij}}{\sum_{i=1}^n R_{ij}} \quad (\text{A.6})$$

$$R_{mi} = \left[\frac{\sum_{j=1}^m \frac{w_j \cdot w_{Ej} \cdot N_A \cdot K_i \cdot R_{oij} / \sum_{i=1}^n (K_i \cdot R_{oij})}{\sum_{i=1}^n (M_{Ii} \cdot (m_{12C}/12) \cdot N_A \cdot K_i \cdot R_{oij} / \sum_{i=1}^n (K_i \cdot R_{oij}))}}{\sum_{j=1}^m \frac{w_j \cdot w_{Ej} \cdot N_A \cdot K_b \cdot R_{obj} / \sum_{i=1}^n (K_i \cdot R_{oij})}{\sum_{i=1}^n (M_{Ii} \cdot (m_{12C}/12) \cdot N_A \cdot K_i \cdot R_{oij} / \sum_{i=1}^n (K_i \cdot R_{oij}))}} \right]^{-1} \quad (\text{A.15})$$

Similarly to (A.1) results the isotope abundance ratio for the mixture (A.7) and (A.8).

$$R_{mi} = \frac{\sum_{j=1}^m N_{ij}}{\sum_{j=1}^m N_{bj}} \quad (\text{A.7})$$

$$R_{mi} = \frac{\sum_{j=1}^m (\sum_{i=1}^n N_{ij}) \cdot h_{tij}}{\sum_{j=1}^m (\sum_{i=1}^n N_{ij}) \cdot h_{tbj}} \quad (\text{A.8})$$

The sum over all atoms of the element (Cd) in the enriched isotope material j :

$$\sum_{i=1}^n N_{ij} = \frac{w_j \cdot w_{Ej}}{M_j} \cdot N_A \quad (\text{A.9})$$

The atomic weight of the element (Cd) in the enriched isotope material j :

$$M_j = \sum_{i=1}^n (M_i \cdot h_{tij}) \quad (\text{A.10})$$

$$M_i = m_i \cdot N_A \quad (\text{A.11})$$

The atomic mass of isotope i (M_i in kg mol^{-1}) is the mass of one atom of isotope i multiplied by the Avogadro constant.

Atomic mass of isotope i (m_i in kg) is the product of atomic mass ratio number multiplied by the atomic mass constant m_u .

$$m_i = M_{Ii} \cdot \frac{m_{12C}}{12} \quad (\text{A.12})$$

$$\frac{m_{12C}}{12} = 1.66053886(28) \cdot 10^{-27} \text{ kg} = 1m_u \quad (\text{A.13})$$

Corrected isotope abundance ratio for isotope i in enriched isotope material j :

$$R_{tij} = K_i \cdot R_{oij} \quad (\text{A.14})$$

Corrected isotope abundance ratio R_{mi} in the mixture prepared from enriched isotope materials.

Insertions give (A.15) ((A.12) in (A.11), (A.11) in (A.10), (A.10) in (A.9), (A.9) in (A.8), (A.6) in (A.8) und (A.14) in (A.8)):

After cancellations in (A.15) follows:

$$R_{mi} = \left[\frac{\sum_{j=1}^m \frac{w_j \cdot w_{Ej} \cdot K_i \cdot R_{oij}}{\sum_{i=1}^n M_{Ii} \cdot K_i \cdot R_{oij}}}{\sum_{j=1}^m \frac{w_j \cdot w_{Ej} \cdot K_b \cdot R_{obj}}{\sum_{i=1}^n M_{Ii} \cdot K_i \cdot R_{oij}}} \right]^{-1} \quad (\text{A.16})$$

Isotope abundance ratio observed in enriched isotope material j , with basic isotope 4 (^{111}Cd):

$$R_{obj} = R_{o4j} \quad (\text{A.17})$$

$$K_b = K_4 \quad (\text{A.18})$$

$$K_4 = 1 \quad (\text{A.19})$$

With (A.17) and (A.18) follows (A.20), which expresses the corrected isotope abundance ratio in the mixture.

$$R_{mi} = \left[\frac{K_i \cdot \sum_{j=1}^m \frac{w_j \cdot w_{Ej} \cdot R_{oij}}{\sum_{i=1}^n M_{Ii} \cdot K_i \cdot R_{oij}}}{K_4 \cdot \sum_{j=1}^m \frac{w_j \cdot w_{Ej} \cdot R_{o4j}}{\sum_{i=1}^n M_{Ii} \cdot K_i \cdot R_{oij}}} \right]^{-1} \quad (\text{A.20})$$

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