

# Supplementary Information

to

## Stable isotope fractionation of metals and metalloids in plants: a review

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**Table S1:** An overview of non-traditional stable isotope methods

Element (symbol)	Stable isotopes (natural abundances, %)	Ratio <sup>a</sup>	Analyte amount <sup>b</sup> ng	Separation procedures	Primary standard	Instrumentation	Isobaric interferences <sup>f</sup>	Mass bias correction	Analytical precision ‰
Boron (B)	10 (19.9) 11 (80.1)	11/10	200-400	Geilert et al. 2015 Rosner et al. 2011	NIST 951 NIST 951a	ICP-Q-MS MC-ICP-MS TIMS		SSB <sup>g</sup>	>0.8
Magnesium (Mg)	24 (78.99) 25 (10.00) 26 (11.01)	25/24 26/24	1000-3000	Bolou-Bi et al. 2009 Opfergelt et al. 2012 Wang et al. 2020	NIST 980 DSM3	MC-ICP-MS		SSB	>0.1
Silicon (Si)	28 (92.230) 29 (4.683) 30 (3.087)	30/28	600-3000 <sup>c</sup>	Schuessler & Blankenburg 2014 Georg et al. 2006 Oelze et al. 2016	NIST 8546	MC-ICP-MS LA-MC-ICP-MS	<sup>15</sup> N <sub>2</sub>	SSB Mg doping	0.10-0.11 (bulk), 0.24 ( <i>in situ</i> )
Potassium (K)	39 (93.2581) 40 (0.012) 41 (6.730)	41/39	3000-10000	Richter et al. 2011 Li et al. 2016 Morgan et al. 2018 Chen et al. 2019	NIST 999b NIST 3141a	MC-ICP-MS (isoprobe)		SSB	0.05 to 0.20
Calcium (Ca)	40 (96.941) 42 (0.647) 43 (0.135) 44 (2.086) 46 (0.004)	44/40	2000-5000	Bullen & Chadwick 2016 Schmitt et al. 2009 Christensen et al., 2018	NIST 915a	TIMS MC-ICP-MS	<sup>40</sup> Ar <sup>20</sup> Ne <sup>2+</sup> <sup>21</sup> Ne <sup>2+</sup> <sup>22</sup> Ne <sup>2+</sup>	Double spike SSB	0.09-0.12
Iron (Fe)	54 (5.845) 56 (91.754), 57 (2.119) 58 (0.282)	57/54 56/54	1500-5000 100-500 <sup>d</sup>	Schoenberg & von Blanckenburg 2005, Teutsch et al. 2005 StreLOW 1980	IRMM-014	MC-ICP-MS	<sup>54</sup> Cr <sup>58</sup> Ni	SSB Ni/Cu-doping	0.05-0.12
Nickel (Ni)	58 (68.077) 60 (26.223) 61 (1.140) 62 (3.635) 64 (0.9256)	60/58	100-200	Quitté and Oberli 2006 Cameron et al. 2009 Ratie et al. 2019	NIST 986	MC-ICP-MS	<sup>58</sup> Fe	Double spike	0.05-0.10
Copper (Cu)	63 (69.17) 65 (30.83)	65/63	100-300	Blotevogel et al. 2018 Borrok et al. 2007 Kidder et al. 2020	NIST 976 <sup>e</sup>	MC-ICP-MS		SSB Ni/Zn/Ga doping	0.02-0.15
Zinc (Zn)	64 (48.63) 66 (27.9) 67 (4.10) 68 (18.75) 70 (20.84)	66/64	50-200	Caldelas et al. 2020 Marković et al. 2017 Moore et al. 2017	JMC-Lyon <sup>e</sup>	MC-ICP-MS	<sup>64</sup> Ni Ba <sup>2+</sup> <sup>70</sup> Ge <sup>35</sup> Cl <sub>2</sub>	Double spike Cu/Ni-doping	0.05-0.10
Molybdenum (Mo)	92 (14.84) 94 (9.25) 95 (15.92) 96 (16.68) 97 (9.55) 98 (24.13) 100 (9.63)	98/95	20-100	Kerl et al. 2017 Malinovsky & Kashulin 2018	NIST 3134	MC-ICP-MS	<sup>92</sup> Zr <sup>94</sup> Zr <sup>96</sup> Zr <sup>98</sup> Ru <sup>100</sup> Ru	Double spike Pd-doping	0.04-0.20
Cadmium (Cd)	106 (1.25) 108 (0.89) 110 (12.49) 111 (12.80) 112 (24.13) 113 (12.22) 114 (28.73) 116 (7.49)	114/110	20-100	Murphy et al. 2016 Wei et al. 2015	NIST 3108	MC-ICP-MS TIMS	<sup>106</sup> Pd <sup>108</sup> Pd <sup>110</sup> Pd <sup>112</sup> Sn <sup>113</sup> In, <sup>113</sup> In <sup>114</sup> Sn <sup>116</sup> Sn	Double spike Ag-doping SSB	0.02-0.10
Thallium (Tl)	203 (29.524) 205 (70.476)	205/203	10-100	Rader et al. 2018 Baker et al. 2009	NIST 997	MC-ICP-MS		SSB Pb-doping	0.04-0.10

<sup>a</sup>Isotope ratio most commonly used to report isotope composition, usually using the delta ( $\delta$ ) notation relative to the primary isotope standard. Other ratios are used to assess whether isotope fractionation is mass dependent or independent.

<sup>b</sup>The range of analyte amount used for isotopic measurement with good analytical precision. The minimum value will provide enough for one measurement, while the maximum value is preferred, to enable analytical repeats. Note that these are indicative values and can increase or decrease depending on mass bias correction method, sensitivity (V/ppm analyte), the uptake rate of the nebuliser (MC-ICP-MS) and wet or dry plasma conditions.

<sup>c</sup> This is the amount used for the isotope measurement, but more (up to 60 ug) is required for the separation procedure (NaOH fusion)

<sup>d</sup> For Fe, measurements with lower analyte amounts can be undertaken using new generation MC-ICP-MS instrumentation

<sup>e</sup> No longer available so others used and then conversion applied to data. For Cu: AE633 or AE647 (Moeller et al. 2012), For Zn: AA-ETH or IRMM-3702 (Archer et al. 2017)

<sup>f</sup> There are also multiple possible molecular interferences including hydrides, nitrides, oxides and argides. For example, potentially problematic molecular interferences for <sup>56</sup>Fe and <sup>63</sup>Cu are <sup>40</sup>Ar<sup>16</sup>O and <sup>23</sup>Na<sup>40</sup>Ar, respectively.

These can be found online. E.g. [https://www.perkinelmer.com/CMSResources/Images/44-74379ATL\\_TableOfPolyatomicInterferences.pdf](https://www.perkinelmer.com/CMSResources/Images/44-74379ATL_TableOfPolyatomicInterferences.pdf)

<sup>g</sup> sample standard bracketing

**Table S2:** List of certified reference materials (CRMs). The CRMs have certified concentrations of various elements so can be used as quality control (QC) for analyte yields for plant and soil analyses. This table lists the studies that have also reported isotope compositions for the materials, as additional QC for isotope analysis and for interlaboratory comparisons.

<b>Material</b>	<b>Type</b>	<b>Element</b>	<b>Reference</b>
BCR 281	Rye grass	Si, Fe, Zn	<b>Frick et al. 2020, Arnold et al. 2010, 2015, Caldelas et al. 2011, Caldelas et al. 2020, Couder et al. 2015</b>
BCR 279	Sea Lettuce	Mg	<b>Bolou-Bi et al. 2009</b>
BCR 381	Rye flour	Mg	<b>Bolou-Bi et al. 2009</b>
BCR 383	Green beans	Mg	<b>Le Goff et al. 2021</b>
BCR 482	Lichen	Mg, Cu, Ni, Zn, Cd	<b>Bolou-Bi et al. 2009, Sillerova et al. 2017, Caldelas et al. 2011, Deng et al. 2014, Cloquet et al. 2006, Borovička et al. 2021</b>
BCR 62	Olive leaves	Zn	Caldelas et al. 2011, Tang et al. 2016
BCR 679	White cabbage	B, Cd	<b>Rosner et al. 2011, Geilert et al. 2015, Geilert et al. 2019, Moore et al. 2020</b>
IGGE GSB-4	Soybean	Ni	<b>Li et al. 2020</b>
IGGE GSB-12	Bean	Ni	<b>Li et al. 2020</b>
INCT TI-1	Tea leaves	Tl	<b>Vanek et al. 2019</b>
INRA V464	Oak leaves	Ni	<b>Zelano et al. 2020</b>
IPE 126	Maize	B	<b>Geilert et al. 2015, Geilert et al. 2019</b>
SRM 1515	Apple leaves	Mg, Fe, Ni	<b>Shalev et al. 2018, Garnier et al. 2017, Ratié et al. 2019</b>
SRM 1547	Peach leaves	B, Cu, Mo	<b>Geilert et al. 2015, Geilert et al. 2019, Rosner et al. 2011, Malinovsky &amp; Kashulin 2018</b>
SRM 1567b	Wheat flour	Zn, Cd	<b>van der Ent et al. 2021, Wigganhauser et al. 2016, Imseng et al. 2018, 2019, Borovička et al. 2021</b>
SRM 1570a	Spinach leaves	Ni, Cd	Ratié et al. 2019, <b>Moore et al. 2020, Borovička et al. 2021</b>
SRM 1573a	Tomato leaves	Cu, Zn, Cd	<b>Ryan et al. 2013, van der Ent et al. 2021, Borovička et al. 2021</b>
SRM 1575a	Pine needles	Fe, Cd	Wu et al. 2021, <b>Borovička et al. 2021</b>
SRM 2384	Baking Chocolate	Cd	<b>Barraza et al. 2019</b>
SRM 8433	Corn Bran	B	<b>Geilert et al. 2015, Geilert et al. 2019, Rosner et al. 2011</b>
BCR 60	Light sandy soil	Zn	Caldelas et al. 2011, Caldelas et al. 2020
IGGE GSS1-7	Soils	Ni, Tl	<b>Li et al. 2020, Kersten et a. 2014</b>
SRM 2709a	San Joaquin soil	Zn, Fe, Cu, Cd	<b>Wigganhauser et al. 2018, van der Ent et al. 2021, Garnier et al. 2017, Blotevogel et al. 2019, Barraza et al. 2019</b>
SRM 2710	Montana soil I	Cd	<b>Zhou et al. 2020, Zhong et al. 2021, 2022</b>
SRM 2710a	Montana soil I	Cu, Ni, Cd	Sillerova et al. 2017, <b>Zhong et al. 2021, 2022</b>
SRM 2711	Montana soil II	Cd	<b>Liu et al. 2020, Zhou et al. 2020, Borovička et al. 2021, Zhong et al. 2021, 2022</b>
SRM 2711a	Montana soil II	Cd	<b>Zhong et al. 2021, 2022</b>
TILL 11	Forest soil	Mg	<b>Bolou-Bi et al. 2009</b>

Bold references used the material for QC of isotope analysis and report isotope compositions, while the others used for yield quantification only.

**Table S3:** Summary of linkages between physiological and physico-chemical processes as well as knowledge gaps and corresponding research priorities. Colors: Blue = enrichment of light isotopes, red = enrichment of heavy isotopes, orange = both/unknown. Font: robust experimental evidence provided (regular), well substantiated hypotheses (italic). Empty cell = research gap.

	root uptake	short distance transport (membrane transport)	long distance transport (xylem/phloem)	metabolic functionalization/storage and compartmentalization	others	proposed research priorities
<b>B</b>		<i>equilibrium fractionation between soluble boric acid (heavy) and borate (light)</i>		<i>structural binding of borate enriches cell walls in light isotopes</i>	<i>distinct B supply, cultivar, and species seems to change B isotope fractionation</i>	- determination of B isotope fractionation during plant uptake by i) providing full B mass balances and ii) using B model plants (e.g. arabidopsis) to e.g. employ genetic approaches - experimental determination of the isotope fractionation factor for cell wall binding of B by separating soluble and non-soluble B fractions from fresh plants (see example Sun et al. 2018 for dried plant material) - determination of isotope fractionation for deficient and adequate B supply in model plants
	<i>cell wall sorption</i>		<i>phloem transport induces enrichment of heavy Mg in reproductive organs</i>	<i>binding of Mg to chlorophyll</i>	<i>low Mg supply changes fractionation during Mg uptake and re-translocation</i>	- identification of the role of distinct membrane proteins on isotope fractionation during Mg uptake by employing genetic approaches with yeast and/or model plants (e.g. arabidopsis) - determination of the role of vacuolar storage of Mg on the isotope fractionation between root and shoot - experimental determination of equilibrium isotope fractionation of Mg binding to molecules other than chlorophyll (e.g. ATP). - identifying the role of sink-source relationships by integrating isotope fractionation factors for cross-membrane transport and binding of elements to organic ligands
<b>Mg</b>	<i>binding of Mg to membrane transporter at low supply</i>	<i>binding of Mg to membrane transporter at low supply</i>	<i>degradation of Mg containing molecules and subsequent re-translocation of Mg</i>			
	<i>diffusion through membrane, with and without Si membrane protein</i>	<i>diffusion through membrane, with and without Si membrane protein</i>	<i>enrichment of heavy Si in tissues along the transpiration stream through precipitation of light Si into phytoliths</i>	<i>precipitation of Si into phytoliths</i>	<i>Si isotope fractionate within leaves</i>	- determination of the role of membrane transport and Si precipitation on isotope fractionation between root and shoot. - determination of the role of Lsi transporters on isotope fractionation using genetic approaches (as exemplified in Köster et al. 2009) by including biological replicates.
<b>Si</b>		<i>precipitation of light Si into phytoliths in roots</i>	<i>membrane transport in the shoot (LSi6)</i>			
	<i>ion channel through distinct ionic radii and dehydration of K</i>	<i>diffusion does not play a role during K membrane transport</i>	<i>binding of heavy isotopes to pectate in roots and leaves</i>			- the method to measure K isotope ratios in plants is developed. Next steps could be to investigate the role of low and high K supply on K isotope fractionation in plants
<b>K</b>	<i>root cell wall sorption</i>			<i>structural binding of light Ca to pectins</i>	<i>distinct isotope fractionation within the shoot with distinct Ca supply</i>	- determination of isotope fraction during Ca uptake by distinct root membrane transporters that dominate at low and high Ca supply - measuring Ca isotopes in storage forms (e.g. by extractions, Schmitt et al. 2018) at different Ca supply and/or in distinct phloem sources - experimental determination of equilibrium and kinetic isotope fractionation of Ca binding to oxalate
	<i>dehydration prior to membrane transport</i>	<i>dehydration prior to membrane transport</i>	<i>heavy Ca in the xylem due to binding of light Ca to pectate in cell walls</i>	<i>binding of Ca to oxalate in roots and leaves</i>		
<b>Ca</b>	<i>reduction prior to membrane transport, (re-)precipitation of light Fe in the apoplast, binding of Fe to phytosiderophores</i>				<i>redox conditions with strong impact on Fe isotopes fractionation in the soil-plant interface</i>	- detailed investigation on Fe membrane transport by employing single cell organisms, model plants (e.g. arabidopsis, rice) as well as genetic approaches - investigation on the effect of distinct Cu supply on Fe isotope fractionation during uptake - determination of the impact on distinct Fe supply on Fe isotope fractionation during Fe uptake and root-to-shoot translocation - focus on Fe re-translocation during grain filling periods by e.g. combined isotope and speciation measurements in the shoots.
			<i>re-translocation of Fe(III) from leaves requires reduction to Fe(II)</i>	<i>storage of Fe e.g. leaves as Fe(III) in proteins</i>		
<b>Fe</b>						

	root uptake	short distance transport (membrane transport)	long distance transport (xylem/phloem)	metabolic functionalization/storage and compartmentalization	others	proposed research priorities
<b>Ni</b>	<i>speciation in nutrient solution, diffusion t favors light Ni</i>	<i>high Ni uptake rates favor light Ni</i>	<i>Ni re-translocation during tree aging reduces Ni fractionation within shoots</i>	<i>binding of Ni to organic acids induces minor isotope fractionation</i>	<i>reduced isotope fractionation during Ni plant uptake with high Zn supply</i>	<ul style="list-style-type: none"> <li>- root extraction to distinguish between apoplastic and symplastic Ni in roots</li> <li>- the role of distinct conditions in the Ni source such as pH, Fe supply, and distinct Ni speciation on Ni isotope fractionation during uptake</li> <li>- identify processes that control the root-to-shoot transport of Ni and a systematic investigation of phloem sink-source relations during reproductive growth stages. Potentially by combining with Ni speciation measurements.</li> </ul>
<b>Cu</b>	<i>reduction prior to membrane transport, Cu speciation in solution</i>	<i>membrane transport with and without reduction prior to transport</i>			<i>Cu supply, has an effect on Cu isotope fractionation during Cu uptake</i>	<ul style="list-style-type: none"> <li>- investigation of fractionation factors associated with different uptake pathways at low and high supply</li> <li>- continuation of the yeast work of Cadiou et al. (2017) by employing similar genetic approaches in model plants</li> <li>- systematic investigation of the role of Cu stress on isotope fractionation between roots and shoots</li> <li>- determination of the role of transpiration during vegetative growth and re-translocation of Cu during reproductive growth phases</li> <li>- systematic comparison of Cu isotope composition in apoplastic and symplastic root pools</li> </ul>
	<i>binding during membrane transport, sorption in the apoplast</i>		<i>Successive fractionation with leaf height (transpiration stream driven)</i>	<i>binding of Cu to thiols for detoxification</i>		
<b>Zn</b>	<i>diffusion, speciation in solution, binding to phytosiderophores and other ligands with O and/or N donors, sorption in the apoplast</i>	<i>high affinity (low uptake rates) transport induces a shift towards heavy isotopes</i>	<i>phloem sinks enriched in light isotopes</i>	<i>Zn storage in root vacuoles to organic acids at high Zn concentrations</i>	<i>extent of isotope fractionation during Zn acquisition depends on Zn supply and uptake rates</i>	<ul style="list-style-type: none"> <li>- determination of the the role of pyhtosiderophores on Zn isotope fractionation by employing genetic approaches</li> <li>- apply genetic approaches to identify transporters and corresponding isotope fractionation at low and high supply</li> <li>- systematically disentangling the role of kinetic vs. equilibrium fractionation during Zn uptake in plants</li> <li>- focus on sink-source relationships during grain filling by combining isotope analyses with genetic and speciation approaches</li> </ul>
	<i>stripping off the hydration shell</i>	<i>binding of Zn to membrane transporter, diffusion prior to membrane transport, binding to phytosiderophores prior to membrane transport</i>	<i>phloem transport of light isotopes due to binding and retention of heavy Zn to O and N containing ligands in senescent leaves</i>			
<b>Mo</b>						<ul style="list-style-type: none"> <li>- the methodology to measure Mo isotopes in plants is set up. Future studies should systematically explore the impact of environmental factors, membrane proteins, and organic ligands on Mo isotope fractionation in plants</li> </ul>
<b>Cd</b>	<i>root uptake by Nramp5 (binding of Cd to the transporter), adsorption to root surface, binding to humic acids enriches ionic Cd in heavy isotopes</i>		<i>xylem to phloem transfer in the nodes by OsHMA2, OsLCT1</i>	<i>sequestration of Cd into vacuoles causes a transport of heavy Cd from root to shoot</i>	<i>distinct isotope fractionation patterns between cereals, cacao, and Cd accumulators</i>	<ul style="list-style-type: none"> <li>- determination of the role of distinct environmental conditions (e.g., high and low pH) on Cd speciation in the source and Cd uptake</li> <li>- disentangling the interplay of distinct uptake transporters on Cd isotope fractionation during plant uptake (e.g., NRAMP5, NRAMP1, IRT-1)</li> <li>- experimental determination of the Cd isotope effect of diffusion and Cd binding to distinct organic ligands</li> <li>- disentangling the role of Cd speciation and membrane transport on isotope fractionation</li> <li>- determination of the role of xylem vs. phloem transport on isotope fractionation in cacao</li> </ul>
	<i>diffusion prior to uptake favors light isotopes</i>	<i>dehydration of Cd prior to transport, binding to S donors of the membrane protein</i>	<i>vacuolar sequestration of light Cd enriches phloem sinks in heavy isotopes</i>	<i>vacuolar sequestration may be driven by tonoplast transport (HMA3) and chelation by thiols such as phytochelatins</i>		
<b>TI</b>	<i>potential involvement of membrane proteins of K</i>			<i>mainly bound to O ligands, S ligands play a minor role</i>	<i>TI strongly fractionated within the plant</i>	<ul style="list-style-type: none"> <li>- determination of the role of distinct K supply on TI isotope fractionation during TI uptake and transport within the plant by including e.g. mutant plants with dysfunctional K uptake membrane transporters</li> <li>- determination of equilibrium isotope fractionation for TI binding to distinct organic ligands</li> </ul>

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