

# **Supplement to: Silicon isotope fractionation and uptake dynamics of three crop plants: laboratory studies with transient silicon concentrations**

Daniel A. Frick<sup>1</sup>, Rainer Remus<sup>2</sup>, Michael Sommer<sup>2,3</sup>, Jürgen Augustin<sup>2</sup>, Friedhelm von Blanckenburg<sup>1,4</sup>

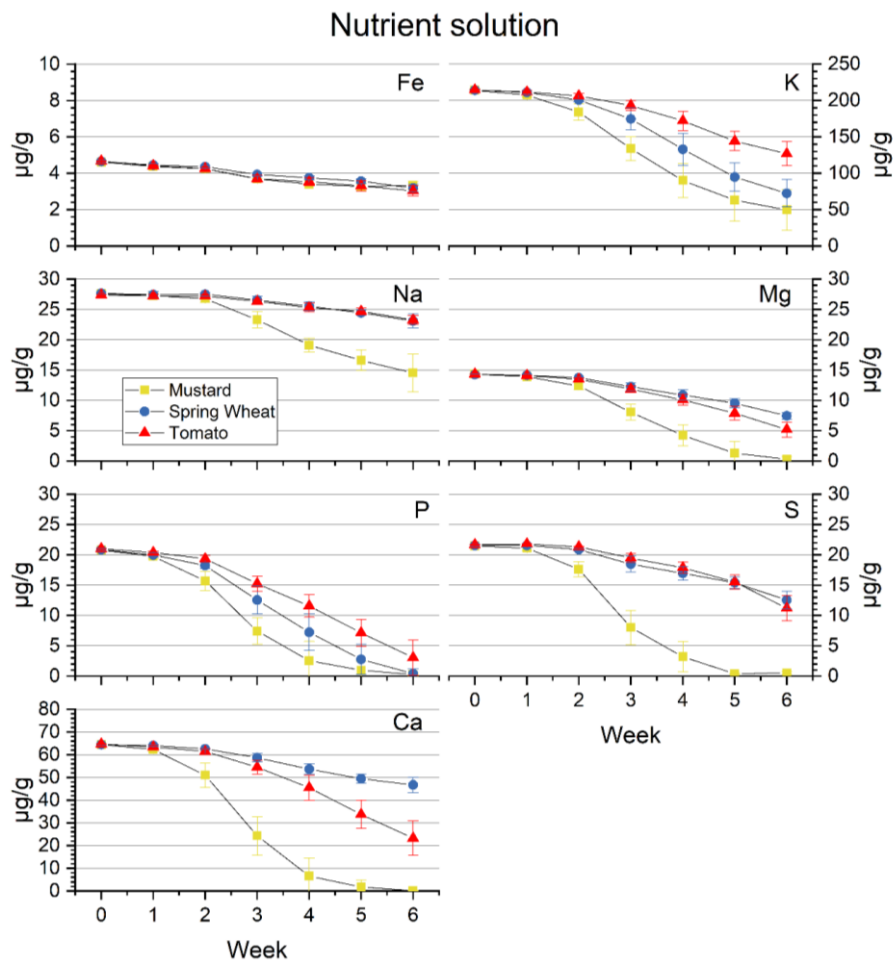
5 <sup>1</sup>GFZ German Research Centre for Geosciences, Potsdam, 14473, Germany.

<sup>2</sup>Leibniz Centre for Agricultural Landscape Research (ZALF), Müncheberg, 15374, Germany.

<sup>3</sup>Institute of Environmental Science and Geography, University of Potsdam, Potsdam, 14476, Germany

<sup>4</sup>Institute of Geological Science, Freie Universität Berlin, Berlin, 12249, Germany.

*Correspondence to:* Daniel A. Frick (dfrick@gfz-potsdam.de)



**S-Figure 1: Temporal evolution of nutrient concentrations during the hydroponic growth of the different plant species. Concentration (Fe, K, Mg, Ca, P, S, Na in  $\mu\text{g}\cdot\text{g}^{-1}$ ) are based on the mean of the three replicated containers, uncertainty shown is 1 standard deviation of those replicated containers.**

## Tables

	<b>Concentration measurements</b>	<b>Si isotope ratio measurements</b>
Instrument	Varian 720ES ICP-OES	ThermoFisher Neptune Plus
Spraychamber	cyclonic, glass	APEX
Nebuliser	concentric, glass	concentric, PFA
Sample uptake rate	ca. 2 ml/min (pumped:15 rpm)	160 $\mu$ L/min
Cones	standard cone	N-sampler / H-skimmer
Plasma RF power	1.0 kW	1200 W
Ar cool gas	15 L/min	15 L/min
Ar aux gas	1.5 L/min	0.8 L/min
Ar nebuliser pressure /flow rate <sup>a</sup>	280 -320 kPa	1.0 L/min
Analysis integration time	10 s	4 s
Integration replicates per analysis	3	30
Rinse time between samples	60 s (pumped at 50 rpm), 0.3 M HNO <sub>3</sub>	160 s, 0.1 M HCl
Analytes (wavelengths in nm for ICP-OES or isotopes for MC-ICP-MS)	Ca 422.673, Fe 238.204, K 769.897, Mg 280.270, Na 588.995, Si 288.158, S 181.972, P 213.618	<sup>24</sup> Mg, <sup>25</sup> Mg, <sup>26</sup> Mg <sup>28</sup> Si, <sup>29</sup> Si, <sup>30</sup> Si medium mass resolution mode: $\Delta m/m$ (5%/95% intensity limits): >5000
<sup>a</sup> Optimised during each analytical session		

**Table S1: Instrument settings for concentration and silicon isotope ratio measurements.**

ERM-CD281				BHVO-2			
$\delta^{29}\text{Si}/^{28}\text{Si}$	2 s	$\delta^{30}\text{Si}/^{28}\text{Si}$	2 s	$\delta^{29}\text{Si}/^{28}\text{Si}$	2 s	$\delta^{30}\text{Si}/^{28}\text{Si}$	2 s
-0.12	0.04	-0.25	0.05	-0.14	0.06	-0.26	0.07
-0.18	0.05	-0.33	0.06	-0.13	0.04	-0.24	0.07
-0.16	0.04	-0.26	0.05	-0.18	0.04	-0.30	0.06
-0.19	0.05	-0.24	0.07	-0.18	0.04	-0.32	0.06
-0.15	0.05	-0.27	0.05	-0.22	0.05	-0.35	0.07
-0.19	0.05	-0.28	0.07	-0.15	0.05	-0.29	0.06
-0.15	0.06	-0.18	0.07	-0.27	0.14	-0.40	0.15
-0.25	0.04	-0.45	0.05	-0.07	0.08	-0.25	0.09
-0.26	0.04	-0.47	0.05	-0.17	0.05	-0.24	0.07
-0.28	0.04	-0.44	0.07	-0.11	0.05	-0.27	0.07
-0.27	0.05	-0.46	0.07	-0.16	0.05	-0.26	0.07
-0.31	0.04	-0.42	0.07	-0.11	0.08	-0.23	0.09
-0.25	0.04	-0.38	0.07	-0.14	0.06	-0.27	0.10
				-0.14	0.04	-0.30	0.06
				-0.17	0.04	-0.29	0.06
				-0.17	0.04	-0.29	0.06
				-0.18	0.05	-0.32	0.07
				-0.14	0.05	-0.22	0.07
				-0.19	0.04	-0.35	0.06
				-0.18	0.05	-0.31	0.07
				-0.15	0.05	-0.29	0.06
				-0.13	0.05	-0.29	0.06
				-0.16	0.06	-0.26	0.07
				-0.22	0.05	-0.32	0.07
				-0.21	0.05	-0.21	0.07
				-0.16	0.04	-0.29	0.05
				-0.16	0.04	-0.33	0.05
				-0.20	0.04	-0.31	0.06
				-0.13	0.06	-0.25	0.09
				-0.16	0.05	-0.35	0.06
				-0.17	0.04	-0.24	0.07
				-0.18	0.05	-0.32	0.07
				-0.18	0.05	-0.30	0.07
				-0.17	0.05	-0.36	0.07
				-0.13	0.04	-0.25	0.05
				-0.12	0.04	-0.29	0.04
				-0.15	0.06	-0.29	0.06
				-0.09	0.04	-0.26	0.07
				-0.16	0.04	-0.27	0.05
				-0.15	0.04	-0.23	0.06

Table S2: Individually repeated analysis of BHVO-2 and ERM-CD281 for their silicon isotope composition.

		Ca	Fe	K	Mg	P	S	Si	$\delta^{30}\text{Si}$	2 SD
		$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	‰	
<b>Mustard</b>	<b>Pot 1</b>	64.2	4.6	210.8	14.3	20.4	21.2	49.3	-0.23	0.12
	<b>Pot 4</b>	64.3	4.6	214.8	14.3	20.9	21.6	49.8	-0.19	0.06
	<b>Pot 7</b>	65.0	4.7	216.1	14.4	21.2	21.6	49.5	-0.15	0.06
<b>Spring Wheat</b>	<b>Pot 2</b>	64.3	4.6	213.2	14.3	20.7	21.3	49.9	-0.18	0.03
	<b>Pot 5</b>	64.5	4.7	214.0	14.3	20.8	21.6	49.4	-0.18	0.13
	<b>Pot 8</b>	64.8	4.6	215.5	14.2	21.0	21.7	49.2	-0.24	0.07
<b>Tomato</b>	<b>Pot 3</b>	64.9	4.7	213.3	14.4	20.9	21.7	49.4	-0.20	0.08
	<b>Pot 6</b>	64.5	4.7	215.4	14.4	21.1	21.6	49.5	-0.25	0.10
	<b>Pot 9</b>	64.7	4.7	214.7	14.2	21.1	21.7	49.4	-0.23	0.02
<b>Average</b>									-0.21	0.07

**Table S3: Starting composition (major element concentration (in  $\mu\text{g g}^{-1}$ ) and silicon isotopic composition) of the nutrient solutions for the individual pots.**

The Table S4 is in on the following pages.

- 25 **Table S4: Dry weight, major element concentration (in  $\text{mg}\cdot\text{g}^{-1}$ ) and Si isotope composition (in ‰) of the plants separated into shoot and root.**





Tomato		Plant ID	dry mass [g]	Ca mg/g	Fe mg/g	K mg/g	Mg mg/g	P mg/g	S mg/g	Si mg/g	δ30Si		δ30Si	
											‰ NBS28	2 s / *95 % CI	‰ nutrient solution	2 s / *95 % CI
Pot 3	Roots	19-5-3R-T1	0.03	8.7	1.53	65.4	4.6	6.1	5.7	7.41	-0.60	0.10	-0.39	0.10
		19-5-3R-T2	1.08	7.3	0.99	81.1	3.8	7.5	2.7	1.77	-0.03	0.04	0.17	0.04
		19-5-3R-T3	0.40	6.8	1.18	58.5	4.6	7.6	2.6	4.32	-0.46	0.03	-0.25	0.03
		19-5-3R-T4	0.44	6.8	2.48	72.5	3.4	9.1	2.8	3.80	-0.19	0.01	0.02	0.01
	Shoot	19-5-3S-T1	0.17	19.5	0.11	79.8	3.2	11.5	2.9	2.45	-0.30	0.09	-0.10	0.09
		19-5-3S-T2	6.18	24.9	0.13	60.2	3.1	7.9	4.6	1.21	-0.77	0.01	-0.56	0.01
		19-5-3S-T3	2.13	28.9	0.28	50.7	5.5	10.9	4.8	1.38	-0.42	0.09	-0.21	0.09
		19-5-3S-T4	3.33	21.5	0.15	70.1	3.9	8.3	4.6	1.23	-0.81	0.06	-0.60	0.06
Pot 6	Roots	19-5-6R-T1	0.45	6.0	1.53	58.7	4.4	10.0	3.1	1.90	0.07	0.10	0.28	0.10
		19-5-6R-T2	0.21	8.6	3.13	62.7	5.6	13.1	3.8	4.12	-0.47	0.10	-0.27	0.10
		19-5-6R-T3	0.45	6.4	2.63	68.7	3.9	12.2	2.3	1.79	0.22	0.10	0.43	0.10
		19-5-6R-T4	0.69	6.7	1.22	76.4	4.7	10.6	2.8	1.92	-0.15	0.07	0.06	0.07
	Shoot	19-5-6S-T1	2.62	14.8	0.14	53.9	4.6	8.0	4.6	0.89	-0.57	0.11	-0.37	0.11
		19-5-6S-T2	1.40	25.9	0.23	61.6	5.1	11.7	6.2	0.98	-0.36	0.14	-0.15	0.14
		19-5-6S-T3	2.52	24.3	0.16	62.6	4.8	11.7	5.1	1.63	-0.70	0.12	-0.49	0.12
		19-5-6S-T4	3.64	25.6	0.15	60.1	4.3	10.0	4.5	1.01	-0.67	0.11	-0.47	0.11
Pot 9	Roots	19-5-9R-T1	0.02	9.4	1.75	99.0	3.1	9.5	9.2	4.65	-0.35	0.07	-0.14	0.07
		19-5-9R-T2	0.05	6.8	1.99	78.2	5.5	15.2	3.9	3.10	-0.34	0.15	-0.14	0.15
		19-5-9R-T3	0.10	8.1	2.82	76.8	5.3	13.0	5.0	5.10	-0.14	0.04	0.07	0.04
		19-5-9R-T4	1.30	6.6	0.70	81.4	3.2	9.8	2.8	1.71	0.12	0.12	0.32	0.12
	Shoot	19-5-9S-T1	0.21	27.6	0.18	80.1	3.8	15.3	4.7	3.16	-0.33	0.12	-0.12	0.12
		19-5-9S-T2	0.44	20.2	0.27	63.9	4.8	9.9	5.0	0.95	-0.43	0.15	-0.23	0.15
		19-5-9S-T3	0.80	21.7	0.16	70.9	4.1	8.9	4.3	0.99	-0.61	0.05	-0.41	0.05
		19-5-9S-T4	7.41	24.3	0.11	60.9	2.9	7.1	3.6	0.78	-0.82	0.08	-0.61	0.08
Average	Roots	0.44	7.35	1.83	73.27	4.34	10.29	3.88	3.47	-0.19	0.16*	0.01	0.16*	
	Shoot	2.57	23.25	0.17	64.56	4.17	10.10	4.59	1.39	-0.57	0.12*	-0.36	0.12*	
Sum	Plants	36.09												

\* Uncertainty based on 95 % CI



## Methods

### Method S1 Preparation of the nutrient solution

30 The nutrient solution was prepared from technical graded salts and dissolved in 10 L of ultrapure water. Macro nutrients 1.23 g MgSO<sub>4</sub>·7H<sub>2</sub>O, 3.54 g Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, 0.33 g Ferric sodium EDTA, 3.6 g KNO<sub>3</sub>, 1.1 g KCl and 0.82 g KH<sub>2</sub>PO<sub>4</sub>. Micro nutrients: 0.55 mg Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 0.28 mg KJ, 0.28 mg KBr, 0.55 mg TiO<sub>2</sub>, 0.28 mg SnCl<sub>2</sub> 2H<sub>2</sub>O, 0.28 mg LiCl, 0.39 mg MnCl<sub>2</sub> 4H<sub>2</sub>O, 6.1 mg H<sub>3</sub>BO<sub>3</sub>, 0.55 mg ZnSO<sub>4</sub>, 0.55 mg CuSO<sub>4</sub> 5H<sub>2</sub>O, 0.55 mg NiSO<sub>4</sub> 6H<sub>2</sub>O, 0.55 mg Co(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O, 0.05 mg As<sub>2</sub>O<sub>3</sub>, 0.28 mg BaCl<sub>2</sub>, 0.05 mg Bi(NO<sub>3</sub>)<sub>3</sub>, 0.05 mg Rb<sub>2</sub>SO<sub>4</sub>, 0.28 mg K<sub>2</sub>CrO<sub>4</sub>, 0.05 mg KF, 0.05 mg PbCl<sub>2</sub>, 0.05 mg HgCl<sub>2</sub>, 0.28 mg 35 MoO<sub>3</sub>, 0.05 mg H<sub>2</sub>SeO<sub>4</sub>, 0.28 mg SrSO<sub>4</sub>, 0.05 mg H<sub>2</sub>WO<sub>4</sub>, 0.05 mg VCl<sub>2</sub>). Silicon: 2.03 g NaSiO<sub>4</sub>. pH was adjusted to 6.0 using HNO<sub>3</sub> (PA grade).

### Method S2 Plant germination and growth conditions

Plant seeds were germinated in in Petri dishes containing a nutrient solution of half the concentration than the solution used for growth experiments (Methods S1) and in the absence of NaSiO<sub>4</sub>. After cotyledons germinated, seeds and roots were 40 clamped in a foam block (3 cm high with a diameter of 2.5 cm) and each seedling (foam block) transferred to a PP vial (50 mL centrifuge tube) filled with half-concentrated nutrient solution without NaSiO<sub>4</sub>. Two weeks later, the foam blocks including young plants were transferred to the experimental containers, four plants per container, 3 replicated container per species. These containers were opaque plastic containers 25.5 cm high, 20.5 cm deep and 20.5 cm wide (with a wall thickness of 0.5 45 cm). In order to reduce evaporation and to prevent algae growth in the nutrient solution, the containers were closed with opaque lids which had holes for the plants (foam blocks). Germination and plant cultivation were performed in a growth chamber under controlled conditions. The temperature in the growth chamber during the day and night was maintained at 18 °C for 14 h and at 15 °C for 10 h, respectively, and the daylight intensity at the top of the container was adjusted to 350 μE m<sup>-2</sup> s<sup>-1</sup>) at the start of the experiment. The relative humidity was maintained at approximately 65 %. For comparability, the cultivation conditions for the three species were the same, knowingly they are not equally suited for all species. The relatively low 50 temperatures may have inhibited the growth of the more thermophilic tomato, while the conditions for mustard and summer wheat were close to their optimum. In order to supply the roots with oxygen, perforated PVC tubes were used to inject (approx. 6 L) room air into the nutrient solution twice a day for two hours each. The transpired water was replenished weekly with ultrapure water.

### 55 **Method S3 Dried plant and nutrient residue digestion and chromatographic purification of Si**

The crucibles containing the sample (dried down nutrient solution or charred plant material with approximately 400 mg NaOH) were placed in a high temperature furnace at 750 °C for 15 min. After cooling down the crucibles were cleaned externally with ultrapure water and placed in precleaned 50mL PP centrifuge tubes and covered with ultrapure water for 24 h. Thereafter, the crucibles were placed in an ultra-sonic bath for 30 min to facilitate the dissolution of the fusion cake. This solution #1 was  
60 decanted and collected in precleaned PP flask. The silver crucibles were then stored for ~3 h in a 0.03 M HCl solution and this solution #2 was combined with solution #1 in the PP flask. Using concentrated HCl the pH was adjusted to 1.5. If the concentration was expected to be above 60 µg g<sup>-1</sup> additional 0.03 M HCl solution was added. 1:10-fold dilution was analysed by ICP-OES to determining the Si content. Approximately 60 µg Si from are loaded onto precleaned and preconditioned columns using a cation exchange resin (1.5 mL, DOWEX 50WX8, Sigma-Aldrich) and eluted using 5 mL ultrapure water.  
65 The cation exchange resin is then regenerated using HCl and HNO<sub>3</sub>. The Si yield of the fusion procedure and the column chemistry was determined in a 1:10-fold dilution by ICP-OES.