

SUPPLEMENTARY INFORMATION

Determination of absolute isotope ratios of vanadium by internal standardisation

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Table S1. Isotope ratio data obtained in individual measurements of NIST SRM 3165 vanadium standard solution (Lot No. 992706) doped with iron standard IRMM-014 in this study, after correction for instrumental blank only. Each measurement consisted of 100 cycles, with each cycle being 8 seconds duration. Standard deviation represents 1- σ level. Values of the RF power of MC-ICP-MS at which the measurements were performed are also shown (see text for details).

Session 1									
	$^{51}\text{V}/^{50}\text{V}$	stdev	$^{56}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{56}\text{Fe}$	stdev	RF power, W
measurement 1	409.89	0.32	16.500	0.002	0.39027	0.00008	0.023653	0.000005	1150
measurement 2	409.82	0.29	16.502	0.002	0.39032	0.00007	0.023653	0.000004	1170
measurement 3	409.88	0.39	16.501	0.001	0.39031	0.00007	0.023654	0.000004	1190
measurement 4	410.08	0.33	16.498	0.003	0.39035	0.00007	0.023660	0.000006	1220
measurement 5	410.09	0.31	16.507	0.002	0.39057	0.00007	0.023661	0.000004	1240
measurement 6	410.19	0.45	16.509	0.002	0.39073	0.00007	0.023667	0.000004	1270
Session 2									
	$^{51}\text{V}/^{50}\text{V}$	stdev	$^{56}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{56}\text{Fe}$	stdev	RF power, W
measurement 1	410.33	0.20	16.492	0.005	0.39020	0.00016	0.023660	0.000004	1200
measurement 2	410.26	0.17	16.509	0.002	0.39056	0.00009	0.023658	0.000004	1250
measurement 3	410.27	0.21	16.510	0.002	0.39059	0.00009	0.023657	0.000004	1300
measurement 4	410.13	0.23	16.514	0.002	0.39075	0.00008	0.023662	0.000004	1350
Session 3									
	$^{51}\text{V}/^{50}\text{V}$	stdev	$^{56}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{56}\text{Fe}$	stdev	RF power, W
measurement 1	409.31	0.42	16.494	0.003	0.38999	0.00013	0.023644	0.000006	1080
measurement 2	408.05	0.67	16.497	0.002	0.39009	0.00014	0.023647	0.000008	960
measurement 3	409.11	0.67	16.507	0.002	0.39035	0.00011	0.023648	0.000007	980
measurement 4	409.44	0.66	16.528	0.002	0.39108	0.00008	0.023662	0.000005	1000

measurement 5	409.55	0.35	16.541	0.002	0.39161	0.00007	0.023674	0.000004	1020
measurement 6	409.72	0.54	16.537	0.002	0.39141	0.00009	0.023669	0.000005	1040
measurement 7	409.70	0.43	16.526	0.002	0.39100	0.00005	0.023659	0.000005	1060
measurement 8	408.72	0.45	16.452	0.002	0.38829	0.00012	0.023601	0.000007	1100
measurement 9	408.15	0.39	16.393	0.003	0.38609	0.00016	0.023551	0.000008	1120
measurement 10	407.58	0.92	16.348	0.006	0.38419	0.00032	0.023501	0.000014	1140
measurement 11	406.55	1.10	16.323	0.004	0.38324	0.00030	0.023478	0.000015	1160
measurement 12	406.55	1.37	16.317	0.005	0.38257	0.00029	0.023446	0.000014	1180
measurement 13	409.36	0.48	16.524	0.002	0.39067	0.00014	0.023643	0.000008	1200
measurement 14	409.44	0.41	16.513	0.003	0.39026	0.00009	0.023633	0.000006	1220
measurement 15	408.98	0.71	16.528	0.002	0.39100	0.00012	0.023656	0.000007	1240
measurement 16	409.32	0.32	16.523	0.002	0.39058	0.00014	0.023639	0.000007	1260
measurement 17	409.27	0.59	16.517	0.002	0.39021	0.00012	0.023625	0.000008	1280
measurement 18	408.94	0.47	16.535	0.003	0.39096	0.00010	0.023645	0.000008	1300
measurement 19	409.05	0.51	16.527	0.002	0.39056	0.00014	0.023632	0.000008	1320
Session 4									
	$^{51}\text{V}/^{50}\text{V}$	stdev	$^{56}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{56}\text{Fe}$	stdev	RF power, W
measurement 1	406.54	1.46	16.474	0.005	0.38929	0.00016	0.023631	0.000007	1100
measurement 2	407.04	1.44	16.479	0.002	0.38964	0.00010	0.023645	0.000007	1140
measurement 3	406.78	1.64	16.474	0.002	0.38952	0.00014	0.023644	0.000008	1080
measurement 4	408.93	0.63	16.492	0.002	0.39000	0.00009	0.023648	0.000006	1060
measurement 5	409.78	0.39	16.525	0.002	0.39118	0.00010	0.023672	0.000006	1040
measurement 6	409.79	0.45	16.506	0.003	0.39041	0.00015	0.023652	0.000007	1020
measurement 7	409.95	0.43	16.529	0.002	0.39123	0.00012	0.023669	0.000008	1000
measurement 8	410.23	0.46	16.526	0.002	0.39111	0.00012	0.023666	0.000006	980
measurement 9	410.10	0.31	16.540	0.002	0.39169	0.00008	0.023681	0.000005	960
measurement 10	410.13	0.48	16.538	0.003	0.39155	0.00011	0.023675	0.000005	940
measurement 11	410.32	0.56	16.529	0.002	0.39123	0.00011	0.023669	0.000006	920
measurement 12	410.45	0.38	16.550	0.003	0.39195	0.00010	0.023683	0.000005	900
measurement 13	410.28	0.35	16.545	0.002	0.39182	0.00011	0.023682	0.000008	880

measurement 14	410.50	0.41	16.545	0.003	0.39173	0.00016	0.023677	0.000007	870
Session 5									
	$^{51}\text{V}/^{50}\text{V}$	stdev	$^{56}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{56}\text{Fe}$	stdev	RF power, W
measurement 1	409.56	0.46	16.519	0.003	0.39083	0.00013	0.023659	0.000005	1100
measurement 2	409.69	0.45	16.521	0.002	0.39089	0.00008	0.023659	0.000004	1080
measurement 3	409.92	0.48	16.524	0.002	0.39096	0.00011	0.023661	0.000006	1060
measurement 4	410.02	0.38	16.521	0.002	0.39088	0.00007	0.023660	0.000004	1040
measurement 5	410.27	0.40	16.539	0.002	0.39143	0.00009	0.023668	0.000006	1020
measurement 6	410.14	0.55	16.542	0.003	0.39154	0.00011	0.023670	0.000005	1000
measurement 7	410.35	0.57	16.534	0.002	0.39133	0.00008	0.023669	0.000006	980
measurement 8	410.29	0.46	16.523	0.002	0.39091	0.00012	0.023659	0.000006	960
measurement 9	410.28	0.31	16.521	0.002	0.39086	0.00010	0.023658	0.000005	940
measurement 10	410.55	0.24	16.536	0.002	0.39137	0.00013	0.023667	0.000006	920
measurement 11	410.23	0.51	16.529	0.002	0.39116	0.00010	0.023665	0.000005	900
measurement 12	410.45	0.44	16.543	0.001	0.39164	0.00012	0.023675	0.000007	890
measurement 13	410.39	0.38	16.548	0.002	0.39183	0.00012	0.023679	0.000006	880
measurement 14	410.67	0.39	16.555	0.001	0.39207	0.00009	0.023683	0.000005	870
measurement 15	410.31	0.50	16.552	0.002	0.39195	0.00011	0.023681	0.000005	860
Session 6									
	$^{51}\text{V}/^{50}\text{V}$	stdev	$^{56}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{56}\text{Fe}$	stdev	RF power, W
measurement 1	405.62	0.19	16.451	0.003	0.38848	0.00011	0.023615	0.000004	1060
measurement 2	406.40	0.19	16.528	0.001	0.39126	0.00005	0.023673	0.000003	1040
measurement 3	406.43	0.17	16.527	0.001	0.39119	0.00004	0.023671	0.000002	1020
measurement 4	406.41	0.18	16.525	0.001	0.39112	0.00005	0.023668	0.000003	1000
measurement 5	406.49	0.19	16.531	0.002	0.39134	0.00005	0.023673	0.000003	980
measurement 6	406.63	0.21	16.531	0.002	0.39135	0.00005	0.023674	0.000004	960
measurement 7	406.59	0.20	16.528	0.001	0.39121	0.00008	0.023670	0.000004	940
measurement 8	406.72	0.18	16.531	0.002	0.39133	0.00007	0.023672	0.000003	920
measurement 9	406.78	0.13	16.538	0.001	0.39155	0.00007	0.023676	0.000004	900
measurement 10	406.89	0.19	16.546	0.001	0.39184	0.00005	0.023682	0.000003	890

measurement 11	406.80	0.12	16.546	0.001	0.39185	0.00006	0.023682	0.000003	880
Session 7									
	$^{51}\text{V}/^{50}\text{V}$	stdev	$^{56}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{56}\text{Fe}$	stdev	RF power, W
measurement 1	406.33	0.18	16.509	0.004	0.39067	0.00016	0.023663	0.000005	870
measurement 2	406.78	0.11	16.544	0.002	0.39183	0.00008	0.023684	0.000003	880
measurement 3	406.83	0.18	16.547	0.001	0.39190	0.00007	0.023684	0.000003	890
measurement 4	406.76	0.15	16.540	0.001	0.39164	0.00004	0.023679	0.000004	900
measurement 5	406.72	0.22	16.543	0.002	0.39173	0.00006	0.023680	0.000003	920
measurement 6	406.74	0.16	16.539	0.002	0.39160	0.00005	0.023677	0.000002	940
measurement 7	406.64	0.14	16.541	0.001	0.39167	0.00004	0.023679	0.000003	960
measurement 8	406.53	0.18	16.530	0.002	0.39123	0.00008	0.023669	0.000003	980
measurement 9	406.65	0.16	16.533	0.001	0.39142	0.00007	0.023674	0.000004	1000
measurement 10	406.55	0.21	16.534	0.001	0.39144	0.00005	0.023675	0.000003	1020
measurement 11	406.43	0.13	16.525	0.001	0.39112	0.00005	0.023668	0.000003	1040
measurement 12	406.44	0.30	16.533	0.002	0.39141	0.00006	0.023674	0.000004	1060
measurement 13	406.29	0.23	16.520	0.002	0.39092	0.00007	0.023664	0.000003	1080
measurement 14	406.32	0.18	16.527	0.002	0.39118	0.00008	0.023669	0.000003	1100
Session 8									
	$^{51}\text{V}/^{50}\text{V}$	stdev	$^{56}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{56}\text{Fe}$	stdev	RF power, W
measurement 1	409.17	0.20	16.550	0.002	0.39201	0.00008	0.023687	0.000004	870
measurement 2	409.04	0.16	16.553	0.001	0.39211	0.00008	0.023688	0.000005	880
measurement 3	409.08	0.13	16.544	0.001	0.39176	0.00007	0.023680	0.000003	890
measurement 4	409.03	0.18	16.548	0.001	0.39195	0.00007	0.023685	0.000004	900
measurement 5	409.01	0.24	16.546	0.002	0.39185	0.00005	0.023682	0.000002	920
measurement 6	408.84	0.17	16.533	0.001	0.39143	0.00007	0.023676	0.000004	960
measurement 7	408.75	0.09	16.527	0.001	0.39125	0.00007	0.023673	0.000004	1000
measurement 8	408.53	0.22	16.528	0.001	0.39118	0.00006	0.023668	0.000005	1060
measurement 9	408.66	0.20	16.536	0.001	0.39158	0.00004	0.023680	0.000003	1100
Session 9									
	$^{51}\text{V}/^{50}\text{V}$	stdev	$^{56}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{56}\text{Fe}$	stdev	RF power, W

measurement 1	408.59	0.29	16.535	0.002	0.39153	0.00006	0.023678	0.000004	1100
measurement 2	408.63	0.12	16.530	0.002	0.39126	0.00008	0.023670	0.000003	1080
measurement 3	408.72	0.22	16.527	0.001	0.39123	0.00005	0.023672	0.000005	1040
measurement 4	408.70	0.16	16.530	0.002	0.39129	0.00007	0.023672	0.000004	1000
measurement 5	408.68	0.21	16.526	0.002	0.39119	0.00010	0.023672	0.000004	960
measurement 6	408.88	0.24	16.540	0.003	0.39167	0.00011	0.023680	0.000004	920
measurement 7	409.26	0.18	16.550	0.001	0.39190	0.00008	0.023680	0.000004	900
measurement 8	409.45	0.21	16.553	0.002	0.39206	0.00009	0.023685	0.000004	890
measurement 9	409.19	0.20	16.533	0.001	0.39137	0.00004	0.023671	0.000003	880
measurement 10	409.32	0.20	16.556	0.001	0.39218	0.00005	0.023688	0.000004	870
Session 10									
	$^{51}\text{V}/^{50}\text{V}$	stdev	$^{56}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{56}\text{Fe}$	stdev	RF power, W
measurement 1	407.16	0.11	16.943	0.045	0.39410	0.00007	0.023261	0.000065	1150
measurement 2	407.12	0.07	16.626	0.003	0.39349	0.00002	0.023667	0.000003	1170
measurement 3	407.17	0.08	16.640	0.012	0.39347	0.00003	0.023646	0.000016	1200
measurement 4	407.11	0.06	16.637	0.001	0.39361	0.00005	0.023659	0.000003	1220
measurement 5	407.13	0.09	16.633	0.001	0.39370	0.00002	0.023670	0.000002	1250
Session 11									
	$^{51}\text{V}/^{50}\text{V}$	stdev	$^{56}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{56}\text{Fe}$	stdev	RF power, W
measurement 1	408.89	0.21	16.654	0.008	0.39502	0.00010	0.023719	0.000003	1120
measurement 2	408.69	0.20	16.678	0.003	0.39597	0.00006	0.023742	0.000002	1090
measurement 3	408.04	0.22	16.677	0.005	0.39690	0.00018	0.023798	0.000004	1050
measurement 4	409.26	0.15	16.666	0.008	0.39498	0.00010	0.023700	0.000006	1150
Session 12									
	$^{51}\text{V}/^{50}\text{V}$	stdev	$^{56}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{54}\text{Fe}$	stdev	$^{57}\text{Fe}/^{56}\text{Fe}$	stdev	RF power, W
measurement 1	409.61	0.13	16.653	0.002	0.39508	0.00010	0.023724	0.000004	1150
measurement 2	409.86	0.12	16.637	0.003	0.39460	0.00013	0.023718	0.000005	1170
measurement 3	409.73	0.12	16.639	0.003	0.39428	0.00002	0.023696	0.000008	1200
measurement 4	409.58	0.18	16.683	0.010	0.39537	0.00013	0.023699	0.000008	1230

Table S2. Isotope abundances of vanadium determined in previous studies and current IUPAC best measurement for vanadium isotopic composition and accepted standard atomic weight. Uncertainties in parentheses are expanded uncertainties.

<i>E</i>	<i>A</i>	Observed interval of isotope-abundance variation in natural materials (isotope-amount fraction, <i>x</i>)*	Best measurement of isotope abundances from a single terrestrial source (isotope-amount fraction, <i>x</i>)**	Standard atomic weight currently accepted by IUPAC, $A_r(V)$ ***
Vanadium	50	0.002487 – 0.002502	0.002497(6)	50.9415(1)
	51	0.997498 – 0.997513	0.997503(6)	

* For details see Meija et al. *Pure Appl. Chem.* 2016; 88(3): 293–306.

** For details see <https://ciaaw.org/best-measurements.htm> and Flesch et al. *Advanced Mass Spectrometry* III, pp. 571, Leiden, London (1966). In the work by Flesch et al. (1966), vanadium isotope ratios were determined by gas source mass spectrometry using vanadium oxytrifluoride, VOF₃, to introduce vanadium into a gas source. Dual collector mass spectrometer was used (Consolidate Electro Dynamics Corporation, Model 21-220, Pasadena, USA). Sample preparation and data treatment were detailed in this paper. The authors reported relative standard deviation of ⁵¹V/⁵⁰V isotope ratios of individual samples they measured as ranging from 0.02% to 0.10%.

*** For details see <https://ciaaw.org/atomic-weights.htm>, Prohaska et al., *Pure Appl. Chem.* 2022; 94(5), 573–600, and Holden et al., *Pure Appl. Chem.* 1979, 51, 405–433.

Additional details of the measurement procedure in this study

- Iron was selected as the calibrant for vanadium isotope ratios because Fe and V are the closest elements by mass that do not have isobaric interferences from each other. Both elements have to be measured in high mass resolution mode. Also, both iron and vanadium are transition metals from the same row of the Periodic Table.
- Self-aspiration through the stable introduction system consisting of tandem quartz spray chamber (cyclone + Scott double pass) was used for sample introduction into the plasma. Concentration of vanadium at 2 mg/l was found most comfortable for the measurements, giving stable signal intensity and avoiding the risk of nebuliser clogging. A desolvating nebuliser was not used in the measurements as not sufficiently tested way of sample introduction, to avoid potential vanadium isotope fractionation during heating of sample aerosol during desolvation (temperature range of 110°C-140°C). It is known that vanadium pentoxide, V₂O₅, the predominant chemical form of the element in aerated acidic solution, exhibits vapor pressure that increases non-linearly from being negligible at room temperature to the melting point of the compound at 690°C. Previous studies also pointed out that the main pathway of V₂O₅ volatilisation at temperatures higher than 100°C is by the formation of volatile hydroxyl compounds with water, and not by an increase of temperature only (*J. Phys. Chem.*, 1968, 72(9):3293-3296, <https://doi.org/10.1021/j100855a035>; *E3S Web of Conferences*, 2021, 268, 01005, <https://doi.org/10.1051/e3sconf/202126801005>).

- In line with practice of the regression model, measurements involved a series of single measurements with incremental changes in the RF power (see section Mass spectrometry in the main text). Different patterns of the RF power changes from the maximum sensitivity setting at ~1100W were used as detailed in the Table S1. This also allowed testing ruggedness of the measurement method.
- Combined standard uncertainties for the measurement results were obtained in accordance with the JCGM “Guide to the Expression of Uncertainty in Measurement” (https://www.bipm.org/documents/20126/2071204/JCGM_100_2008_E.pdf). Combined standard uncertainties of $n(^{51}\text{V})/n(^{50}\text{V})$ values were calculated by propagating standard uncertainties of input variables with the aid of Kragten's numerical method of differentiation using a spreadsheet template made in the MS Excel program. The calculation template with explanatory notes can be found in the Electronic Supplementary Information our previous work (*J. Anal. At. Spectrom.*, 2020, 35, 2723; <https://doi.org/10.1039/D0JA00145G>).