Supporting Information

A study on a natural pyrite sample as a potential reference material for simultaneous measurement of sulfur and iron isotopes using fs-LA-MC-ICP-MSs

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Table S1 Summary of the instrument parameters

Faraday Cup Configurations for Fe isotopes on Neptune Plus and S isotopes on Neptune								
L4	L3	L2	L1	C	H1	H2	H3	H4
	^{53}Cr		^{54}Fe	^{56}Fe	^{57}Fe		^{58}Fe	^{60}Ni
			^{32}S	^{33}S	^{34}S			

Neptune / Neptune Plus MC-ICP-MS		*NWRFemto Laser Ablation System*	
RF power	1200 W	Wavelength	257 nm
Plasma gas	16 L/min (Ar)	Pulse duration	70 ~ 90 fs
Auxiliary gas	0.9 L/min (Ar)	Energy density	Approximate 0.1 J/cm^2 at energy output of 5% for Fe and S isotope ratio analysis
Sample depth	About -0.6 ~ -1.2 mm	Beam size	25 ~ 30 μm and 40 μm for Fe and S isotope ratio analysis, respectively, and 60 μm for simultaneous measurements of Fe-S isotopes
Interface cones	Sample cone: standard cone Skimmer cone: X cone		
Make up gas	About 0.80 ~ 1.3 L/min (Ar)	Pulse repeat rate	3 ~ 8 Hz and 10 ~ 15 Hz for Fe and S isotope ratio analysis, respectively and 20 Hz for simultaneous measurements of Fe-S isotopes
Resolution	High resolution mode (m/Δm ~8000-9000)		
Integration	A single analysis consists of a block of 60 cycles with an integration time of 0.262 s per cycle for Fe and S isotope ratio analysis	Carrier gas (He)	About 700 mL/min for Fe and S isotope ratio analysis and about 900 mL/min for simultaneous measurements of Fe-S isotopes

Table S2 Element concentrations (wt%) of IGGPy-1 by EPMA

Spot No.	Grain No.	Element concentration (wt%)								
		Fe	S	Co	Ni	Cu	Zn	As	Pb	Total
1	IGGPy G01	46.2	52.1	1.47	0.03	-	0.03	-	0.09	99.9
2	IGGPy G02	46.0	51.7	1.46	-	-	0.03	-	0.06	99.3
3	IGGPy G03	46.3	52.0	1.47	0.03	-	-	-	0.10	99.9
4	IGGPy G04	46.1	51.9	1.48	-	-	-	-	0.09	99.6
5	IGGPy G05	46.2	52.2	1.48	-	-	-	-	0.07	99.9
6	IGGPy G06	46.2	52.3	1.45	-	0.03	-	0.05	0.07	100.1
7	IGGPy G07	46.3	52.6	1.48	-	-	-	0.03	-	100.4
8	IGGPy G08	46.2	51.9	1.48	-	-	-	-	0.09	99.8
9	IGGPy G09	46.5	52.1	1.49	-	-	-	0.03	0.07	100.2
10	IGGPy G10	46.4	52.0	1.48	-	-	-	-	0.11	100.0
11	IGGPy G11	46.3	52.0	1.47	0.02	-	-	-	0.07	99.9
12	IGGPy G12	46.3	51.5	1.47	-	-	-	-	0.06	99.3
	average	46.3	52.0	1.47					0.07	99.9
	1S	0.1	0.3	0.01					0.02	0.3
13	IGGPy G13	46.0	51.7	1.49	-	-	-	0.03	0.10	99.3
14		46.0	51.7	1.48	0.02	-	-	-	0.03	99.3
15		46.2	52.0	1.47	-	-	-	-	0.10	99.7
16		46.1	51.7	1.49	0.02	-	-	-	0.09	99.4
17		46.2	51.8	1.45	-	-	0.03	-	0.11	99.6
18		46.0	51.9	1.49	-	-	-	0.02	-	99.5
19		46.1	51.9	1.47	0.02	-	-	-	0.08	99.5
20		46.2	51.7	1.46	-	-	-	-	0.13	99.6
21		46.1	51.8	1.45	0.03	-	-	0.02	0.12	99.5
22		46.1	51.6	1.48	-	-	-	0.02	0.08	99.3
23		46.3	51.9	1.48	-	-	-	-	0.01	99.7
24		45.9	51.5	1.47	-	-	-	0.03	0.09	99.1
25		46.3	51.8	1.48	-	-	-	0.02	0.07	99.7
26		46.1	51.6	1.44	-	0.03	-	0.02	0.08	99.3
27		46.1	51.5	1.46	-	-	-	0.03	0.08	99.2
28		46.2	51.5	1.47	-	-	-	0.03	0.07	99.3
29		46.0	51.6	1.46	0.04	-	-	-	0.10	99.2
30		46.3	51.7	1.47	-	-	-	-	0.07	99.6
31		46.2	51.6	1.44	-	-	-	0.02	0.07	99.4
32		46.0	51.9	1.44	0.03	0.02	-	-	0.04	99.5
33		46.1	51.8	1.47	-	0.03	-	0.03	0.10	99.5
34		46.1	51.9	1.47	0.02	-	-	0.03	-	99.6
35		46.2	51.7	1.46	-	-	-	0.05	0.07	99.5
36		46.0	51.8	1.47	-	-	0.03	0.02	0.06	99.5
37		46.2	51.8	1.47	-	-	-	0.02	-	99.5

Table S2 continued

38		46.2	52.0	1.48	0.02	-	-	-	-	99.8
39		46.1	52.0	1.48	-	-	-	-	0.05	99.7
40		46.1	52.0	1.46	-	-	-	-	0.07	99.7
41		45.9	51.9	1.45	-	-	-	-	0.11	99.4
42		46.2	51.8	1.48	-	-	-	0.02	0.06	99.6
43		46.1	51.9	1.46	-	-	-	-	0.08	99.5
44		46.2	52.0	1.48	0.02	-	0.03	-	0.05	99.8
45		46.2	52.1	1.47	-	-	-	-	0.05	99.9
46		46.0	52.0	1.48	0.02	-	-	0.03	0.07	99.6
47		46.2	51.9	1.49	-	0.04	-	0.02	0.09	99.8
48		46.1	51.7	1.48	0.02	0.02	-	0.03	-	99.4
49		46.1	52.0	1.45	-	-	-	0.04	0.07	99.7
50		46.0	51.8	1.46	-	-	-	-	0.10	99.3
51		46.3	52.2	1.45	0.03	-	-	0.02	0.09	100.0
52		46.1	51.9	1.46	-	-	0.05	0.02	-	99.6
53		46.0	51.8	1.45	-	-	-	-	0.06	99.3
54		46.3	52.0	1.46	-	0.02	-	-	0.05	99.8
55		46.0	51.9	1.46	0.02	-	-	0.02	0.10	99.5
56		46.5	52.1	1.48	-	-	-	0.03	0.10	100.2
57		46.0	52.1	1.45	-	-	-	0.02	0.04	99.6
58		46.2	52.0	1.46	0.03	0.02	-	-	0.04	99.8
59		46.2	52.0	1.47	0.02	-	-	0.03	0.08	99.8
60		46.1	52.2	1.46	-	0.02	-	-	0.09	99.9
61		46.2	52.0	1.46	-	-	-	0.02	0.05	99.7
62		46.2	52.3	1.46	-	-	-	-	0.04	100.0
	average	46.1	51.9	1.47					0.07	99.6
	1S	0.1	0.2	0.01					0.03	0.2
63	IGGPy G14	46.3	52.0	1.47	-	-	-	-	0.09	99.8
64		46.2	51.9	1.45	-	-	-	-	0.11	99.7
65		46.3	52.0	1.46	-	-	-	-	0.14	99.9
66		46.1	51.9	1.48	-	-	-	-	0.07	99.6
67		46.3	52.2	1.48	-	-	-	0.03	0.05	100.1
68		46.0	52.1	1.45	-	-	-	-	0.08	99.7
69		46.2	51.9	1.47	-	-	-	-	0.05	99.5
70		46.2	52.0	1.46	0.02	-	-	-	0.09	99.7
71		46.0	52.1	1.46	-	-	-	0.02	0.05	99.7
72		46.3	52.3	1.45	-	-	-	-	0.06	100.1
73		46.2	52.1	1.47	-	-	-	-	-	99.8
74		46.3	52.1	1.46	-	-	-	0.02	0.05	99.9
75		46.5	52.1	1.47	-	0.03	-	0.03	0.06	100.2
76		46.2	52.0	1.45	-	-	-	-	0.06	99.7

Table S2 continued

77		46.1	52.1	1.47	0.02	-	-	0.02	0.04	99.8
78		46.2	51.9	1.46	-	-	-	0.02	0.09	99.7
79		46.4	52.3	1.47	-	-	-	0.03	0.05	100.2
80		45.9	52.0	1.47	-	-	-	-	0.07	99.5
81		46.3	52.1	1.48	0.02	-	-	0.04	0.07	100.0
82		46.3	52.1	1.46	-	-	0.05	-	0.08	100.0
83		46.1	52.0	1.47	-	-	-	-	0.05	99.7
84		46.1	52.1	1.48	-	-	-	0.02	0.05	99.8
85		46.2	52.2	1.46	-	-	-	-	-	99.8
86		46.2	52.0	1.48	-	-	-	0.02	0.05	99.8
87		46.0	51.9	1.46	-	-	-	0.05	0.07	99.5
88		46.4	52.0	1.48	0.02	-	-	0.03	0.12	100.0
89		46.4	52.3	1.48	-	-	-	0.02	0.05	100.2
90		46.2	52.3	1.48	-	-	-	-	0.07	100.1
91		46.1	52.0	1.46	0.02	-	0.03	-	0.07	99.8
92		46.3	52.0	1.47	-	-	-	-	0.10	99.9
93		46.1	52.2	1.47	-	0.02	-	0.04	0.06	99.9
94		46.3	52.2	1.46	-	-	-	0.02	0.05	100.0
95		46.2	52.1	1.46	-	-	-	0.03	0.07	99.9
96		46.2	52.1	1.44	-	-	-	-	0.09	99.8
97		46.3	52.1	1.47	0.02	-	-	-	0.09	100.0
98		45.9	52.1	1.46	-	-	-	-	0.06	99.6
99		46.0	52.1	1.47	-	0.02	-	-	0.05	99.7
100		46.1	52.1	1.46	-	-	-	-	-	99.7
101		46.0	52.2	1.45	0.02	-	-	0.02	0.05	99.8
102		46.2	52.2	1.46	0.02	-	-	0.02	0.05	99.9
	average	46.2	52.1	1.47					0.06	99.8
	1S	0.1	0.1	0.01					0.03	0.2

'-' indicates 'Not detected'.

Table S3 Position effects within a TV2 cell on iron and sulfur isotope composition measurement

Sample No.	$\delta^{34}S_1$ to 5†	$\delta^{56}Fe_1$ to 5†	$\delta^{34}S_2$ to 5†	$\delta^{56}Fe_2$ to 5†	$\delta^{34}S_3$ to 5†	$\delta^{56}Fe_3$ to 5†	$\delta^{34}S_4$ to 5†	$\delta^{56}Fe_4$ to 5†	$\delta^{34}S_6$ to 5†	$\delta^{56}Fe_6$ to 5†
1	0.12	0.24	0.00	0.01	-0.09	0.06	0.14	0.19	-0.02	0.05
2	-0.03	0.25	0.07	-0.07	-0.12	0.14	0.11	0.08	-0.08	-0.01
3	0.01	0.23	-0.01	0.02	0.00	0.09	0.05	0.22	0.06	-0.02
4	-0.04	0.17	0.10	0.09	-0.03	0.06	0.03	0.24	0.12	-0.05
5	-0.01	0.11	0.08	0.00	0.02	0.05	0.01	0.19	0.14	0.04
6	0.04	0.17	-0.01	-0.03	-0.06	0.05	0.02	0.32	0.11	0.06
7	-0.02	0.28	-0.06	0.10	-0.09	0.04	0.07	0.17	-0.03	0.04
8	-0.04	0.29	0.07	0.04	-0.09	0.08	0.06	0.09	0.02	-0.03
9	-0.03	0.16	0.02	-0.07	-0.11	0.03	0.11	0.22	-0.07	-0.10
10	-0.13	0.16	-0.10	-0.08	-0.17	0.00	0.01	0.09	0.06	-0.02
11	-0.19	0.19	0.01	-0.01	-0.21	0.04	0.10	0.17	0.11	-0.03
12	-0.14	0.16	0.11	-0.05	-0.06	0.17	0.03	0.24	0.07	0.12
13	-0.05	0.06	-0.03	-0.13	-0.04	0.10	0.00	0.10	-0.01	0.10
14	-0.13	0.17	-0.02	-0.10	-0.05	0.09	0.05	0.23	-0.08	0.00
15	-0.23	0.14	-0.01	-0.05	-0.05	0.16	0.07	0.22	0.17	-0.10
16	-0.24	0.07	0.06	-0.08	-0.08	0.17	0.00	0.25	0.00	-0.07
17	-0.22	0.16	0.04	0.00	-0.14	0.16	-0.01	0.14	0.01	-0.04
18	-0.27	0.16	0.02	0.00	-0.09	0.17	-0.02	0.20	0.07	0.08
average	-0.09	0.18	0.02	-0.02	-0.08	0.09	0.05	0.19	0.04	0.00
2S	0.22	0.13	0.11	0.12	0.11	0.11	0.09	0.13	0.15	0.13
*t	3.34	11.31	1.44	1.58	6.00	6.62	4.20	11.58	1.92	0.12
‡$t_{critical}$	2.11									

†: $\delta^{34}S_{x\ to\ 5}$ and $\delta^{56}Fe_{x\ to\ 5}$ (x = 1, 2, 3, 4 and 6, respectively) were the deviations per mil of sulfur and iron isotope composition measured for IGGPy-1 pyrite on the position x relative to that on position 5, respectively.

*: t values calculated using the formula: $t = \frac{|\bar{x} - \mu|}{S}\sqrt{n}$. Here, $\bar{x}$ is the mean of the deviation in iron or sulfur isotopic compositions measured in position 1, 2, 3, 4 and 6, respectively, calibrated against that measured in position 5; S is the standard deviation; n is the number of the values. μ represents the population of the deviations in iron or sulfur isotopic composition measured in position 1, 2, 3, 4 and 6, respectively. if the measurements on iron or sulfur isotopic composition were not influenced by position effects and only random error occurs, then μ = 0.

‡: $t_{critical}$ values calculated using T.INV.2T function (two-tailed hypothesis) in Excel at the significance level of 0.05 and the freedom degree of 17.

Table S4 Matrix effects between IGGPo-1 and IGGPy-1 on Fe and S isotope measurement

Applied technique	fs-LA-MC-ICP-MS	fs-LA-MC-ICP-MS
Analytical No.	$\delta^{34}S_{VCDT}$	$\delta^{56}Fe_{IRMM-014}$
1	0.43	-2.31
2	0.46	-2.29
3	0.66	-2.28
4	0.64	-2.27
5	0.58	-2.24
6	0.56	-2.18
7	0.50	-2.22
8	0.39	-2.20
9	0.61	-2.15
10	0.58	-2.20
11	0.51	-2.14
12	0.65	-2.25
13	0.52	-2.20
14	0.34	-2.15
15	0.48	-2.29
16	0.54	-2.25
17	0.55	-2.17
18	0.53	-2.12
19	0.40	-2.08
20	0.34	-2.20
average	0.51	-2.21
2S	0.20	0.12
†t	47.14	56.69
‡$t_{critical}$	2.09	2.09
Applied technique	EA-IRMS	SN-MC-ICPMS
average	-0.52	-1.43
2S	0.30	0.06
N	2	3

†: t values calculated using the formula: $t = \frac{|\bar{x} - \mu|}{S}\sqrt{n}$. Here, $\bar{x}$ is the mean of the deviation values in iron (or sulfur) isotopic composition measured of IGGPo-1 pyrrhotite calibrated against IGGPy-1 pyrite; S is the standard deviation; n is the number of the values. μ represents the population of deviations in iron (or sulfur) isotopic composition, if the isotopic measurements were not influenced by matrix effects and only random error occurs, then μ should be near to iron (or sulfur) isotopic reference value obtained by SN-MC-ICP-MS (or EA-IRMS).

‡: $t_{critical}$ values calculated using T.INV.2T function (two-tailed hypothesis) in Excel at the significance level of 0.05 and the freedom degree of 19.

Table S5 The results of simultaneous measurement of Fe and S isotopic compositions

Sample	Analysis#	$\delta^{56}Fe_{IRRM014}$	$\delta^{57}Fe_{IRRM014}$	$\delta^{34}S_{VCDT}$	Description
12744a	**Test 1**	Ablated material proportion of 5:1 used for measuring S and Fe isotopes			
	1	0.38	0.59	2.85	
	2	0.47	0.69	2.71	Signal intensities of ^{56}Fe and ^{32}S
	3	0.43	0.60	2.78	were about 10 V and 24 V,
	4	0.52	0.65	2.76	respectively.
	5	0.37	0.58	2.75	
	6	0.38	0.49	2.69	
	7	0.29	0.39	2.61	
	8	0.28	0.34	2.67	
	9	0.34	0.33	2.81	
	10	0.35	0.51	2.77	
	11	0.32	0.60	2.73	
	Average	0.37	0.52	2.74	
	2S	0.15	0.25	0.13	
	Test 2	Ablated material proportion of 3:1 used for measuring S and Fe isotopes			
	12	0.38	0.49	2.74	
	13	0.40	0.45	2.81	Signal intensities of ^{56}Fe and ^{32}S
	14	0.45	0.51	2.52	were about 18 V and 20 V,
	15	0.41	0.68	2.69	respectively.
	16	0.34	0.55	2.76	
	17	0.41	0.64	2.72	
	18	0.39	0.52	2.83	
	19	0.36	0.58	2.68	
	20	0.38	0.48	2.70	
	21	0.38	0.68	2.74	
	22	0.40	0.46	2.76	
	average	0.39	0.55	2.72	
	2S	0.06	0.17	0.17	
	Test 3	Ablated material proportion of 3:2 used for measuring S and Fe isotopes			
	23	0.57	0.76	2.85	
	24	0.49	0.79	2.77	Signal intensities of ^{56}Fe and ^{32}S
	25	0.49	0.69	2.89	were about 32 V and 18 V,
	26	0.44	0.65	2.83	respectively.
	27	0.45	0.72	2.85	
	28	0.40	0.59	2.92	
	29	0.46	0.68	3.02	
	30	0.47	0.69	2.89	
	31	0.43	0.66	2.89	
	32	0.50	0.85	2.85	
	33	0.53	0.85	2.88	
	average	0.47	0.72	2.88	
	2S	0.10	0.17	0.12	

Table S5 continued

H5a		Ablated material proportion of 3:1 used for measuring S and Fe isotopes			
	1	0.50	0.53	17.40	
	2	0.38	0.60	17.54	Signal intensities of ^{56}Fe and ^{32}S were about 18 V and 20 V, respectively.
	3	0.41	0.68	17.15	
	4	0.49	0.59	17.55	
	5	0.57	0.69	17.38	
	6	0.42	0.64	17.33	
	7	0.34	0.55	17.54	
	8	0.48	0.63	17.38	
	9	0.40	0.54	17.34	
	10	0.40	0.53	17.41	
	11	0.42	0.59	17.41	
	average	0.44	0.60	17.40	
	2S	0.13	0.12	0.23	
66030a		Ablated material proportion of 3:1 used for measuring S and Fe isotopes			
	1	0.66	1.02	-2.47	
	2	0.61	0.92	-2.43	Signal intensities of ^{56}Fe and ^{32}S were about 18 V and 20 V, respectively.
	3	0.66	0.96	-2.44	
	4	0.58	0.80	-2.45	
	5	0.68	1.00	-2.52	
	6	0.81	1.04	-2.43	
	7	0.72	0.98	-2.42	
	8	0.61	0.94	-2.42	
	9	0.61	0.80	-2.35	
	10	0.65	0.91	-2.34	
	average	0.66	0.94	-2.43	
	2S	0.13	0.17	0.11	

Fe and S isotopic compositions measured by SN-MC-ICP-MS and SIMS, respectively

Sample	$\delta^{56}Fe_{IRRM014}$	$\delta^{57}Fe_{IRRM014}$	N	$\delta^{34}S_{VCDT}$	N
12744a	0.38 ± 0.06	0.56 ± 0.07	4	2.87 ± 0.27	6
H5a	0.46 ± 0.04	0.67 ± 0.11	4	17.35 ± 0.45	8
66030a	0.64 ± 0.02	0.98 ± 0.11	4	-2.60 ± 0.18	7