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Supporting Online Material for

Early Archaean Microorganisms Preferred Elemental Sulfur, Not Sulfate

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Correction: In table S3 of the originally posted supporting online material, the data in column δ34S were inverted with that of column δ33S.

Materials and Methods (SOM)

All samples analysed here come from the drill cores of the Pilbara Drilling Project collected in August 2004 as part of a scientific collaboration between the Institut de Physique du Globe de Paris and the Geological Survey of Western Australia. Before isotopic analysis, petrographical investigations of all samples were performed on polished thin sections. Special care has been taken in selecting the microscopic sulfide arrays in barite crystals (Fig. 2C and 3C). Detailed examination of a large number of petrographical sections revealed that the vast majority of these arrays have been pervasively infiltrated by hydrothermal fluids as attested by the occurrence of microcrystalline silica, carbonates, micas and recrystallized sulfides and barites lining the individual arrays. Well-preserved microscopic sulfides occur as tiny rounded grains, a few µm to a few tens of µm in size, located in large barite crystals that are free of deformation/recrystallization features. Several well-preserved zones were selected in drill cores PDP2B (samples 84-6 and 89-3) and PDP2C (96-6; Tables S1, S2, Fig. S1). Representative sulfide Ion Mass Spectrometry (IMS) spot analyses were subsequently investigated for their chemical composition and trace element distribution (Table S3, Fig. S1). Most sulfides analyzed are typical pyrite (FeS_2) with trace amounts of transition metals (Ni, Co, Zn). Sulfides from the bedded carbonates can have up to 5.1 wt% As and 1.4 wt% Ni. Well-preserved microscopic sulfides in barite have 0.3 to 3.5 wt% Ni and can contain local inclusions of pentlandite $(Fe,Ni)_9S_8$ and Millerite (NiS; Fig. S1).

Sulfur isotope analysis

Analyses of $\Delta^{33}S$ and $\delta^{34}S$ were made in situ directly on polished thin sections by secondary ion mass spectrometry (SIMS) using the Caméca ims 1270 ion microprobe in multicollector mode at the CRPG, Nancy. This approach has the advantage to resolve isotope anomalies on a grain scale, and therefore provides an independent means of tracing the origin of the sulfur species involved in the formation of the different units. Six bulk analyses were also performed on selected samples (Table S2, Fig. S1) to corroborate our SIMS measurements at the ESSIC Center, University of Maryland, College Park. Sulfur isotopic ratios are given by conventional delta notation in units per mil (‰) relative to CDT, with:

$\delta^{34}S = [(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{CDT}-1]*1000$,

$\delta^{33}S = [(^{33}S/^{32}S)_{sample}/(^{33}S/^{32}S)_{CDT}-1]*1000$,

$\Delta^{33}S = 1000^{*} [(1 + \delta^{33}S/1000) - (1 + \delta^{34}S/1000)^{0.515} -1]$, which is used as a measure of mass-independent fractionation (MIF) relative to the mass-dependent fractionation line.

Ion Microprobe in situ analysis

Sulfur isotopes were analysed as S^- ions produced by a bombardment by a Cs^+ primary beam (8-10 nA intensity) of ~20µm diameter. The entrance slit was 60 µm and the exit slit of the multicollector was 250 µm (n°2). This setting resulted in a mass resolving power (M/ΔM) of 5000. Under these conditions, the interferences of the different sulfur isotopes are completely resolved. S isotopes were measured in multicollection mode using three off-axis Faraday cups (L'2, C and H1). The gains of

Faraday cups L'2, C and H1 were calibrated at the beginning of the analytical session using the Caméca built-in amplifier calibration routine. Typical ion intensities of 5×10^9 counts per second (cps) were obtained on $^{32}S^-$, so that an internal 1σ error better than ± 0.1 ‰ was reached after a few minutes of counting. The stability of the instrument was monitored by multiple measurements of the standards CAR111 and Maine (pyrite, FeS_2, courtesy of Douglas Rumble), Enonkoski (pyrrhotite, FeS), Ka8 (pyrite and pentlandite $(Fe,Ni)_9S_8$), and Miller (Millerite, NiS) (courtesy of C.J. Stanley, Natural History Museum of London). The average external reproducibility, as estimated from replicate measurements of sulfur standards, was generally better than ± 0.5 ‰ for $\delta^{34}S$ and ± 0.1 ‰ for $\Delta^{33}S$. Uncertainties on $\delta^{34}S_{sample}$ and $\Delta^{33}S_{sample}$ are generally better than ± 1.2‰ and ± 0.5‰ (2σ), respectively and were calculated using

$$(2\sigma_{\Delta 33S})_{sample} = [(2\sigma_{\delta 34S})^2_{sample} + (2\sigma_{\delta 33S})^2_{sample}) + (2\sigma_{\Delta 33S})^2_{std}]^{1/2}, \text{ with}$$

$$(2\sigma_{\Delta 33S})_{std} = [(2\sigma_{\delta 34S})^2_{std} + (2\sigma_{\delta 33S})^2_{std})]^{1/2}.$$

For one sample, of macroscopic sulfide laminates (F95.0), $\delta^{34}S$ error (2σ) was not better than ± 3.7‰ due to the poor quality of the standard used (CAR111), which showed altered zones as revealed by scanning electron imaging performed after SIMS analysis. Uncertainties between $\delta^{33}S$ and $\delta^{34}S$ are mass-dependently correlated, resulting in $\Delta^{33}S$ uncertainties that are generally smaller than for $\delta^{33}S$.

We decided to analyze pentlandite and millerite to evaluate the effect of Ni content on sulfur isotope fractionations as both minerals have been found as tiny inclusions in some microscopic sulfides. Results show that the occurrence of pentlandite or millerite has a negligible effect on sulfur isotope fractionations. Calculations performed using a pure NiS end-member (millerite) yielded more negative $\delta^{34}S$ values of about 1 ‰ than using pyrite or pendlantite. This implies that the range of $\delta^{34}S$ values reported here for microscopic sulfides are minimum values. Additionally, the contribution of sulfur emerging from barite has been evaluated for each spot analysis knowing the proportion of barite ionised from backscattered electron images and the yield of sulfur extracted from barite compared to that of sulfides. Calculations indicated that the contribution of barite to the overall isotope signal is less than 1% and therefore must be considered negligible.

Sulfur isotope bulk analysis

Sulfur was extracted from 0.5 g of powdered samples using the sequential extraction method developed by Hsieh & Yang *(S1)*. Samples were placed in a container within in a sealed tub filled with nitrogen gas and then sulfur was extracted by reaction with 15 mL of a solution of 5 N HCl and acidic ~0.3M Cr(II). The evolved sulfide was trapped on an alkaline Zinc trapping solution for 48 hours. The ZnS thus formed was washed and then converted to Ag_2S which was then washed and dried. Sulfate minerals were transferred to a boiling flask that was assembled as a part of an apparatus similar that consisted of a nitrogen purged boiling flask, a water-cooled condenser, a bubbler filled with milli-Q water, and a sulfide trap filled with an acidic Zb acetate trapping solution. All ground glass joints are sealed with PTFE sleeves. Addition of 25 mL of a reduction solution *(S2)* containing preboiled and nitrogen-purged HI, H_2PO_3, and 12N HCl to the boiling flask was followed by heating to near the boiling point. Three hours of heating and purging with nitrogen, approximately 5 mL of Milli-Q water and 5 drops of 0.3 M silver nitrate solution were added to the trapping solution to convert ZnS to Ag_2S. The trapping solutions were left in a dark cabinet overnight, and then silver sulfide was filtered, washed and then dried in a 90 ºC drying oven. The silver sulfide precipitates were weighed, wrapped in Al-foil boats and placed into separate Ni-reaction vessels for fluorination by reaction with ~10 times excess purified F_2-gas at 250 ºC. Product SF_6 was frozen out of the remaining F_2-gas which was passivated by reaction with hot KBr. The product SF_6 was then purified by cryogenic separation at -120 ˚C and gas chromatography using a 1/8 inch diameter composite column consisting of a 6 foot 5A molecular sieve followed by an 8 foot Haysep Q column. The SF_6 peak was trapped as it exited the column and frozen into the sample inlet of a dual inlet ThermoFinnigan MAT 253 where m/z = 127, 128, 129, and 131 were monitored. Reproducibility of these measurements is estimated on the basis of long-term measurements of IAEA reference materials and are generally better than 0.2, 0.01 and 0.2‰ for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$. The $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$ values are normalized to measurements of CDT and the values for the tank gas and this normalization are presented in Ono et al. *(S3)*.

SEM and EPMA Analysis

Sulfide compositions were examined on each IMS spot analysis with backscattered electron (BSE) imaging supplemented by qualitative energy dispersive (EDS) analysis using the ZEISS Microscope Supra 55VP at the Université Paris 6. Accelerating voltage was 15 keV, beam current was 20 nA and diaphragm 120. Quantitative chemical analyses and semi-quantitative X-ray maps of sulfides were performed with a Cameca SX100 electron microprobe at CAMPARIS, Université Paris 6. Synthetic and natural mineral standards of pyrite, NiO, ZnS, Barite, Co and AsGa were used. Accelerating voltage was 15 keV, beam current was 40 nA, nominal spot size was ~3 µm, and count times were ~10 s/pt. Count times for X-ray maps was 100ms/pixel.

Figures and legends (SOM)

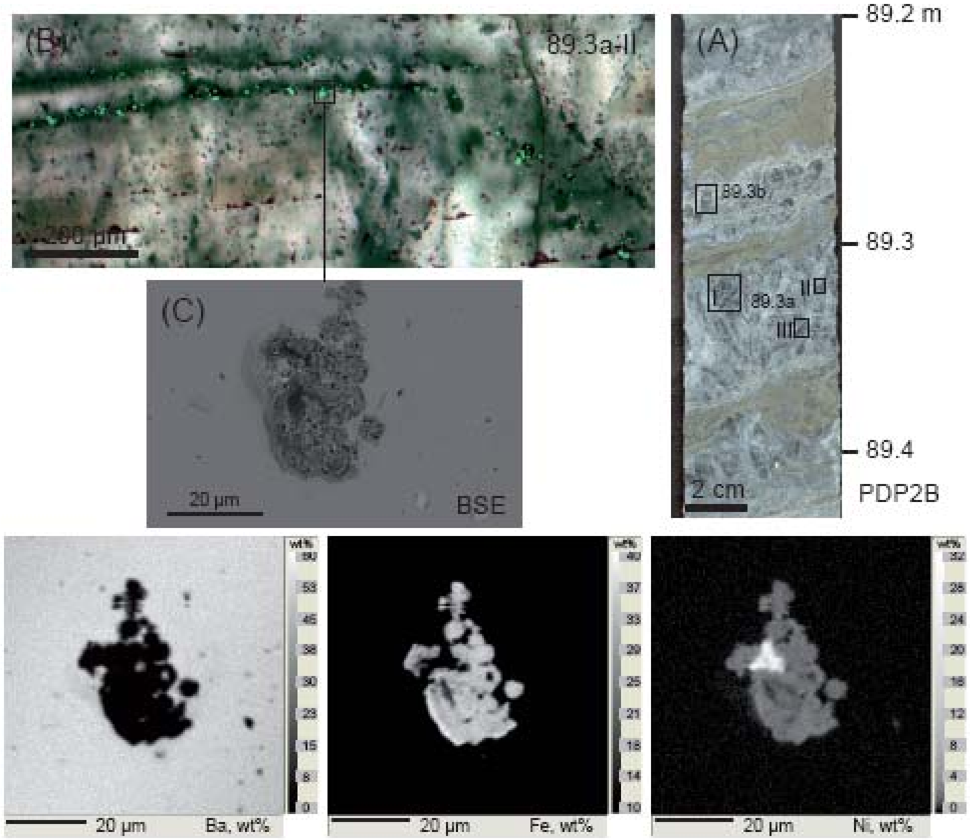

Fig. S1. Textural and compositional characteristics of microscopic sulfides in barite. **(A)** Drill core sample 89.3 (PDP2B) showing barite crystal fans (light grey) alternating with macroscopic sulfide laminates. **(B)** Microscopic sulfides lining barite crystallographic faces (barite grain 89.3a-II). **(C)** Backscattered electron (BSE) imaging and semi-quantitative compositional X-ray maps of Ba, Fe and Ni of a microscopic Ni-bearing pyrite grain containing a µm-scale pentlandite $(Fe,Ni)_9S_8$ inclusion., which was previously analyzed by Ion Mass Spectrometry (IMS). Elemental concentrations (Wt%) are shown on the right handside of each X-ray map.

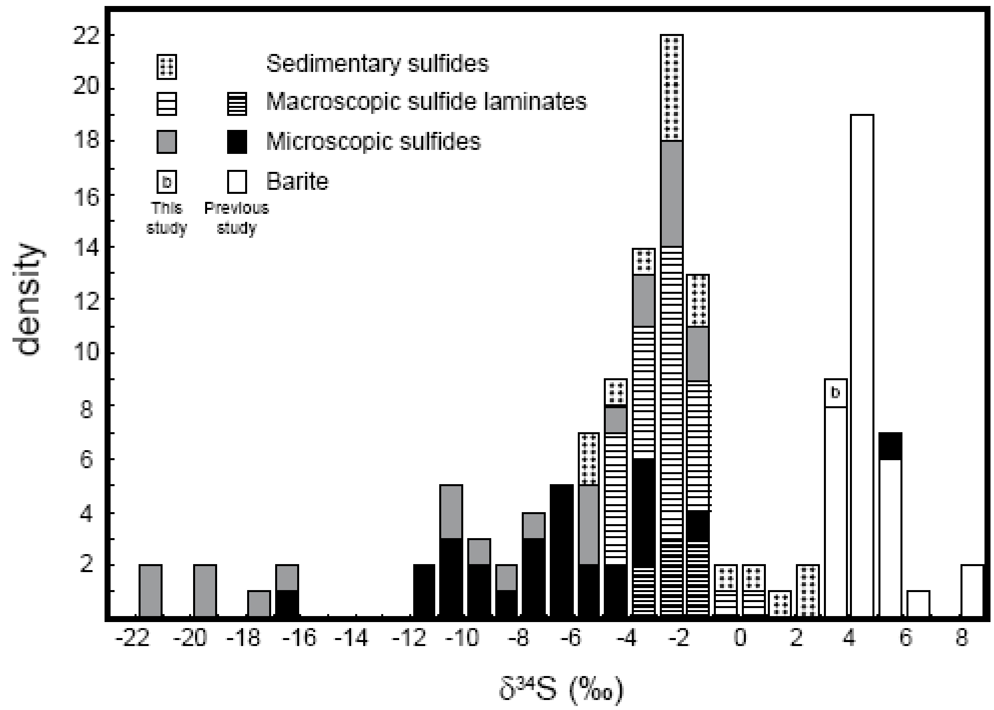

Fig S2. Mass-dependent isotopic composition ($\delta^{34}S$) of sulfur species from the Chert-Barite deposit at North Pole. Previous data from *(1, 14, 24).*

Tables and legends (SOM)

Table S1: Elemental composition of sulfides from North Pole Chert-Barite Deposit

Sample	Rock type (drill core #)	S (wt%)	Fe (wt%)	Ni (wt%)	Co (wt%)	Cu (wt%)	Zn (wt%)	As (wt%)	Total (wt%)	Mineral
92-6b-I	Bedded carbornate (PDP2C)	53.48	46.67	0.02	0.08	0	0.02	1	101.22	pyrite
92-6b-I	Bedded carbornate (2C)	51.52	45.83	0.01	-0.02	0	0	5.13	102.48	pyrite
94-6a-III	Bedded carbornate (2C)	53.18	45.31	1.39	0.24	0	0.01	0.57	100.71	pyrite
94-8-I	Volc. Sandstone (2C)	53.88	46.49	0.18	0.2	0	0.02	0.29	101.06	pyrite
95-35c	Macro-sulfide laminate (2C)	52.89	46.12	0.14	0.06	0	0.02	0.14	99.38	pyrite
95-35c	Macro-sulfide laminate (2C)	53.02	46.29	0.22	0.14	0	0.01	0.04	99.72	pyrite
89-3a-I	Inclusion in Microsulfide (2B)	35.02	33.25	28.99	0.74	0	0.02	0.16	98.19	pentlandite*
89-3a-I	Inclusion in Microsulfide (2B)	33.27	32.02	29.69	0.81	0	0.01	0.18	95.98	pentlandite*
89-3a-I	Microscopic sulfide (2B)	52.1	41.55	2.32	1.04	0	0.02	0.21	97.24	pyrite*
89-3a-I	Microscopic sulfide (2B)	53.48	45.73	0.32	0.66	0	0.02	0.05	100.22	pyrite
89-3a-II	Microscopic sulfide (2B)	51.13	46.05	3.48	0.93	0	0.01	0.13	101.71	pyrite
89-3b-4a	Microscopic sulfide (2B)	52.59	44.05	1.26	0.29	0	0.01	0.11	98.32	pyrite*

** Analysis with total lower than 100 (Wt%) were performed in cavities formed by the Cs+ ion beam of the ion microprobe, which likely affected X-ray detection*

Table S2: Ion probe sulfur isotope compositions of North Pole sulfides and standards

date	Sample name- analysis # (Drill Core #)	mineral	δ34S (‰)	± 2σ (‰)	δ33S (‰)	± 2σ (‰)	Δ33S (‰)	± 2σ (‰)
Standards:								
April-05	car111-16	Pyrite	17.11	1.08	8.79	0.51	-0.02	0.31
April-05	car111-17	Pyrite	16.35	1.08	8.45	0.53	0.03	0.33
June-06	car111-26	Pyrite	17.49	2.45	9.05	1.13	0.05	0.17
June-06	car111-27	Pyrite	16.71	2.45	8.45	1.12	-0.15	0.16
June-06	car111-28	Pyrite	15.62	2.45	8	1.12	-0.04	0.15
June-06	car111-37	Pyrite	18.36	2.45	9.34	1.12	-0.11	0.16
June-06	car111-38	Pyrite	15.49	2.45	8.25	1.13	0.28	0.2
June-06	car111-53	Pyrite	18.83	3.75	9.12	1.54	-0.53	0.27
June-06	car111-54	Pyrite	15.43	3.75	8.14	1.55	0.22	0.3
April-05	enon-18	Pyrrothite	0.86	0.16	0.53	0.29	0.09	0.33
April-05	enon-19	Pyrrothite	0.95	0.18	0.4	0.34	-0.09	0.38
June-06	enon-3	Pyrrothite	0.49	0.78	0.3	0.52	0.05	0.27
June-06	enon-4	Pyrrothite	0.46	0.78	0.17	0.53	-0.07	0.29
June-06	enon-21	Pyrrothite	1.19	0.78	0.72	0.54	0.11	0.31
June-06	enon-22	Pyrrothite	1.21	0.78	0.57	0.54	-0.05	0.31
June-06	enon-23	Pyrrothite	1.15	0.78	0.56	0.54	-0.03	0.31
June-06	enon-31	Pyrrothite	0.77	0.51	0.43	0.19	0.03	0.14
June-06	enon-32	Pyrrothite	1.11	0.51	0.56	0.2	-0.01	0.15
June-06	enon-33	Pyrrothite	1.12	0.51	0.49	0.19	-0.09	0.14
June-06	enon-36	Pyrrothite	0.61	0.51	0.36	0.21	0.04	0.17
June-06	enon-43	Pyrrothite	0.94	0.12	0.54	0.25	0.05	0.21
June-06	enon-44	Pyrrothite	0.96	0.12	0.47	0.3	-0.03	0.27
June-06	enon-50	Pyrrothite	0.49	0.73	0.18	0.79	-0.1	0.27
June-06	enon-51	Pyrrothite	1.08	0.72	0.71	0.78	0.13	0.23
February07	Enon-8	Pyrrothite	1.07	0.5	0.84	0.59	0.29	0.69
February07	Enon-8bis	Pyrrothite	1.22	0.5	0.71	0.58	0.09	0.69
February07	Enon-9	Pyrrothite	1.2	0.5	0.92	0.59	0.31	0.69
February07	Enon-16	Pyrrothite	1	0.49	0.33	0.58	-0.18	0.69
February07	Enon-17	Pyrrothite	0.6	0.5	0.25	0.58	-0.06	0.69
February07	Enon-18	Pyrrothite	0.83	0.49	0.26	0.59	-0.17	0.69

February07	Enon-19	Pyrrothite	0.7	0.5	0.18	0.59	-0.18	0.69
February07	Enon-20	Pyrrothite	0.93	0.5	0.43	0.58	-0.05	0.68
February07	Enon-21	Pyrrothite	0.57	0.5	0.26	0.58	-0.03	0.69
February07	Enon-34	Pyrrothite	0.54	0.49	0.37	0.36	0.1	0.42
February07	Enon-35	Pyrrothite	0.82	0.48	0.54	0.38	0.13	0.43
February07	Enon-36	Pyrrothite	0.57	0.49	0.34	0.38	0.05	0.43
February07	Enon-37	Pyrrothite	0.85	0.49	0.4	0.37	-0.03	0.43
February07	Enon-38	Pyrrothite	0.89	0.48	0.44	0.36	-0.01	0.42
February07	Enon-39	Pyrrothite	0.94	0.47	0.4	0.36	-0.08	0.42
February07	Enon-40	Pyrrothite	1	0.48	0.38	0.38	-0.13	0.43
February07	Enon-78	Pyrrothite	1.26	0.47	0.86	0.38	0.22	0.43
February07	Enon-81	Pyrrothite	0.06	1.18	-0.14	0.79	-0.16	1
February07	Enon-82	Pyrrothite	0.39	1.18	0.04	0.78	-0.16	0.99
February07	Enon-83	Pyrrothite	0.57	1.18	0.19	0.78	-0.1	0.99
February07	Enon-84	Pyrrothite	0.69	1.18	0.29	0.77	-0.06	0.98
February07	Enon-85	Pyrrothite	0.49	1.18	0.26	0.78	0.02	0.99
February07	Enon-86	Pyrrothite	0.61	1.18	0.41	0.79	0.1	1
February07	Enon-87	Pyrrothite	0.67	1.18	0.43	0.79	0.09	1
February07	Enon-100	Pyrrothite	1.55	1.18	0.86	0.77	0.07	0.99
February07	Enon-101	Pyrrothite	1.47	1.18	0.92	0.78	0.17	0.99
February07	Enon-102	Pyrrothite	1.8	1.18	0.93	0.78	0.01	0.99
February07	Enon-103	Pyrrothite	1.59	1.18	0.89	0.79	0.08	1
February07	Enon-200	Pyrrothite	1.64	0.78	1.19	0.76	0.34	0.94
February07	Enon-201	Pyrrothite	0.56	0.78	0.39	0.75	0.1	0.93
February07	Enon-202	Pyrrothite	1.11	0.78	0.81	0.75	0.23	0.94
February07	Enon-203	Pyrrothite	1.17	0.78	0.42	0.75	-0.19	0.93
February07	Enon-208	Pyrrothite	0.35	0.77	-0.03	0.74	-0.21	0.93
February07	Enon-209	Pyrrothite	0.72	0.77	0.34	0.74	-0.04	0.93
February07	Enon-210	Pyrrothite	0.86	0.77	0.07	0.75	-0.38	0.93
February07	Enon-218	Pyrrothite	0.96	0.77	0.53	0.75	0.03	0.93
February07	Enon-219	Pyrrothite	0.74	0.77	0.49	0.76	0.1	0.94
June-06	Maine-1	Pyrite	-19.8	0.69	-10.09	0.39	0.11	0.25
June-06	Maine-2	Pyrite	-19.53	0.69	-9.82	0.36	0.24	0.19
June-06	Maine-5	Pyrite	-19.12	0.69	-9.88	0.37	-0.03	0.21
June-06	Maine-20	Pyrite	-19.44	0.69	-10.18	0.37	-0.17	0.21
June-06	Maine-24	Pyrite	-19.03	0.69	-9.84	0.37	-0.04	0.21
June-06	Maine-41	Pyrite	-18.56	1.22	-9.43	0.83	0.13	0.17
June-06	Maine-42	Pyrite	-19.1	1.21	-9.87	0.83	-0.03	0.17
June-06	Maine-55	Pyrite	-18.9	0.69	-9.84	0.36	-0.11	0.19
February07	Maine-4	Pyrite	-20.29	1.23	-9.96	0.27	0.49	0.7

February07	Maine-5	Pyrite	-19.86	1.23	-9.9	0.31	0.33	0.74
February07	Maine-6	Pyrite	-19.06	1.23	-9.74	0.27	0.08	0.7
February07	Maine-7	Pyrite	-19.48	1.23	-9.99	0.27	0.04	0.7
February07	Maine-22	Pyrite	-18.85	1.23	-10.12	0.25	-0.41	0.68
February07	Maine-23	Pyrite	-18.54	1.23	-9.92	0.26	-0.37	0.69
February07	Maine-24	Pyrite	-19.01	1.23	-9.99	0.26	-0.2	0.69
February07	Maine-31	Pyrite	-19.41	0.23	-10	0.16	0.02	0.17
February07	Maine-32	Pyrite	-19.29	0.22	-9.89	0.15	0.06	0.16
February07	Maine-33	Pyrite	-19.2	0.22	-9.94	0.14	-0.03	0.15
February07	Maine-96	Pyrite	-19.45	0.53	-10.03	0.47	0	0.52
February07	Maine-97	Pyrite	-19.45	0.53	-10.1	0.46	-0.07	0.52
February07	Maine-99	Pyrite	-19	0.52	-9.68	0.47	0.12	0.53
February07	Maine-211	Pyrite	-19.28	0.65	-10.09	0.32	-0.16	0.42
February07	Maine-212	Pyrite	-18.99	0.65	-9.79	0.33	-0.01	0.44
February07	Maine-213	Pyrite	-19.63	0.65	-9.95	0.33	0.16	0.44
February07	KA8-10	Pentlandite	1.74	0.81	1.06	0.58	0.16	0.74
February07	KA8-11	Pentlandite	1.98	0.81	1.08	0.58	0.06	0.74
February07	KA8-12	Pentlandite	2.32	0.81	0.98	0.58	-0.22	0.74
February07	KA8-13	Pentlandite	2.21	0.81	0.96	0.58	-0.18	0.74
February07	KA8-14	Pentlandite	2.81	0.82	1.63	0.6	0.18	0.76
February07	KA8-43	Pentlandite	2.34	0.58	1.15	0.63	-0.05	0.73
February07	KA8-45	Pentlandite	2.27	0.59	1.24	0.64	0.08	0.74
February07	KA8-46	Pentlandite	1.79	0.59	0.72	0.63	-0.2	0.74
February07	KA8-77	Pentlandite	2.43	0.58	1.45	0.63	0.2	0.73
February07	KA8-88	Pentlandite	0.97	0.2	0.54	0.21	0.1	0.09
February07	KA8-89	Pentlandite	0.92	0.2	0.45	0.19	0.1	-0.04
February07	KA8-90	Pentlandite	0.81	0.22	0.41	0.21	0.11	-0.01
February07	Ka8-204	Pentlandite	2.17	0.23	1.08	0.25	-0.04	0.26
February07	Ka8-205	Pentlandite	2.25	0.2	1.2	0.26	0.04	0.27
February07	Miller-49	Millerite	2.65	0.84	1.26	0.59	-0.1	0.74
February07	Miller-50	Millerite	3.18	0.83	1.67	0.58	0.04	0.73
February07	Miller-51	Millerite	2.95	0.83	1.3	0.58	-0.22	0.73
February07	Miller-52	Millerite	2.7	0.83	1.25	0.59	-0.14	0.74
February07	Miller-53	Millerite	2.65	0.83	1.19	0.58	-0.17	0.73
February07	Miller-55	Millerite	2.78	0.83	1.45	0.58	0.02	0.73
February07	Miller-64	Millerite	2.19	0.83	1.36	0.59	0.24	0.75
February07	Miller-69	Millerite	3.63	0.83	2.08	0.58	0.21	0.73
February07	Miller-76	Millerite	2.59	0.84	1.51	0.59	0.18	0.74
February07	Miller-91	Millerite	3.25	1.14	1.66	0.84	-0.01	1.15

February07	Miller-92	Millerite	2.63	1.16	0.91	0.84	-0.44	1.15
February07	Miller-93	Millerite	1.94	1.16	1.15	0.85	0.16	1.16
February07	Miller-94	Millerite	3.33	1.14	1.91	0.85	0.2	1.16
February07	Miller-95	Millerite	2.88	1.15	1.6	0.84	0.12	1.15
February07	Miller-206	Millerite	2.79	0.39	1.5	0.26	0.06	0.3
February07	Miller-207	Millerite	2.84	0.37	1.4	0.31	-0.06	0.35

North pole Sulfides:		**Sulfide in:**						
April-05	92-6b-I-2 (PDP 2C)	Bedded carbonate	-2.38	1.08	-0.51	0.54	0.71	0.34
April-05	92-6b-I-3 (2C)	Bedded carbonate	-2.45	1.08	-0.57	0.53	0.69	0.33
April-05	92-6b-I-4 (2C)	Bedded carbonate	-2.79	1.08	-0.55	0.5	0.88	0.28
April-05	92-6b-I-5 (2C)	Bedded carbonate	-2.99	1.08	-0.83	0.51	0.71	0.29
February07	92-6b-79 (2C)	Bedded carbonate	3.48	0.23	2.25	0.18	0.45	0.15
February07	92-6b-80 (2C)	Bedded carbonate	2.67	0.22	2.15	0.18	0.77	0.15
April-05	94.6a-III-1 (2C)	Bedded carbonate	1.55	1.08	1.63	0.5	0.83	0.28
April-05	94.6a-III-2 (2C)	Bedded carbonate	-0.94	1.08	1.32	0.5	1.8	0.28
April-05	94.6a-III-3 (2C)	Bedded carbonate	1.08	1.08	1.65	0.5	1.09	0.28
April-05	94.6a-III-4 (2C)	Bedded carbonate	0.89	1.08	-0.05	0.5	-0.51	0.28
April-05	94.6a-III-5 (2C)	Bedded carbonate	-1.57	1.08	0.39	0.53	1.19	0.33
April-05	94-8-I-1 (2C)	Volc. sandstone	-5.04	1.08	-1.61	0.51	0.98	0.29
April-05	94-8-I-2 (2C)	Volc. sandstone	-5.39	1.08	-1.14	0.5	1.63	0.28
April-05	94-8-I-3 (2C)	Volc. sandstone	-3.12	1.08	-0.34	0.51	1.26	0.29
April-05	94-8-I-4 (2C)	Volc. sandstone	-4.13	1.08	-0.43	0.51	1.69	0.3
April-05	94-8-I-5 (2C)	Volc. sandstone	-1.74	1.08	0.86	0.51	1.75	0.31
June-06	95-0a-39 (2C)	Macro.sulfide lam.	-2.16	3.75	0.33	1.55	1.41	0.28
June-06	95-0a-40 (2C)	Macro.sulfide lam.	-2.39	3.75	-0.05	1.55	1.14	0.32
June-06	95-0a-41 (2C)	Macro.sulfide lam.	-1.47	3.75	0.13	1.54	0.85	0.25
June-06	95-0a-42 (2C)	Macro.sulfide lam.	-1.82	3.75	-0.18	1.54	0.72	0.25
June-06	95-0a-43 (2C)	Macro.sulfide lam.	0.79	3.75	1.67	1.55	1.24	0.3
June-06	95-0a-44 (2C)	Macro.sulfide lam.	-0.83	3.75	1.67	1.54	2.07	0.23
June-06	95-0a-45 (2C)	Macro.sulfide lam.	-4.06	3.75	-2.38	1.54	-0.33	0.23
June-06	95-0a-46 (2C)	Macro.sulfide lam.	-3.2	3.75	-2.18	1.54	-0.57	0.25
June-06	95-0a-47 (2C)	Macro.sulfide lam.	-3.3	3.75	-2.18	1.54	-0.52	0.27
June-06	95-0a-48 (2C)	Macro.sulfide lam.	-1.78	3.75	-1.26	1.55	-0.38	0.29
June-06	95-0a-49 (2C)	Macro.sulfide lam.	-2.78	3.75	-2.54	1.55	-1.14	0.31
June-06	95-35c-12 (2C)	Macro.sulfide lam.	-4.66	0.69	-2.36	0.38	0.04	0.23
June-06	95-35c-13 (2C)	Macro.sulfide lam.	-1.74	0.69	-1.11	0.38	-0.22	0.23
June-06	95-35c-14 (2C)	Macro.sulfide lam.	-4.55	0.69	-1.96	0.38	0.38	0.23
June-06	95-35c-25 (2C)	Macro.sulfide lam.	-2.3	1.21	-0.91	0.83	0.27	0.19
June-06	95-35c-26 (2C)	Macro.sulfide lam.	-4.26	1.22	-1.76	0.82	0.43	0.17

June-06	95-35c-27 (2C)	Macro.sulfide lam.	-2.84	1.21	-0.86	0.83	0.6	0.21
June-06	95-35c-28 (2C)	Macro.sulfide lam.	-3.1	1.21	-1.49	0.83	0.1	0.21
June-06	95-35c-29 (2C)	Macro.sulfide lam.	-2.65	1.21	-1.32	0.82	0.04	0.15
June-06	95-35c-30 (2C)	Macro.sulfide lam.	-1.73	1.22	-0.35	0.84	0.54	0.25
June-06	95-35c-30bis (2C)	Macro.sulfide lam.	-2.09	1.22	-0.45	0.84	0.62	0.25
June-06	95-35c-31 (2C)	Macro.sulfide lam.	-2.8	1.21	-0.71	0.83	0.73	0.19
June-06	95-35c-32 (2C)	Macro.sulfide lam.	-2.08	1.21	-0.58	0.83	0.49	0.19
June-06	95-35c-33 (2C)	Macro.sulfide lam.	-2.19	1.21	-0.61	0.84	0.52	0.23
June-06	95-35c-34 (2C)	Macro.sulfide lam.	-3.22	1.22	0.44	0.88	2.1	0.35
June-06	95-35c-35 (2C)	Macro.sulfide lam.	-3.64	1.21	-1.09	0.84	0.78	0.25
June-06	95-35c-36 (2C)	Macro.sulfide lam.	-4.79	1.22	-2.67	0.84	-0.2	0.23
June-06	95-35c-37 (2C)	Macro.sulfide lam.	-2.88	1.21	-1.85	0.83	-0.37	0.21
April-05	89-3a-I-1 (2B)	Microscopic sulfide	-19.11	1.08	-10.36	0.51	-0.53	0.31
June-06	84-6-V-35 (2C)	Microscopic sulfide	-1.76	2.45	-0.47	1.12	0.43	0.14
June-06	84-6-V-36 (2C)	Microscopic sulfide	-3.08	2.45	-1.09	1.12	0.49	0.13
June-06	96-6aP-Ib-6 (2C)	Microscopic sulfide	-2.61	0.69	0.24	0.4	1.58	0.27
June-06	96-6aP-Ib-7 (2C)	Microscopic sulfide	-3.05	0.69	0.17	0.44	1.74	0.33
June-06	96-6aP-Ib-8 (2C)	Microscopic sulfide	-5.3	0.7	0.83	0.5	3.56	0.41
June-06	96-6aP-Ib-9 (2C)	Microscopic sulfide	-2.34	0.69	0.03	0.42	1.23	0.29
June-06	89-3b-4a-10 (2B)	Microscopic sulfide	-2.08	0.69	-0.17	0.42	0.9	0.29
June-06	89-3b-4a-11 (2B)	Microscopic sulfide	-2.83	0.69	0	0.4	1.46	0.27
June-06	89-3a-III-15 (2B)	Microscopic sulfide	-9.4	0.69	-1.46	0.57	3.38	0.48
June-06	89-3a-III-16 (2B)	Microscopic sulfide	-10.84	0.7	-4.78	0.5	0.8	0.41
June-06	89-3a-III-17 (2B)	Microscopic sulfide	-10.11	0.69	-1.84	0.55	3.37	0.47
February07	89-3a-I-56 (2B)	Microscopic sulfide	-19.18	0.29	-9.73	0.25	0.15	0.26
February07	89-3a-I-57 (2B)	Microscopic sulfide	-22.64	0.33	-8.79	0.23	2.87	0.26
February07	89-3a-I-58 (2B)	Microscopic sulfide	-22.36	0.38	-7.8	0.36	3.72	0.39
February07	89-3a-I-59 (2B)	Microscopic sulfide	-8.53	0.43	-0.39	0.41	4	0.46
February07	89-3a-I-60 (2B)	Microscopic sulfide	-16.02	0.4	-2.16	0.4	6.09	0.43
February07	89-3a-I-61 (2B)	Microscopic sulfide	-5.18	0.26	0.11	0.4	2.78	0.4
February07	89-3a-I-62 (2B)	Microscopic sulfide	-5.62	0.23	-2.49	0.26	0.4	0.26
February07	89-3a-II-74 (2B)	Microscopic sulfide	-7.86	0.24	0.98	0.18	5.03	0.15
February07	89-3a-II-75 (2B)	Microscopic sulfide	-17.49	0.28	-4.56	0.28	4.45	0.28

Table S3: Bulk sulfur isotope compositions of selected North Pole sulfides and sulfate

Sample	Rock type	mineral	δ34S (‰)	δ33S (‰)	Δ33S (‰)
GIS 93-5	Bedded carbonate	Sulfide	1.84	1.17	0.22
GIS 94-6 a	Bedded carbonate	Sulfide	0.9	0.39	-0.08
GIS 95-0	Macro. sulfide laminate	Sulfide	-1.3	-0.88	-0.21
GIS 96-6	Microscopic sulfide	Sulfide	-1.89	-1.26	-0.28
GIS 96-7	Microscopic sulfide	Sulfide	-4.77	-2.79	-0.33
GIS 96-7	Barite	Sulfate	3.29	0.49	-1.2

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