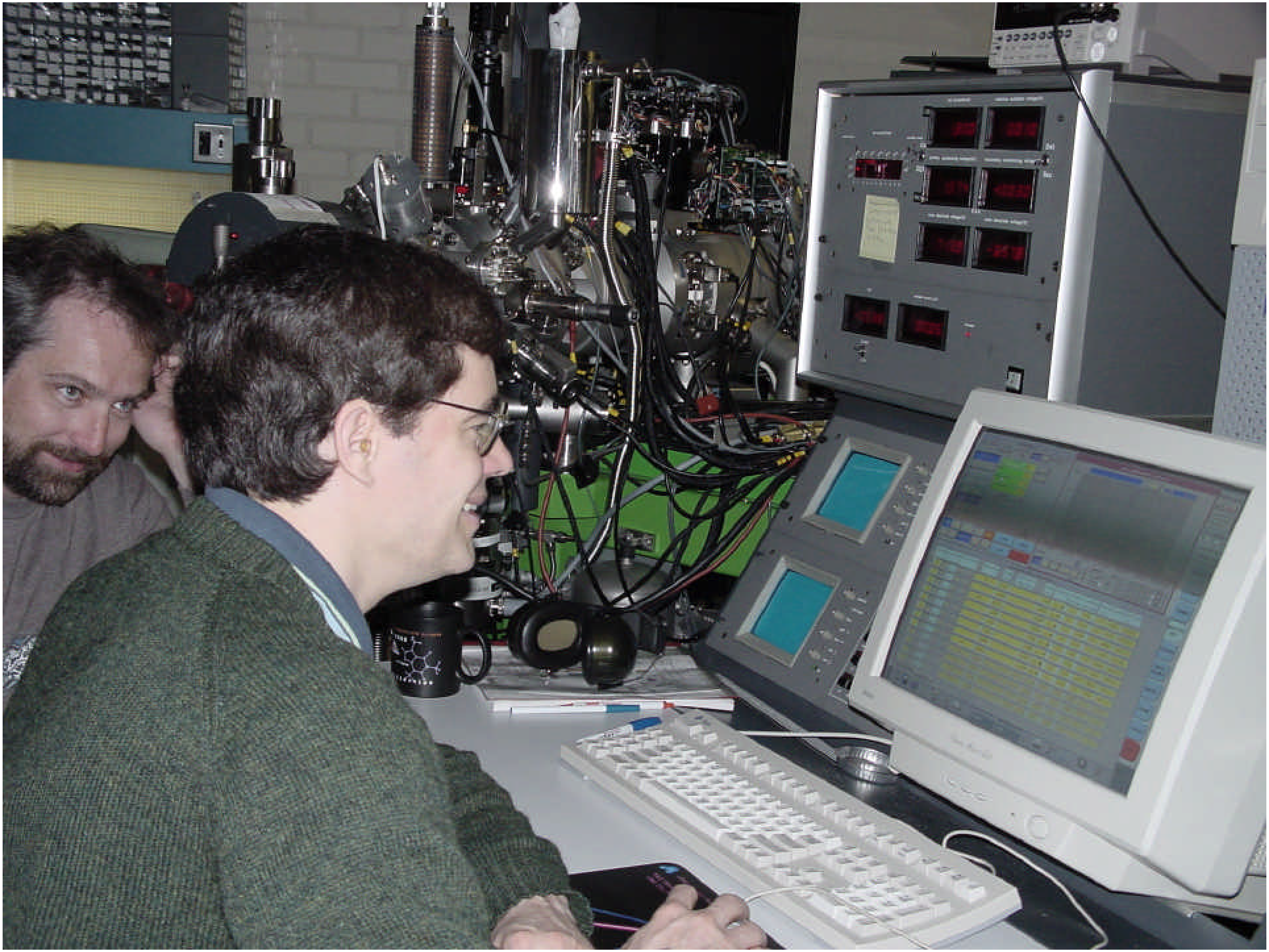
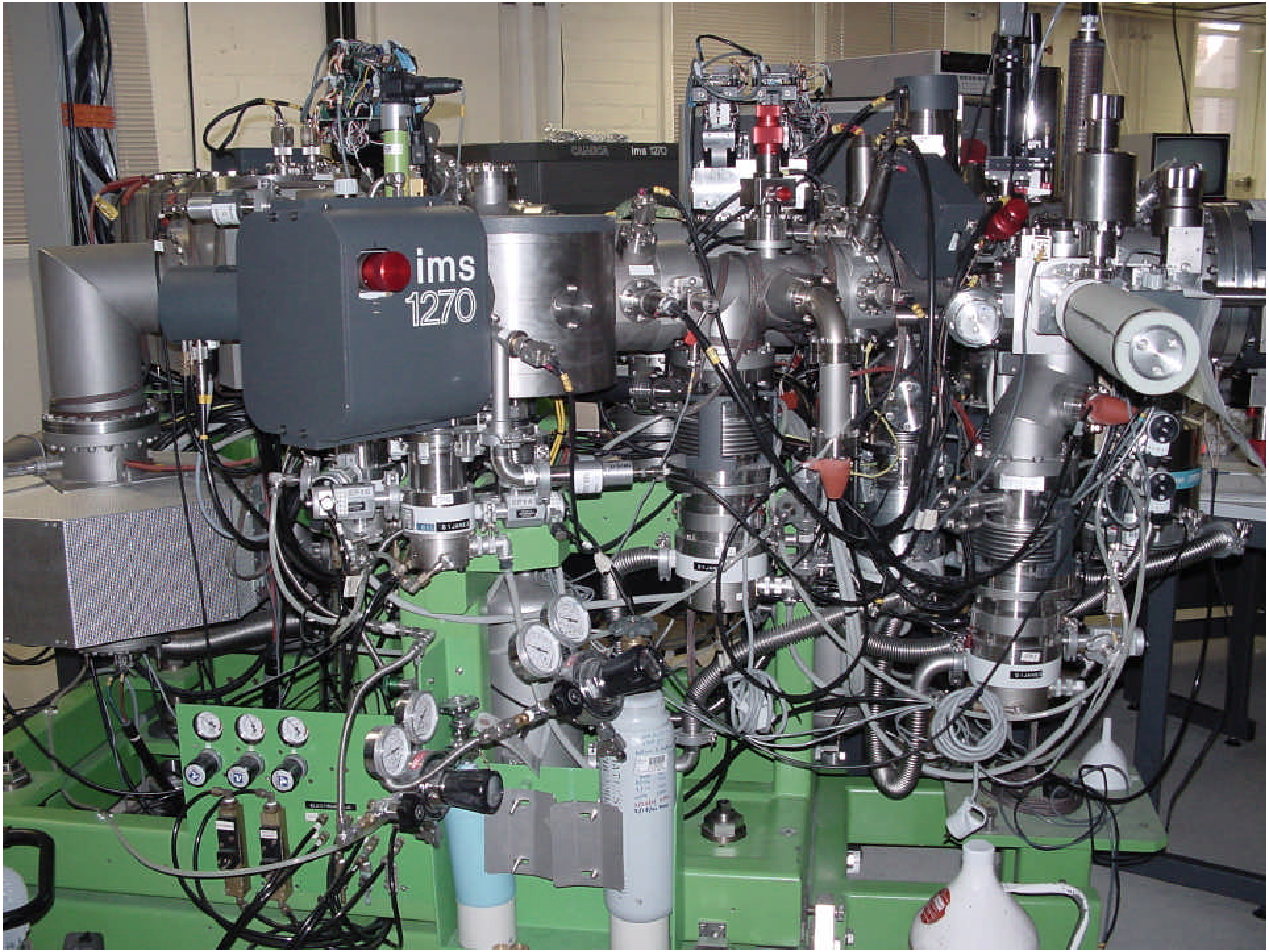
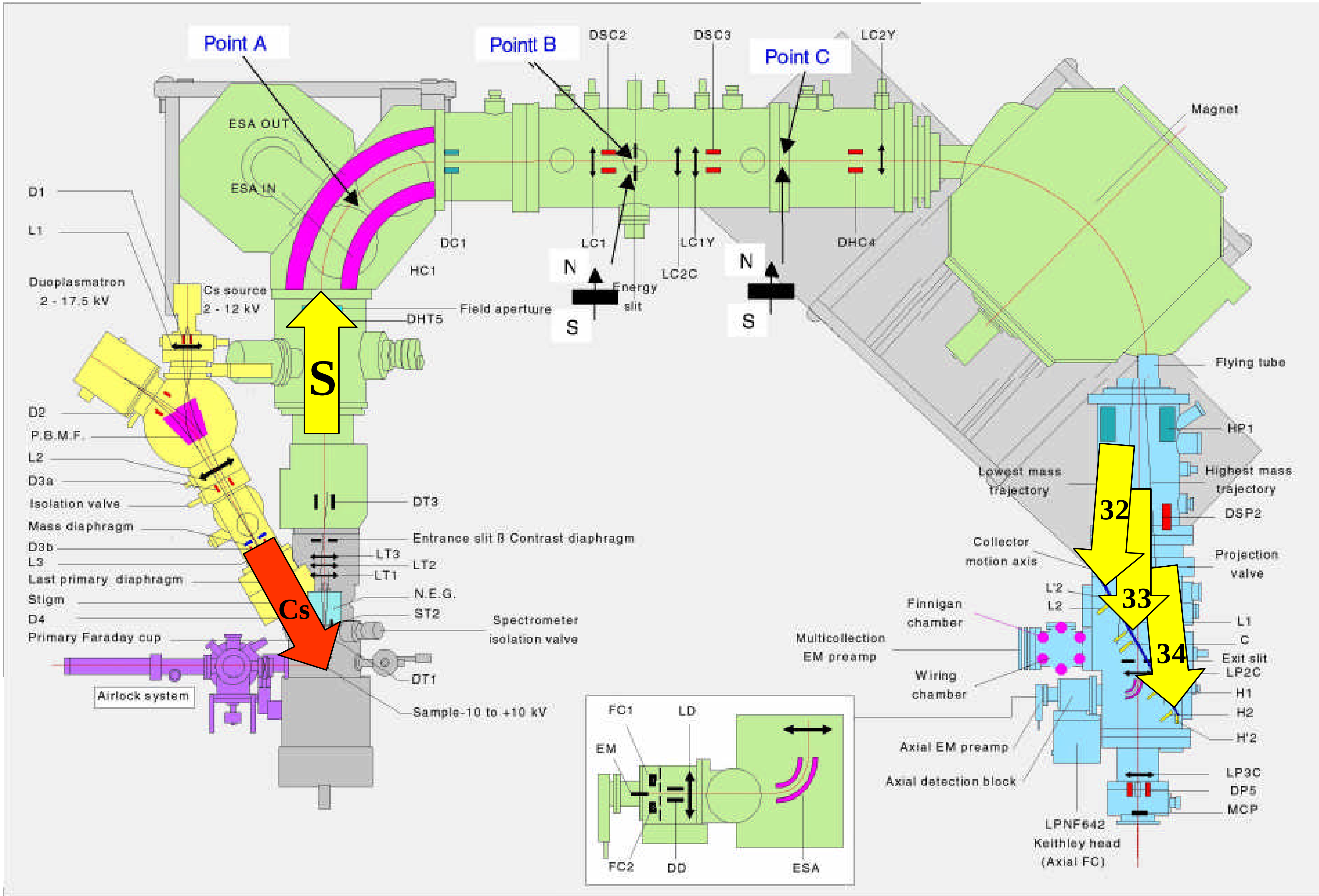
Mass-independent fractionation of sulfur isotopes (^{32}S, ^{33}S, ^{34}S, ^{36}S), sulfur cycling, and the rise of oxygen on the early Earth

Geochemistry and mineralogy –

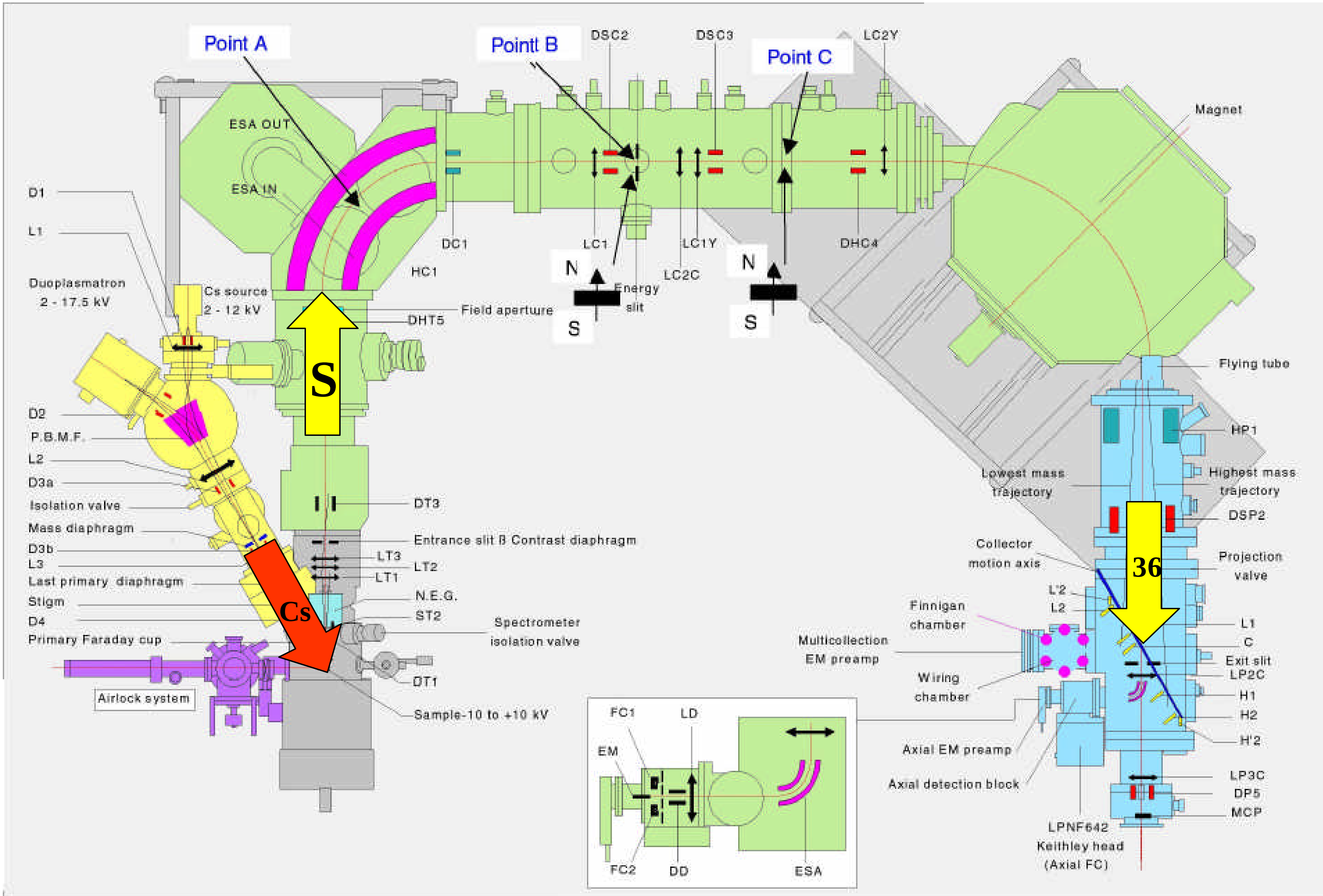
Wayne Dollase, James Lyons , Kevin McKeegan, and Craig Manning, UCLA
Stephen Mojzsis, University of Colorado
Christopher Coath, University of Bristol
James Farquhar, University of Maryland




ims
1270
ims 1270



Keck National Center Cameca ims 1270 ion microprobe



Keck National Center Cameca ims 1270 ion microprobe

Field assistance, Western Australia –

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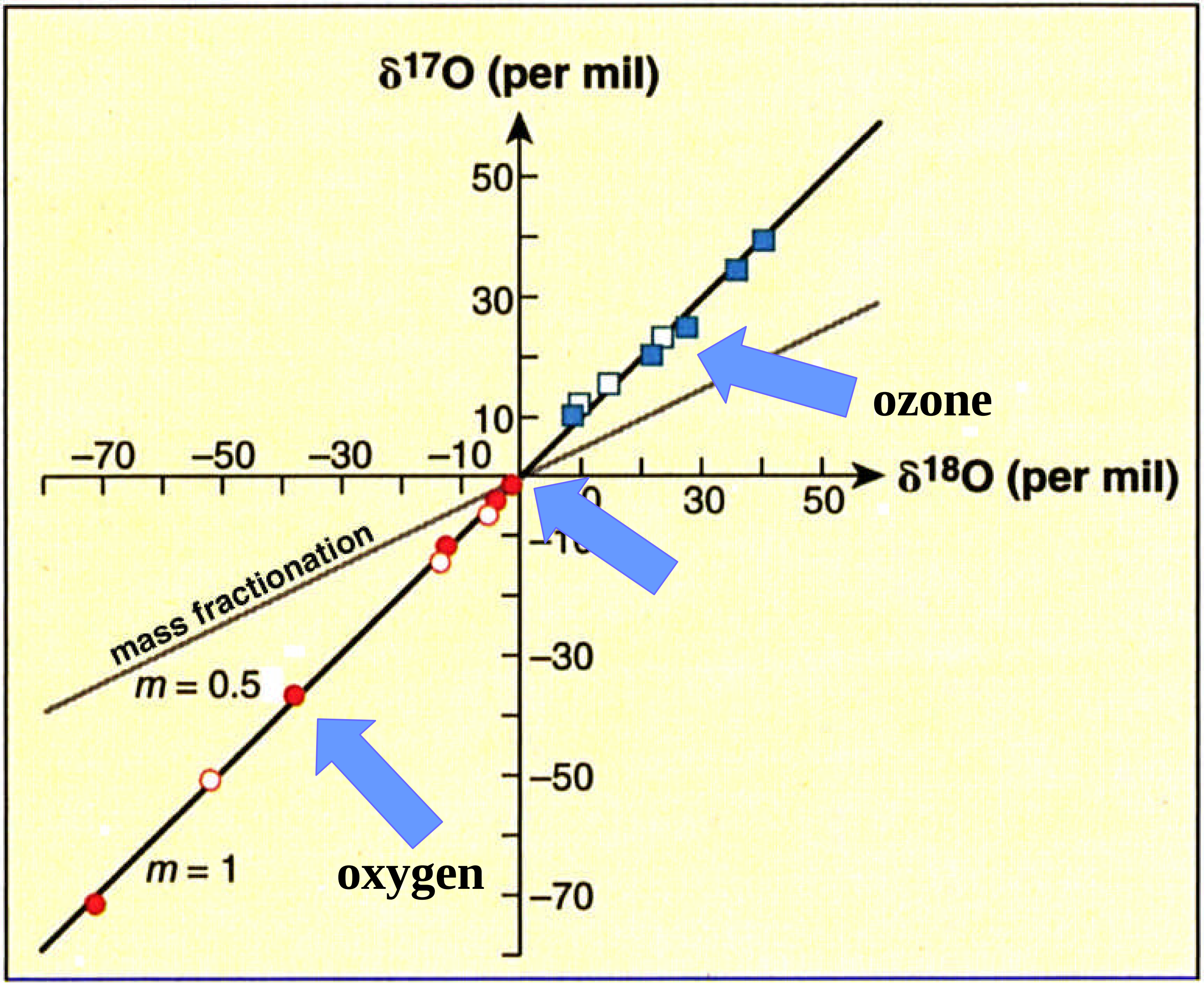
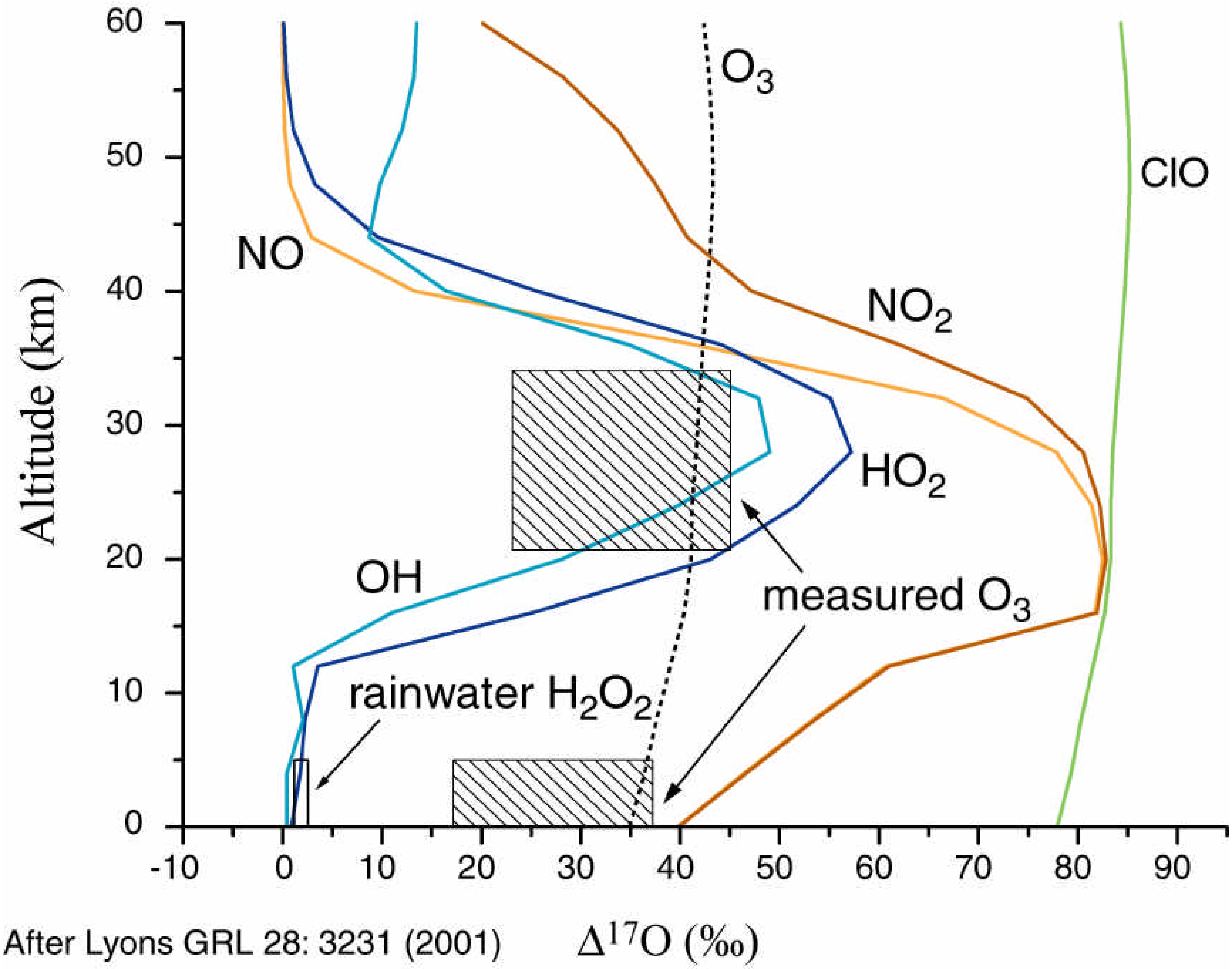
Ian Williams, Geological Survey of WA
Jim Gehling, South Australian Museum
Brent Murdoch, Murdoch Consulting
Roger Buick, University of Washington

Gift of samples –

Peter Morant, Sipa Resources
Don Carslile, Bill Schopf, UCLA
Whitey Hagadorn, Amherst College
Dick Holland, Harvard University
Des Lascelles, Univ. of Western Australia



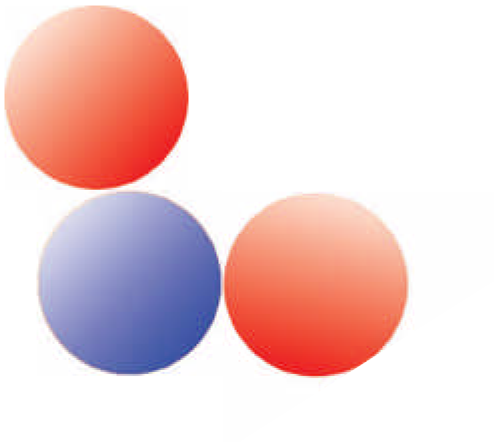
Thiemens and Heidenreich, Science 219, 1073 (1983)

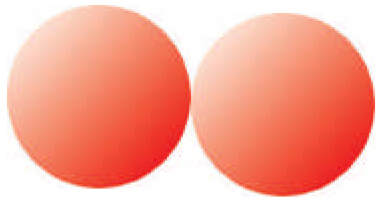


After Lyons GRL 28: 3231 (2001)

$^{18}O + {}^{16}O^{16}O = {}^{18}O^{16}O + {}^{16}O$

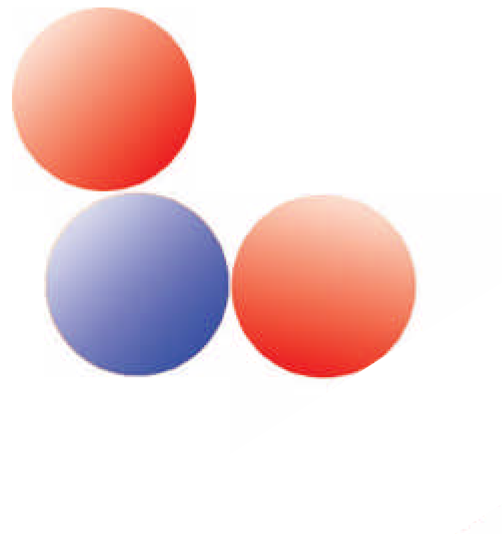
$^{18}O^{16}O + {}^{16}O = {}^{16}O^{18}O^{16}O$

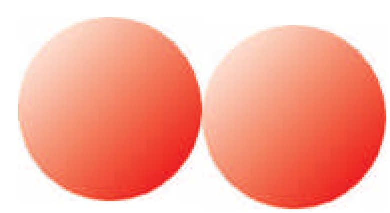




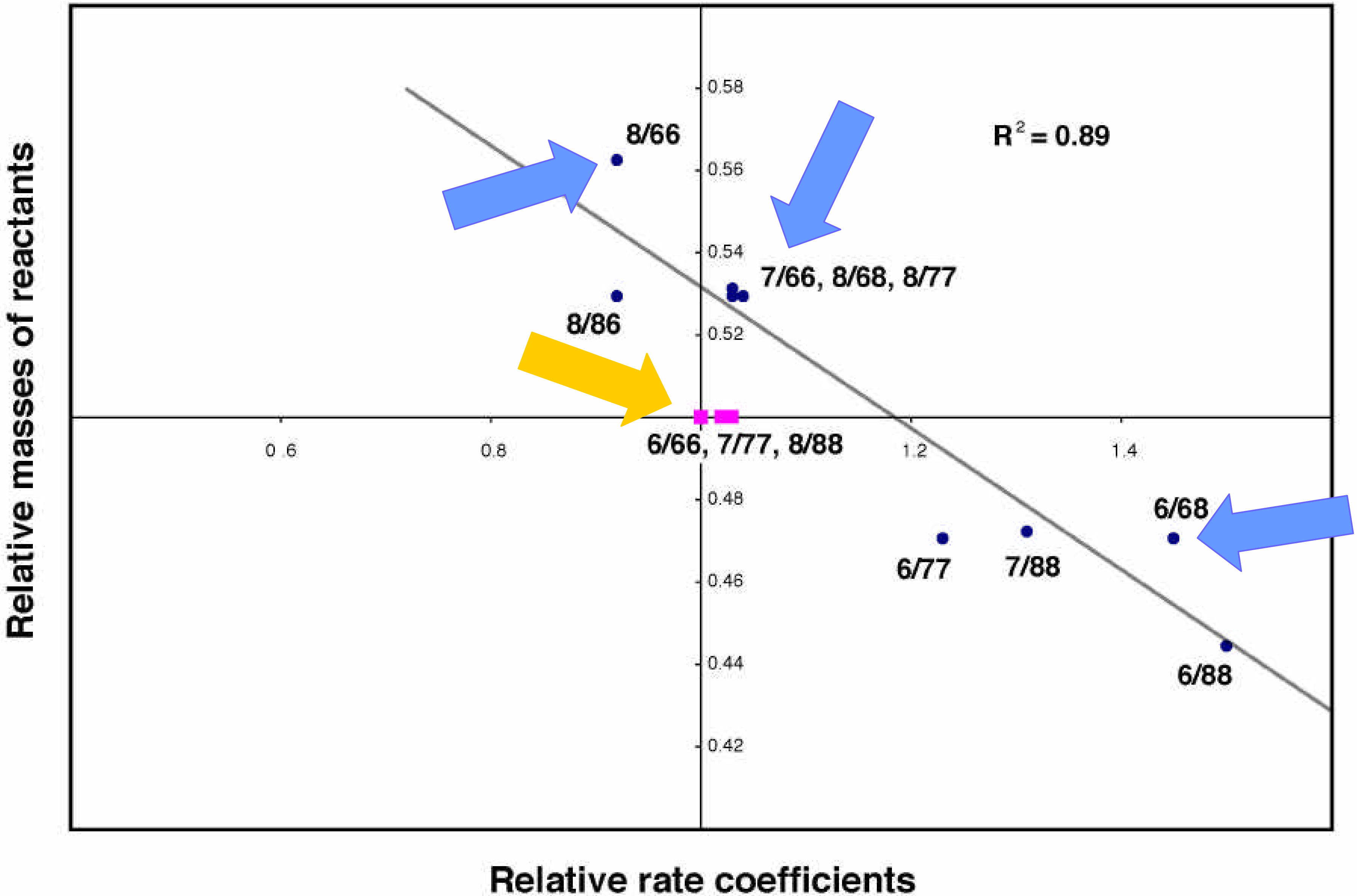
$$^{18}O + {}^{16}O^{16}O = {}^{18}O^{16}O + {}^{16}O$$

$$^{18}O^{16}O + {}^{16}O = {}^{16}O^{18}O^{16}O$$





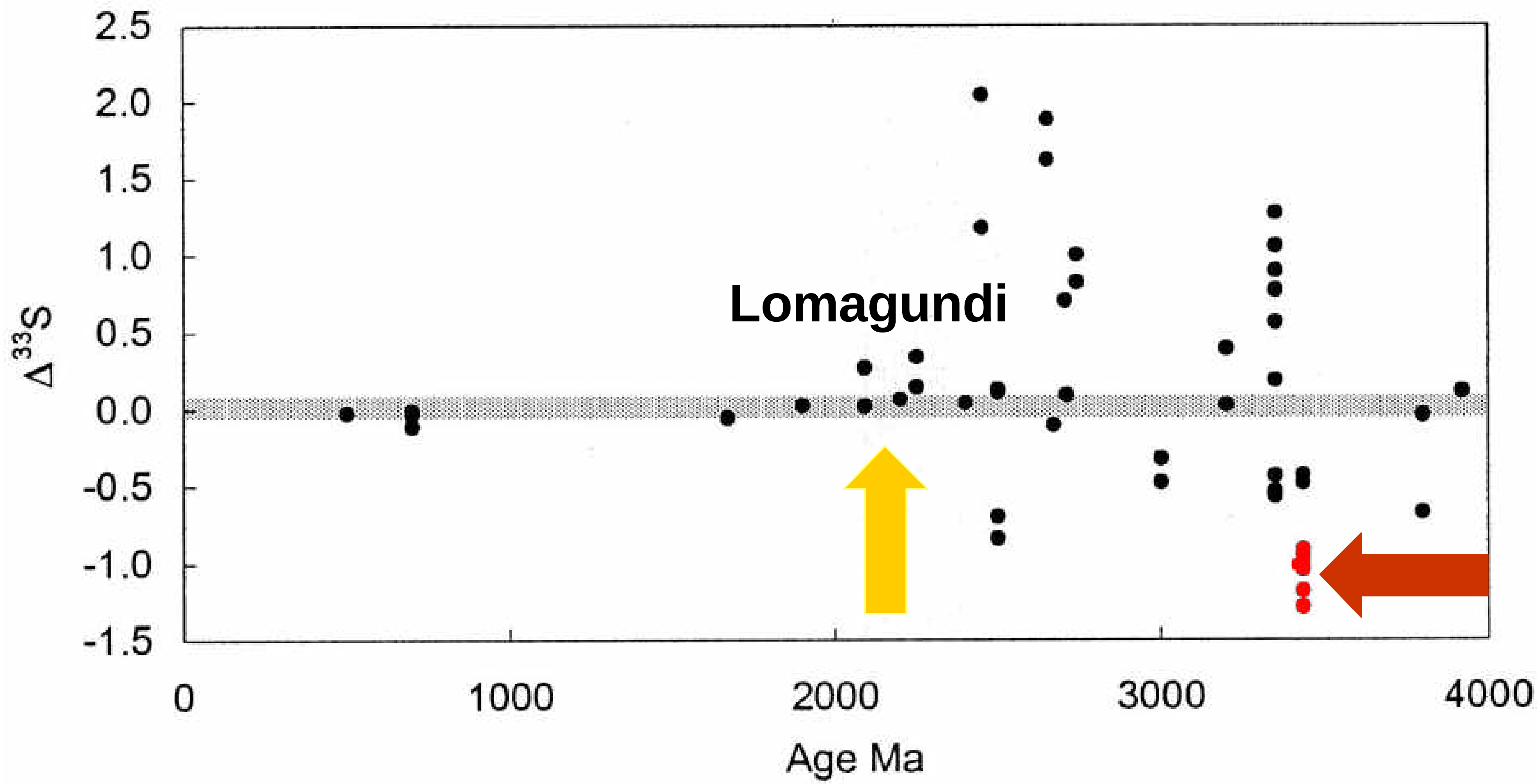
Data from Janssen et al., PCCP 3, 4718 (2001)



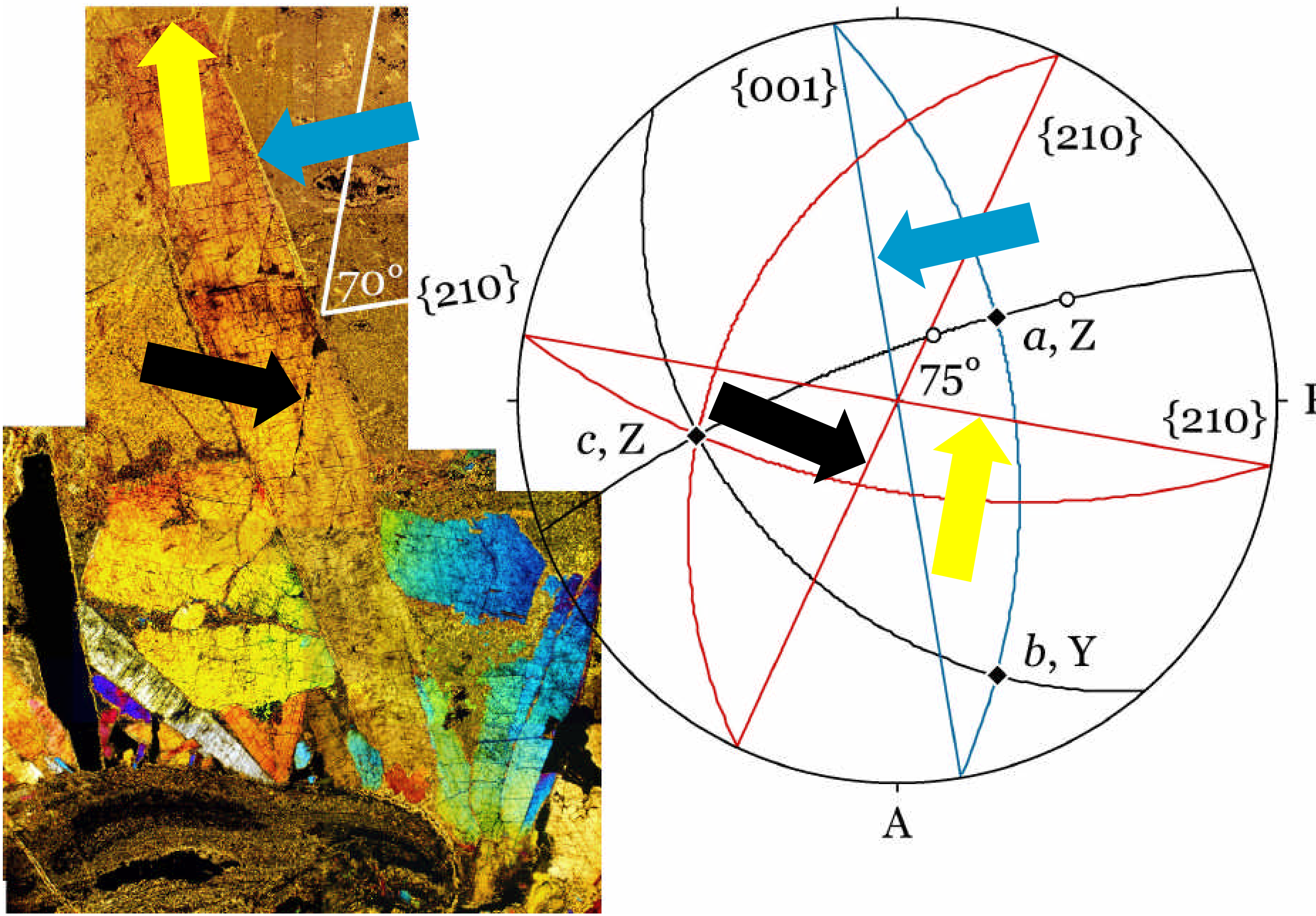
Atmospheric Influence of Earth's Earliest Sulfur Cycle

James Farquhar, Huiming Bao, Mark Thiemens

Science 289: 756-758 (2000)

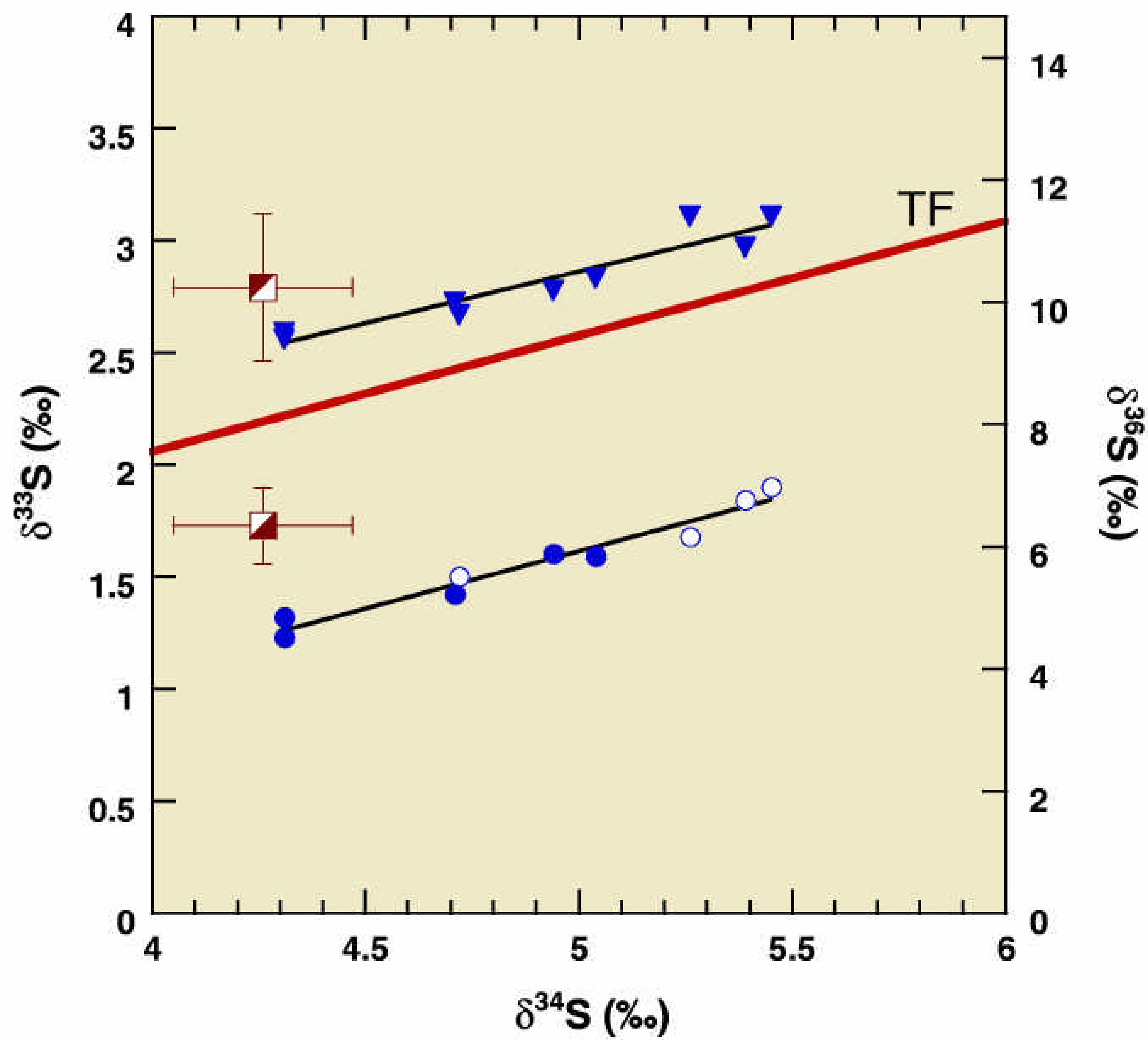


GSWA 169711

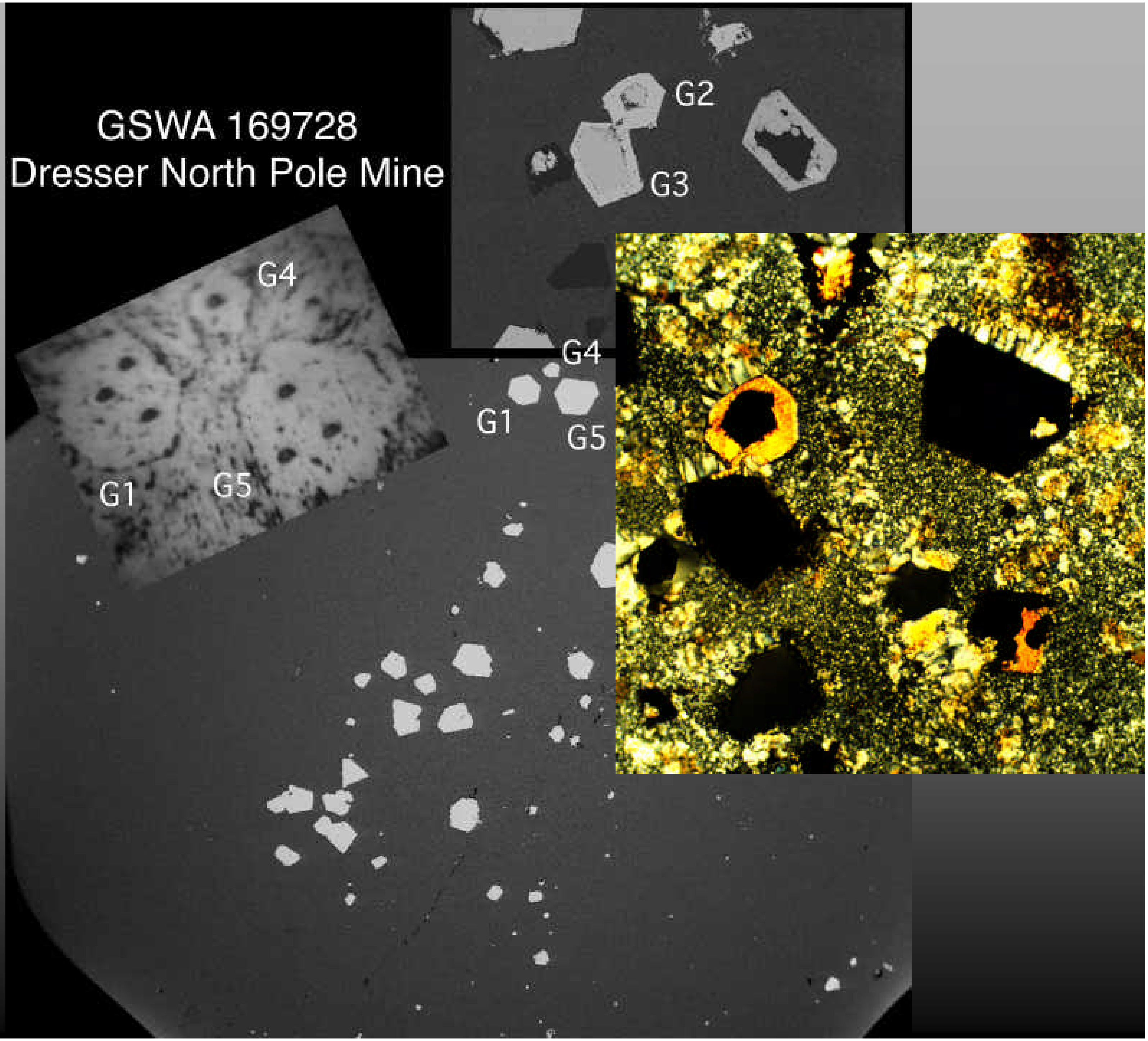


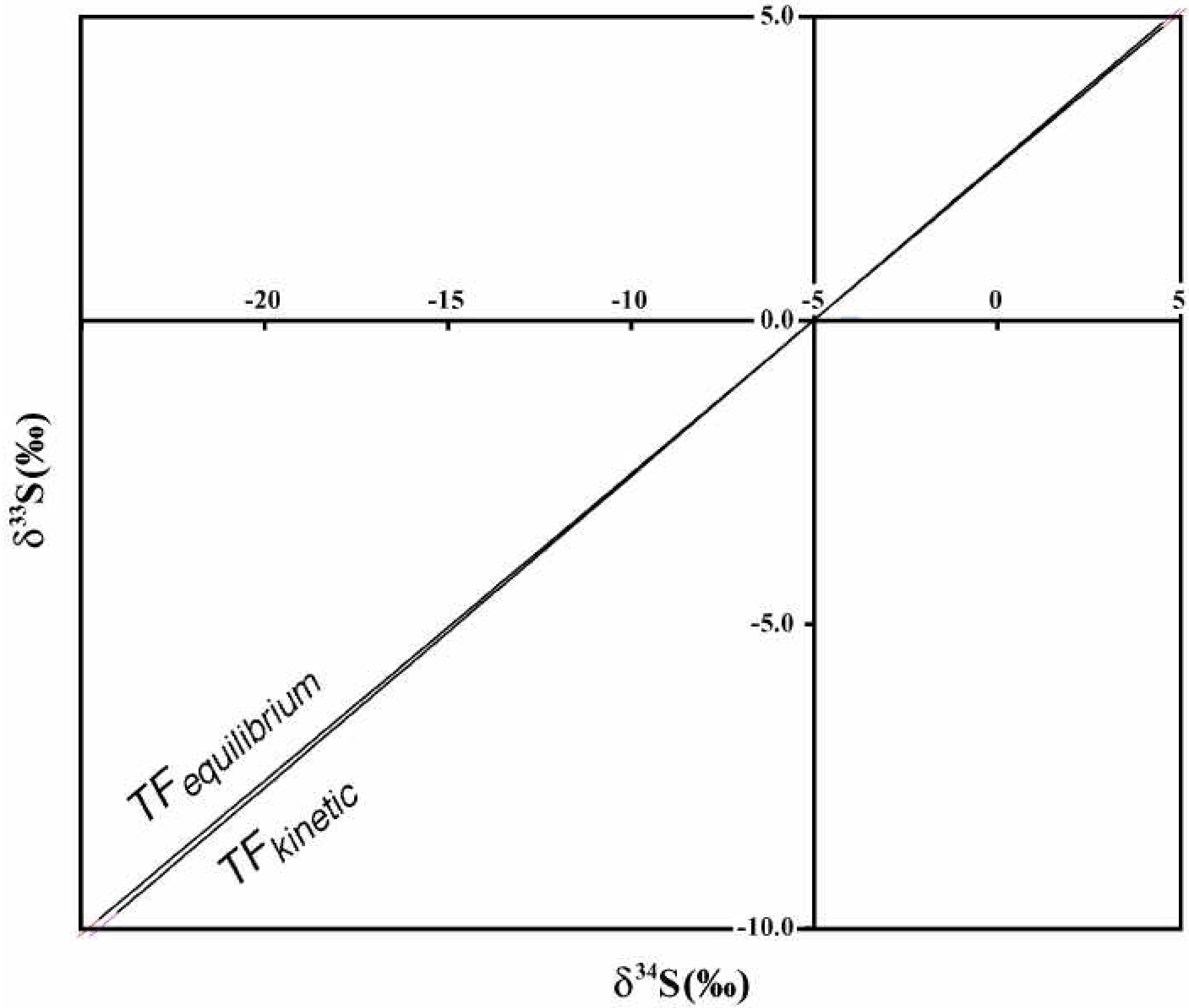
70°
{210}
{001}
{210}
a, Z
75°
P
{210}
c, Z
b, Y
A

Data from Farquhar et al. (2000)

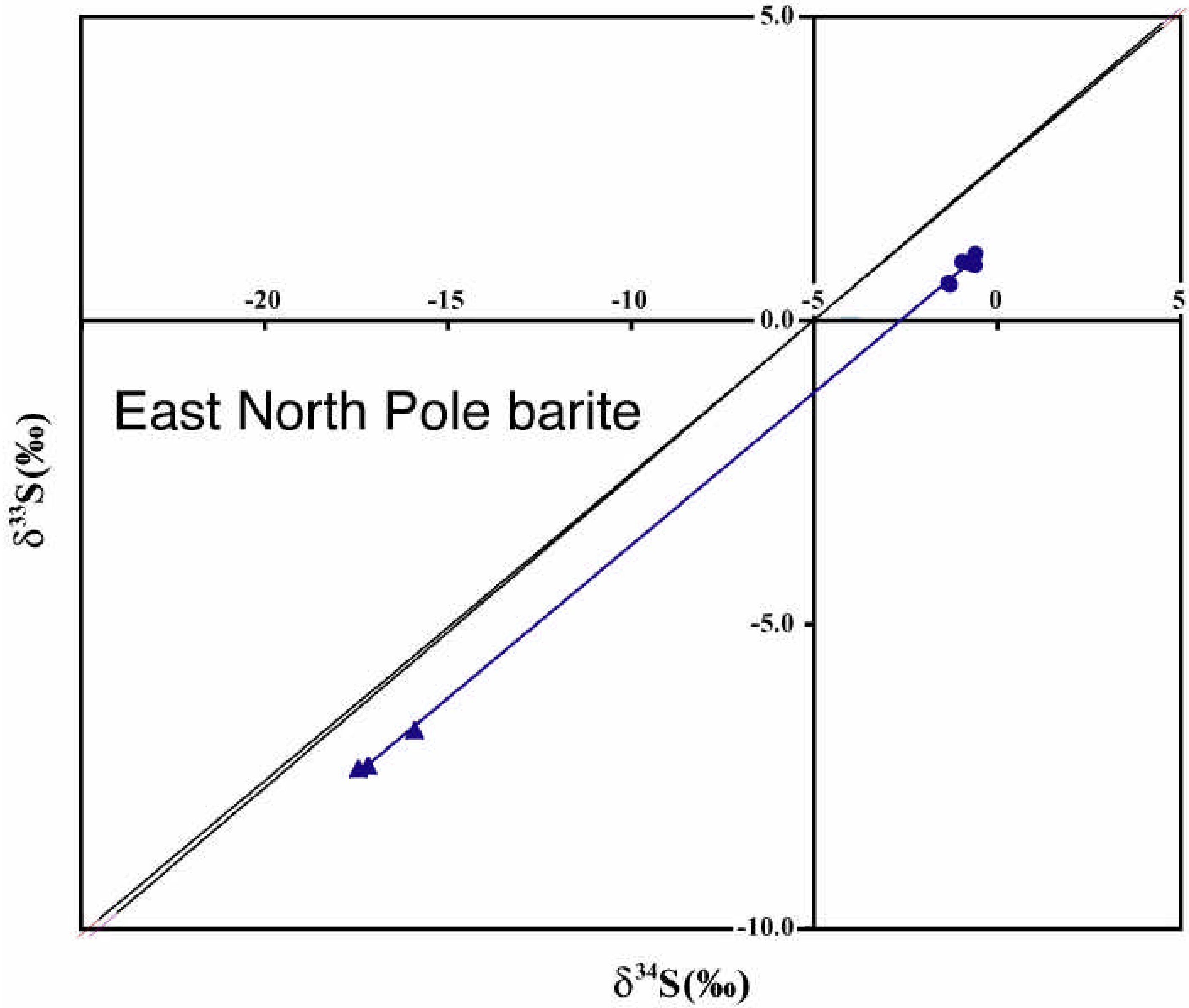



One and a
half inch drill core
Dresser Formation
Warrawoona Group
Western Australia

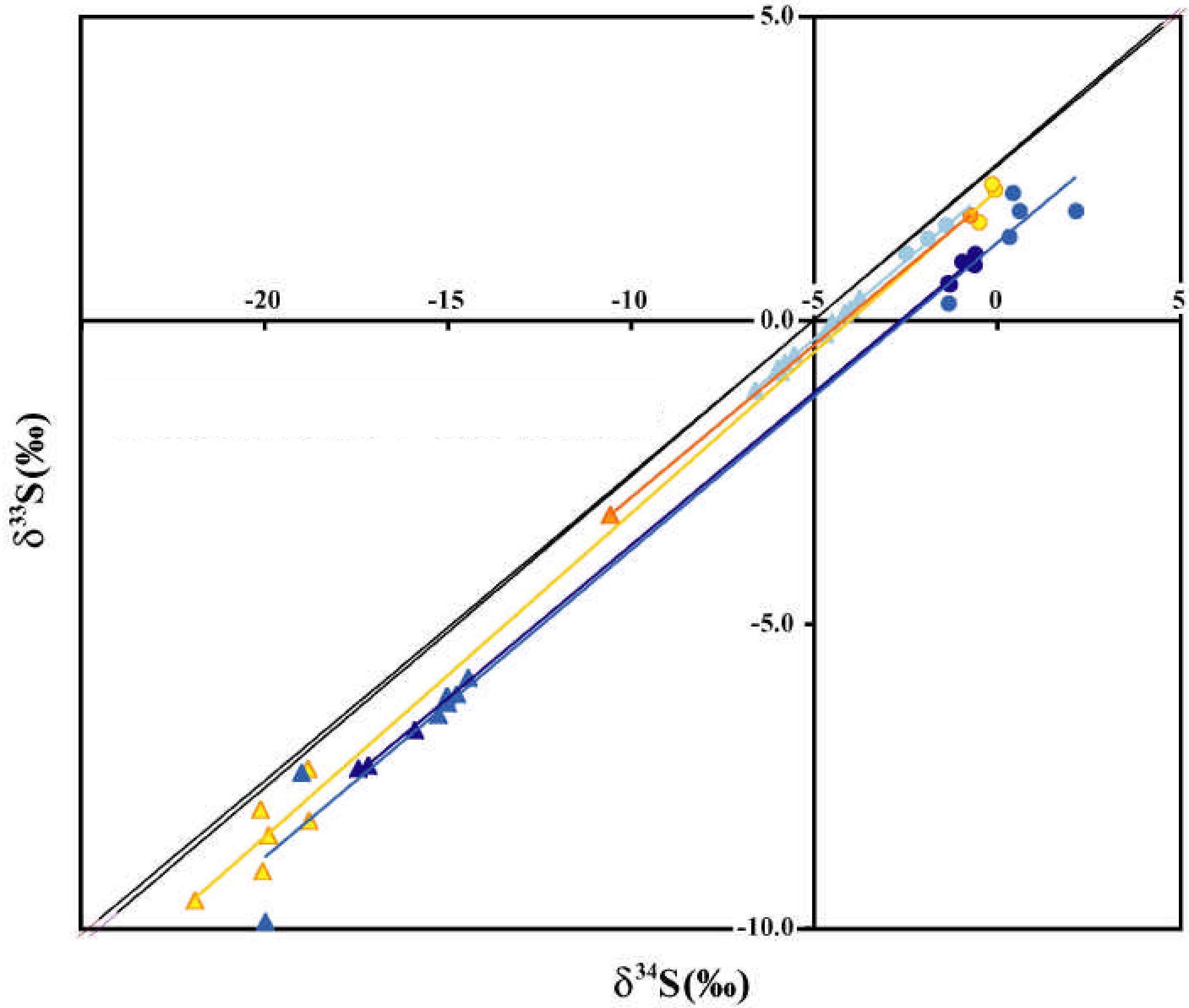

GSWA 169728
Dresser North Pole Mine
G2
G3
G4
G1
G5
G4
G1
G5



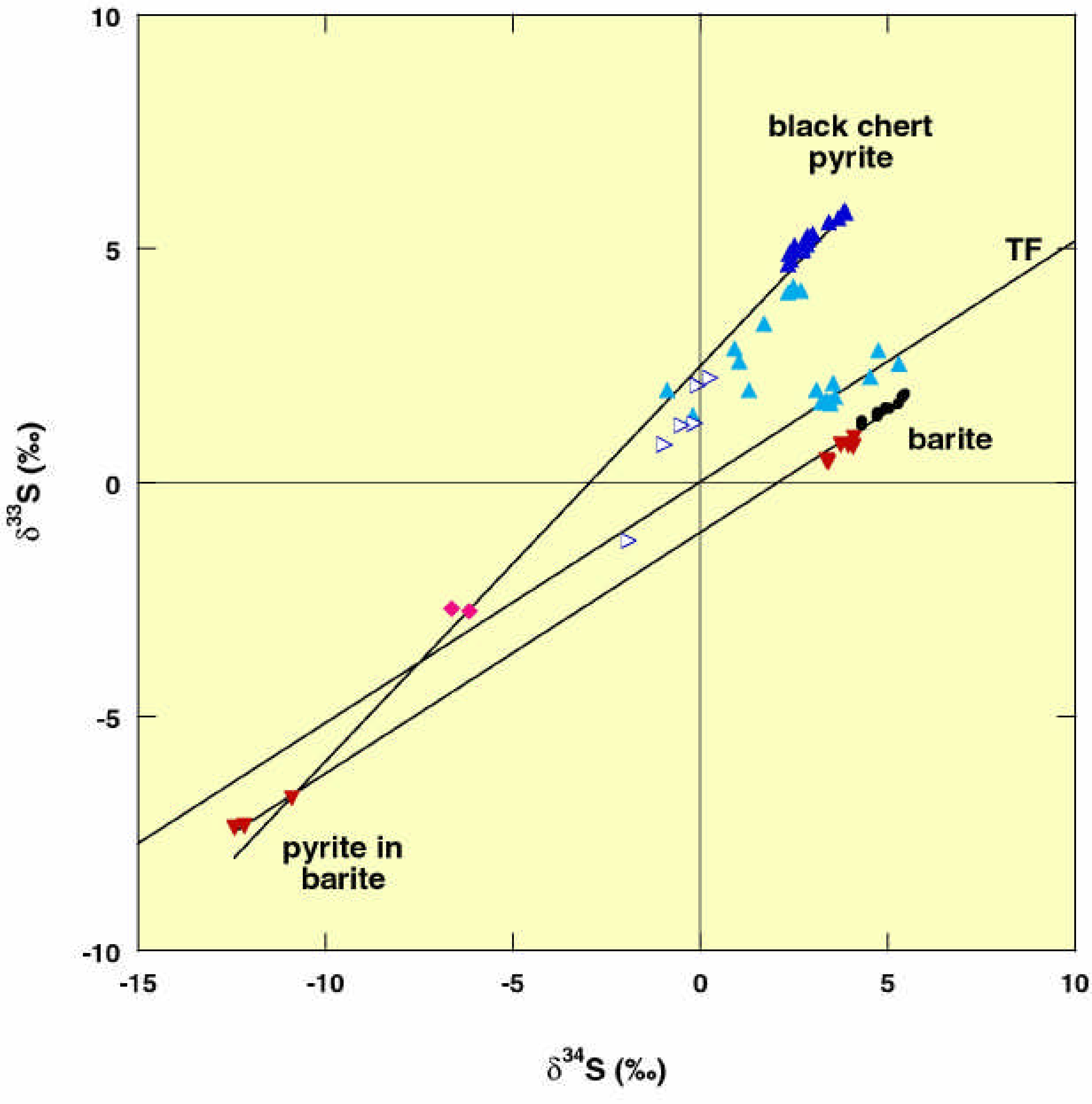
5.0
0.0
-5.0
-10.0
-20
-15
-10
-5
0
5
δ33S(‰)
δ34S(‰)
TF equilibrium
TF kinetic



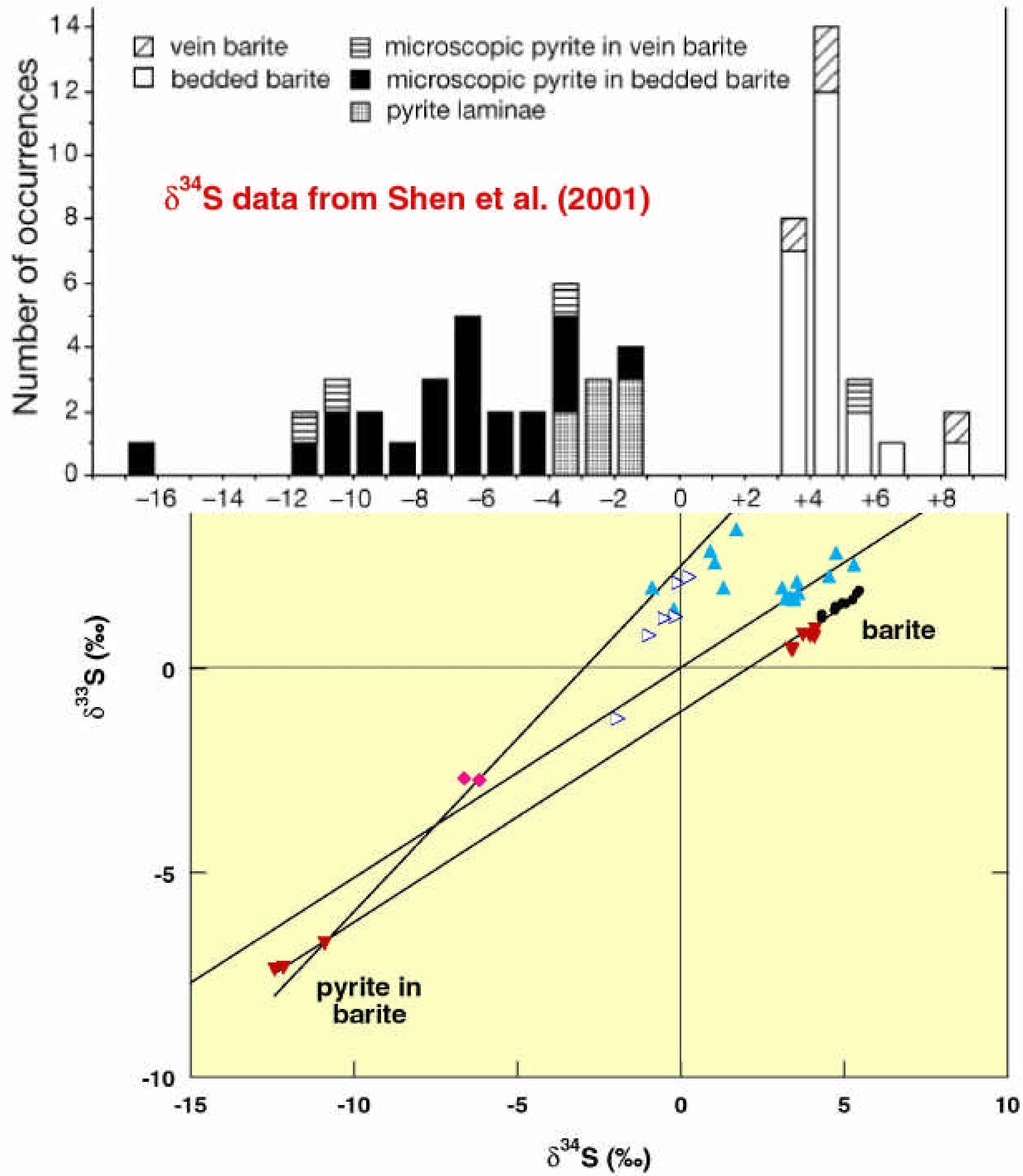
5.0
0.0
-5.0
-10.0
-20
-15
-10
-5
0
5
East North Pole barite
δ33S(‰)
δ34S(‰)

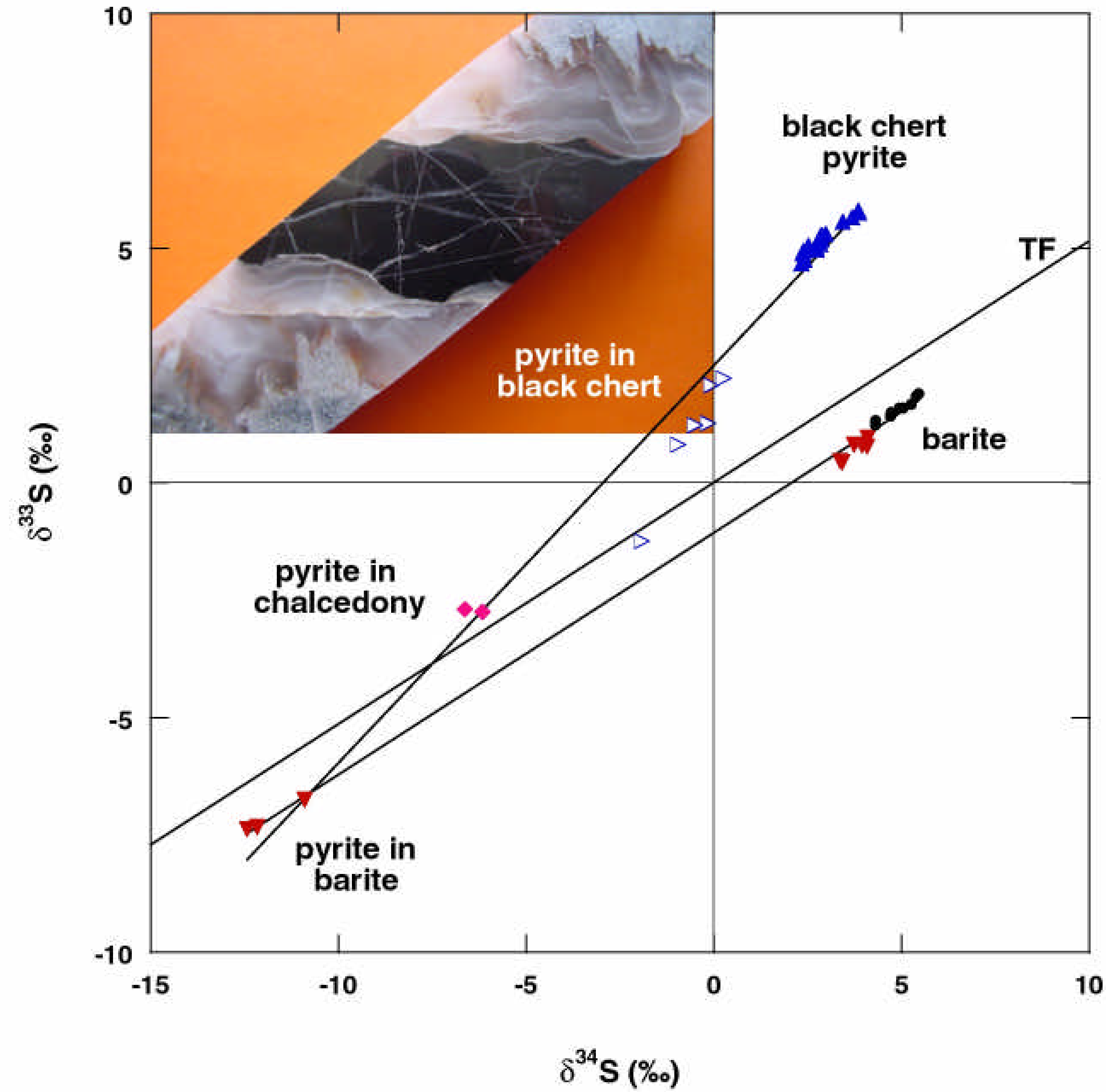


5.0
0.0
-5.0
-10.0
-20
-15
-10
-5
0
5
δ33S(‰)
δ34S(‰)

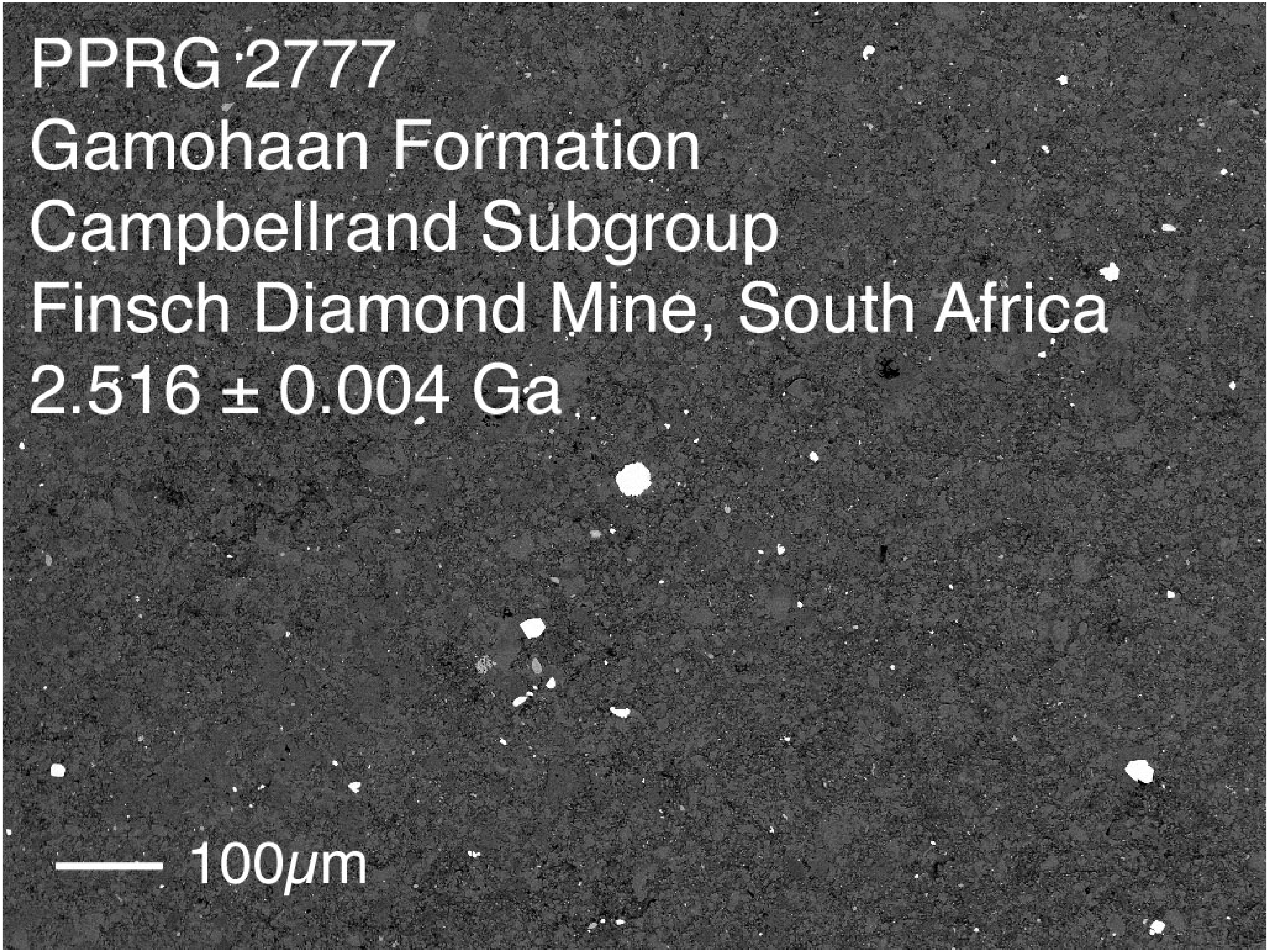


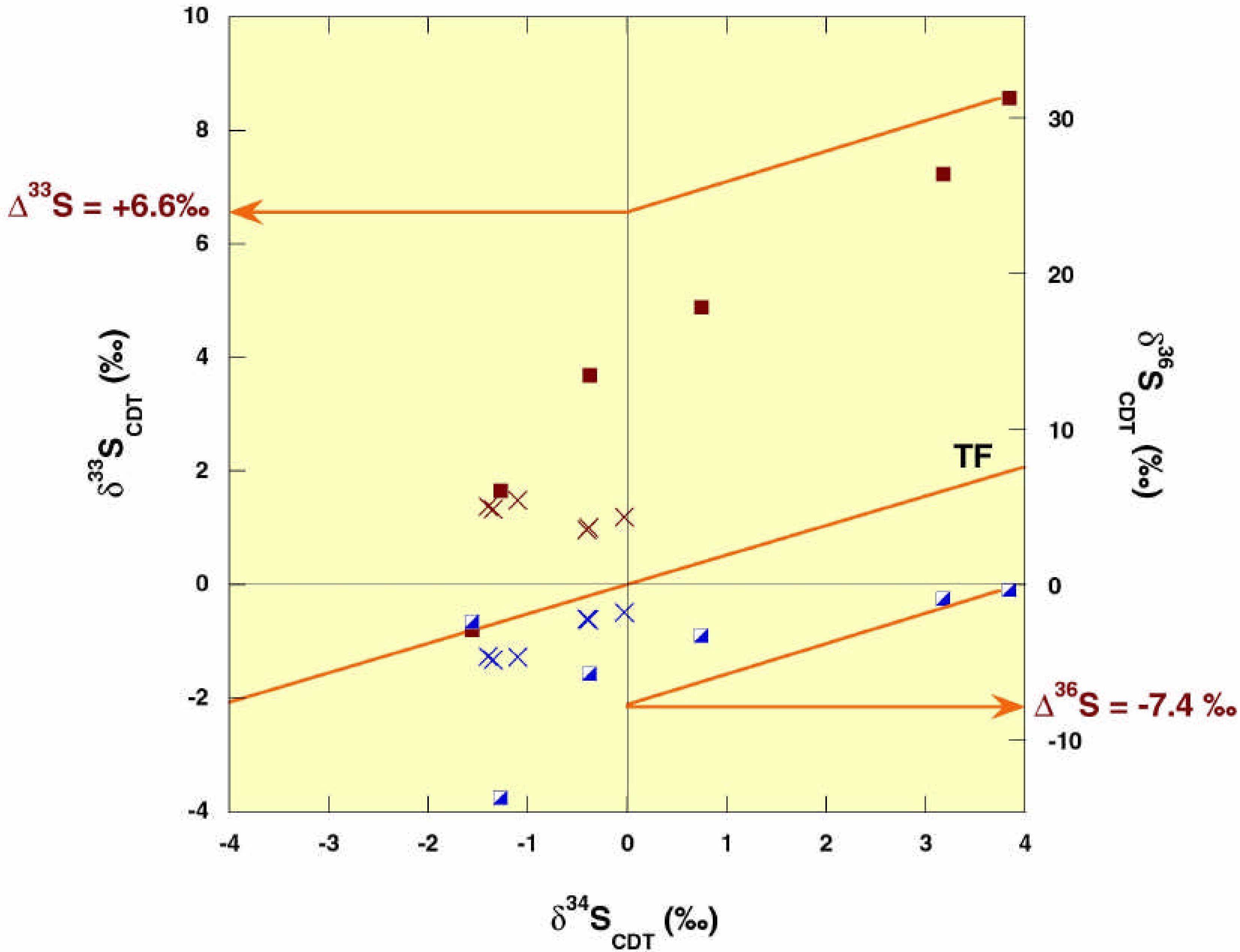
black chert pyrite
TF
barite
pyrite in barite
10
5
0
-5
-10
-15
-10
-5
0
5
10
δ33S (‰)
δ34S (‰)


vein barite
bedded barite
microscopic pyrite in vein barite
microscopic pyrite in bedded barite
pyrite laminae
Number of occurrences
δ^{34}S data from Shen et al. (2001)
barite
pyrite in barite
δ^{33}S (‰)
δ^{34}S (‰)

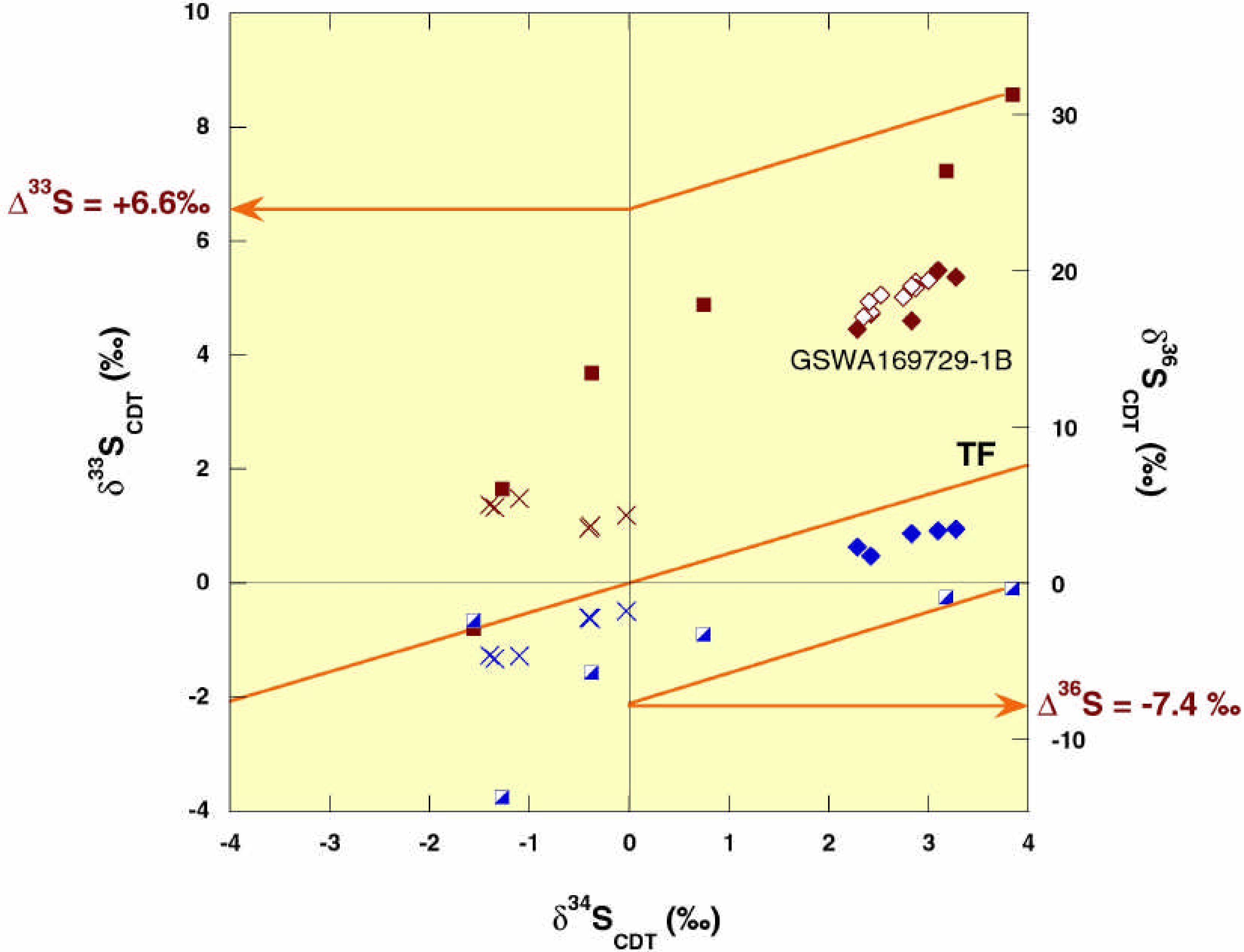


black chert pyrite
TF
pyrite in black chert
barite
pyrite in chalcedony
pyrite in barite
10
5
0
-5
-10
-15
-10
-5
0
5
10
δ33S (‰)
δ34S (‰)

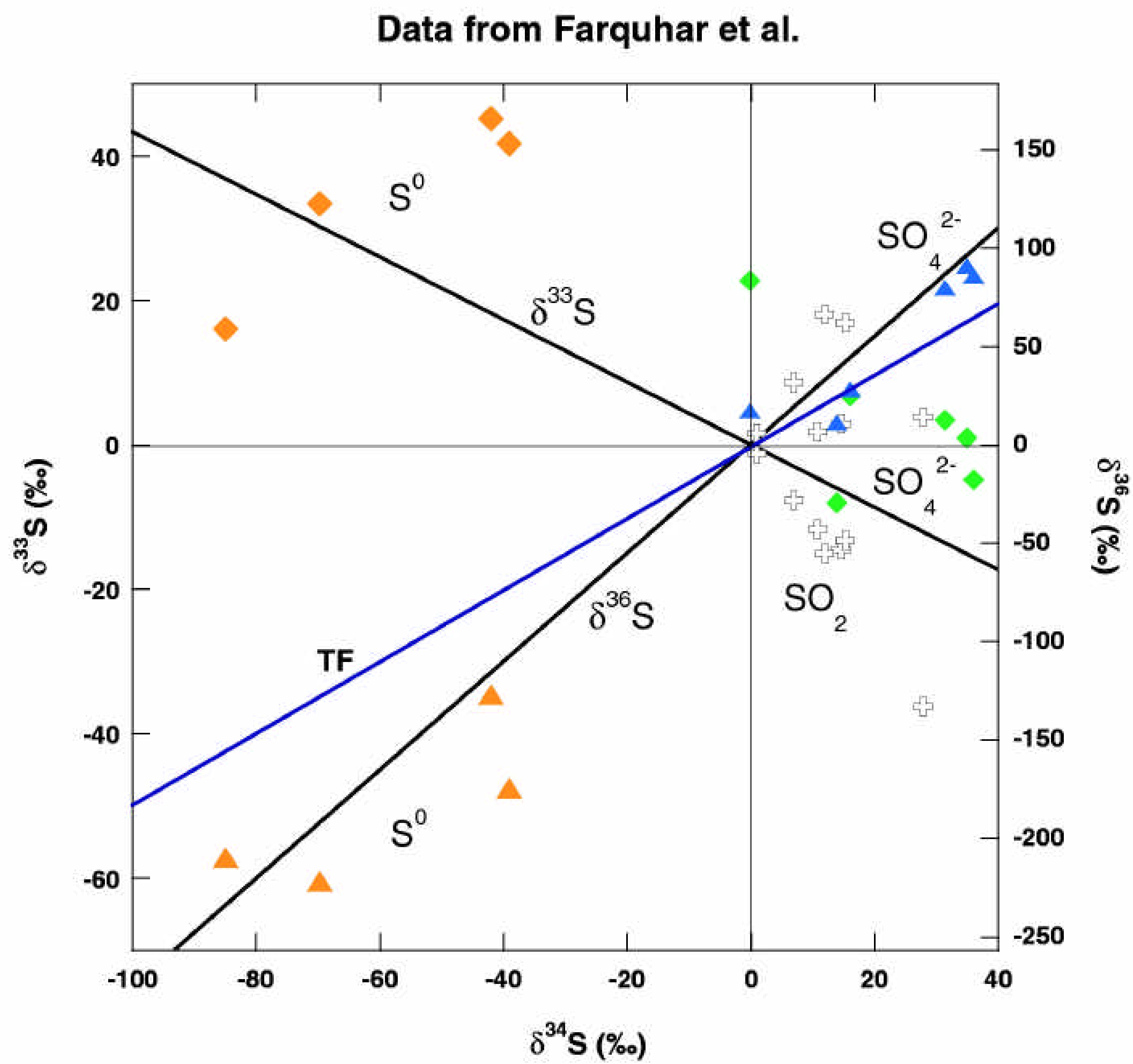

PPRG 2777
Gamohaan Formation
Campbellrand Subgroup
Finsch Diamond Mine, South Africa
2.516 ± 0.004 Ga
100μm



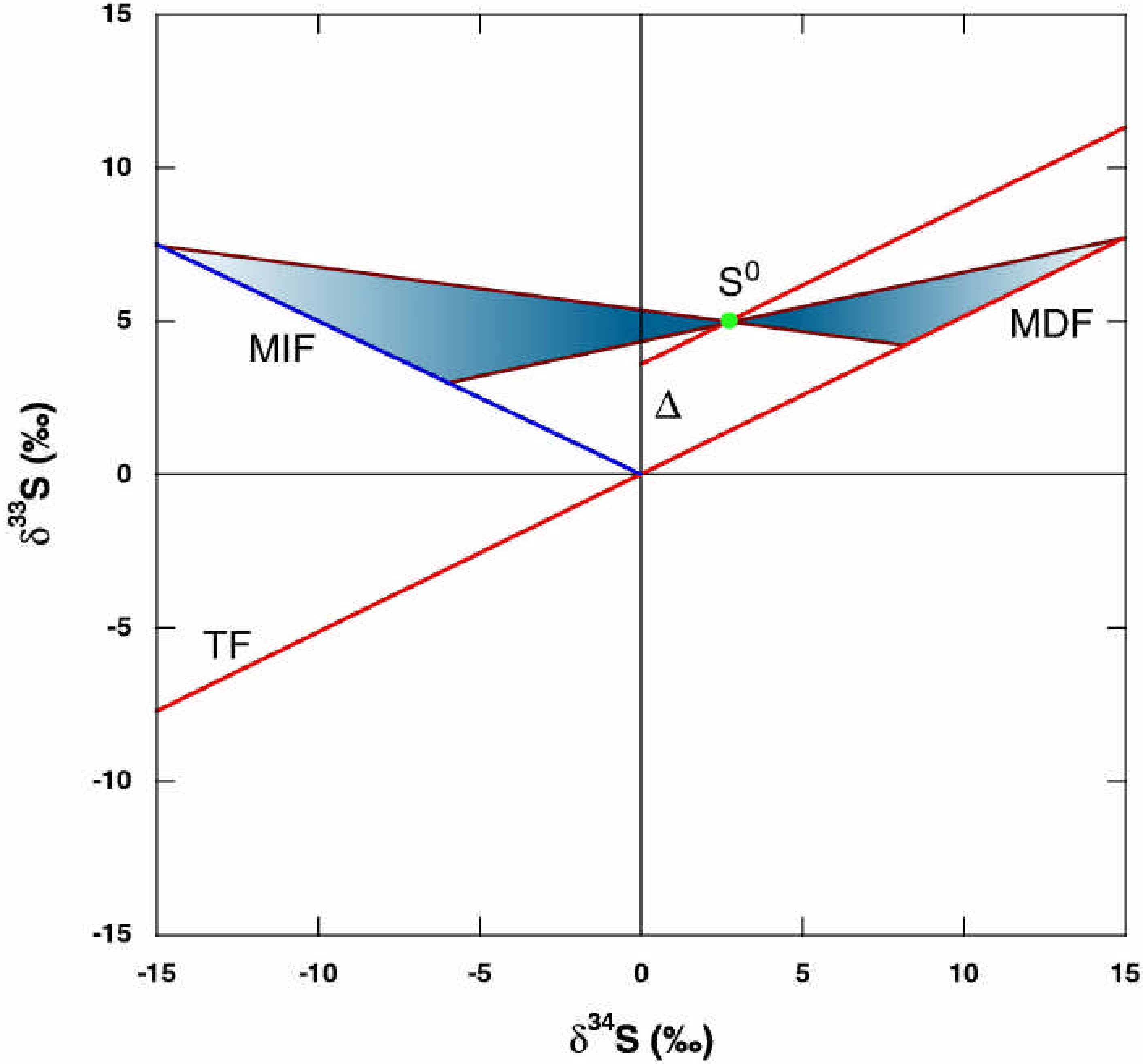
10
8
6
4
2
0
-2
-4
30
20
10
0
-10
-4
-3
-2
-1
0
1
2
3
4
Δ33S = +6.6‰
Δ36S = -7.4 ‰
TF
δ33SCDT (‰)
δ36SCDT (‰)
δ34SCDT (‰)



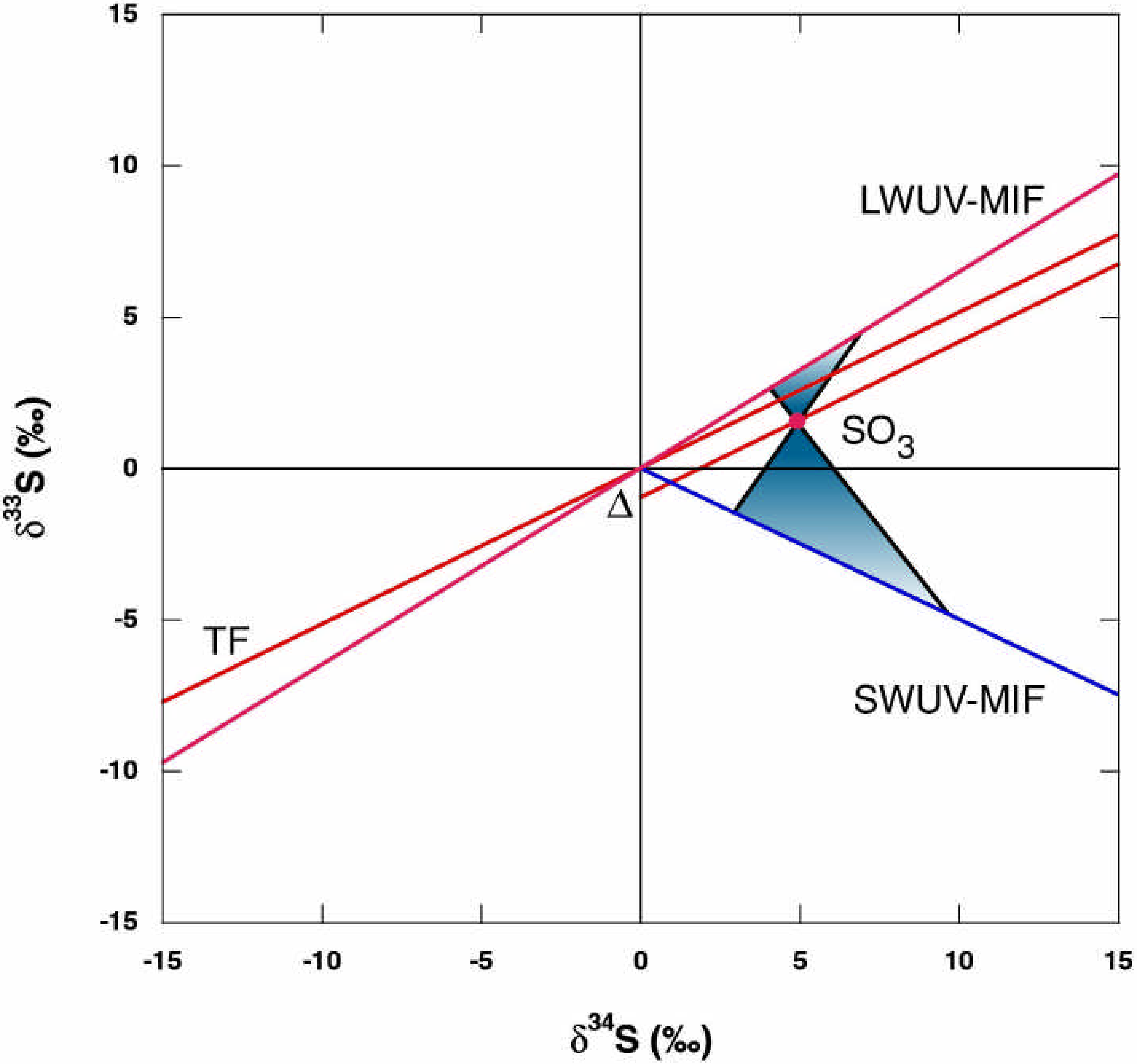
Δ33S = +6.6‰
Δ36S = -7.4 ‰
GSWA169729-1B
TF
δ33S CDT (‰)
δ36S CDT (‰)
δ34S CDT (‰)
10
8
6
4
2
0
-2
-4
30
20
10
0
-10
-4
-3
-2
-1
0
1
2
3
4



Data from Farquhar et al.
S0
δ33S
SO4 2-
SO4 2-
SO2
δ36S
TF
S0
δ33S (‰)
δ34S (‰)
δ36S (‰)
40
20
0
-20
-40
-60
-100
-80
-60
-40
-20
0
20
40
150
100
50
0
-50
-100
-150
-200
-250



15
10
5
0
-5
-10
-15
-15
-10
-5
0
5
10
15
S0
MIF
MDF
Δ
TF
δ33S (‰)
δ34S (‰)



15
10
5
0
-5
-10
-15
-15
-10
-5
0
5
10
15
LWUV-MIF
SO3
Δ
TF
SWUV-MIF
δ33S (‰)
δ34S (‰)

Conclusions:

Archean barites are primary minerals formed from low-temperature (~150°C) hydrothermal fluids –

There is no evidence for gypsum evaporites

Bedded barites and vein barites have the same sulfur source –

Negative ?^{33}S of barites suggests that sulfate was produced photochemically in atmosphere

Conclusions:

Pyrites that are intimately associated with barites have the same negative ?^{33}S (and positive ?^{36}S) as the barites but are lighter in ?^{34}S by as much as 20‰ (five examples from three continents).

This isotopic difference between co-existing sulfate and sulfide is attributed to fractionation in hydrothermal environments. The pyrites inherited their anomalous ?^{33}S and ?^{36}S signatures from UV-oxidized atmospheric SO_2

Conclusions:

Pyrites in black cherts, black shales, and BIFs are anomalously enriched in ^{33}S by as much as 7‰ (?^{33}S > 0, ?^{36}S < 0) and, typically, have ?^{34}S > 0.

The pyrite seems to be derived from elemental sulfur that obtained its anomalous ?^{33}S and ?^{36}S signatures as a result of SWUV-induced reduction of SO_2 to S^0. However, a second source of sulfur (LWUV photodissociation of H_2S?) is required to explain why ?^{34}S > 0.

Conclusions:

Archean atmosphere was anoxic and ocean was probably low in sulfate –

UV photochemistry implies no ozone screen

Evidence for sulfur processing by bacteria is missing from the Archean –

Bacterial oxidation/reduction of sulphur (S^0) may have been widespread but its small isotopic signature makes it difficult to detect

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