Si-isotope exchange experiments – Details

- **Materials:**

  (1) **^{29}Si-spiked Archean Artificial Seawater (AAS):**

  - monosilicic acid (H_4SiO_4) tetrahedron ([Si]≤1mM)
  - $\delta^{29}Si \approx 99‰$; $\delta^{30}Si \approx 0‰$
  - Comparative groups:

    Fe(II)-free: Exp-2a & 3a; **1 mM Fe(II)**: Exp-2b & 3b

  (2) Amorphous Fe(III)-Si gel

  - Si–OH, Si–O–Fe, Si–O–Si network
  - $\delta^{29}Si \approx 0‰$; $\delta^{30}Si \approx 0‰$

- **Experiment conditions:**

  room temperature; pH ~7.3; anoxic

1
00:00:11,730 --> 00:00:09,210
speaking of silicon iron cook passivity

2
00:00:13,759 --> 00:00:11,740
today I'm going to show you some

3
00:00:15,660 --> 00:00:13,769
experiment results I'm silikal I still

4
00:00:17,760 --> 00:00:15,670
fractionation between simulated

5
00:00:22,019 --> 00:00:17,770
precambrian sea water and iron silica

6
00:00:24,179 --> 00:00:22,029
gel so we know the Precambrian was

7
00:00:26,490 --> 00:00:24,189
dramatic different from the model ocean

8
00:00:29,519 --> 00:00:26,500
in particular there was no silica

9
00:00:31,589 --> 00:00:29,529
secreting organism by the time so so the

10
00:00:33,720 --> 00:00:31,599
sim cellular concentration the

11
00:00:35,190 --> 00:00:33,730
Precambrian seawater was over an order

12
00:00:37,530 --> 00:00:35,200
of magnitude higher than the modern

13
00:00:39,450 --> 00:00:37,540

seawater so that actually leads to a

14
00:00:41,490 --> 00:00:39,460
silica flux from the seawater into

15
00:00:43,860 --> 00:00:41,500
segments that's why we see abounded

16
00:00:46,200 --> 00:00:43,870
unusually abounded deposition of silica

17
00:00:48,900 --> 00:00:46,210
rich rock student Cambrian like Church

18
00:00:50,669 --> 00:00:48,910
and bending our information so as we

19
00:00:52,560 --> 00:00:50,679
know the life actually started in this

20
00:00:54,150 --> 00:00:52,570
silicon rate environment so it's quite

21
00:00:57,959 --> 00:00:54,160
important to understand the spherical

22
00:01:00,090 --> 00:00:57,969
psycho during that time so silicon

23
00:01:02,669 --> 00:01:00,100
isotope is a potential proxy for the

24
00:01:06,510 --> 00:01:02,679
silica sonico so silicon has three

25
00:01:08,550 --> 00:01:06,520
stabilized health 28 29 and 30 a silicon

26
00:01:11,639 --> 00:01:08,560
star is expressed by the traditional

27
00:01:13,730 --> 00:01:11,649
doubt a notation in per mil so the high

28
00:01:16,260 --> 00:01:13,740
temperature process do not significantly

29
00:01:18,389 --> 00:01:16,270
fractionated silicon stealth as you can

30
00:01:21,149 --> 00:01:18,399
see is a point 5 ml changing the igneous

31
00:01:23,010 --> 00:01:21,159
rocks but the its variation can be

32
00:01:25,740 --> 00:01:23,020
pretty large at low temperature

33
00:01:28,230 --> 00:01:25,750
environment and over 7 premieres bread

34
00:01:30,510 --> 00:01:28,240
was reported for the Precambrian beefs

35
00:01:33,420 --> 00:01:30,520
and the church so the question is how to

36
00:01:37,200 --> 00:01:33,430
interpret this large spread in the Delta

37
00:01:39,660 --> 00:01:37,210
silica 30 venues so a previous study

38
00:01:41,490 --> 00:01:39,670

proposed the silicon still in the pre

39
00:01:43,469 --> 00:01:41,500
Cambridge church can reflect seawater

40
00:01:45,300 --> 00:01:43,479
temperature at the time based on the

41
00:01:47,340 --> 00:01:45,310
observation that silicon I still follow

42
00:01:49,560 --> 00:01:47,350
a similar train there's oxygen my cell

43
00:01:52,700 --> 00:01:49,570
if you still believe oxygen isotope came

44
00:01:56,429 --> 00:01:52,710
with flexi water after here in jax talk

45
00:01:58,050 --> 00:01:56,439
but later a latest study kind of Charlie

46
00:02:00,300 --> 00:01:58,060
this proposal was challenged by some

47
00:02:02,520 --> 00:02:00,310
later studies so this group of guys

48
00:02:04,230 --> 00:02:02,530
basically look at the silicon stove in

49
00:02:06,569 --> 00:02:04,240
the church against their chemical

50
00:02:08,969 --> 00:02:06,579
composition alumina oxide in this case

51
00:02:12,000 --> 00:02:08,979
and as you can see from this figure and

52
00:02:14,940 --> 00:02:12,010
those data set seems can be explained by

53
00:02:15,660 --> 00:02:14,950
three different end members so so the

54
00:02:17,400 --> 00:02:15,670
disco

55
00:02:19,920 --> 00:02:17,410
just proposed silicon stuff in the

56
00:02:22,800 --> 00:02:19,930
church can can can be used to trace

57
00:02:24,809 --> 00:02:22,810
celica from different sources but

58
00:02:27,120 --> 00:02:24,819
obviously there are other process may

59
00:02:30,270 --> 00:02:27,130
also affect silicon still preserved in

60
00:02:32,040 --> 00:02:30,280
this geological records for example this

61
00:02:34,050 --> 00:02:32,050
to a figure shows the completion of

62
00:02:36,180 --> 00:02:34,060
silicon is the convolution in the

63
00:02:40,140 --> 00:02:36,190

proterozoic bend your information church

64
00:02:42,090 --> 00:02:40,150
and the the black sail the open circle

65
00:02:44,940 --> 00:02:42,100
and the grip are indicated data from

66
00:02:47,490 --> 00:02:44,950
church and the black circle and the

67
00:02:49,860 --> 00:02:47,500
black bars indicate data from the

68
00:02:51,930 --> 00:02:49,870
depending on information so common

69
00:02:54,180 --> 00:02:51,940
observation is that the delta silicates

70
00:02:56,640 --> 00:02:54,190
30 venue in the independent our

71
00:02:59,070 --> 00:02:56,650
formation seems lower than the data

72
00:03:02,400 --> 00:02:59,080
recorded by the church even at the same

73
00:03:04,530 --> 00:03:02,410
time so it's still unclear why this is

74
00:03:06,120 --> 00:03:04,540
the case and maybe it's due to for a

75
00:03:08,070 --> 00:03:06,130
different fractionation factor

76
00:03:09,960 --> 00:03:08,080
associated with formation of these

77
00:03:12,600 --> 00:03:09,970
different type of rocks or due to

78
00:03:14,850 --> 00:03:12,610
different diagenesis so all this

79
00:03:17,130 --> 00:03:14,860
interpretation actually fundamentally

80
00:03:19,050 --> 00:03:17,140
depends on how well we know the

81
00:03:21,539 --> 00:03:19,060
fractionation in different eye on

82
00:03:23,729 --> 00:03:21,549
different systems so this study will

83
00:03:25,830 --> 00:03:23,739
just try to determine the fractionation

84
00:03:29,370 --> 00:03:25,840
factor between the acreage silica and

85
00:03:32,370 --> 00:03:29,380
our silica gel so the the method we use

86
00:03:34,740 --> 00:03:32,380
is called 3i stone method so basically

87
00:03:37,170 --> 00:03:34,750
this method involves ice tub exchange

88
00:03:40,470 --> 00:03:37,180

between two component one are in silica

89
00:03:43,140 --> 00:03:40,480
gel and one a quiz silica so for the

90
00:03:46,140 --> 00:03:43,150
folder are silica gel which has normal

91
00:03:49,319 --> 00:03:46,150
are silicon solution which falls on this

92
00:03:51,479 --> 00:03:49,329
mess dependent fractionation line so all

93
00:03:54,539 --> 00:03:51,489
natural sample should plot on this line

94
00:03:57,060 --> 00:03:54,549
but for another aqueous component we

95
00:04:00,420 --> 00:03:57,070
intentionally add some artificially

96
00:04:02,180 --> 00:04:00,430
enraged silica 29 spike so its

97
00:04:05,069 --> 00:04:02,190
completion just plot of this

98
00:04:07,229 --> 00:04:05,079
fractionation light up here so during

99
00:04:08,970 --> 00:04:07,239
the ice tub exchange the two component

100
00:04:10,800 --> 00:04:08,980
will gradually evolve together and

101
00:04:14,640 --> 00:04:10,810
finally reach the secondary

102
00:04:16,949 --> 00:04:14,650
fractionation line so a good cool thing

103
00:04:19,430 --> 00:04:16,959
about this technique it's one we sample

104
00:04:22,110 --> 00:04:19,440
at different time point we can actually

105
00:04:24,630 --> 00:04:22,120
extrapolate this partially exchange data

106
00:04:26,730 --> 00:04:24,640
point to a hundred percent exchange so

107
00:04:28,800 --> 00:04:26,740
this method actually guarantees do you

108
00:04:31,110 --> 00:04:28,810
get the the fractionation factor

109
00:04:34,680 --> 00:04:31,120
at a complete I silicone ice tub

110
00:04:36,930 --> 00:04:34,690
exchange between the two components so a

111
00:04:40,740 --> 00:04:36,940
little bit details about the experiment

112
00:04:44,220 --> 00:04:40,750
setup so I prepare the the silica 29

113
00:04:47,790 --> 00:04:44,230

spiked a quiz silica in a seawater like

114
00:04:49,530 --> 00:04:47,800
matrix which and try to mimic some some

115
00:04:52,140 --> 00:04:49,540
key feature of the ark in seawater

116
00:04:55,379 --> 00:04:52,150
including high silica concentration and

117
00:04:57,510 --> 00:04:55,389
low sulfate and no auction and the

118
00:04:59,310 --> 00:04:57,520
terminal species silica species in the

119
00:05:02,610 --> 00:04:59,320
aqueous as a monastery stochastic

120
00:05:05,969 --> 00:05:02,620
tetrahedra so silica concentration bow

121
00:05:08,000 --> 00:05:05,979
is about 1 million mo silica 29,000

122
00:05:10,980 --> 00:05:08,010
silica 29 because we spiked it with

123
00:05:14,820 --> 00:05:10,990
silica 29 and artificially in Rachel

124
00:05:18,210 --> 00:05:14,830
silica 29 so it has a venule close to

125
00:05:21,570 --> 00:05:18,220
100 per mil but Delta silica 30 was not

126
00:05:24,780 --> 00:05:21,580
affected by adding this 2029 slick spike

127
00:05:28,170 --> 00:05:24,790
so it has a kind of normal venues cloud

128
00:05:31,080 --> 00:05:28,180
20 per mil so I set up to comparative

129
00:05:33,480 --> 00:05:31,090
group of experiment and one group I just

130
00:05:35,520 --> 00:05:33,490
used the artificial seawater without any

131
00:05:38,340 --> 00:05:35,530
ferris oriental in the sea in the

132
00:05:41,100 --> 00:05:38,350
aqueous phase but for another group I

133
00:05:43,650 --> 00:05:41,110
just adding 1 million mole of a very

134
00:05:46,020 --> 00:05:43,660
fair of first iron in the in the aqueous

135
00:05:48,029 --> 00:05:46,030
phase in the aqueous phase because we

136
00:05:52,080 --> 00:05:48,039
know that our King seawater is kind of

137
00:05:54,480 --> 00:05:52,090
enraged in the in the in the fe 2 so

138
00:05:57,360 --> 00:05:54,490

each group of experiment contain

139
00:05:59,909 --> 00:05:57,370
actually contain to experiment so the

140
00:06:02,400 --> 00:05:59,919
solid phase is the amorphous Anna

141
00:06:04,980 --> 00:06:02,410
Ferrick silica gel as you can see from

142
00:06:08,010 --> 00:06:04,990
the figure here just a kind of amorphous

143
00:06:10,050 --> 00:06:08,020
cool stuff so the silicon atoms in this

144
00:06:12,420 --> 00:06:10,060
in this Joe is actually presenting

145
00:06:14,400 --> 00:06:12,430
different bounding environment silicon

146
00:06:16,860 --> 00:06:14,410
hydroxyl group silicon auction are

147
00:06:20,370 --> 00:06:16,870
inbound in silicon oxygen silicon not a

148
00:06:23,100 --> 00:06:20,380
network so the the are silica gel has

149
00:06:26,159 --> 00:06:23,110
normal siliconized to completion so both

150
00:06:29,400 --> 00:06:26,169
the Delta 29 silica powder silica 30 has

151
00:06:32,310 --> 00:06:29,410
0 per mil so the experiment was

152
00:06:35,430 --> 00:06:32,320
conducted at room temperature and pH new

153
00:06:37,649 --> 00:06:35,440
circum- mph and all the experiment was

154
00:06:40,260 --> 00:06:37,659
done in anaerobic chambers there is a

155
00:06:41,970 --> 00:06:40,270
free of oxygen which to prevent from

156
00:06:48,870 --> 00:06:41,980
prevent the oxidation

157
00:06:50,910 --> 00:06:48,880
fe to ya so here show some results so we

158
00:06:53,880 --> 00:06:50,920
can actually look at the the kinetics of

159
00:06:56,010 --> 00:06:53,890
the siliconix I study change between the

160
00:07:00,060 --> 00:06:56,020
two components by looking at Delta

161
00:07:03,690 --> 00:07:00,070
silica 29 so 442 group of extreme

162
00:07:05,790 --> 00:07:03,700
experiment you can see the the one color

163
00:07:07,680 --> 00:07:05,800

indicate data from the solid from the

164
00:07:10,200 --> 00:07:07,690
aqueous phase and the coat color

165
00:07:13,050 --> 00:07:10,210
indicator data from the from the solid

166
00:07:15,330 --> 00:07:13,060
phase so for both experiment you can see

167
00:07:17,640 --> 00:07:15,340
the the to compile data from two

168
00:07:19,320 --> 00:07:17,650
component just converge which indicate

169
00:07:23,580 --> 00:07:19,330
the ice tub exchange occurred between

170
00:07:27,930 --> 00:07:23,590
these two two components so so we can

171
00:07:30,780 --> 00:07:27,940
actually quantify sorry so we can

172
00:07:36,150 --> 00:07:30,790
actually quantify the extent of this I

173
00:07:39,030 --> 00:07:36,160
stop exchange of this I stock exchange

174
00:07:41,730 --> 00:07:39,040
relative to the equilibrium state so

175
00:07:45,090 --> 00:07:41,740
that's the earth manual as you can sure

176
00:07:47,670 --> 00:07:45,100
as you see here so we can see for the

177
00:07:50,010 --> 00:07:47,680
for the group without any first ironing

178
00:07:52,320 --> 00:07:50,020
in the art if you see water the the

179
00:07:56,040 --> 00:07:52,330
experiment reach about seventy percent I

180
00:08:00,780 --> 00:07:56,050
step exchange and after about 50 to 70

181
00:08:03,240 --> 00:08:00,790
days but for the for the group were

182
00:08:05,790 --> 00:08:03,250
using containing 1 million my affairs

183
00:08:07,590 --> 00:08:05,800
are in the artifice seawater in reach a

184
00:08:09,390 --> 00:08:07,600
higher percentage of I stock exchange

185
00:08:13,350 --> 00:08:09,400
reaching about eighty to ninety percent

186
00:08:15,690 --> 00:08:13,360
I stock exchange within the same amount

187
00:08:18,720 --> 00:08:15,700
of time so that suggests that the

188
00:08:20,700 --> 00:08:18,730

presence of fe to actually make the iso

189
00:08:23,580 --> 00:08:20,710
silicone ice tub exchange between two

190
00:08:27,570 --> 00:08:23,590
components faster so we can expand this

191
00:08:31,860 --> 00:08:27,580
by the fe 2 Fe 3 electron transfer Adam

192
00:08:34,170 --> 00:08:31,870
exchange interaction so imagine so

193
00:08:37,469 --> 00:08:34,180
imagine that's the our silica gel in the

194
00:08:39,810 --> 00:08:37,479
in the eggs to face and that stuff fe 2

195
00:08:42,690 --> 00:08:39,820
in the in the aqueous so when the f you

196
00:08:44,850 --> 00:08:42,700
to absorb on the solid so the electron

197
00:08:47,040 --> 00:08:44,860
from the one election from the f you too

198
00:08:50,340 --> 00:08:47,050
can actually moving into the solid and

199
00:08:52,380 --> 00:08:50,350
moving around so one fe 3 in the solid

200
00:08:54,199 --> 00:08:52,390
can eventually get this lecture and

201
00:08:56,239 --> 00:08:54,209
being reduced and

202
00:08:59,150 --> 00:08:56,249
then released back to the solution so

203
00:09:01,910 --> 00:08:59,160
this process actually leads to the

204
00:09:04,639 --> 00:09:01,920
breaking of silica are impounding so

205
00:09:07,189 --> 00:09:04,649
that's a potential way to accelerate the

206
00:09:10,579 --> 00:09:07,199
silica is the exchange between the

207
00:09:12,499 --> 00:09:10,589
aqueous and solid so we can also look at

208
00:09:15,199 --> 00:09:12,509
the natural fractionation between the

209
00:09:18,379 --> 00:09:15,209
solid and the aqueous by luke and outer

210
00:09:20,569 --> 00:09:18,389
silica 30 venues the same the warm color

211
00:09:23,179 --> 00:09:20,579
indicate data from the from the aqueous

212
00:09:26,449 --> 00:09:23,189
and the code color indicate data from

213
00:09:29,359 --> 00:09:26,459

the solid so we can from both experiment

214
00:09:31,429 --> 00:09:29,369
we can see the the heavy silicon stir

215
00:09:34,460 --> 00:09:31,439
preferentially goes to the a quest and

216
00:09:37,069 --> 00:09:34,470
the device silica preferentially goes to

217
00:09:40,280 --> 00:09:37,079
solid and we can see the two data point

218
00:09:42,710 --> 00:09:40,290
the two curve just diverge so that's

219
00:09:44,900 --> 00:09:42,720
indicated fractionation cup between the

220
00:09:47,960 --> 00:09:44,910
two component and we can extrapolate

221
00:09:50,030 --> 00:09:47,970
this partially exchange data to a

222
00:09:53,419 --> 00:09:50,040
hundred percent exchange so that will

223
00:09:55,669 --> 00:09:53,429
give us the fractionation factor so for

224
00:09:58,220 --> 00:09:55,679
the for the experiment without any in

225
00:10:01,280 --> 00:09:58,230
first iron in in the April's we've got a

226
00:10:05,299 --> 00:10:01,290
fractionation factors about a minus 2.3

227
00:10:07,819 --> 00:10:05,309
pml but for the experiment containing Fe

228
00:10:10,759 --> 00:10:07,829
2 in the APIs we've got slightly larger

229
00:10:14,269 --> 00:10:10,769
fractionation factor at minus 3.2 per

230
00:10:16,879 --> 00:10:14,279
mil so we can compare our results with

231
00:10:20,030 --> 00:10:16,889
some previous studies so this great

232
00:10:22,669 --> 00:10:20,040
that's just a fractionation factor

233
00:10:25,579 --> 00:10:22,679
determined and during the precipitation

234
00:10:28,400 --> 00:10:25,589
of pure silica silica gel from

235
00:10:31,900 --> 00:10:28,410
relatively pure oversaturated silica

236
00:10:34,100 --> 00:10:31,910
solution and as you can see our error

237
00:10:35,419 --> 00:10:34,110
fractionation factor is larger than

238
00:10:38,090 --> 00:10:35,429

those previously determined

239
00:10:40,789 --> 00:10:38,100
fractionation factors so we can also

240
00:10:43,400 --> 00:10:40,799
expand that by electron donation theory

241
00:10:45,859 --> 00:10:43,410
so some theoretical calculations

242
00:10:48,109 --> 00:10:45,869
indicate the fraction that the magnitude

243
00:10:49,970 --> 00:10:48,119
of silica isotope fractionation actually

244
00:10:53,329 --> 00:10:49,980
depends on the overall the average

245
00:10:56,030 --> 00:10:53,339
silicon auction bond strength and so the

246
00:10:58,160 --> 00:10:56,040
weights a weaker the silicon oxygen the

247
00:11:00,470 --> 00:10:58,170
average silicon oxygen bound the larger

248
00:11:02,329 --> 00:11:00,480
the fractionation factor will be so

249
00:11:05,030 --> 00:11:02,339
different atom can be characterized by

250
00:11:06,950 --> 00:11:05,040
these electronegativity values which is

251
00:11:09,230 --> 00:11:06,960
a measure for the tendency that

252
00:11:12,650 --> 00:11:09,240
Adam attract the electron towards itself

253
00:11:15,440 --> 00:11:12,660
so if there's a cat I'm presenting the

254
00:11:17,390 --> 00:11:15,450
the in the system if the qatar has an

255
00:11:20,300 --> 00:11:17,400
election activity value lower than the

256
00:11:22,490 --> 00:11:20,310
silica that means that there will share

257
00:11:24,590 --> 00:11:22,500
more election to this oxygen so that

258
00:11:26,750 --> 00:11:24,600
will shorten this silicon action bound

259
00:11:29,180 --> 00:11:26,760
by the same time that will lengthening

260
00:11:31,700 --> 00:11:29,190
the other three silica action bank so

261
00:11:35,630 --> 00:11:31,710
the overall the average silicon ocean

262
00:11:37,970 --> 00:11:35,640
bound energy will decrease so so so for

263
00:11:41,300 --> 00:11:37,980

our experiment we have learned here so

264
00:11:43,610 --> 00:11:41,310
so that's the that's the reason why the

265
00:11:46,130 --> 00:11:43,620
presence of aren't actually lower the

266
00:11:48,710 --> 00:11:46,140
average silicon oxygen bounding that

267
00:11:50,900 --> 00:11:48,720
leads to larger fractionation factors so

268
00:11:53,090 --> 00:11:50,910
the fe 2 has an activity

269
00:11:56,300 --> 00:11:53,100
electronegativity value even lower than

270
00:11:59,060 --> 00:11:56,310
the fe 3 so the effect of fe 2 in

271
00:12:00,710 --> 00:11:59,070
weakening this RN silica in the silica

272
00:12:02,720 --> 00:12:00,720
action bounding is the stronger than

273
00:12:04,910 --> 00:12:02,730
they feed three so that's why we see

274
00:12:08,900 --> 00:12:04,920
even larger fractionation in the fu two

275
00:12:11,360 --> 00:12:08,910
in fe 2 system so if you still remember

276
00:12:14,480 --> 00:12:11,370
those two figure just show you earlier

277
00:12:15,500 --> 00:12:14,490
so our experiment seems suggests that

278
00:12:18,070 --> 00:12:15,510
there are actually different

279
00:12:21,890 --> 00:12:18,080
fractionation factor associated with

280
00:12:24,200 --> 00:12:21,900
precipitation of pure silica as you can

281
00:12:26,300 --> 00:12:24,210
see from this church sample represented

282
00:12:29,120 --> 00:12:26,310
by this church samples and larger

283
00:12:31,490 --> 00:12:29,130
fractionation associated with this bend

284
00:12:34,160 --> 00:12:31,500
your information samples so maybe that's

285
00:12:37,640 --> 00:12:34,170
why we see lower venues in this in this

286
00:12:40,190 --> 00:12:37,650
spending our information so just to

287
00:12:42,830 --> 00:12:40,200
conclude so our experiments suggest the

288
00:12:45,080 --> 00:12:42,840

first provide first evidence for the fe

289
00:12:47,540 --> 00:12:45,090
to catalyze the siliconized of exchange

290
00:12:49,280 --> 00:12:47,550
and we determine the clipper and

291
00:12:52,070 --> 00:12:49,290
fractionation factor between the iron

292
00:12:55,220 --> 00:12:52,080
silica gel and the quests silica is

293
00:12:57,590 --> 00:12:55,230
about the at two or three per ml and the

294
00:12:59,720 --> 00:12:57,600
presence of fe to actually leads to two

295
00:13:01,970 --> 00:12:59,730
larger fractionation factor so our

296
00:13:04,010 --> 00:13:01,980
experiment kind of suggests the early

297
00:13:06,860 --> 00:13:04,020
diagenetic process and the formation of

298
00:13:10,520 --> 00:13:06,870
these different rock types actually play

299
00:13:13,070 --> 00:13:10,530
a major role in in in the delta celica

300
00:13:19,400 --> 00:13:13,080
30 venules actually proceed preserved in