1
00:00:11,419 --> 00:00:09,589
and so I gave this talk last year but

2
00:00:14,270 --> 00:00:11,429
now with a thousand percent more results

3
00:00:16,310 --> 00:00:14,280
in conclusions so yes this is the

4
00:00:18,380 --> 00:00:16,320
potential photochemical origins of

5
00:00:22,310 --> 00:00:18,390
banded iron formations I'm Parker

6
00:00:24,980 --> 00:00:22,320
casselberry at ASU so first banded iron

7
00:00:27,470 --> 00:00:24,990
formations there are large sedimentary

8
00:00:32,359 --> 00:00:27,480
deposits of iron oxide by large I mean

9
00:00:34,760 --> 00:00:32,369
trillions of tons these are laser these

10
00:00:37,190 --> 00:00:34,770
are very pretty ones in Western

11
00:00:41,350 --> 00:00:37,200
Australia and they're alternating layers

12
00:00:44,720 --> 00:00:41,360
of high iron and low iron minerals and

13
00:00:46,880 --> 00:00:44,730

they're thought to be formed by oxygen

14
00:00:49,639 --> 00:00:46,890
oxidizing iron in seawater that

15
00:00:56,209 --> 00:00:49,649
precipitates and the thought for this

16
00:00:58,639 --> 00:00:56,219
comes from if you look at oxygen levels

17
00:01:01,040 --> 00:00:58,649
in the atmosphere over time and biff

18
00:01:03,470 --> 00:01:01,050
relative abundance they correlate well

19
00:01:06,859 --> 00:01:03,480
there's a lot of this deposited right

20
00:01:09,280 --> 00:01:06,869
around the great oxidation event but

21
00:01:12,380 --> 00:01:09,290
there are some alternatives proposed

22
00:01:15,380 --> 00:01:12,390
there's photo Pharaoh trophy which is a

23
00:01:17,899 --> 00:01:15,390
biological process it's type of an

24
00:01:21,020 --> 00:01:17,909
oxygen acronis asst that directly

25
00:01:22,880 --> 00:01:21,030
oxidizes iron and experiments and

26
00:01:25,190 --> 00:01:22,890
modeling have shown that you could

27
00:01:28,190 --> 00:01:25,200
generate enough oxidized iron to make

28
00:01:31,179 --> 00:01:28,200
Biff's with this and that is a beautiful

29
00:01:34,429 --> 00:01:31,189
lake where photo photography is studied

30
00:01:36,590 --> 00:01:34,439
but there's another idea that is

31
00:01:40,280 --> 00:01:36,600
photooxidation this is a completely

32
00:01:42,679 --> 00:01:40,290
abiotic process and it's ultraviolet

33
00:01:45,499 --> 00:01:42,689
light turning iron 2 into iron 3 and

34
00:01:49,700 --> 00:01:45,509
this is a cartoon I have somewhat

35
00:01:51,859 --> 00:01:49,710
abstracted mechanistic details so you

36
00:01:54,190 --> 00:01:51,869
have an ultraviolet photon from the Sun

37
00:01:59,090 --> 00:01:54,200
hits an iron two species in sea water

38
00:02:03,560 --> 00:01:59,100

turns it into iron hydroxide and then

39
00:02:06,170 --> 00:02:03,570
that will precipitate soluble and then

40
00:02:09,729 --> 00:02:06,180
over time that is transformed into Biff

41
00:02:12,890 --> 00:02:09,739
minerals like hematite and magnetite and

42
00:02:13,790 --> 00:02:12,900
the implication here is that as I said

43
00:02:16,850 --> 00:02:13,800
this is an a

44
00:02:20,360 --> 00:02:16,860
biotic process so you don't need oxygen

45
00:02:23,720 --> 00:02:20,370
or even biological activity so are these

46
00:02:27,740 --> 00:02:23,730
bits that we're seeing really signs of

47
00:02:30,400 --> 00:02:27,750
oxygen in our life or neither so

48
00:02:33,860 --> 00:02:30,410
previous work has been done testing this

49
00:02:36,650 --> 00:02:33,870
in 1983 brighter min at all used a

50
00:02:39,770 --> 00:02:36,660
mercury lamp and they observed reactions

51
00:02:44,570 --> 00:02:39,780
using filters for long wavelengths over

52
00:02:47,420 --> 00:02:44,580
400 nanometers that's in the visible not

53
00:02:49,790 --> 00:02:47,430
even in the UV so that led them to

54
00:02:51,860 --> 00:02:49,800
believe that this iron species feo h+

55
00:02:54,770 --> 00:02:51,870
was responsible because it has

56
00:02:59,170 --> 00:02:54,780
absorbance going out to almost 450

57
00:03:02,710 --> 00:02:59,180
nanometers and this is important because

58
00:03:07,340 --> 00:03:02,720
so this is the solar radiation spectrum

59
00:03:11,600 --> 00:03:07,350
and here's the UV so the earth had no

60
00:03:13,880 --> 00:03:11,610
ozone back then so it was somewhat

61
00:03:18,410 --> 00:03:13,890
proximate to this top of atmosphere

62
00:03:22,010 --> 00:03:18,420
spectrum there and so if you have feo h+

63
00:03:23,900 --> 00:03:22,020

it absorbs a huge region of UV and

64
00:03:26,449 --> 00:03:23,910
getting into the visible where there's a

65
00:03:28,070 --> 00:03:26,459
lot more radiation as one of my

66
00:03:32,930 --> 00:03:28,080
professor said that's the meaty part of

67
00:03:35,930 --> 00:03:32,940
the solar spectrum and Francois took

68
00:03:37,580 --> 00:03:35,940
these results ran with them and made

69
00:03:42,110 --> 00:03:37,590
notion model calculated a mass

70
00:03:44,479 --> 00:03:42,120
cumulation rate and he got about an

71
00:03:48,590 --> 00:03:44,489
order of magnitude more than an

72
00:03:52,600 --> 00:03:48,600
estimated natural rate for a bit so that

73
00:03:57,740 --> 00:03:52,610
led people to conclude this is plausible

74
00:04:00,699 --> 00:03:57,750
but I went back to re-examine this so I

75
00:04:03,790 --> 00:04:00,709
used a quartz reactor with ports for

76
00:04:06,050 --> 00:04:03,800
flowing gas inventing drawing samples

77
00:04:10,009 --> 00:04:06,060
continuously purged with nitrogen co2

78
00:04:13,310 --> 00:04:10,019
gas which 2% co2 is not unreasonable for

79
00:04:16,250 --> 00:04:13,320
the archaean and that's to keep oxygen

80
00:04:19,880 --> 00:04:16,260
out because this is extremely sensitive

81
00:04:22,880 --> 00:04:19,890
doxygen solution was deoxygenated di

82
00:04:27,230 --> 00:04:22,890
water sodium chloride iron and

83
00:04:31,100 --> 00:04:27,240
bicarbonate so this is what I saw

84
00:04:35,390 --> 00:04:31,110
24 hours and in the bottom there are

85
00:04:37,400 --> 00:04:35,400
those kind of orange precipitates Raman

86
00:04:39,499 --> 00:04:37,410
spectroscopy identified those as lipid

87
00:04:44,960 --> 00:04:39,509
ocurro site which is consistent with the

88
00:04:46,760 --> 00:04:44,970

earlier work so then though well the

89
00:04:52,939 --> 00:04:46,770
mercury lamp poorly matches the solar

90
00:04:55,219 --> 00:04:52,949
spectrum it has all these peaks and so I

91
00:04:57,890 --> 00:04:55,229
used a solar simulator as a light source

92
00:05:01,189 --> 00:04:57,900
which is a Zeon arc lamp and special

93
00:05:04,999 --> 00:05:01,199
filters to match the solar spectrum but

94
00:05:09,830 --> 00:05:05,009
if you feo h+ is absorbing then i should

95
00:05:13,730 --> 00:05:09,840
observe a reaction so this is the dark

96
00:05:16,510 --> 00:05:13,740
control no precipitation this iron was

97
00:05:19,219 --> 00:05:16,520
measured on quadrupole icp-ms and

98
00:05:21,230 --> 00:05:19,229
everything was ratio to sodium to

99
00:05:25,430 --> 00:05:21,240
correct for any evaporation because

100
00:05:28,370 --> 00:05:25,440
these experiments took days and dramatic

101
00:05:34,580 --> 00:05:28,380
pause solar simulator also showed

102
00:05:41,390 --> 00:05:34,590
nothing no reaction over 46 hours this

103
00:05:43,939 --> 00:05:41,400
was quite puzzling but the mercury lamp

104
00:05:48,560 --> 00:05:43,949
and the solar simulator have extremely

105
00:05:54,409 --> 00:05:48,570
different spectra so there's just a few

106
00:05:57,290 --> 00:05:54,419
slight differences so what I did is to

107
00:05:59,120 --> 00:05:57,300
test the wavelength dependence you know

108
00:06:02,209 --> 00:05:59,130
which of these differences is important

109
00:06:04,879 --> 00:06:02,219
I performed an experiment using the

110
00:06:08,469 --> 00:06:04,889
mercury lamp and light filters it was

111
00:06:10,879 --> 00:06:08,479
one continuous experiment and

112
00:06:14,629 --> 00:06:10,889
periodically swapping out light filters

113
00:06:16,909 --> 00:06:14,639

and so if I change light filters and saw

114
00:06:23,209 --> 00:06:16,919
a reaction oh that's the wavelength that

115
00:06:26,390 --> 00:06:23,219
caused it so to begin I started with no

116
00:06:31,850 --> 00:06:26,400
light dark control and so I know our

117
00:06:34,370 --> 00:06:31,860
precipitation okay good and then light

118
00:06:37,760 --> 00:06:34,380
longer than 400 nanometers also showed

119
00:06:39,629 --> 00:06:37,770
no effect this is different than what

120
00:06:42,809 --> 00:06:39,639
Khan house are observed or

121
00:06:44,610 --> 00:06:42,819
not seem brighter Minh there's another

122
00:06:48,689 --> 00:06:44,620
paper con Howser that does agree with

123
00:06:51,420 --> 00:06:48,699
this and then light longer than three

124
00:06:53,519 --> 00:06:51,430
hundred and forty five nanometers also

125
00:07:00,269 --> 00:06:53,529
showed no effect so that is getting down

126
00:07:02,309 --> 00:07:00,279
into the UV and then boom 295 2 340 5

127
00:07:06,469 --> 00:07:02,319
nanometers cause significant iron

128
00:07:09,510 --> 00:07:06,479
precipitation in a couple days and then

129
00:07:14,339 --> 00:07:09,520
the full spectrum didn't actually show

130
00:07:16,409 --> 00:07:14,349
an increased rate so I can conclude oh

131
00:07:20,939 --> 00:07:16,419
and precipitation stopped when the light

132
00:07:25,860 --> 00:07:20,949
was turned off just to make sure so I

133
00:07:28,409 --> 00:07:25,870
can conclude that mid UV so 345

134
00:07:35,579 --> 00:07:28,419
nanometers or so is what's causing this

135
00:07:37,439 --> 00:07:35,589
reaction and then so what I did is using

136
00:07:40,950 --> 00:07:37,449
this new wavelength dependence that I

137
00:07:44,010 --> 00:07:40,960
found I went back to the old models

138
00:07:46,469 --> 00:07:44,020

where you calculated it using only that

139
00:07:50,279 --> 00:07:46,479
region that I observed and not the

140
00:07:54,390 --> 00:07:50,289
long-wavelength where you have all of

141
00:07:59,189 --> 00:07:54,400
the higher solar radiation and I

142
00:08:01,709 --> 00:07:59,199
calculated rates that are 6 250 4

143
00:08:03,570 --> 00:08:01,719
milligrams of iron per square centimeter

144
00:08:06,540 --> 00:08:03,580
per year depending on the concentration

145
00:08:08,129 --> 00:08:06,550
of iron too there's a lot of

146
00:08:10,679 --> 00:08:08,139
uncertainties and assumptions that went

147
00:08:14,279 --> 00:08:10,689
into this but that's just to get kind of

148
00:08:17,010 --> 00:08:14,289
a rough estimate and like i said i'm

149
00:08:21,059 --> 00:08:17,020
missing the longer wave absorbance here

150
00:08:23,999 --> 00:08:21,069
so this is five times less than previous

151
00:08:28,980 --> 00:08:24,009
models five times slower but it actually

152
00:08:34,110 --> 00:08:28,990
still compares favorably to estimated

153
00:08:36,060 --> 00:08:34,120
natural rates but looking at I talked

154
00:08:39,870 --> 00:08:36,070
about those alternative theories like

155
00:08:42,269 --> 00:08:39,880
photo Farrah trophy foto para trophy

156
00:08:45,930 --> 00:08:42,279
there's actually you can get numbers of

157
00:08:50,120 --> 00:08:45,940
around 500 milligrams per centimeter per

158
00:08:54,020 --> 00:08:50,130
year for similar iron concentrations

159
00:08:58,480 --> 00:08:54,030
so I can conclude here that I

160
00:09:01,220 --> 00:08:58,490
reevaluated iron photooxidation and

161
00:09:05,120 --> 00:09:01,230
found it sensitive to wavelengths

162
00:09:09,290 --> 00:09:05,130
between 295 and 345 nanometers it

163
00:09:13,610 --> 00:09:09,300

results in photooxidation rates 56 times

164
00:09:16,250 --> 00:09:13,620
slower for a predicted model and so if

165
00:09:19,190 --> 00:09:16,260
photo Farrah trophy was around or like

166
00:09:21,920 --> 00:09:19,200
oxygen for moxa net photosynthesis that

167
00:09:25,370 --> 00:09:21,930
would likely outpace this process but

168
00:09:32,840 --> 00:09:25,380
this still is possible in the absence of

169
00:09:35,030 --> 00:09:32,850
any biology at all so questions actually

170
00:09:39,440 --> 00:09:35,040
I have some time so I can talk a little

171
00:09:42,440 --> 00:09:39,450
bit about future work I said I had

172
00:09:44,420 --> 00:09:42,450
dissolved carbonate in there another

173
00:09:47,300 --> 00:09:44,430
thing I've been wanting to test

174
00:09:50,060 --> 00:09:47,310
different additives to this thing's have

175
00:09:52,270 --> 00:09:50,070
redox interactions with the iron also

176
00:09:54,740 --> 00:09:52,280
the effects of dissolved organic carbon

177
00:09:56,960 --> 00:09:54,750
because I could see a photo reduction

178
00:10:00,170 --> 00:09:56,970
which is what happens a lot in modern

179
00:10:01,760 --> 00:10:00,180
systems so I might actually get some

180
00:10:07,340 --> 00:10:01,770
filtered sea water and do experiments

181
00:10:09,140 --> 00:10:07,350
with that and then after this there's

182
00:10:19,630 --> 00:10:09,150
other things I could look at

183
00:10:27,340 --> 00:10:22,390
and I do have time for questions okay

184
00:10:29,380 --> 00:10:27,350
didn't even have to ask so I had a

185
00:10:33,640 --> 00:10:29,390
question about your relative xenon arc

186
00:10:35,290 --> 00:10:33,650
lamp and it's mercury so um I mean xenon

187
00:10:37,690 --> 00:10:35,300
arc lamps have a lot of output in that

188
00:10:40,480 --> 00:10:37,700

same near UV range that you're you're

189
00:10:42,610 --> 00:10:40,490
looking at so what is the like wattage

190
00:10:44,500 --> 00:10:42,620
of your various lamps like is it just

191
00:10:45,910 --> 00:10:44,510
coming from a difference there cuz if

192
00:10:53,220 --> 00:10:45,920
you look at the spectra using it on our

193
00:11:01,270 --> 00:10:58,120
referring to here yeah yeah um the

194
00:11:06,490 --> 00:11:01,280
wattage it was 300 watts okay I mean mu

195
00:11:09,580 --> 00:11:06,500
I guess my question is um the xenon arc

196
00:11:11,350 --> 00:11:09,590
lamps you know have a lot of energy in

197
00:11:13,510 --> 00:11:11,360
that range too so maybe it's just a

198
00:11:18,220 --> 00:11:13,520
power issue with why you weren't seeing

199
00:11:22,600 --> 00:11:18,230
it it's a power issue um I also I have

200
00:11:27,220 --> 00:11:22,610
ideas the air mass filter that I put on

201
00:11:29,110 --> 00:11:27,230
this because that corrects for more of

202
00:11:33,270 --> 00:11:29,120
the longer wavelengths that I was

203
00:11:39,880 --> 00:11:37,780
yeah is actually having some absorbance

204
00:11:44,920 --> 00:11:39,890
right in this region cutting down on the

205
00:11:47,170 --> 00:11:44,930
xenon arc spectrum so essentially the

206
00:11:49,180 --> 00:11:47,180
air mass filter for a solar simulator

207
00:11:53,980 --> 00:11:49,190
might not actually be the best solar

208
00:11:56,110 --> 00:11:53,990
simulator for these UV wavelengths but

209
00:11:57,790 --> 00:11:56,120
yeah I'm thinking about doing that also

210
00:12:03,040 --> 00:11:57,800
talked about getting a deuterium arc

211
00:12:08,490 --> 00:12:03,050
lamp for a I guess consistent UV

212
00:12:11,210 --> 00:12:08,500
spectrum longer wave or shorter wave but

213
00:12:15,330 --> 00:12:11,220

yes

214
00:12:18,000 --> 00:12:15,340
I was wondering so the solar spectrum

215
00:12:21,660 --> 00:12:18,010
that you're showing here is this for

216
00:12:23,340 --> 00:12:21,670
acquiescence Sun or like a flaring Sun

217
00:12:24,690 --> 00:12:23,350
or this is my solar simulator right

218
00:12:28,980 --> 00:12:24,700
right but it's supposed to simulate

219
00:12:31,800 --> 00:12:28,990
aqueous and yes fun okay i guess i'm

220
00:12:37,110 --> 00:12:31,810
just wondering since you know the Sun

221
00:12:46,800 --> 00:12:37,120
does his evolution that is one of my

222
00:12:50,390 --> 00:12:46,810
favorite questions there we go so here

223
00:12:54,180 --> 00:12:50,400
is the evolution of the solar spectrum

224
00:12:56,700 --> 00:12:54,190
and while the solar simulator didn't

225
00:13:00,810 --> 00:12:56,710
take this into account I actually took

226
00:13:04,590 --> 00:13:00,820
this into account in my models but the

227
00:13:08,430 --> 00:13:04,600
Sun was in 20 25 30 percent fainter

228
00:13:11,070 --> 00:13:08,440
early in its history so this is photon

229
00:13:13,110 --> 00:13:11,080
flux and the black is the modern

230
00:13:16,830 --> 00:13:13,120
spectrum and then these are different

231
00:13:18,720 --> 00:13:16,840
ages for the Sun so 100 million years

232
00:13:23,550 --> 00:13:18,730
700 million years and 2 billion years

233
00:13:25,470 --> 00:13:23,560
old and the interesting thing is that

234
00:13:28,980 --> 00:13:25,480
because I heard a lot of theories well

235
00:13:32,370 --> 00:13:28,990
the Sun was brighter in the UV but

236
00:13:34,950 --> 00:13:32,380
actually that is true but only for

237
00:13:39,240 --> 00:13:34,960
wavelengths under 200 nanometers which

238
00:13:41,480 --> 00:13:39,250

aren't of interest for this reaction so

239
00:13:45,870 --> 00:13:41,490
they're generated by different processes

240
00:13:50,730 --> 00:13:45,880
so does that answer question i think i'm

241
00:13:52,410 --> 00:13:50,740
referring more to the solar cycle so oh

242
00:14:00,430 --> 00:13:52,420
I thinks i see i see how you get on

243
00:14:08,030 --> 00:14:06,440
more questions so given the timing of

244
00:14:10,550 --> 00:14:08,040
biff deposits that we see in the rock

245
00:14:13,070 --> 00:14:10,560
record how much of a contribution do you

246
00:14:14,630 --> 00:14:13,080
think this photo-oxidation had on those

247
00:14:24,350 --> 00:14:14,640
formation of you know real world

248
00:14:30,970 --> 00:14:24,360
deposits right actually as i scroll back

249
00:14:34,190 --> 00:14:30,980
through all my slides yeah so I mean

250
00:14:41,140 --> 00:14:34,200
what i think is entirely possible is

251
00:14:44,030 --> 00:14:41,150
that things like older Biff's here were

252
00:14:47,810 --> 00:14:44,040
deposited by photochemistry and then if

253
00:14:50,720 --> 00:14:47,820
at some point photo farah trophy evolved

254
00:14:54,110 --> 00:14:50,730
or accidental photosynthesis then that

255
00:14:55,850 --> 00:14:54,120
is what caused this huge increase so

256
00:14:58,580 --> 00:14:55,860
there might be some background of

257
00:15:11,570 --> 00:14:58,590
photochemistry and then on top of that a

258
00:15:13,400 --> 00:15:11,580
large biogenic signal okay i am not at

259
00:15:14,990 --> 00:15:13,410
all very familiar with photo chemistry

260
00:15:18,140 --> 00:15:15,000
so I have a very basic question for you

261
00:15:20,840 --> 00:15:18,150
um in foot in the photooxidation of the

262
00:15:24,470 --> 00:15:20,850
reduced iron where is the oxygen coming

263
00:15:27,080 --> 00:15:24,480

from the oxen oh so you're saying is it

264
00:15:29,570 --> 00:15:27,090
like dissolved carbonate that oxygen

265
00:15:33,890 --> 00:15:29,580
yeah that oxygen come from water

266
00:15:35,900 --> 00:15:33,900
actually the oxidized iron takes a

267
00:15:49,770 --> 00:15:35,910
nearby water molecule and is like gimme

268
00:15:57,190 --> 00:15:55,930
so since the UM oh um the OA chums from

269
00:16:02,020 --> 00:15:57,200
the water don't you get a build up of

270
00:16:05,530 --> 00:16:02,030
hydrogen gas that's reducing well you

271
00:16:08,500 --> 00:16:05,540
get hydrogen gas yes but actually this

272
00:16:10,600 --> 00:16:08,510
is in the ocean and it actually escaped

273
00:16:13,870 --> 00:16:10,610
and goes into the app so in your setup

274
00:16:15,880 --> 00:16:13,880
it's not an ocean it's smaller so what

275
00:16:17,890 --> 00:16:15,890
what does what do you do with the

276
00:16:19,960 --> 00:16:17,900
hydrogen nuts well I'm continuously

277
00:16:22,390 --> 00:16:19,970
flowing gas through my experiment oh so

278
00:16:26,170 --> 00:16:22,400
there's an in and out yes oh um in fact

279
00:16:28,690 --> 00:16:26,180
I didn't talk about it but I didn't talk

280
00:16:31,630 --> 00:16:28,700
about a gas flow rate but i'm actually

281
00:16:34,870 --> 00:16:31,640
at 500 milliliters per minute I have a

282
00:16:37,300 --> 00:16:34,880
huge doer of liquid nitrogen to keep

283
00:16:39,640 --> 00:16:37,310
this experiment going okay I have tried

284
00:16:43,300 --> 00:16:39,650
lower flow rates but oxygen actually

285
00:16:46,720 --> 00:16:43,310
defuses in because a few i calculated a

286
00:16:49,470 --> 00:16:46,730
few ppm oxygen will give me oxidation

287
00:16:55,540 --> 00:16:49,480
rates that I observed with the lights

288
00:16:59,520 --> 00:16:55,550

okay so um just maybe this may be a

289
00:17:01,960 --> 00:16:59,530
mother geological question along it so

290
00:17:03,730 --> 00:17:01,970
due to the fact I guess there's certain

291
00:17:05,410 --> 00:17:03,740
period of time where parts of the rocky

292
00:17:06,760 --> 00:17:05,420
mountains were actually underwater so is

293
00:17:10,150 --> 00:17:06,770
this actually how they're getting the

294
00:17:14,520 --> 00:17:10,160
the the bands on certain rock formations

295
00:17:20,440 --> 00:17:14,530
that are actually are on land today hmm

296
00:17:31,280 --> 00:17:23,990
but I mean yeah I'm not sure about