432: PCE_3 Presents Origins, Inventories & Geologic Settings of the Building Blocks of Life IV

1
00:00:05,269 --> 00:00:02,070
all right so we're going to go ahead and

2
00:00:07,190 --> 00:00:05,279
get started uh welcome to this session

3
00:00:09,030 --> 00:00:07,200
this is the prebiotic chemistry and

4
00:00:10,950 --> 00:00:09,040
early earth environment session on the

5
00:00:13,030 --> 00:00:10,960
origins inventories and geologic

6
00:00:14,870 --> 00:00:13,040
settings of the building blocks of life

7
00:00:16,870 --> 00:00:14,880
we're your session chairs i'm lori barge

8
00:00:18,870 --> 00:00:16,880
from nasa jpl and this is danielle

9
00:00:20,630 --> 00:00:18,880
simkis from nasa goddard

10
00:00:24,790 --> 00:00:20,640
and so then introducing our first

11
00:00:29,109 --> 00:00:26,550
thank you very much

12
00:00:31,429 --> 00:00:29,119
i hope you'll hear and see my

13
00:00:33,110 --> 00:00:31,439

presentation

14
00:00:36,630 --> 00:00:33,120
so this is uh

15
00:00:38,869 --> 00:00:36,640
this is my abs icon talk uh welcome to

16
00:00:41,030 --> 00:00:38,879
to this presentation uh titled the

17
00:00:42,229 --> 00:00:41,040
effects of geological and environmental

18
00:00:44,549 --> 00:00:42,239
conditions

19
00:00:46,389 --> 00:00:44,559
on the rise of probiotic peptides on

20
00:00:49,029 --> 00:00:46,399
mineral surfaces

21
00:00:51,110 --> 00:00:49,039
uh i'm thomas lostoler a phd candidate i

22
00:00:53,830 --> 00:00:51,120
work at roger boshkovich institute in

23
00:00:55,029 --> 00:00:53,840
croatia here are my contact details and

24
00:00:57,670 --> 00:00:55,039
i thank

25
00:01:00,790 --> 00:00:57,680
all co-authors with whom i worked on

26
00:01:06,070 --> 00:01:01,590
so

27
00:01:08,469 --> 00:01:06,080
the importance of prebiotic peptides

28
00:01:10,550 --> 00:01:08,479
in a probiotic world is obvious it is

29
00:01:13,590 --> 00:01:10,560
hypothesized that they were included in

30
00:01:14,630 --> 00:01:13,600
molecular symbiosis with nucleic acids

31
00:01:17,190 --> 00:01:14,640
and

32
00:01:18,390 --> 00:01:17,200
they have really important catalytic

33
00:01:19,910 --> 00:01:18,400
properties

34
00:01:22,830 --> 00:01:19,920
there are different literature

35
00:01:25,590 --> 00:01:22,840
approaches on how to synthesize

36
00:01:28,070 --> 00:01:25,600
oligopeptides and they mostly uh

37
00:01:30,789 --> 00:01:28,080
understandably so rely on

38
00:01:33,350 --> 00:01:30,799

reactions in aqueous solutions

39
00:01:36,310 --> 00:01:33,360
however from a thermodynamic standpoint

40
00:01:38,630 --> 00:01:36,320
condensation of free amino acids

41
00:01:40,390 --> 00:01:38,640
in aqueous solution is thermodynamically

42
00:01:42,550 --> 00:01:40,400
unfavorable process

43
00:01:44,950 --> 00:01:42,560
and here i would refer to everett

44
00:01:47,830 --> 00:01:44,960
shock's talk at apps icon

45
00:01:49,510 --> 00:01:47,840
when he said that when seeking a biotic

46
00:01:53,030 --> 00:01:49,520
organic synthesis

47
00:01:54,550 --> 00:01:53,040
we should stop fighting thermodynamics

48
00:01:56,389 --> 00:01:54,560
if we do that if we stop fighting

49
00:01:58,950 --> 00:01:56,399
thermodynamics we would have to move

50
00:02:01,429 --> 00:01:58,960
away from aqueous solutions

51
00:02:03,830 --> 00:02:01,439
and we would end up in dry environments

52
00:02:05,030 --> 00:02:03,840
so the availability of dry land on

53
00:02:06,950 --> 00:02:05,040
prebiotic

54
00:02:09,430 --> 00:02:06,960
earth is often discussed

55
00:02:11,350 --> 00:02:09,440
but it is considered that there was some

56
00:02:12,630 --> 00:02:11,360
land available on the emerging

57
00:02:15,510 --> 00:02:12,640
continents

58
00:02:18,470 --> 00:02:15,520
and near volcanoes

59
00:02:20,150 --> 00:02:18,480
if you want to do uh organic synthesis

60
00:02:22,949 --> 00:02:20,160
in the solid state

61
00:02:25,190 --> 00:02:22,959
uh probably uh one of the best options

62
00:02:28,309 --> 00:02:25,200
would be to use a mechanochemist

63
00:02:30,869 --> 00:02:28,319

mechanochemistry is a very uh vibrant

64
00:02:33,030 --> 00:02:30,879
research research field

65
00:02:35,670 --> 00:02:33,040
that is compliant with the principles of

66
00:02:39,030 --> 00:02:35,680
green chemistry it uses mechanical

67
00:02:41,670 --> 00:02:39,040
activation to induce chemical reactivity

68
00:02:44,550 --> 00:02:41,680
in the absence of solvents

69
00:02:47,190 --> 00:02:44,560
and there are uh different types of

70
00:02:49,830 --> 00:02:47,200
mechanochemical instruments which exert

71
00:02:51,350 --> 00:02:49,840
different mechanical forces on the

72
00:02:54,150 --> 00:02:51,360
reaction mixtures

73
00:02:57,509 --> 00:02:54,160
there are vibratory ball mills planetary

74
00:02:59,030 --> 00:02:57,519
ball mills and extruders

75
00:03:02,149 --> 00:02:59,040
and when talking about

76
00:03:04,390 --> 00:03:02,159
mechanical energy on the

77
00:03:06,070 --> 00:03:04,400
prebiotic earth and in the context of

78
00:03:09,190 --> 00:03:06,080
origin of life

79
00:03:10,949 --> 00:03:09,200
it is mostly associated with uh surface

80
00:03:12,710 --> 00:03:10,959
impact events

81
00:03:15,110 --> 00:03:12,720
however the relevance for probiotic

82
00:03:17,430 --> 00:03:15,120
chemistry is hard to predict

83
00:03:20,309 --> 00:03:17,440
given the uncertainty and frequency of

84
00:03:22,309 --> 00:03:20,319
their appearance over time

85
00:03:24,149 --> 00:03:22,319
but the sources of

86
00:03:26,470 --> 00:03:24,159
mechanical energy on early earth could

87
00:03:30,229 --> 00:03:26,480
have been much more diverse

88
00:03:32,949 --> 00:03:30,239

for example they could have included

89
00:03:35,670 --> 00:03:32,959
tectonics earthquakes

90
00:03:38,229 --> 00:03:35,680
but also geomorphological processes such

91
00:03:40,710 --> 00:03:38,239
as erosion and weathering

92
00:03:42,869 --> 00:03:40,720
uh specifically erosion weathering are

93
00:03:45,509 --> 00:03:42,879
known to occur more frequently and are

94
00:03:47,990 --> 00:03:45,519
capable of exchanging matter

95
00:03:49,589 --> 00:03:48,000
on the planetary surface

96
00:03:51,830 --> 00:03:49,599
the use of

97
00:03:53,589 --> 00:03:51,840
mechanochemistry in probiotic chemistry

98
00:03:55,270 --> 00:03:53,599
has been demonstrated

99
00:03:57,030 --> 00:03:55,280
in the literature

100
00:04:01,270 --> 00:03:57,040
in the cases of

101
00:04:04,949 --> 00:04:01,280
amino acid derivatives and sugars

102
00:04:07,910 --> 00:04:05,990
we

103
00:04:09,670 --> 00:04:07,920
try to obtain oligopeptides by

104
00:04:11,990 --> 00:04:09,680
mechanochemistry and we explore

105
00:04:14,070 --> 00:04:12,000
different reaction parameters

106
00:04:16,069 --> 00:04:14,080
namely the effects of temperature

107
00:04:17,110 --> 00:04:16,079
mechanical loading

108
00:04:18,469 --> 00:04:17,120
time

109
00:04:20,229 --> 00:04:18,479
atmosphere

110
00:04:22,390 --> 00:04:20,239
real mineral surfaces

111
00:04:24,150 --> 00:04:22,400
and different combinations of amino

112
00:04:26,070 --> 00:04:24,160
acids

113
00:04:28,230 --> 00:04:26,080

so when considering the effect of

114
00:04:31,990 --> 00:04:28,240
temperature

115
00:04:35,270 --> 00:04:32,000
we milled glycine with titanium dioxide

116
00:04:37,590 --> 00:04:35,280
in a in a ball mill uh we used uh this

117
00:04:40,629 --> 00:04:37,600
kind of setup that was developed in our

118
00:04:41,909 --> 00:04:40,639
lab which enables us to perform

119
00:04:43,990 --> 00:04:41,919
temperature temperature-controlled

120
00:04:45,749 --> 00:04:44,000
mechanochemical reactions

121
00:04:48,790 --> 00:04:45,759
uh some of these findings have already

122
00:04:50,629 --> 00:04:48,800
been published last year

123
00:04:52,550 --> 00:04:50,639
and by iron pairing high performance

124
00:04:54,310 --> 00:04:52,560
liquid chromatography

125
00:04:56,390 --> 00:04:54,320
we could

126
00:04:57,670 --> 00:04:56,400
see that by increasing the the milling

127
00:05:00,870 --> 00:04:57,680
temperature

128
00:05:03,590 --> 00:05:00,880
we obtained a longer glycine oligomers

129
00:05:06,310 --> 00:05:03,600
alongside with the formation of a

130
00:05:08,230 --> 00:05:06,320
predominant uh

131
00:05:11,430 --> 00:05:08,240
part of the reaction mixture which was

132
00:05:14,629 --> 00:05:11,440
uh cyclic dicatopirazine

133
00:05:17,189 --> 00:05:14,639
so total yield of linear oligomers

134
00:05:19,909 --> 00:05:17,199
uh was the highest around 10 percent

135
00:05:21,830 --> 00:05:19,919
when the reaction was performed at 100

136
00:05:24,230 --> 00:05:21,840
degrees celsius

137
00:05:26,390 --> 00:05:24,240
where we obtained glee 8

138
00:05:29,510 --> 00:05:26,400

oligomer

139
00:05:32,790 --> 00:05:29,520
also we validated some of the results by

140
00:05:35,189 --> 00:05:32,800
lcms quadruple time of flight analysis

141
00:05:36,870 --> 00:05:35,199
here we see the results for the reaction

142
00:05:40,230 --> 00:05:36,880
where glycine was milled with titanium

143
00:05:42,710 --> 00:05:40,240
dioxide at 130 degrees celsius

144
00:05:45,189 --> 00:05:42,720
where we observe the ligomers up to glee

145
00:05:48,310 --> 00:05:45,199
11.

146
00:05:49,510 --> 00:05:48,320
next we turn two uh different amino

147
00:05:51,990 --> 00:05:49,520
acids

148
00:05:54,310 --> 00:05:52,000
so this is a chromatogram for milling

149
00:05:57,430 --> 00:05:54,320
glycine with alanine with titanium

150
00:05:59,749 --> 00:05:57,440
dioxide at 100 degrees celsius

151
00:06:02,309 --> 00:05:59,759
we can see that there are

152
00:06:04,309 --> 00:06:02,319
several peaks which would indicate that

153
00:06:07,430 --> 00:06:04,319
there was some reactivity

154
00:06:09,350 --> 00:06:07,440
and by direct injection to ms uh we

155
00:06:11,909 --> 00:06:09,360
could confirm that

156
00:06:13,909 --> 00:06:11,919
uh glycine and alanine dipeptides as

157
00:06:15,830 --> 00:06:13,919
well as tripeptides have been

158
00:06:17,590 --> 00:06:15,840
synthesized in this way

159
00:06:19,909 --> 00:06:17,600
thus demonstrating that

160
00:06:23,430 --> 00:06:19,919
other amino acids can be incorporated

161
00:06:24,870 --> 00:06:23,440
into a growing peptide chain

162
00:06:25,670 --> 00:06:24,880
after that

163
00:06:26,870 --> 00:06:25,680

we

164
00:06:28,309 --> 00:06:26,880
explored

165
00:06:30,469 --> 00:06:28,319
the

166
00:06:32,070 --> 00:06:30,479
different amounts of mechanical loading

167
00:06:33,110 --> 00:06:32,080
that is transferred to the reaction

168
00:06:35,430 --> 00:06:33,120
mixture

169
00:06:38,469 --> 00:06:35,440
we could do that simply by

170
00:06:40,150 --> 00:06:38,479
variation of the milling frequency

171
00:06:41,830 --> 00:06:40,160
so for example

172
00:06:43,909 --> 00:06:41,840
uh when the reaction

173
00:06:46,150 --> 00:06:43,919
of milling glycine with silicon dioxide

174
00:06:48,710 --> 00:06:46,160
at room temperature for 96 hours was

175
00:06:49,909 --> 00:06:48,720
performed at five hertz

176
00:06:51,189 --> 00:06:49,919
we could

177
00:06:54,469 --> 00:06:51,199
detect

178
00:06:57,990 --> 00:06:54,479
the presence of glycine tripeptide

179
00:07:01,350 --> 00:06:58,000
so a milling frequency of 5 hertz

180
00:07:03,990 --> 00:07:01,360
is a very low frequency which could

181
00:07:05,670 --> 00:07:04,000
mimic for example erosion or weathering

182
00:07:07,589 --> 00:07:05,680
processes

183
00:07:13,110 --> 00:07:07,599
so

184
00:07:15,350 --> 00:07:13,120
titanium dioxide using three hand-picked

185
00:07:18,070 --> 00:07:15,360
stones as milling media

186
00:07:21,029 --> 00:07:18,080
for 18 hours at 20 hertz and ambient

187
00:07:24,870 --> 00:07:21,039
temperature uh results from

188
00:07:27,510 --> 00:07:24,880

iphplc show that glycine ligaments up to

189
00:07:29,270 --> 00:07:27,520
tetrapeptide have been formed in this

190
00:07:31,830 --> 00:07:29,280
way

191
00:07:33,430 --> 00:07:31,840
after that we explored uh the effects of

192
00:07:35,350 --> 00:07:33,440
time

193
00:07:38,469 --> 00:07:35,360
so as hypothesized

194
00:07:40,070 --> 00:07:38,479
uh it was demonstrated that time is an

195
00:07:41,830 --> 00:07:40,080
important parameter

196
00:07:44,710 --> 00:07:41,840
so when comparing reactions that were

197
00:07:46,629 --> 00:07:44,720
performed from one hour up to 96 hours

198
00:07:48,230 --> 00:07:46,639
or four days

199
00:07:51,430 --> 00:07:48,240
we could see that there is almost

200
00:07:54,150 --> 00:07:51,440
exponential increase in the total yield

201
00:07:56,150 --> 00:07:54,160
of linear oligomers around 2.5 percent

202
00:07:58,550 --> 00:07:56,160
when the reaction was performed

203
00:08:02,950 --> 00:07:58,560
at 40 degrees celsius

204
00:08:06,230 --> 00:08:05,270
we also explored the effects of

205
00:08:07,909 --> 00:08:06,240
different

206
00:08:08,950 --> 00:08:07,919
atmospheres

207
00:08:09,830 --> 00:08:08,960
so

208
00:08:10,790 --> 00:08:09,840
here

209
00:08:13,749 --> 00:08:10,800
we

210
00:08:14,950 --> 00:08:13,759
used nitrogen and carbon dioxide as one

211
00:08:16,950 --> 00:08:14,960
of the two

212
00:08:18,790 --> 00:08:16,960
primary components of early earth

213
00:08:21,670 --> 00:08:18,800

atmosphere and by

214
00:08:23,589 --> 00:08:21,680
lcms triple quadruple

215
00:08:29,350 --> 00:08:23,599
we could

216
00:08:31,670 --> 00:08:29,360
up to glyce 7

217
00:08:34,070 --> 00:08:31,680
were formed when milling in in nitrogen

218
00:08:37,029 --> 00:08:34,080
atmosphere and glycine oligomers up to

219
00:08:38,550 --> 00:08:37,039
glycine 6 were formed when milling was

220
00:08:41,990 --> 00:08:38,560
performed in

221
00:08:47,190 --> 00:08:44,870
uh finally we turned to uh milling with

222
00:08:48,550 --> 00:08:47,200
real mineral surfaces

223
00:08:49,910 --> 00:08:48,560
we managed to

224
00:08:51,350 --> 00:08:49,920
obtain

225
00:08:55,190 --> 00:08:51,360
10 different

226
00:08:57,590 --> 00:08:55,200
classes of minerals representing

227
00:09:02,550 --> 00:08:57,600
different different mineral classes

228
00:09:06,230 --> 00:09:02,560
and by lcms triple quadruple analysis

229
00:09:08,790 --> 00:09:06,240
we could detect that one of the best

230
00:09:11,350 --> 00:09:08,800
minerals for uh

231
00:09:14,230 --> 00:09:11,360
producing oligopeptides were calcite and

232
00:09:16,310 --> 00:09:14,240
magnesite where we formed glycine

233
00:09:18,710 --> 00:09:16,320
tetrapeptides

234
00:09:22,630 --> 00:09:18,720
but the best was quartz so crystalline

235
00:09:25,190 --> 00:09:22,640
silica uh where we detected glycine

236
00:09:27,750 --> 00:09:25,200
hepta peptide

237
00:09:30,949 --> 00:09:27,760
for example here are the chromatograms

238
00:09:33,990 --> 00:09:30,959

of lcms triple quadruple analysis

239
00:09:35,670 --> 00:09:34,000
using magnesite where gly4 is observed

240
00:09:39,190 --> 00:09:35,680
and quartz

241
00:09:43,030 --> 00:09:39,200
uh oligopeptides up to uh glycine seven

242
00:09:47,829 --> 00:09:45,110
finally at the end we were interested to

243
00:09:51,190 --> 00:09:47,839
see uh if the oligomerization

244
00:09:54,389 --> 00:09:51,200
under mechanochemical conditions also uh

245
00:09:57,590 --> 00:09:54,399
proceeds if amino acids are uh reacted

246
00:09:59,430 --> 00:09:57,600
with hydroxy acid acids to form depth

247
00:10:01,509 --> 00:09:59,440
peptides

248
00:10:02,949 --> 00:10:01,519
therefore we milk glycine and glycolic

249
00:10:05,190 --> 00:10:02,959
acids and

250
00:10:06,150 --> 00:10:05,200
we could observe by

251
00:10:09,670 --> 00:10:06,160
maldi

252
00:10:12,310 --> 00:10:09,680
time of flight analysis that uh

253
00:10:15,430 --> 00:10:12,320
dimer uh deputy peptide dammer was

254
00:10:18,150 --> 00:10:15,440
formed this way alongside at least four

255
00:10:19,990 --> 00:10:18,160
other depths peptides

256
00:10:22,550 --> 00:10:20,000
and the uh

257
00:10:24,790 --> 00:10:22,560
longest depth peptide obtained in this

258
00:10:27,110 --> 00:10:24,800
way so by milling glycine and glycolic

259
00:10:30,150 --> 00:10:27,120
acid with silicon dioxide at room

260
00:10:31,509 --> 00:10:30,160
temperature for 16 hours and at 30 hertz

261
00:10:32,550 --> 00:10:31,519
we obtained

262
00:10:33,910 --> 00:10:32,560
uh

263
00:10:35,590 --> 00:10:33,920

illegal

264
00:10:36,710 --> 00:10:35,600
debsi peptides

265
00:10:39,190 --> 00:10:36,720
containing

266
00:10:42,630 --> 00:10:39,200
three glycine residues as well as three

267
00:10:44,870 --> 00:10:42,640
glycolic acid residues so in summary

268
00:10:46,310 --> 00:10:44,880
the formation of peptides is operational

269
00:10:48,150 --> 00:10:46,320
under different geological and

270
00:10:49,750 --> 00:10:48,160
environmental scenarios in a dry

271
00:10:51,269 --> 00:10:49,760
probiotic setting

272
00:10:53,110 --> 00:10:51,279
this might have implications for

273
00:10:54,949 --> 00:10:53,120
astrobiology research and

274
00:10:56,710 --> 00:10:54,959
reconsideration of extraterrestrial

275
00:10:58,150 --> 00:10:56,720
conditions that can give rise to

276
00:11:00,550 --> 00:10:58,160
peptides

277
00:11:03,110 --> 00:11:00,560
for example a weathering of amino acids

278
00:11:05,829 --> 00:11:03,120
in dry settings on mineral surfaces

279
00:11:08,150 --> 00:11:05,839
might result in peptides

280
00:11:09,430 --> 00:11:08,160
with this i want to end and thank

281
00:11:10,790 --> 00:11:09,440
all of my

282
00:11:13,910 --> 00:11:10,800
co-authors

283
00:11:16,230 --> 00:11:13,920
and the funding agency and i thank you

284
00:11:18,150 --> 00:11:16,240
for your attention and i'm now open for

285
00:11:24,790 --> 00:11:18,160
taking questions

286
00:11:27,829 --> 00:11:24,800
[Applause]

287
00:11:29,509 --> 00:11:27,839
you have time for a couple questions

288
00:11:32,230 --> 00:11:29,519

for an interesting talk john yen

289
00:11:35,670 --> 00:11:32,240
university of wisconsin um in your

290
00:11:37,430 --> 00:11:35,680
characterization of peptides on minerals

291
00:11:39,670 --> 00:11:37,440
i wonder

292
00:11:41,430 --> 00:11:39,680
did you do this on a mass basis of

293
00:11:43,750 --> 00:11:41,440
mineral or

294
00:11:46,470 --> 00:11:43,760
do you have some way of

295
00:11:48,150 --> 00:11:46,480
quantifying the surface area i think the

296
00:11:49,350 --> 00:11:48,160
minerals you showed have a number of

297
00:11:51,350 --> 00:11:49,360
different

298
00:11:54,790 --> 00:11:51,360
probably surface areas per volume could

299
00:11:59,910 --> 00:11:56,629
thank you very much for your question i

300
00:12:04,150 --> 00:11:59,920
will just share the this screen again

301
00:12:06,710 --> 00:12:04,160
so uh what we did uh was we used an

302
00:12:09,829 --> 00:12:06,720
excess of mineral surface

303
00:12:13,110 --> 00:12:09,839
with respect to the uh glycine amino

304
00:12:17,110 --> 00:12:13,120
acids you know we wanted to respect that

305
00:12:21,509 --> 00:12:19,590
more available available in organic

306
00:12:23,670 --> 00:12:21,519
material when compared to organic

307
00:12:25,750 --> 00:12:23,680
material for example on early earth

308
00:12:26,949 --> 00:12:25,760
therefore we used five to one molar

309
00:12:30,150 --> 00:12:26,959
ratio

310
00:12:34,069 --> 00:12:30,160
in favor of excess of minerals

311
00:12:36,949 --> 00:12:34,079
so this is the the variable that we used

312
00:12:39,509 --> 00:12:36,959
uh so far we still didn't

313
00:12:42,629 --> 00:12:39,519

check the surface areas

314
00:12:45,269 --> 00:12:42,639
but this is still an ongoing study so

315
00:12:49,350 --> 00:12:45,279
we will have more data on this i hope

316
00:12:53,030 --> 00:12:51,509
um hey really amazing talk i'm luke

317
00:12:55,190 --> 00:12:53,040
stella from the australian center for

318
00:12:56,710 --> 00:12:55,200
astrobiology i was really interested

319
00:12:58,710 --> 00:12:56,720
with the time

320
00:13:00,790 --> 00:12:58,720
experiments you did and curious why you

321
00:13:02,230 --> 00:13:00,800
stopped at 96 hours when it seemed to be

322
00:13:04,150 --> 00:13:02,240
getting really good like could you run

323
00:13:05,990 --> 00:13:04,160
it for months or i don't know like

324
00:13:08,550 --> 00:13:06,000
what's the end

325
00:13:11,910 --> 00:13:08,560
and limit there

326
00:13:14,150 --> 00:13:11,920
thank you very much luke uh

327
00:13:16,230 --> 00:13:14,160
funny that you asked this question

328
00:13:17,590 --> 00:13:16,240
because my research group is

329
00:13:19,829 --> 00:13:17,600
predominantly

330
00:13:22,069 --> 00:13:19,839
in the mechanochemistry let's say

331
00:13:23,829 --> 00:13:22,079
research area i'm the only one working

332
00:13:24,710 --> 00:13:23,839
in the prebiotic chemistry or origin of

333
00:13:27,030 --> 00:13:24,720
life

334
00:13:29,430 --> 00:13:27,040
therefore we have several

335
00:13:32,150 --> 00:13:29,440
milling instruments and a big research

336
00:13:34,710 --> 00:13:32,160
group so the time that is available to

337
00:13:36,790 --> 00:13:34,720
perform the experiment is limited

338
00:13:39,110 --> 00:13:36,800

and believe me i pushed as far as i

339
00:13:40,470 --> 00:13:39,120
could i almost got expelled from my

340
00:13:43,829 --> 00:13:40,480
research group

341
00:13:47,189 --> 00:13:43,839
uh just just just joking of course but

342
00:13:50,230 --> 00:13:47,199
this is the only reason basically why

343
00:13:53,990 --> 00:13:50,240
we stopped at 96 hours

344
00:13:55,590 --> 00:13:54,000
we could of course do longer milling but

345
00:13:57,910 --> 00:13:55,600
this also

346
00:13:59,509 --> 00:13:57,920
puts a lot of stress on the milling

347
00:14:03,269 --> 00:13:59,519
instrument which

348
00:14:03,990 --> 00:14:03,279
of course is prone to breaking

349
00:14:07,110 --> 00:14:04,000
so

350
00:14:09,829 --> 00:14:07,120
yes thank you maybe maybe we will

351
00:14:13,430 --> 00:14:09,839
try try to also do one experiment at

352
00:14:14,790 --> 00:14:13,440
least uh with longer milling time

353
00:14:16,389 --> 00:14:14,800
leave it over the summer holidays or

354
00:14:17,509 --> 00:14:16,399
something and come back in three months

355
00:14:19,430 --> 00:14:17,519
and yeah

356
00:14:21,189 --> 00:14:19,440
no thank you it's great

357
00:14:22,389 --> 00:14:21,199
thank you very much

358
00:14:24,470 --> 00:14:22,399
one more question

359
00:14:25,430 --> 00:14:24,480
do we have time or no time for one more

360
00:14:27,910 --> 00:14:25,440
okay

361
00:14:29,430 --> 00:14:27,920
hi i'm ellie from cu boulder and i saw

362
00:14:31,269 --> 00:14:29,440
that you had three different minerals

363
00:14:32,150 --> 00:14:31,279

that you um were saying were really good

364
00:14:33,750 --> 00:14:32,160
at this

365
00:14:35,430 --> 00:14:33,760
is there anything universal about the

366
00:14:37,670 --> 00:14:35,440
surface chemistries between these three

367
00:14:39,509 --> 00:14:37,680
minerals that are kind of good at

368
00:14:41,030 --> 00:14:39,519
promoting this kind of reaction like

369
00:14:42,790 --> 00:14:41,040
what is it about the surface chemistry

370
00:14:44,310 --> 00:14:42,800
that's leading to this and can we use

371
00:14:46,629 --> 00:14:44,320
that to predict what other minerals

372
00:14:48,470 --> 00:14:46,639
would be good at this

373
00:14:51,030 --> 00:14:48,480
thank you very much for your question as

374
00:14:52,550 --> 00:14:51,040
i said this is still an ongoing part of

375
00:14:55,509 --> 00:14:52,560
the project

376
00:14:58,150 --> 00:14:55,519
maybe i could give the best answer

377
00:14:59,670 --> 00:14:58,160
for quartz mineral since most of our

378
00:15:03,269 --> 00:14:59,680
reactions

379
00:15:05,670 --> 00:15:03,279
we used uh silicon dioxide you know

380
00:15:06,629 --> 00:15:05,680
the same commercial one that

381
00:15:10,550 --> 00:15:06,639
people

382
00:15:16,629 --> 00:15:13,750
so it's not surprising that quartz which

383
00:15:19,910 --> 00:15:16,639
is a crystal and silicon dioxide uh

384
00:15:22,150 --> 00:15:19,920
would have like similar uh

385
00:15:24,710 --> 00:15:22,160
similar activity and ability to produce

386
00:15:25,509 --> 00:15:24,720
oligopeptides

387
00:15:30,230 --> 00:15:25,519
uh

388
00:15:33,269 --> 00:15:30,240

go into mechanistic studies but

389
00:15:35,590 --> 00:15:33,279
what i can tell you from the literature

390
00:15:38,150 --> 00:15:35,600
is that titanium dioxide as well as

391
00:15:40,150 --> 00:15:38,160
silicon dioxide there have been some

392
00:15:41,350 --> 00:15:40,160
computational studies uh you know

393
00:15:43,350 --> 00:15:41,360
showing that

394
00:15:44,150 --> 00:15:43,360
they have absorption properties as well

395
00:15:46,550 --> 00:15:44,160
as

396
00:15:48,870 --> 00:15:46,560
properties of binding water molecules

397
00:15:51,749 --> 00:15:48,880
that are released uh during the reaction

398
00:15:54,470 --> 00:15:51,759
when oligopeptides are are formed

399
00:15:56,389 --> 00:15:54,480
so there is this kind of dual role

400
00:15:58,550 --> 00:15:56,399
but of course these studies are on very

401
00:16:01,509 --> 00:15:58,560
let's say simple minerals as i said

402
00:16:03,509 --> 00:16:01,519
titanium dioxide or silicon dioxide so

403
00:16:05,910 --> 00:16:03,519
at this moment i could not give you a

404
00:16:08,069 --> 00:16:05,920
better answer but this is certainly very

405
00:16:09,749 --> 00:16:08,079
interesting

406
00:16:10,790 --> 00:16:09,759
thank you very much

407
00:16:18,710 --> 00:16:10,800
all right we're gonna move on to our

408
00:16:18,720 --> 00:16:30,389
our next speaker is kelvin smith

409
00:16:33,430 --> 00:16:32,550
myself

410
00:16:36,870 --> 00:16:33,440
okay

411
00:16:37,829 --> 00:16:36,880
thank you very much uh my name is kelvin

412
00:16:41,189 --> 00:16:37,839
smith

413
00:16:43,430 --> 00:16:41,199

um i'm a six year phd uh student a phd

414
00:16:45,749 --> 00:16:43,440
candidate from georgia tech and i want

415
00:16:46,870 --> 00:16:45,759
to thank apps.com for having me speak

416
00:16:47,590 --> 00:16:46,880
today

417
00:16:50,949 --> 00:16:47,600
so

418
00:16:52,870 --> 00:16:50,959
my presentation is on thermodynamic and

419
00:16:54,949 --> 00:16:52,880
kinetic investigation

420
00:16:57,269 --> 00:16:54,959
of oligomerization and degradation of

421
00:16:59,910 --> 00:16:57,279
density peptides under prebiotic earth

422
00:17:02,550 --> 00:16:59,920
conditions let's get started

423
00:17:04,710 --> 00:17:02,560
so to introduce a topic i want to um say

424
00:17:08,309 --> 00:17:04,720
why is research is important the origins

425
00:17:09,270 --> 00:17:08,319
of life is a long lasting puzzle that

426
00:17:11,829 --> 00:17:09,280
has been

427
00:17:13,350 --> 00:17:11,839
trying to be deciphered for many years

428
00:17:19,829 --> 00:17:13,360
um

429
00:17:22,990 --> 00:17:19,839
it is through peptide bond

430
00:17:24,949 --> 00:17:23,000
formation because of the formation of

431
00:17:26,390 --> 00:17:24,959
diketoperazine and thermodynamic

432
00:17:27,510 --> 00:17:26,400
unfavorability

433
00:17:29,830 --> 00:17:27,520
of that

434
00:17:31,350 --> 00:17:29,840
sort of reaction so how is that able to

435
00:17:32,549 --> 00:17:31,360
be formed under plausibly prebiotic

436
00:17:34,150 --> 00:17:32,559
conditions

437
00:17:37,350 --> 00:17:34,160
and

438
00:17:39,990 --> 00:17:37,360

one molecule it's a simple molecule

439
00:17:41,590 --> 00:17:40,000
but it's a paramount importance um so

440
00:17:43,909 --> 00:17:41,600
much so that it's studied in the

441
00:17:47,590 --> 00:17:43,919
literature quite a bit in lactic acid

442
00:17:50,070 --> 00:17:47,600
and how it can form uh polyesters which

443
00:17:52,390 --> 00:17:50,080
could be the first step into forming a

444
00:17:53,430 --> 00:17:52,400
uh a depth of peptide

445
00:18:01,750 --> 00:17:53,440
so

446
00:18:04,310 --> 00:18:01,760
know is in the kinetics of lactic acid

447
00:18:07,909 --> 00:18:04,320
we are aware of certain mechanisms such

448
00:18:10,549 --> 00:18:07,919
as backbiting and uh singing so bad body

449
00:18:14,310 --> 00:18:10,559
forms a six-membered ring on an o-h

450
00:18:17,110 --> 00:18:14,320
terminus of a dipeptide um to form a

451
00:18:18,070 --> 00:18:17,120
cyclic ester or cyclic amide

452
00:18:20,470 --> 00:18:18,080
um

453
00:18:23,590 --> 00:18:20,480
incision can cleave off

454
00:18:24,950 --> 00:18:23,600
a certain ester moiety on

455
00:18:30,870 --> 00:18:24,960
any sort of

456
00:18:31,909 --> 00:18:30,880
also know thanks to um

457
00:18:35,669 --> 00:18:31,919
you know

458
00:18:37,750 --> 00:18:35,679
um from dr j forsythe about estrogen

459
00:18:39,909 --> 00:18:37,760
exchange that there's a plausible

460
00:18:42,470 --> 00:18:39,919
pathway towards

461
00:18:43,190 --> 00:18:42,480
peptides but what we don't know

462
00:18:44,710 --> 00:18:43,200
is

463
00:18:46,070 --> 00:18:44,720

what are the thermodynamic driving

464
00:18:49,510 --> 00:18:46,080
forces

465
00:18:51,750 --> 00:18:49,520
um that go towards exchange and

466
00:18:54,230 --> 00:18:51,760
this uh oligomerization or sterification

467
00:18:57,430 --> 00:18:54,240
of lactic acid or similar

468
00:19:00,789 --> 00:18:57,440
hydroxy acids and can we and are we able

469
00:19:03,350 --> 00:19:00,799
to quantify them so that's what um what

470
00:19:04,710 --> 00:19:03,360
our experiment our research is about i

471
00:19:06,710 --> 00:19:04,720
make a

472
00:19:08,230 --> 00:19:06,720
uh chemical model

473
00:19:09,190 --> 00:19:08,240
um that would help

474
00:19:11,830 --> 00:19:09,200
create

475
00:19:13,430 --> 00:19:11,840
uh energy plots gibbs energy plots as a

476
00:19:15,270 --> 00:19:13,440
function of ph

477
00:19:18,070 --> 00:19:15,280
and pka

478
00:19:20,310 --> 00:19:18,080
of monomers and dimers and the contour

479
00:19:23,510 --> 00:19:20,320
map and i also make contour maps that

480
00:19:26,230 --> 00:19:23,520
display conversions towards products

481
00:19:28,789 --> 00:19:26,240
and the hypothesis so we hypothesize is

482
00:19:30,950 --> 00:19:28,799
ph and pka do play a major role in the

483
00:19:33,830 --> 00:19:30,960
thermodynamic driving forces

484
00:19:35,110 --> 00:19:33,840
um mainly the pka shift between monitors

485
00:19:37,110 --> 00:19:35,120
and dimers

486
00:19:39,750 --> 00:19:37,120
uh but the temperature because of the

487
00:19:42,710 --> 00:19:39,760
thermal neutrality um

488
00:19:43,510 --> 00:19:42,720

from whitski and vu for um

489
00:19:45,750 --> 00:19:43,520
um

490
00:19:49,510 --> 00:19:45,760
simple elimination of esters kind of

491
00:19:52,789 --> 00:19:49,520
plays plays a little bit of a minor role

492
00:19:55,830 --> 00:19:52,799
so um so my methods is i first start

493
00:19:58,150 --> 00:19:55,840
with a working reaction a very simple

494
00:20:00,789 --> 00:19:58,160
overall reaction of

495
00:20:03,270 --> 00:20:00,799
sterification and i break it down into

496
00:20:06,950 --> 00:20:03,280
dissociation states and each of those

497
00:20:09,270 --> 00:20:06,960
association states are a function of ph

498
00:20:11,270 --> 00:20:09,280
the amount is dependent on ph

499
00:20:12,950 --> 00:20:11,280
and that and that amount is

500
00:20:14,710 --> 00:20:12,960
further dictated from stoichiometric

501
00:20:17,430 --> 00:20:14,720
coefficients which are the mole

502
00:20:20,230 --> 00:20:17,440
fractions of these association states

503
00:20:22,470 --> 00:20:20,240
then i will perform an atom balance so i

504
00:20:25,029 --> 00:20:22,480
deal with carbon nitrogen oxygen

505
00:20:28,789 --> 00:20:25,039
hydrogen on broken down

506
00:20:31,590 --> 00:20:28,799
uh reactions and depending on the ph

507
00:20:34,470 --> 00:20:31,600
the the hydrogen balance especially may

508
00:20:35,909 --> 00:20:34,480
not be satisfied as written so then we

509
00:20:38,070 --> 00:20:35,919
would have i would then need to add

510
00:20:40,710 --> 00:20:38,080
appropriate number of hydrogens as

511
00:20:42,870 --> 00:20:40,720
needed to um the reaction while still

512
00:20:44,630 --> 00:20:42,880
making sure that the reaction is

513
00:20:47,270 --> 00:20:44,640

satisfied

514
00:20:49,590 --> 00:20:47,280
um let's see next is the thermodynamic

515
00:20:51,750 --> 00:20:49,600
calculation so all the gives and

516
00:20:53,990 --> 00:20:51,760
energies and enthalpies of formation

517
00:20:55,909 --> 00:20:54,000
were required using density functional

518
00:20:58,470 --> 00:20:55,919
theory or dft

519
00:21:00,230 --> 00:20:58,480
uh the conversions were

520
00:21:02,950 --> 00:21:00,240
the equations for the conversions were

521
00:21:05,909 --> 00:21:02,960
either derived or for the case of a

522
00:21:08,310 --> 00:21:05,919
sterification there was a closed system

523
00:21:10,950 --> 00:21:08,320
uh equation provided in the literature

524
00:21:13,590 --> 00:21:10,960
by harshi um that would allow us to

525
00:21:15,669 --> 00:21:13,600
compute uh these conversions

526
00:21:17,590 --> 00:21:15,679
and then i make a van haul

527
00:21:19,430 --> 00:21:17,600
plot where i compute equilibrium

528
00:21:21,270 --> 00:21:19,440
constants for different

529
00:21:22,630 --> 00:21:21,280
temperatures provided that the enthalpy

530
00:21:28,830 --> 00:21:22,640
is

531
00:21:31,190 --> 00:21:28,840
constant across temperature

532
00:21:33,510 --> 00:21:31,200
range so here's a list of all the

533
00:21:34,549 --> 00:21:33,520
important alpha hydroxy acids these are

534
00:21:37,110 --> 00:21:34,559
also

535
00:21:38,710 --> 00:21:37,120
a molecules you see um from

536
00:21:41,430 --> 00:21:38,720
groundbreaking experiments such as the

537
00:21:44,549 --> 00:21:41,440
miller urane experiment in the 1950s

538
00:21:45,830 --> 00:21:44,559

you see uh the glycolic acid and lactic

539
00:21:48,149 --> 00:21:45,840
acid

540
00:21:50,710 --> 00:21:48,159
and their

541
00:21:55,270 --> 00:21:50,720
their anionic forms and also in their

542
00:21:58,070 --> 00:21:56,149
so

543
00:22:00,390 --> 00:21:58,080
i want to go through you know step by

544
00:22:02,390 --> 00:22:00,400
step to see where um

545
00:22:04,870 --> 00:22:02,400
the process on how i conducted the

546
00:22:07,190 --> 00:22:04,880
research so we solve a working reaction

547
00:22:09,510 --> 00:22:07,200
we have two lactic acid residues going

548
00:22:11,510 --> 00:22:09,520
to a dimer and water

549
00:22:13,110 --> 00:22:11,520
now the reaction as you see there is not

550
00:22:15,190 --> 00:22:13,120
going to occur all the time

551
00:22:17,750 --> 00:22:15,200
for instance at ph 7

552
00:22:20,470 --> 00:22:17,760
uh the lactic acid monomer and the dinos

553
00:22:22,230 --> 00:22:20,480
is going to be in their anionic state so

554
00:22:24,549 --> 00:22:22,240
we would have to break that reaction

555
00:22:27,190 --> 00:22:24,559
down further into

556
00:22:31,190 --> 00:22:27,200
uh this reaction you see down here where

557
00:22:34,070 --> 00:22:31,200
you see x1 and x2 all the mole fractions

558
00:22:35,510 --> 00:22:34,080
of each of these association states a

559
00:22:37,830 --> 00:22:35,520
and a a

560
00:22:39,270 --> 00:22:37,840
and also i use alpha beta and gamma i

561
00:22:41,350 --> 00:22:39,280
even broke down water into that

562
00:22:43,750 --> 00:22:41,360
association states

563
00:22:46,390 --> 00:22:43,760

and using that broken down reaction i

564
00:22:47,590 --> 00:22:46,400
then do atom balances to be able to

565
00:22:49,750 --> 00:22:47,600
figure out

566
00:22:51,510 --> 00:22:49,760
what relationship exists

567
00:22:52,710 --> 00:22:51,520
um

568
00:22:54,870 --> 00:22:52,720
between

569
00:22:57,110 --> 00:22:54,880
the circumvention coefficients

570
00:22:59,990 --> 00:22:57,120
and um

571
00:23:01,750 --> 00:23:00,000
ph and pka which is what this next slide

572
00:23:03,510 --> 00:23:01,760
is going to be talking about so the

573
00:23:05,669 --> 00:23:03,520
stoichiometric coefficients that you saw

574
00:23:07,430 --> 00:23:05,679
are tied to the pka

575
00:23:10,390 --> 00:23:07,440
of each species

576
00:23:12,630 --> 00:23:10,400
and i calculate them using this uh ratio

577
00:23:13,510 --> 00:23:12,640
you see here of um a henderson house of

578
00:23:16,549 --> 00:23:13,520
back

579
00:23:19,190 --> 00:23:16,559
type of equation we have ph of solutions

580
00:23:21,669 --> 00:23:19,200
equal to pka of species

581
00:23:23,990 --> 00:23:21,679
plus the logarithm of the conjugate base

582
00:23:25,990 --> 00:23:24,000
and the acid and that ratio in the

583
00:23:27,750 --> 00:23:26,000
logarithmic term dictates what the

584
00:23:29,909 --> 00:23:27,760
coefficients are

585
00:23:31,430 --> 00:23:29,919
and the mole fraction of each of those

586
00:23:32,470 --> 00:23:31,440
association

587
00:23:35,750 --> 00:23:32,480
states

588
00:23:38,390 --> 00:23:35,760

from that ratio can be found using

589
00:23:40,630 --> 00:23:38,400
this expression uh mole fraction of

590
00:23:42,149 --> 00:23:40,640
dissociation state j of a particular

591
00:23:44,630 --> 00:23:42,159
species m

592
00:23:46,789 --> 00:23:44,640
can be found using that so by combining

593
00:23:49,510 --> 00:23:46,799
those two equations we get the result

594
00:23:52,549 --> 00:23:49,520
that the mole fraction is of each

595
00:23:54,310 --> 00:23:52,559
species in solution at a particular ph

596
00:23:56,070 --> 00:23:54,320
meaning well out of cyclical shapes is

597
00:23:58,870 --> 00:23:56,080
actually a function of both the ph

598
00:24:01,110 --> 00:23:58,880
itself and also the pka

599
00:24:03,510 --> 00:24:01,120
now some of the pkas were experimentally

600
00:24:05,430 --> 00:24:03,520
undetermined so for instance the lactoil

601
00:24:06,470 --> 00:24:05,440
lactic acid hasn't

602
00:24:07,590 --> 00:24:06,480
been

603
00:24:09,590 --> 00:24:07,600
determined

604
00:24:13,029 --> 00:24:09,600
is pka hasn't been experimentally

605
00:24:15,830 --> 00:24:13,039
undetermined so instead i use benchmarks

606
00:24:19,269 --> 00:24:15,840
of a compound that i use before i mean

607
00:24:20,870 --> 00:24:19,279
of a compound that has been

608
00:24:22,950 --> 00:24:20,880
used like

609
00:24:27,350 --> 00:24:22,960
acetyl acetyl lactic acid which had a

610
00:24:30,630 --> 00:24:27,360
pka of 2.74 or i do a small grid search

611
00:24:32,549 --> 00:24:30,640
to vary them as i um conduct

612
00:24:36,310 --> 00:24:32,559
um

613
00:24:39,990 --> 00:24:36,320

as i make my model in matlab

614
00:24:42,789 --> 00:24:40,000
here's the expanded delta g of reaction

615
00:24:44,870 --> 00:24:42,799
where we have it's just a classical

616
00:24:47,269 --> 00:24:44,880
product known as reactants and we see

617
00:24:49,510 --> 00:24:47,279
the mole fractions you can consider the

618
00:24:50,789 --> 00:24:49,520
mole fractions of each species as a

619
00:24:53,190 --> 00:24:50,799
weight

620
00:24:56,390 --> 00:24:53,200
of uh

621
00:24:57,990 --> 00:24:56,400
on the delta g of formation of these uh

622
00:25:00,870 --> 00:24:58,000
of all these species which are found

623
00:25:02,870 --> 00:25:00,880
from dft and because delta h is a state

624
00:25:04,630 --> 00:25:02,880
function we can use the exact same

625
00:25:06,950 --> 00:25:04,640
formulation except instead of delta g we

626
00:25:10,310 --> 00:25:06,960
use those

627
00:25:12,870 --> 00:25:10,320
so if we combine that we get a graph

628
00:25:15,029 --> 00:25:12,880
that looks like this so we though so

629
00:25:17,510 --> 00:25:15,039
here we see the p the delta g of

630
00:25:18,710 --> 00:25:17,520
formation as a function of ph

631
00:25:21,269 --> 00:25:18,720
um

632
00:25:24,149 --> 00:25:21,279
for the oligomerization of lactic acid

633
00:25:25,110 --> 00:25:24,159
just for monomer to dimer and we can see

634
00:25:29,590 --> 00:25:25,120
that

635
00:25:31,669 --> 00:25:29,600
pka does play a major factor here um

636
00:25:36,630 --> 00:25:31,679
and we can see that around

637
00:25:38,230 --> 00:25:36,640
ph of 3.7 3.8 if the pka is around three

638
00:25:41,029 --> 00:25:38,240

we can see that it's at its most

639
00:25:43,990 --> 00:25:41,039
spontaneous at around that point

640
00:25:47,510 --> 00:25:44,000
but um there are other places where

641
00:25:49,190 --> 00:25:47,520
delta g is very highly unfavorable but

642
00:25:52,549 --> 00:25:49,200
there are certain

643
00:25:55,510 --> 00:25:52,559
uh ph ranges where this reaction is

644
00:25:57,830 --> 00:25:55,520
naturally spontaneous

645
00:25:59,190 --> 00:25:57,840
and here's a van hof plot

646
00:26:01,750 --> 00:25:59,200
and we can see here that the

647
00:26:04,950 --> 00:26:01,760
temperatures are that the profiles of

648
00:26:07,430 --> 00:26:04,960
the delta g are very tightly packed uh

649
00:26:10,470 --> 00:26:07,440
this suggests that it does the thermal

650
00:26:12,950 --> 00:26:10,480
neutrality does hold

651
00:26:16,710 --> 00:26:12,960
temperature does play a small role but

652
00:26:19,029 --> 00:26:16,720
not as major role as the pkas

653
00:26:22,470 --> 00:26:19,039
and then um here we talk about the

654
00:26:24,950 --> 00:26:22,480
conversions so the color contours

655
00:26:26,470 --> 00:26:24,960
are the conversions of lactic acid and

656
00:26:28,710 --> 00:26:26,480
these conversions were computed using

657
00:26:29,750 --> 00:26:28,720
this equation you see to your left from

658
00:26:32,230 --> 00:26:29,760
hershey

659
00:26:34,950 --> 00:26:32,240
where we use the equilibrium constant

660
00:26:37,350 --> 00:26:34,960
uh the initial water content w zero and

661
00:26:39,750 --> 00:26:37,360
then lambda one zero which

662
00:26:42,470 --> 00:26:39,760
harshi describes as the first moment of

663
00:26:44,549 --> 00:26:42,480

monomer uh so basically it's just saying

664
00:26:45,909 --> 00:26:44,559
how much initial monomer do we have in

665
00:26:48,549 --> 00:26:45,919
solution

666
00:26:50,950 --> 00:26:48,559
and this red line you see here is from

667
00:26:55,269 --> 00:26:50,960
an author named holton who has done ph

668
00:26:57,830 --> 00:26:55,279
and thermal work on poly lactic acid um

669
00:27:00,870 --> 00:26:57,840
um acidification at room temperature but

670
00:27:02,870 --> 00:27:00,880
he didn't um report conversion data but

671
00:27:05,269 --> 00:27:02,880
i did just i just bought it but he did

672
00:27:06,870 --> 00:27:05,279
have ph and w0 so i was able to plot

673
00:27:11,510 --> 00:27:06,880
that

674
00:27:13,830 --> 00:27:11,520
dry down

675
00:27:15,029 --> 00:27:13,840
though while holding ph constant we can

676
00:27:18,070 --> 00:27:15,039
see that

677
00:27:22,950 --> 00:27:18,080
conversions do increase as we would

678
00:27:25,430 --> 00:27:22,960
expect but we can see that we can also

679
00:27:27,590 --> 00:27:25,440
increase ph at the same water content by

680
00:27:30,389 --> 00:27:27,600
decreasing um ph

681
00:27:32,549 --> 00:27:30,399
by increasing the yield of

682
00:27:35,669 --> 00:27:32,559
uh

683
00:27:37,590 --> 00:27:35,679
longer ligaments of lactic acid

684
00:27:39,590 --> 00:27:37,600
so conclusion we can see that the poly

685
00:27:42,070 --> 00:27:39,600
condensation thermodynamics is driven by

686
00:27:43,430 --> 00:27:42,080
both pka and the removal of water from

687
00:27:45,830 --> 00:27:43,440
the system

688
00:27:48,710 --> 00:27:45,840

um polycondensation could proceed from

689
00:27:51,190 --> 00:27:48,720
both neutron and ionic states thanks to

690
00:27:52,789 --> 00:27:51,200
the atom balances and the ph and pka

691
00:27:57,110 --> 00:27:52,799
considerations

692
00:27:59,750 --> 00:27:57,990
okay

693
00:28:01,990 --> 00:27:59,760
kairat and even though i didn't say it

694
00:28:03,830 --> 00:28:02,000
in position but chirality whether the

695
00:28:05,909 --> 00:28:03,840
diastereomers do play a minor role in

696
00:28:07,430 --> 00:28:05,919
thermodynamic driving forces

697
00:28:09,029 --> 00:28:07,440
and dissociation states were critical

698
00:28:10,710 --> 00:28:09,039
and understanding the ester bond leakage

699
00:28:12,950 --> 00:28:10,720
thermo

700
00:28:14,630 --> 00:28:12,960
and uh future steps i was going to work

701
00:28:16,710 --> 00:28:14,640
on the second part of the coin which is

702
00:28:20,070 --> 00:28:16,720
about depth peptide

703
00:28:22,230 --> 00:28:20,080
exchange swapping an estrophon and i'm

704
00:28:24,870 --> 00:28:22,240
doing work with these a similar

705
00:28:26,549 --> 00:28:24,880
thermodynamic analysis that reaction

706
00:28:28,310 --> 00:28:26,559
so i want to say thank you very much i

707
00:28:29,909 --> 00:28:28,320
want to thank my advisors dr martha

708
00:28:31,830 --> 00:28:29,919
grofer and dr charles leota for

709
00:28:33,510 --> 00:28:31,840
supporting me and dr moran frankel

710
00:28:35,029 --> 00:28:33,520
penner and dr j forsyth for supporting

711
00:28:37,590 --> 00:28:35,039
me throughout my

712
00:28:41,029 --> 00:28:37,600
um journey through my phd at my email

713
00:28:42,149 --> 00:28:41,039

you can see casemill427 gotech.edu if

714
00:28:43,510 --> 00:28:42,159
you want to contact me for more

715
00:28:45,410 --> 00:28:43,520
questions

716
00:28:52,230 --> 00:28:45,420
thank you very much

717
00:29:01,830 --> 00:28:52,240
[Applause]

718
00:29:07,430 --> 00:29:04,710
thanks for the nice talk um do you

719
00:29:10,830 --> 00:29:07,440
also account for reverse reactions where

720
00:29:13,510 --> 00:29:10,840
you hydrolyze the

721
00:29:15,750 --> 00:29:13,520
products i'm sorry can you um i couldn't

722
00:29:18,070 --> 00:29:15,760
hear you i'm sorry yes i was just

723
00:29:19,830 --> 00:29:18,080
wondering if you uh consider the

724
00:29:22,230 --> 00:29:19,840
hydrolysis of your products if you

725
00:29:25,990 --> 00:29:22,240
consider the reverse reactions or are

726
00:29:31,909 --> 00:29:26,000
they uh fine to neglect

727
00:29:37,830 --> 00:29:35,269
i did include reversibility and um

728
00:29:39,750 --> 00:29:37,840
in my model i did take into

729
00:29:42,470 --> 00:29:39,760
consideration the

730
00:29:44,470 --> 00:29:42,480
equilibrium constant of products over

731
00:29:46,070 --> 00:29:44,480
reactants but in terms of whether it

732
00:29:48,710 --> 00:29:46,080
mattered

733
00:29:50,310 --> 00:29:48,720
a lot i'm not

734
00:29:53,430 --> 00:29:50,320
entirely sure

735
00:29:55,750 --> 00:29:53,440
about that um

736
00:29:58,389 --> 00:29:55,760
so um

737
00:30:01,029 --> 00:29:58,399
i'll have to get i i can get back to you

738
00:30:03,029 --> 00:30:01,039

on um i can get back to you on that if

739
00:30:04,549 --> 00:30:03,039
you need more detail on that but i'm not

740
00:30:07,510 --> 00:30:04,559
entirely

741
00:30:09,190 --> 00:30:07,520
i can't i'm at all time processing that

742
00:30:11,029 --> 00:30:09,200
right

743
00:30:15,029 --> 00:30:11,039
okay thanks

744
00:30:15,039 --> 00:30:19,430
any other questions

745
00:30:19,440 --> 00:30:29,430
if not let's thank our speaker

746
00:30:33,830 --> 00:30:32,070
so our next talk has been is withdrawn

747
00:30:35,750 --> 00:30:33,840
and so in order to stay on time for the

748
00:30:37,909 --> 00:30:35,760
future talks we'll start with our next

749
00:44:44,390 --> 00:30:37,919
speaker at 3 45 so we'll take a short

750
00:44:47,750 --> 00:44:46,230
nice starting one

751
00:44:58,630 --> 00:44:47,760
i guess whenever i'm ready maybe next

752
00:45:04,870 --> 00:45:00,390
all right we're gonna get started again

753
00:45:09,670 --> 00:45:07,109
hi everyone my name is laura rodriguez

754
00:45:11,589 --> 00:45:09,680
and i am a jpl postdoc and today i'm

755
00:45:13,990 --> 00:45:11,599
going to be talking about my research

756
00:45:15,990 --> 00:45:14,000
which is focused on studying conditions

757
00:45:17,910 --> 00:45:16,000
that are conducive for phosphorylating

758
00:45:20,870 --> 00:45:17,920
or adding a phosphate group onto

759
00:45:23,109 --> 00:45:20,880
organics and aqueous solutions

760
00:45:24,950 --> 00:45:23,119
so phosphorus is really important for

761
00:45:26,470 --> 00:45:24,960
life all life on earth today and it's

762
00:45:28,710 --> 00:45:26,480
thought to have been critical for the

763
00:45:30,550 --> 00:45:28,720

origins of life on the early earth

764
00:45:32,470 --> 00:45:30,560
however in its most common form as

765
00:45:33,750 --> 00:45:32,480
phosphate

766
00:45:35,510 --> 00:45:33,760
it would have been difficult to

767
00:45:38,230 --> 00:45:35,520
accumulate in the oceans and that's

768
00:45:39,990 --> 00:45:38,240
because as shown in this diagram here

769
00:45:42,150 --> 00:45:40,000
look at my math shows

770
00:45:44,470 --> 00:45:42,160
under a wide range of ph from acidic

771
00:45:46,630 --> 00:45:44,480
solutions to alkaline conditions you

772
00:45:48,150 --> 00:45:46,640
have to contend with common cations

773
00:45:51,670 --> 00:45:48,160
chelating the phosphate and

774
00:45:53,510 --> 00:45:51,680
precipitating out as insoluble minerals

775
00:45:55,589 --> 00:45:53,520
in addition to that phosphorylating is

776
00:45:57,589 --> 00:45:55,599
thermodynamically not favorable under

777
00:45:59,670 --> 00:45:57,599
aqueous conditions and that's because

778
00:46:01,510 --> 00:45:59,680
it's a condensation reaction which means

779
00:46:03,990 --> 00:46:01,520
that it produces water

780
00:46:05,750 --> 00:46:04,000
as one of the products and when you are

781
00:46:07,030 --> 00:46:05,760
in water you're essentially surrounded

782
00:46:09,430 --> 00:46:07,040
by one of the products and so

783
00:46:13,030 --> 00:46:09,440
equilibrium is pushed towards back

784
00:46:15,270 --> 00:46:13,040
back towards the reactants

785
00:46:18,309 --> 00:46:15,280
there are um mechanisms to get around

786
00:46:19,670 --> 00:46:18,319
that issue if you do the reaction in a

787
00:46:21,589 --> 00:46:19,680
non-aqueous solvents or

788
00:46:23,349 --> 00:46:21,599

semihydrosolvents

789
00:46:25,190 --> 00:46:23,359
but for the purposes of this work i was

790
00:46:27,670 --> 00:46:25,200
interested in focusing on aqueous

791
00:46:29,910 --> 00:46:27,680
conditions and that's because this is um

792
00:46:31,270 --> 00:46:29,920
more representative of the kind of

793
00:46:33,589 --> 00:46:31,280
solutions you would encounter in the

794
00:46:35,750 --> 00:46:33,599
deep sea or on the early earth as well

795
00:46:37,589 --> 00:46:35,760
as the oceans of other worlds such as

796
00:46:39,990 --> 00:46:37,599
enceladus and europa

797
00:46:41,990 --> 00:46:40,000
so a potential workaround instead is

798
00:46:44,870 --> 00:46:42,000
phosphite which is a reduced form of

799
00:46:47,030 --> 00:46:44,880
phosphorus it's hpo3 and you can

800
00:46:49,670 --> 00:46:47,040
actually get phosphite from phosphate by

801
00:46:51,910 --> 00:46:49,680
reducing heating with ferrous minerals

802
00:46:53,990 --> 00:46:51,920
or through lightning strikes

803
00:46:55,910 --> 00:46:54,000
and phosphate unlike phosphate is

804
00:46:57,750 --> 00:46:55,920
actually much more soluble in the water

805
00:46:59,109 --> 00:46:57,760
so you can overcome that solubility

806
00:47:00,309 --> 00:46:59,119
problem

807
00:47:02,550 --> 00:47:00,319
in addition

808
00:47:04,870 --> 00:47:02,560
pasek and colleagues in 2008 showed him

809
00:47:07,270 --> 00:47:04,880
a way to get around the thermodynamic

810
00:47:09,109 --> 00:47:07,280
problem by coupling phosphide oxidation

811
00:47:11,190 --> 00:47:09,119
with fenton chemistry to produce

812
00:47:13,990 --> 00:47:11,200
phosphorylating compounds

813
00:47:15,910 --> 00:47:14,000

so bend chemistry is just the oxidation

814
00:47:17,910 --> 00:47:15,920
of ferrous iron shown in the first line

815
00:47:20,870 --> 00:47:17,920
here with a strong oxidant like hydrogen

816
00:47:23,030 --> 00:47:20,880
peroxide and you can produce ferric iron

817
00:47:25,109 --> 00:47:23,040
as well as a hydroxyl radical and the

818
00:47:27,190 --> 00:47:25,119
hydroxyl radical can then go on to react

819
00:47:28,309 --> 00:47:27,200
with the phosphite producing a phosphite

820
00:47:30,230 --> 00:47:28,319
radical

821
00:47:31,510 --> 00:47:30,240
and then you can form phosphates and

822
00:47:33,270 --> 00:47:31,520
then you can have phosphite and

823
00:47:35,470 --> 00:47:33,280
phosphate radicals combine to form

824
00:47:37,349 --> 00:47:35,480
pyrophosphate triphosphate and

825
00:47:39,030 --> 00:47:37,359
trimetaphosphate and these are all

826
00:47:40,710 --> 00:47:39,040
phosphorylating agents which means they

827
00:47:43,349 --> 00:47:40,720
are readily give up their phosphate

828
00:47:45,109 --> 00:47:43,359
groups onto organic compounds

829
00:47:46,069 --> 00:47:45,119
and so now we have actually a new

830
00:47:47,670 --> 00:47:46,079
problem

831
00:47:50,390 --> 00:47:47,680
which is this reaction actually

832
00:47:52,549 --> 00:47:50,400
generates hydroxyl radicals that can

833
00:47:54,150 --> 00:47:52,559
react with organics and actually destroy

834
00:47:56,069 --> 00:47:54,160
any organic you want to phosphorylate in

835
00:47:58,309 --> 00:47:56,079
the water and so that comes to my

836
00:48:00,069 --> 00:47:58,319
research where i am interested in

837
00:48:01,349 --> 00:48:00,079
looking at condition spaces where you

838
00:48:03,510 --> 00:48:01,359

can generate a lot of these

839
00:48:05,750 --> 00:48:03,520
polyphosphates while minimizing organic

840
00:48:07,750 --> 00:48:05,760
degradation and typically these

841
00:48:10,230 --> 00:48:07,760
reactions are done with dissolved iron

842
00:48:12,230 --> 00:48:10,240
at around ph4 and so i was interested in

843
00:48:13,430 --> 00:48:12,240
doing the reactions with manganese and

844
00:48:16,309 --> 00:48:13,440
that's because manganese is an

845
00:48:18,309 --> 00:48:16,319
antioxidant as well as at higher ph's

846
00:48:20,870 --> 00:48:18,319
and that's because not only are those

847
00:48:23,190 --> 00:48:20,880
higher ph's more relevant for

848
00:48:25,270 --> 00:48:23,200
earth's early oceans but also because at

849
00:48:27,670 --> 00:48:25,280
higher ph iron and manganese crash out

850
00:48:29,910 --> 00:48:27,680
to form oxyhydroxide minerals which

851
00:48:31,670 --> 00:48:29,920
themselves could potentially provide an

852
00:48:34,309 --> 00:48:31,680
avenue for preserving the organic

853
00:48:36,549 --> 00:48:34,319
compounds

854
00:48:38,549 --> 00:48:36,559
so for this work i generated my own

855
00:48:40,870 --> 00:48:38,559
minerals using ferrous chloride or

856
00:48:43,670 --> 00:48:40,880
manganese chloride and titrating with

857
00:48:45,910 --> 00:48:43,680
sodium hydroxide to either ph five six

858
00:48:47,750 --> 00:48:45,920
point five or eight and then i added a

859
00:48:49,990 --> 00:48:47,760
solution of phosphate glycerol also

860
00:48:51,030 --> 00:48:50,000
titrated to the corresponding ph and

861
00:48:53,829 --> 00:48:51,040
then

862
00:48:56,390 --> 00:48:53,839
oxidized it last with hydrogen peroxide

863
00:48:58,790 --> 00:48:56,400

at 500 millimolar all these reactions

864
00:49:01,109 --> 00:48:58,800
were done under anaerobic conditions and

865
00:49:02,870 --> 00:49:01,119
the results were anal and the reactions

866
00:49:07,750 --> 00:49:02,880
were analyzed using nuclear magnetic

867
00:49:12,309 --> 00:49:10,470
so shown here is 31 phosphorus nmr so

868
00:49:14,470 --> 00:49:12,319
each of these peaks corresponds to a

869
00:49:16,470 --> 00:49:14,480
phosphorous species so pa is

870
00:49:18,549 --> 00:49:16,480
phosphonoacetic acid that's the standard

871
00:49:20,710 --> 00:49:18,559
we spiked in

872
00:49:22,710 --> 00:49:20,720
hpo3 is our starting phosphite and you

873
00:49:25,349 --> 00:49:22,720
can see there are two products phosphate

874
00:49:27,349 --> 00:49:25,359
and pyrophosphate and so this goes to

875
00:49:29,589 --> 00:49:27,359
show this reaction was done at ph 8 at

876
00:49:31,030 --> 00:49:29,599
room temperature and so at this ph iron

877
00:49:33,430 --> 00:49:31,040
is mostly present in the mineral

878
00:49:35,030 --> 00:49:33,440
oxyhydroxide and so this is just showing

879
00:49:38,150 --> 00:49:35,040
that the mineral is capable of

880
00:49:39,589 --> 00:49:38,160
facilitating this reaction

881
00:49:41,510 --> 00:49:39,599
we also looked at it at a higher

882
00:49:42,950 --> 00:49:41,520
temperature so in this case 70c because

883
00:49:44,470 --> 00:49:42,960
we wanted to see if that could really

884
00:49:46,710 --> 00:49:44,480
facilitate the formation of

885
00:49:50,470 --> 00:49:46,720
pyrophosphate but what we found is that

886
00:49:53,510 --> 00:49:50,480
it didn't actually increase the yield of

887
00:49:55,430 --> 00:49:53,520
the yield of phosphite oxidation and

888
00:49:57,270 --> 00:49:55,440

instead decreased the amount of

889
00:49:59,589 --> 00:49:57,280
pyrophosphate present and that's because

890
00:50:00,870 --> 00:49:59,599
pyrophosphate is actually unstable under

891
00:50:03,430 --> 00:50:00,880
high temperature so it was just

892
00:50:05,349 --> 00:50:03,440
hydrolyzing back to phosphate so moving

893
00:50:08,230 --> 00:50:05,359
forward we decided to do our reactions

894
00:50:09,750 --> 00:50:08,240
at room temperature

895
00:50:11,670 --> 00:50:09,760
what this diagram is showing is a

896
00:50:13,349 --> 00:50:11,680
comparison over time of the amount of

897
00:50:15,030 --> 00:50:13,359
phosphite that's oxidized over the

898
00:50:17,829 --> 00:50:15,040
course of a month

899
00:50:19,910 --> 00:50:17,839
when we did the reactions at ph 5 6.5 or

900
00:50:21,190 --> 00:50:19,920
8. so you can see here that within 24

901
00:50:22,549 --> 00:50:21,200
hours the reaction is essentially

902
00:50:25,589 --> 00:50:22,559
complete

903
00:50:27,190 --> 00:50:25,599
under all conditions and in general the

904
00:50:30,069 --> 00:50:27,200
reaction yields are pretty high so

905
00:50:31,750 --> 00:50:30,079
between 75 to like 95 percent um

906
00:50:33,829 --> 00:50:31,760
dissolved iron was

907
00:50:35,910 --> 00:50:33,839
uh promoted the reaction more than when

908
00:50:38,069 --> 00:50:35,920
the iron is trapped in the mineral

909
00:50:40,710 --> 00:50:38,079
but overall we had good yields even with

910
00:50:44,470 --> 00:50:40,720
the mineral and in general pyrophosphate

911
00:50:45,990 --> 00:50:44,480
formation was between 10 to 18

912
00:50:48,069 --> 00:50:46,000
so then we decided to look to see what

913
00:50:49,829 --> 00:50:48,079

was happening to our organic in solution

914
00:50:51,109 --> 00:50:49,839
in this case we used glycerol and that's

915
00:50:52,710 --> 00:50:51,119
because if you can phosphorylate

916
00:50:54,950 --> 00:50:52,720
glycerol that's an important component

917
00:50:57,270 --> 00:50:54,960
for phospholipids

918
00:51:00,630 --> 00:50:57,280
and what this top graph is showing here

919
00:51:02,870 --> 00:51:00,640
a top plot is a proton nmr so we have

920
00:51:04,470 --> 00:51:02,880
our phosphonoacetic acid our glycerol

921
00:51:05,910 --> 00:51:04,480
and our starting phosphate and this is

922
00:51:08,230 --> 00:51:05,920
just showing that with the mineral the

923
00:51:09,910 --> 00:51:08,240
glycerol is stable but as soon as we add

924
00:51:12,150 --> 00:51:09,920
peroxide and get the fenton chemistry

925
00:51:14,150 --> 00:51:12,160
going it degrades and forms all of these

926
00:51:15,829 --> 00:51:14,160
different peaks this large peak here

927
00:51:17,910 --> 00:51:15,839
actually correspond corresponds to

928
00:51:19,829 --> 00:51:17,920
formate and so what this is showing is

929
00:51:21,990 --> 00:51:19,839
that even with the mineral we get

930
00:51:24,390 --> 00:51:22,000
glycerol oxidation so it's not it isn't

931
00:51:26,870 --> 00:51:24,400
able to prevent oxidation of the organic

932
00:51:29,190 --> 00:51:26,880
compound what the diagram showing over

933
00:51:30,790 --> 00:51:29,200
here is uh it just i was just showing

934
00:51:32,870 --> 00:51:30,800
that there's been a lot of work looking

935
00:51:34,309 --> 00:51:32,880
at glycerol oxidation with hydroxyl

936
00:51:37,030 --> 00:51:34,319
radicals so here are just some of the

937
00:51:39,109 --> 00:51:37,040
products you would expect to find

938
00:51:40,549 --> 00:51:39,119

so even though it can't prevent glycerol

939
00:51:42,390 --> 00:51:40,559
oxidation i wanted to see how it

940
00:51:44,309 --> 00:51:42,400
compared to

941
00:51:45,829 --> 00:51:44,319
how much glycerol was oxidized under the

942
00:51:48,069 --> 00:51:45,839
other conditions so that is what this

943
00:51:49,670 --> 00:51:48,079
plot is showing here the percentage of

944
00:51:51,030 --> 00:51:49,680
glycerol oxidation over time over the

945
00:51:54,390 --> 00:51:51,040
course of a month

946
00:51:56,470 --> 00:51:54,400
what you can see is as expected at ph 5

947
00:51:58,390 --> 00:51:56,480
more glycerol is oxidized compared to ph

948
00:52:00,790 --> 00:51:58,400
6.5 and 8. so that's not surprising

949
00:52:02,790 --> 00:52:00,800
considering that more phosphite was also

950
00:52:04,150 --> 00:52:02,800
oxidized under these conditions

951
00:52:05,190 --> 00:52:04,160
and in fact it's about a one-to-one

952
00:52:07,990 --> 00:52:05,200
ratio

953
00:52:10,069 --> 00:52:08,000
um intriguingly the ph 6.5 we actually

954
00:52:12,150 --> 00:52:10,079
have proportionally more glycerol being

955
00:52:15,030 --> 00:52:12,160
oxidized than we did have phosphite

956
00:52:16,309 --> 00:52:15,040
being oxidized um and so it was actually

957
00:52:19,270 --> 00:52:16,319
a little bit more than a one-to-one

958
00:52:21,510 --> 00:52:19,280
ratio and then um the opposite is true

959
00:52:23,190 --> 00:52:21,520
for ph eight where we had

960
00:52:24,790 --> 00:52:23,200
about seven if you recall about 75

961
00:52:27,990 --> 00:52:24,800
percent of the phosphite was being

962
00:52:29,670 --> 00:52:28,000
oxidized and um the significantly less

963
00:52:31,589 --> 00:52:29,680

glycerol is oxidized so it's a less than

964
00:52:33,589 --> 00:52:31,599
one to one ratio so although glycerol

965
00:52:36,150 --> 00:52:33,599
still oxidized under these conditions

966
00:52:39,510 --> 00:52:36,160
it's somewhat the oxidation is somewhat

967
00:52:42,390 --> 00:52:39,520
inhibited at pha

968
00:52:43,910 --> 00:52:42,400
so then if we switch gears to manganese

969
00:52:45,829 --> 00:52:43,920
all three of these spectra are

970
00:52:49,270 --> 00:52:45,839
phosphorous nmr of the manganese

971
00:52:50,870 --> 00:52:49,280
reactions at ph 5 ph 6.5 and ph 8 over

972
00:52:53,030 --> 00:52:50,880
the course of a month

973
00:52:55,109 --> 00:52:53,040
and what you can see here

974
00:52:56,390 --> 00:52:55,119
is a phosphate peak is present in all of

975
00:52:58,390 --> 00:52:56,400
them so that's just showing that

976
00:53:00,470 --> 00:52:58,400
manganese can facilitate this kind of

977
00:53:02,230 --> 00:53:00,480
chemistry under all of the conditions so

978
00:53:04,470 --> 00:53:02,240
whether dissolved or whether present as

979
00:53:06,549 --> 00:53:04,480
an oxyhydroxide mineral

980
00:53:08,630 --> 00:53:06,559
we only actually observed pyrophosphate

981
00:53:10,309 --> 00:53:08,640
you can see this trace peak here

982
00:53:11,990 --> 00:53:10,319
in the des when it was present as a

983
00:53:14,390 --> 00:53:12,000
dissolved metal

984
00:53:16,790 --> 00:53:14,400
in fact the reaction is just very very

985
00:53:18,470 --> 00:53:16,800
slow even at ph five

986
00:53:20,230 --> 00:53:18,480
but it's especially slow when it is

987
00:53:22,230 --> 00:53:20,240
trapped as an oxyhydroxide mineral as

988
00:53:24,230 --> 00:53:22,240

you can see by the overall yield shown

989
00:53:25,829 --> 00:53:24,240
here

990
00:53:28,630 --> 00:53:25,839
looking at the

991
00:53:32,150 --> 00:53:28,640
proton nmr spectra to see how glycerol

992
00:53:34,870 --> 00:53:32,160
behaved we found so the top spectra is

993
00:53:37,349 --> 00:53:34,880
the reaction with manganese at ph 5

994
00:53:39,510 --> 00:53:37,359
after 24 hours so we had about 8

995
00:53:42,390 --> 00:53:39,520
phosphite oxidized at that time point

996
00:53:44,710 --> 00:53:42,400
and the bottom is at ph 6.5 after the

997
00:53:46,630 --> 00:53:44,720
course of a month so about half of the

998
00:53:47,430 --> 00:53:46,640
amount of phosphite was oxidized at this

999
00:53:48,790 --> 00:53:47,440
point

1000
00:53:51,030 --> 00:53:48,800
and what you can see here on the top

1001
00:53:53,030 --> 00:53:51,040
part is that when manganese is dissolved

1002
00:53:54,950 --> 00:53:53,040
the glycerol still oxidizes so we see a

1003
00:53:57,109 --> 00:53:54,960
really large formate peak here so it

1004
00:53:59,109 --> 00:53:57,119
didn't prevent oxidation but when it's

1005
00:54:01,030 --> 00:53:59,119
present as an oxyhydroxide mineral we

1006
00:54:03,109 --> 00:54:01,040
did not observe any oxidation of the

1007
00:54:05,190 --> 00:54:03,119
glycerol and that was surprising because

1008
00:54:07,510 --> 00:54:05,200
even though it was relatively

1009
00:54:09,270 --> 00:54:07,520
low yields of a phosphite that was

1010
00:54:11,030 --> 00:54:09,280
oxidized you would still expect to see

1011
00:54:14,390 --> 00:54:11,040
at least a small trace peak of the

1012
00:54:16,069 --> 00:54:14,400
format but we did not see anything

1013
00:54:17,910 --> 00:54:16,079

so that seems to suggest that maybe this

1014
00:54:19,910 --> 00:54:17,920
is an avenue for generating

1015
00:54:22,790 --> 00:54:19,920
polyphosphates while minimizing organic

1016
00:54:25,349 --> 00:54:22,800
degradation and in fact previous work

1017
00:54:27,270 --> 00:54:25,359
has found that when looking at the

1018
00:54:29,670 --> 00:54:27,280
fenton chemistry facilitated by

1019
00:54:30,790 --> 00:54:29,680
manganese either dissolved or at ph

1020
00:54:33,190 --> 00:54:30,800
greater than six where it is

1021
00:54:35,190 --> 00:54:33,200
precipitated out it uh proceeds through

1022
00:54:36,789 --> 00:54:35,200
two different mechanisms so when it's

1023
00:54:39,190 --> 00:54:36,799
dissolved it's like iron it produces

1024
00:54:41,670 --> 00:54:39,200
hydroxyl radicals but at ph greater than

1025
00:54:43,670 --> 00:54:41,680
six it produces reducing radicals that

1026
00:54:45,430 --> 00:54:43,680
actually react with organics differently

1027
00:54:47,510 --> 00:54:45,440
in this case perhaps those reducing

1028
00:54:49,109 --> 00:54:47,520
radicals are not reacting with the

1029
00:54:50,789 --> 00:54:49,119
glycerol

1030
00:54:53,109 --> 00:54:50,799
so while this is a promising avenue

1031
00:54:55,030 --> 00:54:53,119
these reactions are very very slow

1032
00:54:56,710 --> 00:54:55,040
and so we would ideally like to run them

1033
00:54:59,990 --> 00:54:56,720
for much longer than a month to actually

1034
00:55:02,309 --> 00:55:00,000
see if this trend holds true when more

1035
00:55:04,069 --> 00:55:02,319
phosphite is actually oxidized

1036
00:55:05,910 --> 00:55:04,079
but that did lead us to question whether

1037
00:55:07,510 --> 00:55:05,920
mixed iron manganese minerals could be a

1038
00:55:08,950 --> 00:55:07,520

good avenue for

1039
00:55:11,030 --> 00:55:08,960
maximizing

1040
00:55:14,150 --> 00:55:11,040
this kind of reaction so what this is

1041
00:55:15,990 --> 00:55:14,160
showing is a range of iron and manganese

1042
00:55:18,789 --> 00:55:16,000
at different ratios and as predicted you

1043
00:55:22,150 --> 00:55:18,799
can see that at 100 iron we had the most

1044
00:55:23,510 --> 00:55:22,160
oxidized and that it decreases with iron

1045
00:55:26,549 --> 00:55:23,520
and then when looking at the amount of

1046
00:55:29,109 --> 00:55:26,559
organic that's oxidized you can see

1047
00:55:31,030 --> 00:55:29,119
100 iron that a lot of the glycerol was

1048
00:55:33,670 --> 00:55:31,040
oxidized as predicted and we do see that

1049
00:55:35,829 --> 00:55:33,680
trace formate peak and other reactions

1050
00:55:37,750 --> 00:55:35,839
but really what really intrigued me is

1051
00:55:39,190 --> 00:55:37,760
that the glycerol peak just disappeared

1052
00:55:41,829 --> 00:55:39,200
all together when we had mixed iron

1053
00:55:43,430 --> 00:55:41,839
manganese minerals which was strange um

1054
00:55:44,549 --> 00:55:43,440
i'm not quite sure what happened to the

1055
00:55:46,950 --> 00:55:44,559
glycerol

1056
00:55:48,789 --> 00:55:46,960
we did have controls so we did run it

1057
00:55:50,069 --> 00:55:48,799
without the peroxide and the glycerol

1058
00:55:51,349 --> 00:55:50,079
was stable

1059
00:55:53,030 --> 00:55:51,359
so i don't think it's absorbing to the

1060
00:55:54,390 --> 00:55:53,040
mineral unless it only absorbs to the

1061
00:55:56,069 --> 00:55:54,400
oxidized mineral but that would be

1062
00:55:57,270 --> 00:55:56,079
surprising giving the structure of

1063
00:55:59,109 --> 00:55:57,280

glycerol

1064
00:56:01,430 --> 00:55:59,119
and if we zoom here on the formate peak

1065
00:56:03,990 --> 00:56:01,440
you do see that trace formate peak

1066
00:56:05,190 --> 00:56:04,000
in the reactions and so

1067
00:56:06,710 --> 00:56:05,200
it's actually a lot less than you would

1068
00:56:09,190 --> 00:56:06,720
expect considering how much phosphite

1069
00:56:12,150 --> 00:56:09,200
was oxidized so no matter what the

1070
00:56:14,230 --> 00:56:12,160
oxidation of glycerol seems to be

1071
00:56:16,390 --> 00:56:14,240
inhibited but where it went remains

1072
00:56:19,829 --> 00:56:16,400
uncertain and so these are the overall

1073
00:56:21,589 --> 00:56:19,839
conclusions and i would like to thank my

1074
00:56:23,829 --> 00:56:21,599
advisor dr lori barge as well as my

1075
00:56:25,670 --> 00:56:23,839
other co-authors dr david vanderveld and

1076
00:56:28,130 --> 00:56:25,680
dr matthew pasek and thank you all for

1077
00:56:33,349 --> 00:56:28,140
your time and attention

1078
00:56:33,359 --> 00:56:46,390
time for a couple of questions

1079
00:56:50,870 --> 00:56:49,190
hi laura matt hazen usf um

1080
00:56:52,630 --> 00:56:50,880
so i'm curious where your glossary went

1081
00:56:54,549 --> 00:56:52,640
then i mean is there

1082
00:56:56,309 --> 00:56:54,559
do you have any i guess you have some

1083
00:56:57,589 --> 00:56:56,319
amount of speculation but anything

1084
00:56:59,190 --> 00:56:57,599
specific

1085
00:57:01,589 --> 00:56:59,200
about the glycerol yeah

1086
00:57:03,910 --> 00:57:01,599
yeah um so i was thinking that

1087
00:57:05,589 --> 00:57:03,920
perhaps that since it is a different

1088
00:57:06,549 --> 00:57:05,599

radical that forms with the manganese

1089
00:57:08,309 --> 00:57:06,559
when it's

1090
00:57:10,150 --> 00:57:08,319
crashed out as a precipitate that that

1091
00:57:12,390 --> 00:57:10,160
different radical is

1092
00:57:13,990 --> 00:57:12,400
reacting with the glycerol and the

1093
00:57:15,910 --> 00:57:14,000
reason that you don't see that with just

1094
00:57:18,150 --> 00:57:15,920
manganese is perhaps having that iron

1095
00:57:20,870 --> 00:57:18,160
there really promotes that reaction as

1096
00:57:22,630 --> 00:57:20,880
well um but at this point it's kind of

1097
00:57:24,710 --> 00:57:22,640
speculation i just find it i just

1098
00:57:26,630 --> 00:57:24,720
wouldn't expect it to actually absorb to

1099
00:57:28,710 --> 00:57:26,640
the oxyhydroxide mineral that doesn't

1100
00:57:30,710 --> 00:57:28,720
seem likely but we will test that just

1101
00:57:32,950 --> 00:57:30,720
to make sure

1102
00:57:33,750 --> 00:57:32,960
while we're at it do you have it i'm

1103
00:57:35,829 --> 00:57:33,760
here

1104
00:57:37,829 --> 00:57:35,839
do you happen to know what the

1105
00:57:38,950 --> 00:57:37,839
oxidation states that were sampled by

1106
00:57:40,710 --> 00:57:38,960
the manganese i mean you were

1107
00:57:43,349 --> 00:57:40,720
introducing it manganese three i'm

1108
00:57:45,829 --> 00:57:43,359
assuming did you see manganese iv i'm

1109
00:57:48,630 --> 00:57:45,839
assuming you never saw manganese seven

1110
00:57:50,230 --> 00:57:48,640
but did you oh no we didn't investigate

1111
00:57:52,630 --> 00:57:50,240
the oxidation state of manganese i just

1112
00:57:55,109 --> 00:57:52,640
know that it started at manganese two

1113
00:57:56,710 --> 00:57:55,119

we are getting a cation um

1114
00:57:58,630 --> 00:57:56,720
icy though so that is one of the things

1115
00:58:01,190 --> 00:57:58,640
that i'm interested in looking at it

1116
00:58:06,829 --> 00:58:01,200
didn't turn purple it didn't turn purple

1117
00:58:06,839 --> 00:58:11,030
brown any other questions

1118
00:58:13,270 --> 00:58:12,470
in that way of time so i'll ask a

1119
00:58:15,430 --> 00:58:13,280
question

1120
00:58:17,270 --> 00:58:15,440
so um what do you think would hap would

1121
00:58:19,270 --> 00:58:17,280
be the effect of if your iron was in

1122
00:58:21,430 --> 00:58:19,280
varying redox states such as if it

1123
00:58:24,069 --> 00:58:21,440
wasn't just an fe2 hydroxide but a mixed

1124
00:58:26,950 --> 00:58:24,079
fe2 fe3 hydroxide

1125
00:58:28,789 --> 00:58:26,960
good question uh i believe matt has

1126
00:58:30,789 --> 00:58:28,799
actually done some work on that and the

1127
00:58:32,549 --> 00:58:30,799
reaction still proceeded with ferric

1128
00:58:33,670 --> 00:58:32,559
iron right in fact i think it was

1129
00:58:36,230 --> 00:58:33,680
actually

1130
00:58:38,549 --> 00:58:36,240
more efficient with the ferric iron or i

1131
00:58:40,230 --> 00:58:38,559
forget what the actual result was but

1132
00:58:42,150 --> 00:58:40,240
um

1133
00:58:46,470 --> 00:58:42,160
that is a good question i'm not quite

1134
00:58:46,480 --> 00:58:55,349
thank you all right thanks very much

1135
00:58:55,359 --> 00:59:14,069
our next speaker is matt pasek

1136
00:59:19,510 --> 00:59:16,309
hello everyone uh thank you kindly for

1137
00:59:21,349 --> 00:59:19,520
uh the invitation to speak and and today

1138
00:59:23,829 --> 00:59:21,359

i should note as well that this is

1139
00:59:25,589 --> 00:59:23,839
actually uh mahingal is should be the

1140
00:59:28,950 --> 00:59:25,599
lead author on it on this paper but

1141
00:59:31,270 --> 00:59:28,960
instead has uh has two small kids and

1142
00:59:33,589 --> 00:59:31,280
asked me to present in her stead so it

1143
00:59:36,150 --> 00:59:33,599
is a continuation similarly of what

1144
00:59:39,190 --> 00:59:36,160
laura just presented on fenton chemistry

1145
00:59:41,589 --> 00:59:39,200
and reduced phosphorus and the potential

1146
00:59:43,430 --> 00:59:41,599
of doing something interesting with that

1147
00:59:45,430 --> 00:59:43,440
and i'll show you some of the results

1148
00:59:47,030 --> 00:59:45,440
here and so

1149
00:59:49,309 --> 00:59:47,040
her title here is an early earth

1150
00:59:51,430 --> 00:59:49,319
predisposed to phosphonylation and

1151
00:59:53,190 --> 00:59:51,440
phosphorylation by reduced oxidation

1152
00:59:54,789 --> 00:59:53,200
state phosphorus compounds so

1153
00:59:56,789 --> 00:59:54,799
phosphorylation is the addition of

1154
00:59:59,750 --> 00:59:56,799
phosphate phosphonylation is the

1155
01:00:01,990 --> 00:59:59,760
addition of phosphite

1156
01:00:04,390 --> 01:00:02,000
sorry for the names uh the phosphorus

1157
01:00:06,150 --> 01:00:04,400
people got a hold of things and added

1158
01:00:07,829 --> 01:00:06,160
you know many years ago and it becomes

1159
01:00:09,589 --> 01:00:07,839
very hectic especially when you start

1160
01:00:11,150 --> 01:00:09,599
talking about all the various forms of

1161
01:00:13,910 --> 01:00:11,160
phosphorus including things like

1162
01:00:15,910 --> 01:00:13,920
hypophosphite which is shown here is one

1163
01:00:18,309 --> 01:00:15,920

and phosphite which is two and there's a

1164
01:00:20,950 --> 01:00:18,319
hypophosphate which is a plus four

1165
01:00:23,270 --> 01:00:20,960
oxidation state and there's uh uh

1166
01:00:25,230 --> 01:00:23,280
phosphate which is shown here and then

1167
01:00:28,950 --> 01:00:25,240
pyrophosphate and there's a

1168
01:00:30,230 --> 01:00:28,960
pyrophosphite it gets confusing quick

1169
01:00:31,990 --> 01:00:30,240
but

1170
01:00:34,870 --> 01:00:32,000
what we have been looking at is the

1171
01:00:38,390 --> 01:00:34,880
potential of reduced forms of phosphorus

1172
01:00:40,549 --> 01:00:38,400
being able to oxidize and form reactive

1173
01:00:42,470 --> 01:00:40,559
phosphate compounds that could then

1174
01:00:44,309 --> 01:00:42,480
perform key reactions

1175
01:00:45,670 --> 01:00:44,319
and mckeen specifically was

1176
01:00:47,190 --> 01:00:45,680
investigating the reactions between

1177
01:00:48,950 --> 01:00:47,200
reduced oxidation state phosphorus

1178
01:00:50,789 --> 01:00:48,960
compound hypophosphite and that's what

1179
01:00:53,270 --> 01:00:50,799
we'll show specifically here so instead

1180
01:00:54,309 --> 01:00:53,280
of phosphite it is a one plus oxidation

1181
01:00:58,069 --> 01:00:54,319
state

1182
01:01:00,470 --> 01:00:58,079
that can then react with uh the oxide of

1183
01:01:01,990 --> 01:01:00,480
generated by the the fenton chemistry

1184
01:01:03,270 --> 01:01:02,000
and produce reactive phosphorus

1185
01:01:05,030 --> 01:01:03,280
compounds

1186
01:01:07,349 --> 01:01:05,040
we specifically investigated the

1187
01:01:10,549 --> 01:01:07,359
reactions of uridine and adenosine in

1188
01:01:12,309 --> 01:01:10,559

this experiment as well so the

1189
01:01:14,069 --> 01:01:12,319
generation of reduced oxidation state

1190
01:01:16,150 --> 01:01:14,079
phosphorus compounds laura showed kind

1191
01:01:18,549 --> 01:01:16,160
of the uh the general scheme of it right

1192
01:01:20,710 --> 01:01:18,559
here it's a radical induced reaction the

1193
01:01:23,589 --> 01:01:20,720
fenton chemistry specifically forms

1194
01:01:26,069 --> 01:01:23,599
hydroxyl radicals when using iron two

1195
01:01:28,630 --> 01:01:26,079
and those iron those hydroxyl radicals

1196
01:01:31,030 --> 01:01:28,640
rip up that hydrogen phosphorus bond and

1197
01:01:32,710 --> 01:01:31,040
slowly start to oxidize it and the

1198
01:01:36,150 --> 01:01:32,720
interesting thing is you can get a sort

1199
01:01:39,270 --> 01:01:36,160
of possibly a reactive intermediate that

1200
01:01:42,309 --> 01:01:39,280
can form the pyrophosphate triphosphate

1201
01:01:44,950 --> 01:01:42,319
and the cyclic triphosphate as uh sort

1202
01:01:49,589 --> 01:01:44,960
of the oxidized final products it's

1203
01:01:51,270 --> 01:01:49,599
roughly a 70 to 20 to maybe three uh my

1204
01:01:54,789 --> 01:01:51,280
i guess my mass not adding up right

1205
01:01:57,270 --> 01:01:54,799
there 70 to 25 to three to two ratio of

1206
01:01:59,349 --> 01:01:57,280
those four types of compounds here and

1207
01:02:01,349 --> 01:01:59,359
so you use origin originally you use

1208
01:02:03,190 --> 01:02:01,359
some reduced forms of phosphorus oxidize

1209
01:02:05,349 --> 01:02:03,200
those and you can create condensed forms

1210
01:02:07,910 --> 01:02:05,359
of phosphorus condensed phosphates that

1211
01:02:09,829 --> 01:02:07,920
have been used uh previously in several

1212
01:02:11,990 --> 01:02:09,839
reactions to promote phosphorylation

1213
01:02:13,750 --> 01:02:12,000

reactions so the question of course then

1214
01:02:15,589 --> 01:02:13,760
you might have is where are these things

1215
01:02:16,870 --> 01:02:15,599
coming from uh reduced phosphorus you

1216
01:02:19,589 --> 01:02:16,880
can ask

1217
01:02:21,270 --> 01:02:19,599
there's roots from diagenesis uh where

1218
01:02:23,349 --> 01:02:21,280
you take iron two and react with

1219
01:02:25,349 --> 01:02:23,359
phosphate at 200 degrees celsius you can

1220
01:02:27,589 --> 01:02:25,359
make phosphite you can do lightening you

1221
01:02:29,270 --> 01:02:27,599
can have meteoritic materials corrode

1222
01:02:31,109 --> 01:02:29,280
and they will release some phosphate too

1223
01:02:32,870 --> 01:02:31,119
there are some other sources that are

1224
01:02:34,549 --> 01:02:32,880
that we're working on even now that

1225
01:02:36,950 --> 01:02:34,559
there it may have been an important

1226
01:02:39,349 --> 01:02:36,960
constituent on a prebiotic earth

1227
01:02:41,670 --> 01:02:39,359
peroxide is a pretty strong oxidant but

1228
01:02:44,870 --> 01:02:41,680
it is also formed through uv photolysis

1229
01:02:46,789 --> 01:02:44,880
of water um it's found as sort of an ice

1230
01:02:48,870 --> 01:02:46,799
photolysis or radialis product for

1231
01:02:51,670 --> 01:02:48,880
instance on europa so there are ways of

1232
01:02:53,270 --> 01:02:51,680
making a pretty strong oxidant and a

1233
01:02:55,109 --> 01:02:53,280
pretty strong reducing form of

1234
01:02:56,549 --> 01:02:55,119
phosphorus now the interesting thing is

1235
01:02:59,750 --> 01:02:56,559
that reduced phosphorus is actually

1236
01:03:03,190 --> 01:02:59,760
pretty stable we have left a vial of

1237
01:03:05,510 --> 01:03:03,200
phosphite in water stored under air sit

1238
01:03:08,870 --> 01:03:05,520

for five years and had point one percent

1239
01:03:10,309 --> 01:03:08,880
oxidation so this is not a a unstable

1240
01:03:12,150 --> 01:03:10,319
compound that is something that you

1241
01:03:14,630 --> 01:03:12,160
would need to worry about oxidation from

1242
01:03:16,789 --> 01:03:14,640
air or other compound or other oxidants

1243
01:03:19,270 --> 01:03:16,799
in the environment most of what we do is

1244
01:03:21,349 --> 01:03:19,280
phosphorus 31 nmr which is uh the ppm

1245
01:03:23,510 --> 01:03:21,359
scale down here and so this is starting

1246
01:03:25,109 --> 01:03:23,520
material this is hypophosphite

1247
01:03:27,270 --> 01:03:25,119
and it is a triplet because there's two

1248
01:03:29,589 --> 01:03:27,280
hydrogens bound to the phosphorus and

1249
01:03:32,309 --> 01:03:29,599
then when you add the iron and peroxide

1250
01:03:33,589 --> 01:03:32,319
to that you will form uh the phosphite

1251
01:03:35,589 --> 01:03:33,599
in addition to

1252
01:03:37,990 --> 01:03:35,599
to phosphate here and the phosphites

1253
01:03:39,510 --> 01:03:38,000
peak b phosphate is a peak c here and

1254
01:03:41,589 --> 01:03:39,520
there are the pyrophosphate and

1255
01:03:44,549 --> 01:03:41,599
triphosphate that are formed at lower

1256
01:03:47,670 --> 01:03:44,559
concentrations uh further uh up

1257
01:03:50,390 --> 01:03:47,680
uh up field here as well

1258
01:03:53,109 --> 01:03:50,400
so what maheen did uh specifically was

1259
01:03:56,069 --> 01:03:53,119
take a nucleoside in this case uridine

1260
01:03:56,950 --> 01:03:56,079
and then after so i should note after

1261
01:04:04,470 --> 01:03:56,960
the

1262
01:04:06,150 --> 01:04:04,480
it kind of finished she added uridine as

1263
01:04:07,829 --> 01:04:06,160

well as a couple other compounds such as

1264
01:04:11,029 --> 01:04:07,839
urea or

1265
01:04:13,349 --> 01:04:11,039
ammonium hydroxide and then took a look

1266
01:04:15,750 --> 01:04:13,359
and see what you have and so again going

1267
01:04:17,750 --> 01:04:15,760
from the more uh the sort of oxidized

1268
01:04:19,589 --> 01:04:17,760
products of this prior sort of uh

1269
01:04:21,589 --> 01:04:19,599
inorganic spectrum right here and then

1270
01:04:23,910 --> 01:04:21,599
adding after

1271
01:04:25,270 --> 01:04:23,920
the fact a nucleoside you see there's a

1272
01:04:28,069 --> 01:04:25,280
lot of new compounds that have come

1273
01:04:30,710 --> 01:04:28,079
about and these compounds are a number

1274
01:04:31,950 --> 01:04:30,720
of different styles of organics

1275
01:04:34,150 --> 01:04:31,960
mostly

1276
01:04:35,990 --> 01:04:34,160
organophosphonates but also a fair bit

1277
01:04:38,309 --> 01:04:36,000
of organophosphates

1278
01:04:40,390 --> 01:04:38,319
and so these include two prime three

1279
01:04:42,950 --> 01:04:40,400
prime uh five prime phosphites of

1280
01:04:44,549 --> 01:04:42,960
uridine as well as a phosphates there

1281
01:04:46,549 --> 01:04:44,559
appears to be some dimer and i'll show

1282
01:04:49,190 --> 01:04:46,559
you some of that in a little bit and we

1283
01:04:51,430 --> 01:04:49,200
do have some cyclic diester as well the

1284
01:04:54,230 --> 01:04:51,440
total amount of organic phosphorus that

1285
01:04:56,230 --> 01:04:54,240
she is reporting from the integration of

1286
01:04:59,190 --> 01:04:56,240
the the nmr shown here is on the order

1287
01:05:01,589 --> 01:04:59,200
of 22 to 76 percent and

1288
01:05:03,270 --> 01:05:01,599

the you know that is as a fraction of

1289
01:05:05,910 --> 01:05:03,280
phosphorus that is visible within the

1290
01:05:08,549 --> 01:05:05,920
phosphorus nmr

1291
01:05:10,309 --> 01:05:08,559
so sort of a larger perspective of this

1292
01:05:12,230 --> 01:05:10,319
in a sort of more whole field we as well

1293
01:05:14,470 --> 01:05:12,240
use phosphonyl acetic acid as our

1294
01:05:18,870 --> 01:05:14,480
standard which pops up at our ph at

1295
01:05:21,990 --> 01:05:18,880
about uh ph uh about 15.5 ppm and then

1296
01:05:23,190 --> 01:05:22,000
over at uh the sort of 20 ppm is the

1297
01:05:27,829 --> 01:05:23,200
cyclic

1298
01:05:30,150 --> 01:05:27,839
prime uridine phosphate and then you see

1299
01:05:31,750 --> 01:05:30,160
that the inorganic uh phosphorus

1300
01:05:33,549 --> 01:05:31,760
compounds as well as the organic

1301
01:05:35,750 --> 01:05:33,559
phosphates and organic phos

1302
01:05:38,390 --> 01:05:35,760
organophosphonates are present at these

1303
01:05:39,109 --> 01:05:38,400
lower ranges right here and then blown

1304
01:05:42,230 --> 01:05:39,119
up

1305
01:05:44,390 --> 01:05:42,240
right around minus one is what we

1306
01:05:47,029 --> 01:05:44,400
believe to be diesters so that is

1307
01:05:50,309 --> 01:05:47,039
uridine phosphate uridine phosphate

1308
01:05:52,470 --> 01:05:50,319
uridine and there is a sort of chemistry

1309
01:05:54,470 --> 01:05:52,480
that's going on with this this is a

1310
01:05:56,950 --> 01:05:54,480
add this stuff to the compound and then

1311
01:05:59,190 --> 01:05:56,960
let it sit and slowly dry out i should

1312
01:06:02,069 --> 01:05:59,200
add that she is doing this at around 58

1313
01:06:03,270 --> 01:06:02,079

to 65 degrees celsius um

1314
01:06:05,670 --> 01:06:03,280
and then to see what sorts of

1315
01:06:07,430 --> 01:06:05,680
phos-related organics she is producing

1316
01:06:09,589 --> 01:06:07,440
and uh again you have some of the

1317
01:06:11,349 --> 01:06:09,599
uridine uh the we spike this with

1318
01:06:13,990 --> 01:06:11,359
austenitic sample of uradine uh

1319
01:06:16,789 --> 01:06:14,000
five-prime monophosphate and indeed the

1320
01:06:19,349 --> 01:06:16,799
the peak e here is one that rises uh

1321
01:06:21,109 --> 01:06:19,359
when when spiked here

1322
01:06:24,069 --> 01:06:21,119
so to summarize what she sees with

1323
01:06:25,349 --> 01:06:24,079
uridine uh we have our uridine starting

1324
01:06:27,589 --> 01:06:25,359
product and then we have the uridine

1325
01:06:29,190 --> 01:06:27,599
phosphates uh from the phi prime the two

1326
01:06:31,190 --> 01:06:29,200
prime to three prime and then the cyclic

1327
01:06:33,349 --> 01:06:31,200
three two prime three prime in addition

1328
01:06:34,789 --> 01:06:33,359
there are the phosphites also probably

1329
01:06:37,589 --> 01:06:34,799
in the similar condition but you do not

1330
01:06:39,190 --> 01:06:37,599
form the cyclic uridine phosphite um

1331
01:06:40,470 --> 01:06:39,200
because there is no negative charge on

1332
01:06:42,950 --> 01:06:40,480
the phosphite to kind of keep it

1333
01:06:45,589 --> 01:06:42,960
stabilized and then as well there are

1334
01:06:48,069 --> 01:06:45,599
the dimers that are being produced there

1335
01:06:49,910 --> 01:06:48,079
and then if you take adenosine you see

1336
01:06:52,549 --> 01:06:49,920
something very similar the adenosine

1337
01:06:55,190 --> 01:06:52,559
also forms adenosine monophosphates and

1338
01:06:57,349 --> 01:06:55,200

adenosine monophosphites as well as the

1339
01:07:00,230 --> 01:06:57,359
adenosine cyclic two three two prime

1340
01:07:02,549 --> 01:07:00,240
three prime uh phosphate there is also

1341
01:07:05,109 --> 01:07:02,559
this peak corresponding to a dimer as

1342
01:07:07,910 --> 01:07:05,119
well um i should add that when sampled

1343
01:07:09,750 --> 01:07:07,920
by uh m uh mass spectrometry the these

1344
01:07:12,710 --> 01:07:09,760
peaks were all matched to a specific

1345
01:07:14,710 --> 01:07:12,720
gamma or z uh but um

1346
01:07:16,230 --> 01:07:14,720
so there is mass spec

1347
01:07:17,910 --> 01:07:16,240
evidence for each of these compounds as

1348
01:07:19,190 --> 01:07:17,920
well

1349
01:07:20,789 --> 01:07:19,200
so

1350
01:07:22,870 --> 01:07:20,799
again very similar compounds that are

1351
01:07:25,510 --> 01:07:22,880
formed with using adenosine in place of

1352
01:07:27,109 --> 01:07:25,520
uridine suggesting that this style

1353
01:07:29,270 --> 01:07:27,119
chemistry could work

1354
01:07:31,270 --> 01:07:29,280
again after the fact as opposed to being

1355
01:07:34,150 --> 01:07:31,280
subjected to the oxidizing conditions of

1356
01:07:35,430 --> 01:07:34,160
the fenton chemistry and then using a

1357
01:07:36,829 --> 01:07:35,440
two

1358
01:07:40,309 --> 01:07:36,839
deoxyri

1359
01:07:42,470 --> 01:07:40,319
and subjecting that to the these

1360
01:07:44,549 --> 01:07:42,480
conditions we took a look at to see if

1361
01:07:46,309 --> 01:07:44,559
the similar chemistry would come about

1362
01:07:49,910 --> 01:07:46,319
and intriguingly you see here that there

1363
01:07:51,910 --> 01:07:49,920

is no peak corresponding to the um to

1364
01:07:54,069 --> 01:07:51,920
the dimer in this case the dimer would

1365
01:07:56,870 --> 01:07:54,079
appear between zero and and minus two

1366
01:07:58,950 --> 01:07:56,880
right here and it's not there and there

1367
01:08:00,630 --> 01:07:58,960
is additionally no cyclic two prime

1368
01:08:04,069 --> 01:08:00,640
three prime because there it is not

1369
01:08:07,430 --> 01:08:04,079
possible with uh the deoxy adenosine and

1370
01:08:09,270 --> 01:08:07,440
suggesting perhaps that the cyclic uh

1371
01:08:11,270 --> 01:08:09,280
uridine or adenosine two prime three

1372
01:08:13,910 --> 01:08:11,280
prime is the key intermediate forming

1373
01:08:16,870 --> 01:08:13,920
the dimer here

1374
01:08:18,709 --> 01:08:16,880
so the late addition of the organics to

1375
01:08:20,630 --> 01:08:18,719
the solution so after the fenton

1376
01:08:23,829 --> 01:08:20,640
chemistry is kind of burned off much of

1377
01:08:25,349 --> 01:08:23,839
the oxygen appears to be necessary and

1378
01:08:27,590 --> 01:08:25,359
laura showed that very well that

1379
01:08:30,229 --> 01:08:27,600
glycerol is getting ripped up by the

1380
01:08:31,669 --> 01:08:30,239
fentany conditions pretty clearly uh we

1381
01:08:33,669 --> 01:08:31,679
took a look to see the stability of

1382
01:08:37,030 --> 01:08:33,679
adenosine so if you take adenosine this

1383
01:08:39,189 --> 01:08:37,040
is a carbon-13 nmr uh sort of the

1384
01:08:42,630 --> 01:08:39,199
the standard adenosine and then

1385
01:08:43,990 --> 01:08:42,640
subjected to one day of reaction in phen

1386
01:08:46,390 --> 01:08:44,000
chemistry you see some of these peaks

1387
01:08:48,709 --> 01:08:46,400
are starting to drop down two days and

1388
01:08:51,189 --> 01:08:48,719

then three days right here effectively

1389
01:08:53,910 --> 01:08:51,199
all the carbon has become carbonate or

1390
01:08:55,110 --> 01:08:53,920
similar fully oxidized forms of carbon

1391
01:08:57,510 --> 01:08:55,120
so the

1392
01:08:59,430 --> 01:08:57,520
addition of organics it would it

1393
01:09:00,870 --> 01:08:59,440
unfortunately is not a one pot reaction

1394
01:09:02,709 --> 01:09:00,880
that we often seek in prebiotic

1395
01:09:04,550 --> 01:09:02,719
chemistry but is at least a two pot

1396
01:09:07,269 --> 01:09:04,560
reaction in this case

1397
01:09:08,870 --> 01:09:07,279
problematic but there is some promise as

1398
01:09:10,789 --> 01:09:08,880
far as forming dimers and other

1399
01:09:13,430 --> 01:09:10,799
compounds in this chemistry here

1400
01:09:16,630 --> 01:09:13,440
so to kind of summarize uh the best

1401
01:09:18,630 --> 01:09:16,640
reactions between 70 and 80 yield of

1402
01:09:20,309 --> 01:09:18,640
total organic phosphorus that includes

1403
01:09:23,349 --> 01:09:20,319
the organophosphates as well as the

1404
01:09:25,510 --> 01:09:23,359
organic phosphates uh it occurs when you

1405
01:09:28,229 --> 01:09:25,520
use urea and ammonium

1406
01:09:30,950 --> 01:09:28,239
as constituents of this chemistry

1407
01:09:32,709 --> 01:09:30,960
she's done this experiment now several

1408
01:09:35,349 --> 01:09:32,719
dozen times and has been able to get

1409
01:09:37,430 --> 01:09:35,359
these results at least reproducibly and

1410
01:09:39,269 --> 01:09:37,440
her chemistry suggests that the ammonia

1411
01:09:40,709 --> 01:09:39,279
compounds including ammonia from urea

1412
01:09:42,470 --> 01:09:40,719
seems to be kind of

1413
01:09:44,149 --> 01:09:42,480

very helpful in generating reactive

1414
01:09:46,789 --> 01:09:44,159
phosphorus compounds

1415
01:09:48,630 --> 01:09:46,799
that promote condensed phosphates uh

1416
01:09:51,669 --> 01:09:48,640
that we are looking for in sort of our

1417
01:09:53,349 --> 01:09:51,679
prebiotic chemistry and the dimers seem

1418
01:09:55,590 --> 01:09:53,359
to be coming out in this chemistry as

1419
01:09:57,270 --> 01:09:55,600
well and organics could potentially

1420
01:09:58,390 --> 01:09:57,280
survive some of the harsh peroxide

1421
01:10:00,550 --> 01:09:58,400
conditions

1422
01:10:02,229 --> 01:10:00,560
it they're gone in about three days but

1423
01:10:04,470 --> 01:10:02,239
one day there's still some adenosine

1424
01:10:06,550 --> 01:10:04,480
left as well so with that i'll say

1425
01:10:16,470 --> 01:10:06,560
thanks to our collaborators and our

1426
01:10:16,480 --> 01:10:28,950
we have time for a couple questions

1427
01:10:32,790 --> 01:10:31,030
great dog so i have a question how much

1428
01:10:34,870 --> 01:10:32,800
peroxide do you need to have those

1429
01:10:36,630 --> 01:10:34,880
reactions is this probiotically

1430
01:10:38,790 --> 01:10:36,640
plausible

1431
01:10:40,709 --> 01:10:38,800
that is a good question so you need a

1432
01:10:43,910 --> 01:10:40,719
fair bit more stoichiometric peroxide

1433
01:10:47,510 --> 01:10:43,920
than iron so roughly uh you need four

1434
01:10:49,590 --> 01:10:47,520
equivalents of peroxide to every phos

1435
01:10:51,750 --> 01:10:49,600
hypophosphite or two equivalents for

1436
01:10:53,990 --> 01:10:51,760
every phosphite

1437
01:10:56,870 --> 01:10:54,000
that's a fair bit

1438
01:10:58,390 --> 01:10:56,880

it is added you can add it slowly over

1439
01:11:00,070 --> 01:10:58,400
the course of a day or you can add it

1440
01:11:01,189 --> 01:11:00,080
all at once

1441
01:11:02,709 --> 01:11:01,199
there is

1442
01:11:04,630 --> 01:11:02,719
not really a lot of difference in the

1443
01:11:05,669 --> 01:11:04,640
chemistry the final resulting chemistry

1444
01:11:08,229 --> 01:11:05,679
but

1445
01:11:10,709 --> 01:11:08,239
it is on the order in this case of

1446
01:11:16,550 --> 01:11:10,719
hundreds of millimoles so and that's

1447
01:11:20,550 --> 01:11:18,550
hey matt great talk um luke stella from

1448
01:11:22,070 --> 01:11:20,560
the australian center for astrobiology

1449
01:11:23,590 --> 01:11:22,080
um i was really interested seeing those

1450
01:11:26,470 --> 01:11:23,600
dimers come up and i was wondering if

1451
01:11:28,790 --> 01:11:26,480
you saw anything longer um anymore like

1452
01:11:30,630 --> 01:11:28,800
yeah longer polymerization and right if

1453
01:11:32,470 --> 01:11:30,640
not what you could do to maybe promote

1454
01:11:35,350 --> 01:11:32,480
that and get some nice little polymers

1455
01:11:38,470 --> 01:11:35,360
for me that is a fantastic question um

1456
01:11:40,390 --> 01:11:38,480
by mass so unfortunately with nmr you're

1457
01:11:42,310 --> 01:11:40,400
kind of looking at either monomeric

1458
01:11:45,030 --> 01:11:42,320
phosphate or dimeric phosphate or

1459
01:11:47,189 --> 01:11:45,040
polymeric phosphate if you will

1460
01:11:48,149 --> 01:11:47,199
dimeric and polymeric phosphate look the

1461
01:11:50,149 --> 01:11:48,159
same

1462
01:11:51,270 --> 01:11:50,159
when we looked by mass spec we only saw

1463
01:11:53,510 --> 01:11:51,280

the dimer

1464
01:11:56,229 --> 01:11:53,520
so trimer would be excellent but we

1465
01:11:57,910 --> 01:11:56,239
didn't happen to see that far ahead so

1466
01:11:59,590 --> 01:11:57,920
right now only the dimers i can say

1467
01:12:05,669 --> 01:11:59,600
conclusively

1468
01:12:09,590 --> 01:12:06,950
i have a question

1469
01:12:11,590 --> 01:12:09,600
so um so thinking about the last two

1470
01:12:13,110 --> 01:12:11,600
talks so if you have ammonia that's

1471
01:12:14,790 --> 01:12:13,120
required for this reaction do you think

1472
01:12:16,630 --> 01:12:14,800
it's possible that that ammonia could be

1473
01:12:18,870 --> 01:12:16,640
generated by some of these iron

1474
01:12:21,350 --> 01:12:18,880
hydroxides from say reduction of nitrate

1475
01:12:22,390 --> 01:12:21,360
or nitrite right right so you know of

1476
01:12:24,229 --> 01:12:22,400
course there's

1477
01:12:25,990 --> 01:12:24,239
the the mixing of this chemistry

1478
01:12:28,149 --> 01:12:26,000
involves very reduced phases very

1479
01:12:29,990 --> 01:12:28,159
oxidizing phases the ammonia is a pretty

1480
01:12:32,390 --> 01:12:30,000
reduced phase as well

1481
01:12:35,270 --> 01:12:32,400
so yeah i mean i suppose that if you had

1482
01:12:38,470 --> 01:12:35,280
an environment that

1483
01:12:40,229 --> 01:12:38,480
you had pretty spatially different

1484
01:12:42,149 --> 01:12:40,239
types of disequilibrium maybe something

1485
01:12:45,350 --> 01:12:42,159
like that could arise where you had your

1486
01:12:47,270 --> 01:12:45,360
reduced ammonium and phosphite in one

1487
01:12:48,950 --> 01:12:47,280
area that then came in contact with

1488
01:12:50,390 --> 01:12:48,960

peroxide and the iron as sort of the

1489
01:12:52,550 --> 01:12:50,400
boundary that would be a

1490
01:13:03,669 --> 01:12:52,560
an interesting possibility

1491
01:13:26,630 --> 01:13:04,630
all maybe

1492
01:13:33,189 --> 01:13:30,630
okay uh hello everyone i am yuta hiroko

1493
01:13:35,750 --> 01:13:33,199
a phd student at the university

1494
01:13:37,270 --> 01:13:35,760
in japan today i will talk about the

1495
01:13:39,510 --> 01:13:37,280
effects of bull rate

1496
01:13:40,630 --> 01:13:39,520
on selective phosphorylation arrivals on

1497
01:13:42,630 --> 01:13:40,640
the areas

1498
01:13:44,470 --> 01:13:42,640
my research interest is the origin of

1499
01:13:47,669 --> 01:13:44,480
rna and the

1500
01:13:50,390 --> 01:13:47,679
original nucleotide

1501
01:13:52,950 --> 01:13:50,400
and the rna is one of the most important

1502
01:13:56,070 --> 01:13:52,960
molecules for the original life and it

1503
01:13:58,550 --> 01:13:56,080
can hold the information and catalyze

1504
01:14:01,270 --> 01:13:58,560
some chemical reactions in your body

1505
01:14:02,950 --> 01:14:01,280
so many researchers suppose that

1506
01:14:06,310 --> 01:14:02,960
primordial life

1507
01:14:09,189 --> 01:14:06,320
used rna for their supplication

1508
01:14:12,709 --> 01:14:09,199
this this theory is called rna world

1509
01:14:15,750 --> 01:14:12,719
hypothesis and based on this hypothesis

1510
01:14:18,070 --> 01:14:15,760
the rna formation is a crucial step for

1511
01:14:21,590 --> 01:14:18,080
the original life

1512
01:14:24,950 --> 01:14:21,600
and rna is a polymer of ribonucleotide

1513
01:14:27,830 --> 01:14:24,960

so we need to make ribonucleotide first

1514
01:14:30,310 --> 01:14:27,840
and ribonucleotide is consists of three

1515
01:14:32,470 --> 01:14:30,320
components ribose

1516
01:14:34,470 --> 01:14:32,480
nucleus and

1517
01:14:36,390 --> 01:14:34,480
phosphate

1518
01:14:38,870 --> 01:14:36,400
whilst i'll introduce

1519
01:14:41,510 --> 01:14:38,880
the previous research of prebiotic

1520
01:14:42,550 --> 01:14:41,520
nucleotide formation

1521
01:14:45,350 --> 01:14:42,560
and

1522
01:14:47,830 --> 01:14:45,360
many many previous researches many

1523
01:14:51,030 --> 01:14:47,840
researchers have tried nucleotide

1524
01:14:53,590 --> 01:14:51,040
synthesis and red figure shows

1525
01:14:55,510 --> 01:14:53,600
the nucleotide synthesis pathway and

1526
01:14:57,590 --> 01:14:55,520
right figures of the side

1527
01:14:59,830 --> 01:14:57,600
phosphorylation

1528
01:15:02,470 --> 01:14:59,840
nucleotide synthesis generally needs

1529
01:15:05,270 --> 01:15:02,480
step by step reaction using small

1530
01:15:07,669 --> 01:15:05,280
reactive molecules like cyanomolecules

1531
01:15:09,110 --> 01:15:07,679
or cyanoacetamine

1532
01:15:11,430 --> 01:15:09,120
on the other hand

1533
01:15:14,390 --> 01:15:11,440
the nuclear site phosphorylation is a

1534
01:15:15,750 --> 01:15:14,400
one pole reaction using small catalysts

1535
01:15:17,990 --> 01:15:15,760
like urea

1536
01:15:21,669 --> 01:15:18,000
and common point of this previous

1537
01:15:24,550 --> 01:15:21,679
research is the reaction order

1538
01:15:26,550 --> 01:15:24,560

nuclear site synthesis first and flowing

1539
01:15:29,910 --> 01:15:26,560
postulation

1540
01:15:31,750 --> 01:15:29,920
on the other hand we can also assume the

1541
01:15:34,470 --> 01:15:31,760
alternative pathway

1542
01:15:35,830 --> 01:15:34,480
labels phosphorylation first and

1543
01:15:37,350 --> 01:15:35,840
nuclear based

1544
01:15:38,870 --> 01:15:37,360
addition later

1545
01:15:41,030 --> 01:15:38,880
however

1546
01:15:44,229 --> 01:15:41,040
the previous research focusing on this

1547
01:15:46,149 --> 01:15:44,239
alternative pathway is limited

1548
01:15:48,870 --> 01:15:46,159
some paper shows

1549
01:15:51,750 --> 01:15:48,880
nucleotide formation from ribose 5 prime

1550
01:15:53,830 --> 01:15:51,760
phosphate but as far as we know nobody

1551
01:15:55,189 --> 01:15:53,840
reported the ribose 5 brain phosphate

1552
01:15:57,430 --> 01:15:55,199
formation from

1553
01:16:00,149 --> 01:15:57,440
ribose and of phosphate under the

1554
01:16:03,110 --> 01:16:00,159
prioritically plausible condition

1555
01:16:05,669 --> 01:16:03,120
this motivated us to investigate the

1556
01:16:08,470 --> 01:16:05,679
ribose frustration on the areas

1557
01:16:11,910 --> 01:16:08,480
and so why is it difficult to form

1558
01:16:13,990 --> 01:16:11,920
ribose fibrin phosphate

1559
01:16:16,950 --> 01:16:14,000
there are two reasons

1560
01:16:20,390 --> 01:16:16,960
stability and selectivity

1561
01:16:22,870 --> 01:16:20,400
first of all ribose is very unstable

1562
01:16:25,669 --> 01:16:22,880
sugars in heat condition

1563
01:16:27,590 --> 01:16:25,679

and phosphorylation generally needs heat

1564
01:16:31,110 --> 01:16:27,600
and dry condition

1565
01:16:33,350 --> 01:16:31,120
but ribose is easily broke down in and

1566
01:16:35,830 --> 01:16:33,360
reacting each other in such condition

1567
01:16:38,470 --> 01:16:35,840
and turn to brown tau

1568
01:16:41,110 --> 01:16:38,480
and second it is difficult to

1569
01:16:42,709 --> 01:16:41,120
phosphorylate at right position of

1570
01:16:47,669 --> 01:16:42,719
ribose

1571
01:16:50,310 --> 01:16:47,679
for solution but right was one prime

1572
01:16:52,470 --> 01:16:50,320
phosphate was selectively formed not

1573
01:16:56,470 --> 01:16:52,480
fibrin phosphate for the chemical

1574
01:16:59,110 --> 01:16:56,480
evolution to rna we need right structure

1575
01:17:02,709 --> 01:16:59,120
molecules so it is necessary to form

1576
01:17:05,110 --> 01:17:02,719
ribose 5-prime phosphate

1577
01:17:07,510 --> 01:17:05,120
these two issues make it difficult to

1578
01:17:10,229 --> 01:17:07,520
form ribose fiber and phosphate

1579
01:17:13,350 --> 01:17:10,239
so to solve this problem

1580
01:17:15,669 --> 01:17:13,360
we focused on bull rate

1581
01:17:18,950 --> 01:17:15,679
bullet will have existed on the

1582
01:17:21,910 --> 01:17:18,960
biopolitic environment on the areas and

1583
01:17:24,709 --> 01:17:21,920
where it can stabilize rivals by forming

1584
01:17:27,270 --> 01:17:24,719
rival at this rival sport complex

1585
01:17:30,950 --> 01:17:27,280
so bullet ridge environment could have

1586
01:17:33,669 --> 01:17:30,960
accumulated rivals on the areas

1587
01:17:36,149 --> 01:17:33,679
buried also contribute to the original

1588
01:17:38,630 --> 01:17:36,159

selective phosphorylation

1589
01:17:41,110 --> 01:17:38,640
this previous research reported the

1590
01:17:43,350 --> 01:17:41,120
nucleotide phosphorylation at

1591
01:17:46,310 --> 01:17:43,360
five prime hydroxy

1592
01:17:48,950 --> 01:17:46,320
so we consider that this bullet that we

1593
01:17:51,669 --> 01:17:48,960
can apply these bullet abilities to

1594
01:17:54,550 --> 01:17:51,679
ribose phosphorylation so the objective

1595
01:17:56,470 --> 01:17:54,560
of this research is to investigate the

1596
01:17:59,270 --> 01:17:56,480
factor bullet and bullet ridge

1597
01:18:01,830 --> 01:17:59,280
environment on the phosphorylation of

1598
01:18:04,550 --> 01:18:01,840
ribose to find a new root a new

1599
01:18:07,030 --> 01:18:04,560
alternative route to nucleotide

1600
01:18:08,790 --> 01:18:07,040
okay let's move on to the experimental

1601
01:18:11,830 --> 01:18:08,800
method

1602
01:18:14,070 --> 01:18:11,840
for the ribose for the liposolation we

1603
01:18:15,669 --> 01:18:14,080
perform the thermal evaporation

1604
01:18:19,510 --> 01:18:15,679
experiment

1605
01:18:21,990 --> 01:18:19,520
simple

1606
01:18:23,590 --> 01:18:22,000
first we prepare the acquisition

1607
01:18:27,110 --> 01:18:23,600
containing

1608
01:18:28,790 --> 01:18:27,120
ribose and distortion more phosphate

1609
01:18:32,070 --> 01:18:28,800
and boric acid

1610
01:18:35,590 --> 01:18:32,080
and urea as a phosphorylation catalyst

1611
01:18:38,310 --> 01:18:35,600
the solution was heated for 24 hours at

1612
01:18:40,870 --> 01:18:38,320
80 degrees c with the with the leads

1613
01:18:42,950 --> 01:18:40,880

open to evaporate the solution

1614
01:18:46,229 --> 01:18:42,960
after the experiment we added the

1615
01:18:49,510 --> 01:18:46,239
sulfuric acid solution to the sample and

1616
01:18:53,110 --> 01:18:49,520
heated it for one hour at 90 degrees c

1617
01:18:55,830 --> 01:18:53,120
to separate bullet and urea from ribose

1618
01:18:58,470 --> 01:18:55,840
and then we analyze the sample by hpl

1619
01:19:03,750 --> 01:19:01,270
here is the result the upper figure is

1620
01:19:04,870 --> 01:19:03,760
the standard of rivals what rivals

1621
01:19:07,030 --> 01:19:04,880
phosphate

1622
01:19:08,390 --> 01:19:07,040
and lower figure the experimental

1623
01:19:11,510 --> 01:19:08,400
product

1624
01:19:14,630 --> 01:19:11,520
and x-axis is the retention time

1625
01:19:17,669 --> 01:19:14,640
and y-axis is the intensity

1626
01:19:19,750 --> 01:19:17,679
the block line is the standard of rivals

1627
01:19:21,030 --> 01:19:19,760
fibrin phosphate and this is the target

1628
01:19:24,310 --> 01:19:21,040
material

1629
01:19:27,189 --> 01:19:24,320
and the blue line in the ribose two

1630
01:19:29,110 --> 01:19:27,199
prime phosphate and aeroline the ribose

1631
01:19:32,470 --> 01:19:29,120
three point phosphate standard

1632
01:19:35,590 --> 01:19:32,480
and red figures uh the fragment pattern

1633
01:19:38,070 --> 01:19:35,600
spectra of ribose fibrin phosphate and

1634
01:19:40,550 --> 01:19:38,080
experimental product

1635
01:19:43,830 --> 01:19:40,560
this this data showed that ribose

1636
01:19:45,990 --> 01:19:43,840
5-prime phosphate was selectively formed

1637
01:19:48,470 --> 01:19:46,000
in the in the reaction

1638
01:19:50,870 --> 01:19:48,480

and these fragment pattern spectra also

1639
01:19:52,870 --> 01:19:50,880
indicate that this peak is ribose

1640
01:19:55,430 --> 01:19:52,880
5-prime phosphate

1641
01:19:57,910 --> 01:19:55,440
we calculated the yield based on the

1642
01:20:00,630 --> 01:19:57,920
peak area and it was

1643
01:20:02,630 --> 01:20:00,640
22 percent and this yield is

1644
01:20:05,669 --> 01:20:02,640
significantly high as a probiotic

1645
01:20:11,510 --> 01:20:09,350
here is the result in our sense of void

1646
01:20:13,830 --> 01:20:11,520
we could detect the ribose fibrin

1647
01:20:16,149 --> 01:20:13,840
phosphate and this fragment pattern

1648
01:20:19,189 --> 01:20:16,159
spectra also indicates this peak is

1649
01:20:23,270 --> 01:20:19,199
ribose fibrin phosphate but

1650
01:20:25,910 --> 01:20:23,280
the yield was only four percent so

1651
01:20:29,189 --> 01:20:25,920
these data show that ribose uh sorry uh

1652
01:20:32,790 --> 01:20:29,199
borage can improve the yield of ribose

1653
01:20:38,870 --> 01:20:36,709
we also evaluate the product amount of

1654
01:20:40,629 --> 01:20:38,880
each other pentoses in addition to

1655
01:20:44,070 --> 01:20:40,639
ribose because

1656
01:20:47,590 --> 01:20:44,080
why ribose was selected as uh the soil

1657
01:20:49,910 --> 01:20:47,600
rna component is also a significant

1658
01:20:51,510 --> 01:20:49,920
problem for the original life

1659
01:20:54,390 --> 01:20:51,520
here is the result

1660
01:20:56,070 --> 01:20:54,400
the upper left figure is the result of

1661
01:20:58,229 --> 01:20:56,080
ribose experiment

1662
01:20:59,510 --> 01:20:58,239
and upper right is the robinus

1663
01:21:02,310 --> 01:20:59,520

experiment

1664
01:21:03,830 --> 01:21:02,320
and lower left is xylose and lower right

1665
01:21:05,750 --> 01:21:03,840
is rig source

1666
01:21:08,550 --> 01:21:05,760
and each yields

1667
01:21:11,189 --> 01:21:08,560
for 22 percent in ribose

1668
01:21:13,350 --> 01:21:11,199
8 percent in your abinos

1669
01:21:15,750 --> 01:21:13,360
4 percent in xyros

1670
01:21:18,870 --> 01:21:15,760
and eleven percent in rick's cells

1671
01:21:20,950 --> 01:21:18,880
so surprisingly ribose experiment had

1672
01:21:24,709 --> 01:21:20,960
the highest yield among all other

1673
01:21:27,590 --> 01:21:24,719
pentoses in the presence of borate

1674
01:21:31,430 --> 01:21:27,600
on the other hand in our sense of bullet

1675
01:21:33,510 --> 01:21:31,440
each yields were four percent arrivals

1676
01:21:35,030 --> 01:21:33,520
four percent in arabinose

1677
01:21:40,629 --> 01:21:35,040
two percent in

1678
01:21:43,110 --> 01:21:40,639
there was no apparent difference in the

1679
01:21:46,229 --> 01:21:43,120
yield in the absence of bullet

1680
01:21:49,270 --> 01:21:46,239
so this result suggests that bullet can

1681
01:21:51,910 --> 01:21:49,280
improve the increased selectivity of

1682
01:21:58,310 --> 01:21:55,590
so ribose is very unstable sugars and

1683
01:22:01,350 --> 01:21:58,320
other sugars must have existed on the

1684
01:22:04,950 --> 01:22:01,360
probiotic earth so it remains unclear

1685
01:22:07,590 --> 01:22:04,960
why ribose was selected as surrounding

1686
01:22:10,149 --> 01:22:07,600
rna component

1687
01:22:11,990 --> 01:22:10,159
some previous research reported that a

1688
01:22:14,950 --> 01:22:12,000

bullet can contribute to the

1689
01:22:16,709 --> 01:22:14,960
preferential formation of rivals and in

1690
01:22:18,709 --> 01:22:16,719
this research

1691
01:22:21,189 --> 01:22:18,719
we also

1692
01:22:24,470 --> 01:22:21,199
found that bullet can contribute to the

1693
01:22:27,030 --> 01:22:24,480
preferential phosphorylation arrivals

1694
01:22:28,950 --> 01:22:27,040
in other words bullet can increase the

1695
01:22:31,990 --> 01:22:28,960
selectivity of libels

1696
01:22:35,669 --> 01:22:32,000
not only sugar formation but also

1697
01:22:41,750 --> 01:22:38,950
okay let me summarize my presentation

1698
01:22:43,110 --> 01:22:41,760
this figure shows the reaction pathway

1699
01:22:46,629 --> 01:22:43,120
reaction root

1700
01:22:50,070 --> 01:22:46,639
or to nucleotide in biosynthesis

1701
01:22:52,629 --> 01:22:50,080
this study and previous research

1702
01:22:55,270 --> 01:22:52,639
in this study we found that ribose

1703
01:22:57,750 --> 01:22:55,280
5-prime phosphate was formed

1704
01:23:00,870 --> 01:22:57,760
with 22 percent yield

1705
01:23:02,870 --> 01:23:00,880
this reaction is one pole reaction and

1706
01:23:04,470 --> 01:23:02,880
the yield was significantly high in the

1707
01:23:07,270 --> 01:23:04,480
presence of bullet

1708
01:23:10,229 --> 01:23:07,280
so we can consider that this reaction is

1709
01:23:11,590 --> 01:23:10,239
geologically possible

1710
01:23:13,910 --> 01:23:11,600
on the other hand

1711
01:23:16,790 --> 01:23:13,920
previous research nuclear cell synthesis

1712
01:23:20,070 --> 01:23:16,800
needs step-by-step reaction using very

1713
01:23:21,430 --> 01:23:20,080

unstable molecules and very complicated

1714
01:23:23,350 --> 01:23:21,440
procedure

1715
01:23:25,350 --> 01:23:23,360
on the earliest

1716
01:23:29,030 --> 01:23:25,360
the vampire reaction must have

1717
01:23:31,270 --> 01:23:29,040
preferentially occurred compared to the

1718
01:23:33,669 --> 01:23:31,280
step-by-step reaction

1719
01:23:37,030 --> 01:23:33,679
these findings open the new route to

1720
01:23:39,590 --> 01:23:37,040
nucleotide and this route is

1721
01:23:42,070 --> 01:23:39,600
phosphorylation code first and

1722
01:23:44,790 --> 01:23:42,080
nuclear waste combined later

1723
01:23:47,910 --> 01:23:44,800
this route is more geologically possible

1724
01:23:52,629 --> 01:23:47,920
than previous research route and it also

1725
01:23:54,149 --> 01:23:52,639
close to the order of biosynthesis

1726
01:23:56,709 --> 01:23:54,159
in conclusion

1727
01:23:59,189 --> 01:23:56,719
we found that borate and blood rich

1728
01:24:01,669 --> 01:23:59,199
environment could have contributed to

1729
01:24:03,669 --> 01:24:01,679
the preferential formation of ribose

1730
01:24:06,149 --> 01:24:03,679
5-prime phosphate

1731
01:24:08,310 --> 01:24:06,159
and further chemical evolution to rna

1732
01:24:09,590 --> 01:24:08,320
will have a chord say in the same

1733
01:24:12,070 --> 01:24:09,600
environment

1734
01:24:14,229 --> 01:24:12,080
so these findings

1735
01:24:15,430 --> 01:24:14,239
for these findings

1736
01:24:18,950 --> 01:24:15,440
show that

1737
01:24:21,590 --> 01:24:18,960
the bullet voltage environment

1738
01:24:25,430 --> 01:24:21,600

could have been a probable place for the

1739
01:24:27,750 --> 01:24:25,440
origin of nucleotide and rna

1740
01:24:36,070 --> 01:24:27,760
this is the summary and endometrites

1741
01:24:36,080 --> 01:24:47,270
time for a couple questions

1742
01:24:51,990 --> 01:24:49,189
steve banner very nice talk thank you

1743
01:24:53,350 --> 01:24:52,000
very much for that as you know your

1744
01:24:56,229 --> 01:24:53,360
supervisor

1745
01:24:57,750 --> 01:24:56,239
yoshi furukawa has isolated with

1746
01:25:00,709 --> 01:24:57,760
students

1747
01:25:04,149 --> 01:25:00,719
ribose from meteorites yes

1748
01:25:05,990 --> 01:25:04,159
is there borate in those meteorites

1749
01:25:10,229 --> 01:25:06,000
um

1750
01:25:12,629 --> 01:25:10,239
actually we don't find what minerals in

1751
01:25:14,629 --> 01:25:12,639
the meteorites so

1752
01:25:15,910 --> 01:25:14,639
this is a recovery speculation as to how

1753
01:25:17,430 --> 01:25:15,920
ribose

1754
01:25:18,790 --> 01:25:17,440
got into the meteor i mean it seemed to

1755
01:25:20,070 --> 01:25:18,800
me that it would be very nice to have

1756
01:25:22,870 --> 01:25:20,080
bori there

1757
01:25:26,550 --> 01:25:22,880
because of your work yeah um

1758
01:25:28,550 --> 01:25:26,560
yes we fought we tried to find the

1759
01:25:31,110 --> 01:25:28,560
reaction pathway in

1760
01:25:33,350 --> 01:25:31,120
forming ribose in meteorites so

1761
01:25:39,990 --> 01:25:33,360
simulating meteorites condition

1762
01:25:43,910 --> 01:25:42,229
basic uh usf uh so you might have said

1763
01:25:45,830 --> 01:25:43,920

that but what is your phosphate source

1764
01:25:48,709 --> 01:25:45,840
in this case um

1765
01:25:49,669 --> 01:25:48,719
alpha space starts

1766
01:25:51,350 --> 01:25:49,679
um

1767
01:25:54,149 --> 01:25:51,360
yeah

1768
01:25:56,709 --> 01:25:54,159
yes

1769
01:25:58,390 --> 01:25:56,719
hey utah um luke stiller again um big

1770
01:26:00,870 --> 01:25:58,400
fan of your work love everything you're

1771
01:26:03,510 --> 01:26:00,880
doing um i was just wondering what ph

1772
01:26:05,590 --> 01:26:03,520
you're using at those experiments and

1773
01:26:07,830 --> 01:26:05,600
in light of that um we had a chat before

1774
01:26:10,470 --> 01:26:07,840
around how some bored minerals can be

1775
01:26:12,550 --> 01:26:10,480
very insoluble at higher phs and i was

1776
01:26:14,390 --> 01:26:12,560
wondering if you thought about um yeah

1777
01:26:16,149 --> 01:26:14,400
like what mineral source you would have

1778
01:26:18,470 --> 01:26:16,159
for your boric acid and how that might

1779
01:26:19,750 --> 01:26:18,480
be impacted by the ph

1780
01:26:22,310 --> 01:26:19,760
um

1781
01:26:23,270 --> 01:26:22,320
i don't i

1782
01:26:26,709 --> 01:26:23,280
in my

1783
01:26:31,030 --> 01:26:26,719
experiment

1784
01:26:33,270 --> 01:26:31,040
i don't use symbolic void minerals and

1785
01:26:36,390 --> 01:26:33,280
but we

1786
01:26:39,430 --> 01:26:36,400
we assume that some turmeric void rich

1787
01:26:43,110 --> 01:26:39,440
minerals is a

1788
01:26:46,149 --> 01:26:43,120

potential bullet flows because with the

1789
01:26:49,830 --> 01:26:46,159
bullet the solubility was found in

1790
01:26:51,910 --> 01:26:49,840
argent metal sediment and so we can we

1791
01:26:54,070 --> 01:26:51,920
consider that well the tolerance is the

1792
01:26:56,950 --> 01:26:54,080
best candidate for the

1793
01:26:59,510 --> 01:26:56,960
voice source in your experiment

1794
01:27:00,310 --> 01:26:59,520
and what ph is the experiment

1795
01:27:02,149 --> 01:27:00,320
uh

1796
01:27:07,830 --> 01:27:02,159
the ph is around nine

1797
01:27:14,550 --> 01:27:10,100
thank you very much thank you very much

1798
01:27:17,750 --> 01:27:16,310
so that concludes our session so thank