
AbSciCon
2019

1
00:00:00,790 --> 00:00:07,320
[Music]

2
00:00:12,140 --> 00:00:09,470
[Applause]

3
00:00:14,820 --> 00:00:12,150
general Adama graduate student at the

4
00:00:17,220 --> 00:00:14,830
University of South Florida and Tampa I

5
00:00:18,780 --> 00:00:17,230
work under dr. Matthew Pasic in

6
00:00:21,540 --> 00:00:18,790
collaboration with the Center for

7
00:00:24,330 --> 00:00:21,550
chemical evolution my work revolves

8
00:00:26,700 --> 00:00:24,340
around geochemistry with the

9
00:00:33,299 --> 00:00:26,710
incorporating phosphate into your

10
00:00:36,090 --> 00:00:33,309
biomolecules let's see so just a brief

11
00:00:39,450 --> 00:00:36,100
overview of the phosphorylation problem

12
00:00:41,700 --> 00:00:39,460
in prebiotic chemistry incorporating

13
00:00:43,710 --> 00:00:41,710

phosphorus into your biomolecules has

14
00:00:46,380 --> 00:00:43,720
been a known problem that has been

15
00:00:48,180 --> 00:00:46,390
studied for years it's actually a

16
00:00:51,240 --> 00:00:48,190
two-part problem part of it being

17
00:00:53,310 --> 00:00:51,250
phosphate itself that the predominant

18
00:00:55,139 --> 00:00:53,320
phosphorus containing minerals on the

19
00:00:57,420 --> 00:00:55,149
Haiti and earth would have come from the

20
00:00:59,540 --> 00:00:57,430
apatite mineral group the calcium

21
00:01:02,880 --> 00:00:59,550
phosphates which were actually very

22
00:01:05,760 --> 00:01:02,890
insoluble in water the other non

23
00:01:07,440 --> 00:01:05,770
biogenic non biogenic phosphorus

24
00:01:10,889 --> 00:01:07,450
containing minerals would have actually

25
00:01:13,410 --> 00:01:10,899
been more rare and in niche environments

26
00:01:15,750 --> 00:01:13,420
so I have been sticking with the apatite

27
00:01:18,030 --> 00:01:15,760
mineral group but that leads into the

28
00:01:20,880 --> 00:01:18,040
next problem with phosphorus which is

29
00:01:24,120 --> 00:01:20,890
that as I said it's insoluble and water

30
00:01:26,250 --> 00:01:24,130
your appetite as the phosphorylation

31
00:01:27,810 --> 00:01:26,260
reaction itself requires a dehydration

32
00:01:31,520 --> 00:01:27,820
step which of course would be

33
00:01:33,899 --> 00:01:31,530
unfavorable in a water-based solution so

34
00:01:35,700 --> 00:01:33,909
historically scientists have used

35
00:01:38,149 --> 00:01:35,710
multiple routes in order to overcome

36
00:01:41,520 --> 00:01:38,159
this problem they've incorporated

37
00:01:44,670 --> 00:01:41,530
condensing agents into their systems

38
00:01:46,440 --> 00:01:44,680

such as your your cyanamide they've done

39
00:01:48,840 --> 00:01:46,450
high temperature heating in order to

40
00:01:50,999 --> 00:01:48,850
drive off water within the system and

41
00:01:53,749 --> 00:01:51,009
others have used non-aqueous solvents

42
00:01:56,670 --> 00:01:53,759
such as formamide or the deep eutectic

43
00:01:58,560 --> 00:01:56,680
solvent of urea calling chloride and

44
00:02:00,749 --> 00:01:58,570
more recently out of the Center for

45
00:02:04,679 --> 00:02:00,759
chemical evolution dr. Parker had worked

46
00:02:07,469 --> 00:02:04,689
with a alternative solvent called a UAF

47
00:02:10,259 --> 00:02:07,479
w which is urea ammonium formate and

48
00:02:12,780 --> 00:02:10,269
water there's a lot of unique features

49
00:02:15,319 --> 00:02:12,790
that we discovered with this UAF w we

50
00:02:18,390 --> 00:02:15,329
found that just in this system alone

51
00:02:20,410 --> 00:02:18,400
formamide is actually created under mild

52
00:02:23,140 --> 00:02:20,420
heating conditions

53
00:02:24,940 --> 00:02:23,150
actually increases the solubility of

54
00:02:27,520 --> 00:02:24,950
phosphate containing minerals and

55
00:02:30,550 --> 00:02:27,530
promotes phosphorylation it has very

56
00:02:33,730 --> 00:02:30,560
broad temperature stability ammonium

57
00:02:35,140 --> 00:02:33,740
formate and urea itself forms a solution

58
00:02:36,970 --> 00:02:35,150
with the freezing point as low as

59
00:02:40,240 --> 00:02:36,980
negative 30 C and it's used throughout

60
00:02:42,520 --> 00:02:40,250
industry as a de-icing agent and the

61
00:02:44,800 --> 00:02:42,530
components of at the urea the ammonium

62
00:02:48,220 --> 00:02:44,810
formate in the water were all prebiotic

63
00:02:51,220 --> 00:02:48,230

available components now as I said dr.

64
00:02:52,720 --> 00:02:51,230
Burke our and his collaborators at the

65
00:02:55,870 --> 00:02:52,730
Center for chemical evolution have

66
00:02:58,479 --> 00:02:55,880
published paper in 2016 utilizing this

67
00:03:01,090 --> 00:02:58,489
alternative salva in a 1 to 2 to 4 molar

68
00:03:03,190 --> 00:03:01,100
ratio not only was he able to

69
00:03:05,770 --> 00:03:03,200
phosphorylate adenosine within this

70
00:03:07,960 --> 00:03:05,780
system but he also showed that by doping

71
00:03:12,160 --> 00:03:07,970
in some magnesium chloride he was able

72
00:03:15,670 --> 00:03:12,170
to actually convert hydroxyl apatite 20

73
00:03:18,670 --> 00:03:15,680
more soluble mineral called struvite it

74
00:03:22,510 --> 00:03:18,680
is important to note that in his work he

75
00:03:24,699 --> 00:03:22,520
did use a urea water system without any

76
00:03:28,740 --> 00:03:24,709
ammonium formate available and was

77
00:03:32,740 --> 00:03:28,750
actually got no detectable results of

78
00:03:35,320 --> 00:03:32,750
phosphorylation so this led into my work

79
00:03:37,210 --> 00:03:35,330
with this alternative solvent what I

80
00:03:40,330 --> 00:03:37,220
wanted to do was to determine the actual

81
00:03:43,270 --> 00:03:40,340
robustness of the solvent in more than

82
00:03:45,550 --> 00:03:43,280
just the 1 to 2 to 4 molar ratio and to

83
00:03:48,009 --> 00:03:45,560
determine how prebiotic aliy available

84
00:03:50,650 --> 00:03:48,019
would it have been geologically on the

85
00:03:53,080 --> 00:03:50,660
early Earth so we started with urea

86
00:03:55,870 --> 00:03:53,090
formation and we know that urea has been

87
00:03:58,990 --> 00:03:55,880
detected and excuse me detected in

88
00:04:01,930 --> 00:03:59,000

comets and meteorites and that urea is

89
00:04:03,940 --> 00:04:01,940
actually just as urea formation comes

90
00:04:07,210 --> 00:04:03,950
from a simple reaction between ammonia

91
00:04:09,820 --> 00:04:07,220
gas and carbon dioxide so we did some

92
00:04:14,140 --> 00:04:09,830
thermodynamic work and just plotted the

93
00:04:16,449 --> 00:04:14,150
urea formation on a log-log plot of the

94
00:04:19,420 --> 00:04:16,459
partial pressures of carbon dioxide to

95
00:04:21,729 --> 00:04:19,430
ammonia and found that even in a lower

96
00:04:25,270 --> 00:04:21,739
ammonia atmosphere that you would have

97
00:04:28,060 --> 00:04:25,280
urea formation from temperatures the red

98
00:04:30,370 --> 00:04:28,070
line let's see the red line at the

99
00:04:32,589 --> 00:04:30,380
bottom is when the temperatures are at

100
00:04:33,820 --> 00:04:32,599
zero degrees anything about that you're

101
00:04:36,339 --> 00:04:33,830
going to create the

102
00:04:38,559 --> 00:04:36,349
excuse me you're gonna create urea and

103
00:04:41,080 --> 00:04:38,569
then I also plotted it at a hundred

104
00:04:43,480 --> 00:04:41,090
degrees C and you can see that you would

105
00:04:46,029 --> 00:04:43,490
have urea formation up there so we were

106
00:04:48,159 --> 00:04:46,039
satisfied with the fact that urea itself

107
00:04:49,869 --> 00:04:48,169
would probably have been available in a

108
00:04:52,059 --> 00:04:49,879
lot of different geological settings

109
00:04:53,770 --> 00:04:52,069
just made out of the atmosphere so we

110
00:04:56,469 --> 00:04:53,780
wanted to move on to the ammonium

111
00:04:58,869 --> 00:04:56,479
formate now for the ammonium formate we

112
00:05:02,200 --> 00:04:58,879
envision more of a Darwin's warm little

113
00:05:05,920 --> 00:05:02,210

pond theory so this is a model system of

114
00:05:09,100 --> 00:05:05,930
a lake with an input of hydrogen cyanide

115
00:05:11,230 --> 00:05:09,110
from the atmosphere now hydrogen cyanide

116
00:05:13,240 --> 00:05:11,240
hydrolysis and product is ammonium

117
00:05:15,459 --> 00:05:13,250
formate and of course the mid product of

118
00:05:18,760 --> 00:05:15,469
that being formamide which has been used

119
00:05:21,100 --> 00:05:18,770
throughout prebiotic chemistry so what

120
00:05:25,209 --> 00:05:21,110
we did was took a just a small lake

121
00:05:28,990 --> 00:05:25,219
added in a daily input of hydrogen

122
00:05:32,670 --> 00:05:29,000
cyanide to it coming from Mal cows keys

123
00:05:36,820 --> 00:05:32,680
not sure the pronunciation of the name

124
00:05:38,980 --> 00:05:36,830
2002 paper and PA and PNAS that showed

125
00:05:43,149 --> 00:05:38,990
that just a small amount of hydrogen

126
00:05:45,339 --> 00:05:43,159
cyanide over time would actually form in

127
00:05:48,430 --> 00:05:45,349
earth would fall into this lake and

128
00:05:50,860 --> 00:05:48,440
hydrolysis into ammonium formate and as

129
00:05:53,140 --> 00:05:50,870
you can see here in just 20 years we can

130
00:05:56,700 --> 00:05:53,150
actually get a molar concentration in

131
00:05:59,769 --> 00:05:56,710
the lake of about four point four five

132
00:06:03,219 --> 00:05:59,779
point four point four five moles of

133
00:06:05,320 --> 00:06:03,229
ammonium formate so we said okay we know

134
00:06:07,089 --> 00:06:05,330
water is going to be available ammonium

135
00:06:08,559 --> 00:06:07,099
formate urea it seems like it would be

136
00:06:11,320 --> 00:06:08,569
plausible in a lot of different

137
00:06:14,890 --> 00:06:11,330
conditions but what happens in different

138
00:06:19,420 --> 00:06:14,900

molar ratios of this because a 1 to 2 to

139
00:06:22,689 --> 00:06:19,430
4 molar ratio is very specific and might

140
00:06:25,930 --> 00:06:22,699
only be found in certain areas so what I

141
00:06:29,559 --> 00:06:25,940
did here is I just took multiple

142
00:06:32,050 --> 00:06:29,569
different molar ratios of the UAF w

143
00:06:34,899 --> 00:06:32,060
plotted them on a ternary diagram and

144
00:06:36,939 --> 00:06:34,909
after three days just took a look at the

145
00:06:44,079 --> 00:06:36,949
physical characteristics and you can see

146
00:06:46,870 --> 00:06:44,089
from the oops there we go you can see

147
00:06:47,320 --> 00:06:46,880
from the top picture up here that in a

148
00:06:49,629 --> 00:06:47,330
lot

149
00:06:52,899 --> 00:06:49,639
the molar ratios where you have urea and

150
00:06:56,140 --> 00:06:52,909
an excess in three days the system dries

151
00:06:58,990 --> 00:06:56,150
out to a completely dry system but it's

152
00:07:01,180 --> 00:06:59,000
at 72 degrees open to the atmosphere to

153
00:07:03,520 --> 00:07:01,190
allow the volatile to escape and there

154
00:07:06,790 --> 00:07:03,530
are some molar ratios that remain liquid

155
00:07:10,420 --> 00:07:06,800
so on the ternary diagram I just plotted

156
00:07:12,339 --> 00:07:10,430
the the green dots being what remained a

157
00:07:14,230 --> 00:07:12,349
liquid and the red being a solid and you

158
00:07:16,390 --> 00:07:14,240
can see that there's actually quite a

159
00:07:18,070 --> 00:07:16,400
decent area in there in which you would

160
00:07:20,680 --> 00:07:18,080
have remained a liquid environment

161
00:07:22,779 --> 00:07:20,690
within just the three days now this is

162
00:07:25,559 --> 00:07:22,789
not doing any wet/dry cycling this is

163
00:07:28,420 --> 00:07:25,569

just allowing it to sit open in the oven

164
00:07:30,369 --> 00:07:28,430
at the same time I wanted to see what

165
00:07:33,249 --> 00:07:30,379
the solubility of hydroxyl apatite

166
00:07:35,529 --> 00:07:33,259
itself would be within this you afw at

167
00:07:38,140 --> 00:07:35,539
the different molar ratios so again we

168
00:07:40,510 --> 00:07:38,150
created up 10 milliliters of each of the

169
00:07:43,390 --> 00:07:40,520
different molar ratios added in some

170
00:07:45,999 --> 00:07:43,400
hydroxyl apatite put them in an oven at

171
00:07:48,070 --> 00:07:46,009
74 C left open to the environment to

172
00:07:51,159 --> 00:07:48,080
allow the escape of the volatile sand

173
00:07:55,059 --> 00:07:51,169
and after 14 days we analyze these

174
00:07:58,540 --> 00:07:55,069
samples on an icp-oes and that was

175
00:08:01,120 --> 00:07:58,550
actually through our University and in

176
00:08:03,700 --> 00:08:01,130
collaboration with st. Louis University

177
00:08:07,870 --> 00:08:03,710
with Paul Baraka and Rio Fabry

178
00:08:09,909 --> 00:08:07,880
and the results that we got from that we

179
00:08:12,309 --> 00:08:09,919
plotted again on a ternary diagram and

180
00:08:15,700 --> 00:08:12,319
it was actually quite surprising what we

181
00:08:19,930 --> 00:08:15,710
found was that and you can see here that

182
00:08:21,519 --> 00:08:19,940
in the result says free phosphorus

183
00:08:23,559 --> 00:08:21,529
there's actually quite a bit of the

184
00:08:25,719 --> 00:08:23,569
molar ratios where we had seventy to a

185
00:08:29,589 --> 00:08:25,729
hundred percent of free phosphorus

186
00:08:32,939 --> 00:08:29,599
available in this you afw meaning that

187
00:08:37,149 --> 00:08:32,949
the UAF w itself actually sell you lies

188
00:08:39,339 --> 00:08:37,159

appetite there's a decent amount there

189
00:08:42,339 --> 00:08:39,349
that is within the 30 to 70 percent

190
00:08:45,460 --> 00:08:42,349
range which is still remarkable compared

191
00:08:48,430 --> 00:08:45,470
to not soluble in water but then there's

192
00:08:50,530 --> 00:08:48,440
also a very specific area in which there

193
00:08:52,060 --> 00:08:50,540
was no free phosphorus or very little

194
00:08:54,360 --> 00:08:52,070
free phosphorus available in this

195
00:08:57,150 --> 00:08:54,370
solution and

196
00:08:59,340 --> 00:08:57,160
see here so on the dotted line I drew

197
00:09:01,650 --> 00:08:59,350
there it you can see that it actually

198
00:09:03,150 --> 00:09:01,660
follows the trend between where you have

199
00:09:05,820 --> 00:09:03,160
a high amount of free phosphorus

200
00:09:08,250 --> 00:09:05,830
available versus a moderate to low

201
00:09:10,530 --> 00:09:08,260
amount and what we found was that the

202
00:09:12,690 --> 00:09:10,540
more urea that is in the solution

203
00:09:16,950 --> 00:09:12,700
compared to the ammonium formate molar

204
00:09:20,370 --> 00:09:16,960
ratio you actually decrease the your

205
00:09:22,800 --> 00:09:20,380
solubility of the solution so urea is

206
00:09:26,430 --> 00:09:22,810
actually seeming to inhibit the

207
00:09:31,200 --> 00:09:26,440
solubility of hydroxyl apatite within

208
00:09:33,930 --> 00:09:31,210
the system but urea actually seems to be

209
00:09:36,630 --> 00:09:33,940
somewhat necessary within the system in

210
00:09:39,329 --> 00:09:36,640
order to drive down the water because as

211
00:09:42,810 --> 00:09:39,339
I said it apatite is insoluble in water

212
00:09:44,550 --> 00:09:42,820
so if we have any water in the system we

213
00:09:46,860 --> 00:09:44,560

need to drive up enough of it off in

214
00:09:50,700 --> 00:09:46,870
order to soluble eyes this phosphorus

215
00:09:53,850 --> 00:09:50,710
mineral and so there's a point at which

216
00:09:56,550 --> 00:09:53,860
about 75% water if you have more than

217
00:09:59,730 --> 00:09:56,560
that available you no longer have the

218
00:10:02,070 --> 00:09:59,740
solubility of this hydroxyl apatite but

219
00:10:04,500 --> 00:10:02,080
again when you're talking about the fact

220
00:10:06,690 --> 00:10:04,510
that is the system robust we can see

221
00:10:08,760 --> 00:10:06,700
that there's still quite a range here in

222
00:10:11,250 --> 00:10:08,770
which of molar ratios that you're going

223
00:10:13,019 --> 00:10:11,260
to have this system available that will

224
00:10:16,260 --> 00:10:13,029
soluble eyes your hydroxyl apatite

225
00:10:19,110 --> 00:10:16,270
minerals so just a quick conclusion to

226
00:10:21,240 --> 00:10:19,120
go over it the solubility of phosphate

227
00:10:25,100 --> 00:10:21,250
minerals is actually controlled by the

228
00:10:27,630 --> 00:10:25,110
molar ratios of this UAF W system

229
00:10:30,510 --> 00:10:27,640
dissolution of phosphate requires a

230
00:10:32,220 --> 00:10:30,520
liquid medium but at the same time we

231
00:10:35,010 --> 00:10:32,230
don't want too much of the water

232
00:10:37,230 --> 00:10:35,020
available and as long as the UAF W

233
00:10:39,540 --> 00:10:37,240
remains in this liquid system the

234
00:10:41,699 --> 00:10:39,550
solubility of the phosphate mineral will

235
00:10:43,800 --> 00:10:41,709
be enhanced and greater enhancement

236
00:10:46,440 --> 00:10:43,810
comes with a higher amount of ammonium

237
00:10:48,630 --> 00:10:46,450
formate versus the urea we're

238
00:10:51,510 --> 00:10:48,640

hypothesizing that ureas role within

239
00:10:54,120 --> 00:10:51,520
this system is actually as a condensing

240
00:10:56,370 --> 00:10:54,130
agent that it doesn't do anything for

241
00:10:58,320 --> 00:10:56,380
the soluble izing of the phosphate or

242
00:11:00,180 --> 00:10:58,330
freeing of the phosphate but that it is

243
00:11:03,000 --> 00:11:00,190
actually helping to drive off the water

244
00:11:05,160 --> 00:11:03,010
within the system and make a eutectic

245
00:11:07,129 --> 00:11:05,170
and that the ammonium formate is

246
00:11:10,400 --> 00:11:07,139
actually the key leading age

247
00:11:13,460 --> 00:11:10,410
that is taking the phosphate out of the

248
00:11:16,569 --> 00:11:13,470
calcium phosphate mineral and with that

249
00:11:18,769 --> 00:11:16,579
I would like to acknowledge my

250
00:11:21,259 --> 00:11:18,779
collaboration within the CCE

251
00:11:23,539 --> 00:11:21,269
my lab mates at USF for all their help

252
00:11:34,039 --> 00:11:23,549
and encouragement and of course our

253
00:11:43,640 --> 00:11:34,049
funding God's NSF and NASA Thank You

254
00:11:50,610 --> 00:11:47,490
Dave your first time yeah I got her in

255
00:11:54,390 --> 00:11:50,620
an open system with ammonium formate yes

256
00:11:57,600 --> 00:11:54,400
the ammonia nh3 will leave the system

257
00:12:00,630 --> 00:11:57,610
right it'll become more acid oh my god

258
00:12:03,260 --> 00:12:00,640
maybe behind formic acid therefore acid

259
00:12:06,720 --> 00:12:03,270
alone can solubilize the appetite

260
00:12:09,510 --> 00:12:06,730
absolutely and I would like to and have

261
00:12:11,040 --> 00:12:09,520
not done yet to determine the final PHS

262
00:12:13,110 --> 00:12:11,050
but as you could see in that picture

263
00:12:17,250 --> 00:12:13,120

because we're using just a small amount

264
00:12:20,220 --> 00:12:17,260
of the UAF w solution it's very

265
00:12:22,110 --> 00:12:20,230
difficult to get an actual pH on those

266
00:12:24,360 --> 00:12:22,120
amounts at the end I'd like to try a

267
00:12:32,360 --> 00:12:24,370
larger based experiment so that we can

268
00:12:32,370 --> 00:12:35,600
okay

269
00:12:41,690 --> 00:12:38,740
perfect thank you I'll do that thank you

270
00:12:43,210 --> 00:12:41,700
if there are no more questions I'd like