

A Possible Path to Prebiotic Peptides

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1
00:00:13,669 --> 00:00:09,580

[Music]

2
00:00:17,029 --> 00:00:13,679

yeah just a real quick plug that I and a

3
00:00:20,060 --> 00:00:17,039

lot of my courts are cool researchers

4
00:00:22,400 --> 00:00:20,070

chemical origins apply and we're proud

5
00:00:24,410 --> 00:00:22,410

I'm a proud member of the Center for

6
00:00:26,960 --> 00:00:24,420

chemical evolution I'm kind of like what

7
00:00:28,820 --> 00:00:26,970

a body was saying that we understand

8
00:00:32,179 --> 00:00:28,830

that biopolymers are the constituents of

9
00:00:35,030 --> 00:00:32,189

life and we look at poly nucleic acids

10
00:00:38,150 --> 00:00:35,040

polysaccharides polypeptides and really

11
00:00:39,950 --> 00:00:38,160

we look at proto poly nucleic acids

12
00:00:43,819 --> 00:00:39,960

polypeptides and I'll be talking about

13
00:00:45,619 --> 00:00:43,829

our proto polypeptides and we really

14

00:00:49,490 --> 00:00:45,629

like to embrace the evolution and the

15

00:00:54,639 --> 00:00:49,500

transformation of these systems so to

16

00:00:56,540 --> 00:00:54,649

put the proto in polypeptide me up to

17

00:00:58,279 --> 00:00:56,550

motivate that we have to consider some

18

00:01:00,349 --> 00:00:58,289

of the challenges of poly condensation

19

00:01:03,380 --> 00:01:00,359

of amino acids in the early Earth

20

00:01:05,509 --> 00:01:03,390

environment the direct condensation does

21

00:01:08,090 --> 00:01:05,519

require high temperatures it can also be

22

00:01:10,820 --> 00:01:08,100

achieved with a complex catalyst that

23

00:01:13,520 --> 00:01:10,830

may not be periodically plausible and of

24

00:01:17,240 --> 00:01:13,530

course sometimes called the dkp trap

25

00:01:20,810 --> 00:01:17,250

this cyclic dimer that occurs after you

26
00:01:24,410 --> 00:01:20,820
get your first condensation that is a

27
00:01:31,520 --> 00:01:24,420
trap towards further linear polymers of

28
00:01:35,600 --> 00:01:31,530
amino acids so we look for we look in

29
00:01:38,390 --> 00:01:35,610
two places meteorite examples and and

30
00:01:42,289 --> 00:01:38,400
also spark experiments are two of

31
00:01:45,170 --> 00:01:42,299
probably many and we have to acknowledge

32
00:01:48,380 --> 00:01:45,180
that the prebiotic molecular inventory

33
00:01:51,109 --> 00:01:48,390
is more diverse than the Vinge's what we

34
00:01:54,319 --> 00:01:51,119
have in our bodies right now so this an

35
00:01:56,270 --> 00:01:54,329
analog to amino acids hydroxy acids are

36
00:01:57,590 --> 00:01:56,280
quite similar except they have a

37
00:02:00,200 --> 00:01:57,600
hydroxyl group and therefore I can

38
00:02:02,959 --> 00:02:00,210

deform ester bonds instead of Arab bonds

39

00:02:05,899 --> 00:02:02,969

which are you know chemically distinct

40

00:02:08,210 --> 00:02:05,909

and these are plausible of course

41

00:02:10,419 --> 00:02:08,220

because they do appear in samples like

42

00:02:13,660 --> 00:02:10,429

the Murchison meteorite and

43

00:02:18,580 --> 00:02:13,670

in abundance in spark to charge model

44

00:02:22,420 --> 00:02:18,590

prebiotic systems and so what we have

45

00:02:24,970 --> 00:02:22,430

found in our search to have this proto

46

00:02:26,289 --> 00:02:24,980

apply peptide is an ester mediated amide

47

00:02:28,509 --> 00:02:26,299

bond formation

48

00:02:31,059 --> 00:02:28,519

so in evaporative conditions at mild

49

00:02:32,349 --> 00:02:31,069

temperatures eighty five and we've

50

00:02:36,129 --> 00:02:32,359

explored some of the mperatures as well

51
00:02:40,449 --> 00:02:36,139
but we as I've mentioned here the direct

52
00:02:41,740 --> 00:02:40,459
peptide formation can lead to the cyclic

53
00:02:45,879 --> 00:02:41,750
dimerization kind of the end of that

54
00:02:48,220 --> 00:02:45,889
cycle we don't see in Mason conditions

55
00:02:51,220 --> 00:02:48,230
we don't see applied glycine or poly

56
00:02:52,149 --> 00:02:51,230
amino acids but hydroxy I think there's

57
00:02:54,129 --> 00:02:52,159
actually lack of gasps what are we

58
00:02:55,929 --> 00:02:54,139
talking about a lot today they wrap

59
00:02:58,720 --> 00:02:55,939
readily form polyesters in these

60
00:03:01,990 --> 00:02:58,730
conditions so if we combine these two

61
00:03:04,690 --> 00:03:02,000
this co polymerizing system at this at

62
00:03:07,330 --> 00:03:04,700
this after the carbon of this ester site

63
00:03:10,539 --> 00:03:07,340

is activated for the nucleophilic attack

64

00:03:13,449 --> 00:03:10,549

by the amino acid and we get this we

65

00:03:16,479 --> 00:03:13,459

call exchange and this can be repeated

66

00:03:20,379 --> 00:03:16,489

so this esterification exchange until we

67

00:03:22,539 --> 00:03:20,389

get something that has a mix and ester

68

00:03:25,000 --> 00:03:22,549

backbone that we refer to as a deputy

69

00:03:29,460 --> 00:03:25,010

peptide and this can go on indefinitely

70

00:03:33,689 --> 00:03:29,470

and we get shown here a wide variety of

71

00:03:38,140 --> 00:03:33,699

sequences and compositions of oligomers

72

00:03:41,789 --> 00:03:38,150

with appreciable lengths and this can

73

00:03:45,580 --> 00:03:41,799

just go off like a shot so we get these

74

00:03:50,789 --> 00:03:45,590

copolymers that like I said have ester

75

00:03:53,199 --> 00:03:50,799

and the deck bones so way back to the

76

00:03:56,469 --> 00:03:53,209

Brinell hypothesis but just that

77

00:03:58,839 --> 00:03:56,479

minerals have been as ever-present steam

78

00:04:03,520 --> 00:03:58,849

in prebiotic chemistry their ubiquity

79

00:04:05,110 --> 00:04:03,530

their diversity and the unique dynamics

80

00:04:08,020 --> 00:04:05,120

that go on at the inner feet at the

81

00:04:09,969 --> 00:04:08,030

interface necessitate their their

82

00:04:11,710 --> 00:04:09,979

consideration and especially in

83

00:04:16,149 --> 00:04:11,720

evaporative systems will be drive off

84

00:04:18,249 --> 00:04:16,159

water to promote condensation if and you

85

00:04:19,990 --> 00:04:18,259

know in dilutes systems which are very

86

00:04:21,969 --> 00:04:20,000

plausible that the substrates will

87

00:04:23,470 --> 00:04:21,979

almost like always be in contact with

88

00:04:24,870 --> 00:04:23,480

the molecules

89

00:04:28,450 --> 00:04:24,880

their interactions need to be considered

90

00:04:31,990 --> 00:04:28,460

so focusing on the composition of deputy

91

00:04:35,230 --> 00:04:32,000

peptides you can have for say a six mark

92

00:04:37,420 --> 00:04:35,240

and anything from a holy peptide to

93

00:04:40,590 --> 00:04:37,430

something a polyester and of course the

94

00:04:45,910 --> 00:04:40,600

EPI peptides are somewhere in between so

95

00:04:48,520 --> 00:04:45,920

using mass spectrometry we can have a

96

00:04:49,870 --> 00:04:48,530

reaction and then understand the

97

00:04:54,610 --> 00:04:49,880

relative abundances of the different

98

00:04:58,930 --> 00:04:54,620

compositions here the dominant species

99

00:05:02,620 --> 00:04:58,940

present in this population is a six

100

00:05:05,320 --> 00:05:02,630

month six MERS has three lactic acids

101

00:05:08,310 --> 00:05:05,330

and in this case three glycine's and

102

00:05:11,800 --> 00:05:08,320

what we can also do is compare different

103

00:05:15,010 --> 00:05:11,810

conditions so an addition of in this

104

00:05:18,130 --> 00:05:15,020

case fumed silica presents a completely

105

00:05:20,740 --> 00:05:18,140

different composition distribution here

106

00:05:25,270 --> 00:05:20,750

we see that the dominant species only

107

00:05:26,830 --> 00:05:25,280

contains one hydroxy acid lactic acid so

108

00:05:29,860 --> 00:05:26,840

this is much more peptide like in

109

00:05:32,250 --> 00:05:29,870

character and through other mass

110

00:05:34,810 --> 00:05:32,260

spectometry means it's likely that this

111

00:05:38,070 --> 00:05:34,820

one hydroxy acid is actually on the end

112

00:05:41,530 --> 00:05:38,080

so we have a core of amino acids a

113

00:05:42,910 --> 00:05:41,540

peptide so this enrichment of amino

114

00:05:45,370 --> 00:05:42,920

acids is very important it's very

115

00:05:48,340 --> 00:05:45,380

interesting and occurs in the presence

116

00:05:50,320 --> 00:05:48,350

of silica so just some quick

117

00:05:51,790 --> 00:05:50,330

experimental notes this reaction a lot

118

00:05:55,120 --> 00:05:51,800

of you have been doing at 85 degrees

119

00:06:00,010 --> 00:05:55,130

Celsius and open file and this is an

120

00:06:02,470 --> 00:06:00,020

acidic pH s and this not only works for

121

00:06:04,690 --> 00:06:02,480

this enrichment of amino acids not only

122

00:06:08,140 --> 00:06:04,700

occurs for a glycine lactic acid system

123

00:06:11,410 --> 00:06:08,150

but also alanine so I have more slightly

124

00:06:13,930 --> 00:06:11,420

more complex amino acid at 85 we see

125

00:06:17,680 --> 00:06:13,940

that there from the black red and the

126

00:06:20,170 --> 00:06:17,690

Rev the black and red inset that a lower

127

00:06:23,650 --> 00:06:20,180

atomic mass is actually something that

128

00:06:27,310 --> 00:06:23,660

is more peptide rich because nitrogen

129

00:06:29,260 --> 00:06:27,320

has a lower tonic past and oxygen and

130

00:06:31,750 --> 00:06:29,270

for Allen again even at higher

131

00:06:34,630 --> 00:06:31,760

temperatures that the distributions are

132

00:06:36,300 --> 00:06:34,640

distinct and there are other ways to

133

00:06:38,250 --> 00:06:36,310

verify this

134

00:06:40,500 --> 00:06:38,260

acid and enrichment in the presence of

135

00:06:42,450 --> 00:06:40,510

silica we can look at NMR and I won't go

136

00:06:45,380 --> 00:06:42,460

into how we assign these Peaks but we

137

00:06:47,820 --> 00:06:45,390

can identify these key bonding motifs

138

00:06:50,400 --> 00:06:47,830

some associated esters and we see in the

139

00:06:52,940 --> 00:06:50,410

first one that is present in the no

140

00:06:55,820 --> 00:06:52,950

substrate control and its absence in the

141

00:07:00,410 --> 00:06:55,830

silica samples something that

142

00:07:02,910 --> 00:07:00,420

corresponds to internal amid linkages is

143

00:07:04,590 --> 00:07:02,920

much more abundant in the silicon

144

00:07:07,590 --> 00:07:04,600

containing samples than in the control

145

00:07:10,650 --> 00:07:07,600

and another example of a motif

146

00:07:12,240 --> 00:07:10,660

associated with polyesterification that

147

00:07:15,660 --> 00:07:12,250

is present in the control and not the

148

00:07:17,280 --> 00:07:15,670

silicon panning samples so that's that

149

00:07:19,500 --> 00:07:17,290

was very interesting and so our next

150

00:07:21,810 --> 00:07:19,510

step and to kind of understand maybe how

151
00:07:24,780 --> 00:07:21,820
this was happening was to kind of break

152
00:07:27,840 --> 00:07:24,790
up the reaction in two steps so first we

153
00:07:30,150 --> 00:07:27,850
were reacting the silica with the

154
00:07:34,320 --> 00:07:30,160
hydroxy acid lactic acid incubated it

155
00:07:37,980 --> 00:07:34,330
then watched it to remove maybe any non

156
00:07:40,440 --> 00:07:37,990
covalently bound species and then added

157
00:07:46,110 --> 00:07:40,450
our amino acid afterwards and what we

158
00:07:49,440 --> 00:07:46,120
got was a population of depth C peptides

159
00:07:53,910 --> 00:07:49,450
that had no esters so they only won a

160
00:07:58,680 --> 00:07:53,920
lactic acid on the C terminus and so

161
00:08:00,810 --> 00:07:58,690
that if we were to form these poly or

162
00:08:04,280 --> 00:08:00,820
these Amin's we would have to have had a

163
00:08:06,870 --> 00:08:04,290

an ester present to be the activator and

164

00:08:09,900 --> 00:08:06,880

so that kind of got us thinking of what

165

00:08:12,510 --> 00:08:09,910

may be occurring on a hydroxyl

166

00:08:14,520 --> 00:08:12,520

terminated silica surface that we could

167

00:08:18,960 --> 00:08:14,530

perhaps have formed these inter facial

168

00:08:22,320 --> 00:08:18,970

esters that when the glycine is present

169

00:08:25,260 --> 00:08:22,330

later these were active sites as I

170

00:08:27,720 --> 00:08:25,270

expressed earlier for ester Damon

171

00:08:31,920 --> 00:08:27,730

exchange and that we were able to form a

172

00:08:34,980 --> 00:08:31,930

Dead Sea peptide so - to begin to

173

00:08:39,540 --> 00:08:34,990

confirm this we thought about modifying

174

00:08:41,520 --> 00:08:39,550

our hydroxy acid so we now it's a

175

00:08:46,490 --> 00:08:41,530

methoxy propionic acid so this is now a

176

00:08:49,560 --> 00:08:46,500

mono functional molecule that cannot

177

00:08:51,570 --> 00:08:49,570

cannot participate in esterification

178

00:08:55,260 --> 00:08:51,580

though for other Pitts purposes such as

179

00:08:58,950 --> 00:08:55,270

the the acidity and the pKa of the acid

180

00:09:02,550 --> 00:08:58,960

are quite similar to lactic acid we

181

00:09:05,220 --> 00:09:02,560

reacted that with an amino acid and as

182

00:09:08,820 --> 00:09:05,230

it turns out in the absence of silica we

183

00:09:10,410 --> 00:09:08,830

do not get only trace amounts of the

184

00:09:13,050 --> 00:09:10,420

condensation products but in the

185

00:09:17,310 --> 00:09:13,060

presence of silica we get you know up to

186

00:09:20,580 --> 00:09:17,320

four or so glycine's attached to this

187

00:09:23,820 --> 00:09:20,590

one to methoxy propionic acid and this

188

00:09:26,610 --> 00:09:23,830

suggests that the silica can participate

189

00:09:30,510 --> 00:09:26,620

in the formation of an ester therefore

190

00:09:33,360 --> 00:09:30,520

an active site that can allow for an

191

00:09:38,280 --> 00:09:33,370

amid synthesis and at the temperatures

192

00:09:42,350 --> 00:09:38,290

and also we can look at other or at

193

00:09:47,550 --> 00:09:42,360

other substrates some minerals TiO_2 and

194

00:09:49,860 --> 00:09:47,560

hydroxide and see that titania does

195

00:09:53,610 --> 00:09:49,870

produce some economization products and

196

00:09:58,680 --> 00:09:53,620

all the NO_x hydroxide does not and I

197

00:10:02,850 --> 00:09:58,690

think that's interesting so just to

198

00:10:05,040 --> 00:10:02,860

conclude that we are able to form deputy

199

00:10:07,980 --> 00:10:05,050

peptides in presence of silica and that

200

00:10:10,740 --> 00:10:07,990

the presence of silica enriches the

201
00:10:14,010 --> 00:10:10,750
population in amino acids both glycine

202
00:10:18,090 --> 00:10:14,020
alanine we can be sure about that

203
00:10:20,880 --> 00:10:18,100
because ester linkages are reduced in

204
00:10:25,320 --> 00:10:20,890
presence of silica and ammon linkages

205
00:10:30,240 --> 00:10:25,330
are increased and that it is suggested

206
00:10:31,410 --> 00:10:30,250
that the the amide synthesis in the

207
00:10:35,970 --> 00:10:31,420
presence of silica is actually

208
00:10:39,330 --> 00:10:35,980
facilitated by a interfacial ester and

209
00:10:41,820 --> 00:10:39,340
so going back to the last level we

210
00:10:44,070 --> 00:10:41,830
showed some other minerals what

211
00:10:46,290 --> 00:10:44,080
characteristic of the mineral would

212
00:10:49,710 --> 00:10:46,300
would be most predictive of its ability

213
00:10:51,840 --> 00:10:49,720

to enrich the system a peptide farming

214

00:10:54,900 --> 00:10:51,850

system definitely forming system with

215

00:10:58,760 --> 00:10:54,910

amino acids is unclear now but

216

00:11:01,890 --> 00:10:58,770

that's the target of present work and

217

00:11:16,860 --> 00:11:01,900

that's yeah it's like that right now

218

00:11:18,930 --> 00:11:16,870

thank you okay cool

219

00:11:21,780 --> 00:11:18,940

that was a great talk thank you I have a

220

00:11:24,870 --> 00:11:21,790

question about a kind of comment

221

00:11:28,290 --> 00:11:24,880

question about silica that's because we

222

00:11:30,840 --> 00:11:28,300

think that silica availability on earth

223

00:11:32,730 --> 00:11:30,850

has changed a lot through time now it's

224

00:11:35,040 --> 00:11:32,740

controlled a lot by biology because

225

00:11:36,930 --> 00:11:35,050

there's shale formation so do you think

226

00:11:39,900 --> 00:11:36,940

that because silica might have been more

227

00:11:45,180 --> 00:11:39,910

available back in Earth history would

228

00:11:46,440 --> 00:11:45,190

that affect your your results so a lot

229

00:11:48,360 --> 00:11:46,450

of these studies didymus fused silica

230

00:11:50,130 --> 00:11:48,370

which I wouldn't even consider formally

231

00:11:54,030 --> 00:11:50,140

a mineral that's you know pyrolysis

232

00:11:55,769 --> 00:11:54,040

created the question of the abundance of

233

00:11:57,060 --> 00:11:55,779

silica I'm not exactly sure I think

234

00:11:59,610 --> 00:11:57,070

they're probably other minerals that are

235

00:12:05,850 --> 00:11:59,620

far more abundant co2 may have been one

236

00:12:08,430 --> 00:12:05,860

I I don't I don't mean to say that silk

237

00:12:10,170 --> 00:12:08,440

is the only way that we can enrich I

238

00:12:12,840 --> 00:12:10,180

mean you know the use any mineral to

239

00:12:16,140 --> 00:12:12,850

enrich deputy peptide systems with amino

240

00:12:18,860 --> 00:12:16,150

acids you can cycle these you can add

241

00:12:21,420 --> 00:12:18,870

more of one monomer but the chemistry

242

00:12:23,310 --> 00:12:21,430

with a mineral and a deputy peptide

243

00:12:25,650 --> 00:12:23,320

system needs to be studied and is

244

00:12:28,650 --> 00:12:25,660

distinct from a mineral and a purely

245

00:12:32,460 --> 00:12:28,660

amino acid system which has been looked

246

00:12:44,150 --> 00:12:32,470

at extensively in the past and so I

247

00:12:53,220 --> 00:12:47,640

distinctively limiting the the length of

248

00:12:57,630 --> 00:12:53,230

the oligomers that you can form one of

249

00:13:02,430 --> 00:12:57,640

them could be I mean besides besides

250

00:13:10,770 --> 00:13:02,440

like a monomer I think solubility of the

251

00:13:14,310 --> 00:13:10,780

if we get too too large then they the

252

00:13:15,170 --> 00:13:14,320

oligomers may conform in some way where

253

00:13:43,070 --> 00:13:15,180

the