



Cover Page for Proposal
Submitted to the
National Aeronautics and
Space Administration

NASA Proposal Number

17-EW17_2-0024

NASA PROCEDURE FOR HANDLING PROPOSALS

This proposal shall be used and disclosed for evaluation purposes only, and a copy of this Government notice shall be applied to any reproduction or abstract thereof. Any authorized restrictive notices that the submitter places on this proposal shall also be strictly complied with. Disclosure of this proposal for any reason outside the Government evaluation purposes shall be made only to the extent authorized by the Government.

SECTION I - Proposal Information

Principal Investigator Matthew Pasek		E-mail Address mpasek@lpl.arizona.edu		Phone Number 813-974-8979	
Street Address (1) 4202 E Fowler Ave			Street Address (2) SCA 528		
City Tampa		State / Province FL		Postal Code 33620-9951	
Country Code US					

Proposal Title : **Phosphorus mineral cosmochemistry in the emerging solar system**

Proposed Start Date	Proposed End Date	Total Budget	Year 1 Budget	Year 2 Budget	Year 3 Budget	Year 4 Budget
05 / 01 / 2018	04 / 30 / 2021	406,440.00	137,771.00	134,117.00	134,552.00	0.00

SECTION II - Application Information

NASA Program Announcement Number NNH17ZDA001N-EW		NASA Program Announcement Title Emerging Worlds			
For Consideration By NASA Organization <i>(the soliciting organization, or the organization to which an unsolicited proposal is submitted)</i> Planetary Science					
Date Submitted 05 / 31 / 2017		Submission Method Electronic Submission Only		Applicant Proposal Identifier	
Type of Application New	Predecessor Award Number		Other Federal Agencies to Which Proposal Has Been Submitted		
International Participation No	Type of International Participation				

SECTION III - Submitting Organization Information

DUNS Number 069687242	CAGE Code 1F202	Employer Identification Number (EIN or TIN)	Organization Type 2A		
Organization Name (Standard/Legal Name) University Of South Florida, Tampa				Company Division UNIVERSITY OF SOUTH FLORIDA	
Organization DBA Name UNIVERSITY OF SOUTH FLORIDA				Division Number	
Street Address (1) 4202 E FOWLER AVE			Street Address (2)		
City TAMPA		State / Province FL		Postal Code 33620	
Country Code USA					

SECTION IV - Proposal Point of Contact Information

Name Matthew Pasek	Email Address mpasek@usf.edu	Phone Number 813-974-8979
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SECTION V - Certification and Authorization

Certification of Compliance with Applicable Executive Orders and U.S. Code

By submitting the proposal identified in the Cover Sheet/Proposal Summary in response to this Research Announcement, the Authorizing Official of the proposing organization (or the individual proposer if there is no proposing organization) as identified below:

- certifies that the statements made in this proposal are true and complete to the best of his/her knowledge;
- agrees to accept the obligations to comply with NASA award terms and conditions if an award is made as a result of this proposal; and
- confirms compliance with all provisions, rules, and stipulations set forth in this solicitation.

Willful provision of false information in this proposal and/or its supporting documents, or in reports required under an ensuing award, is a criminal offense (U.S. Code, Title 18, Section 1001).

Authorized Organizational Representative (AOR) Name Arthur Santos	AOR E-mail Address arthursantos@usf.edu	Phone Number 813-974-7393
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AOR Signature *(Must have AOR's original signature. Do not sign "for" AOR.)* _____ Date _____

PI Name : Matthew Pasek		NASA Proposal Number	
Organization Name : University Of South Florida, Tampa		17-EW17_2-0024	
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system			
SECTION VI - Team Members			
Team Member Role PI	Team Member Name Matthew Pasek	Contact Phone 813-974-8979	E-mail Address mpasek@lpl.arizona.edu
Organization/Business Relationship University Of South Florida, Tampa		Cage Code 1F202	DUNS# 069687242
International Participation No	U.S. Government Agency		Total Funds Requested 0.00

PI Name : Matthew Pasek	NASA Proposal Number
Organization Name : University Of South Florida, Tampa	17-EW17_2-0024
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system	

SECTION VII - Project Summary

The element phosphorus (P) is generally classified as a minor or trace element in terrestrial and extraterrestrial samples. However, despite its relative scarcity in the Solar System, phosphorus has received a significant amount of attention from the cosmochemical community, due both to its role in capturing trace elements in phosphate mineral crystal lattices, and in the astrobiological implications of phosphorus to the development of life on the earth (e.g., Pasek 2015).

Despite the role of phosphorus in cosmochemical evolution, several facets of phosphorus cosmochemistry remain unclear, including 1) the extent of volatile forms of phosphorus present within the early Solar System, including the gas phosphine (PH₃), 2) the oxidation reactions between siderophilic (metal-loving) P minerals such as schreibersite (Fe,Ni)₃P and silicates and oxides to give phosphate, and 3) a detailed analysis of why specific phosphate minerals are more common in meteorites than on planetary bodies. We propose to investigate these key aspects of phosphorus cosmochemistry to better constrain the phases and forms that govern the distribution of this key element in our Solar System. This objective will be accomplished by experimental analyses that are fed into Solar System and planet chemistry models.

1. The gas phosphine (PH₃) has been proposed to be the major P species in cold environments in the solar system. We believe this to be incorrect, and instead argue that phosphorus is highly reactive towards metal. We propose that metal is phosphidized by phosphorus gases at high temperatures (500-1200K), and diffusion distributes gaseous phosphorus towards this extensive phosphorus sink, and results in the depletion of volatile phosphorus throughout the solar nebula. As a result, phosphine and other volatile P forms are less likely to dominate in the outer solar system. This will be examined by detailed metal phosphidation studies that establish reactions kinetics that then apply this data to solar system models.

2. The formation of phosphates from phosphides is predicted to occur at about 800 K, and produces calcium phosphate minerals such as apatite. The kinetic controls on this oxidation are unknown. In equilibrated chondrites most of the phosphorus is in phosphates, whereas in unequilibrated chondrites, the phosphorus is more distributed between phosphates and phosphides. This suggests that oxidation timescales may be of the order of thousands of years, requiring longer-term metamorphism. Phosphate-phosphide equilibrium and kinetics will be investigated using controlled reactions in a tube furnace, and will attempt to constrain the timescale of oxidation. By doing so, this data may help constrain the metamorphic history of asteroids.

3. The phosphate minerals that are found in meteorites include apatite—well known from terrestrial mineralogy—and merrillite/whitlockite, which are both minerals quite rare on the earth. The dominance of calcium phosphate is surprising as recent work has demonstrated these phosphates are susceptible to alteration to Mg/NH₄ phosphates. Here we will research the apatite-struvite transition using mineral reactions in a vacuum manifold under a controlled temperature, and attempt to determine the rates and specific chemistry required to form these different phosphate mineral classes.

This work is directly relevant to Emerging Worlds as it deals with the primordial chemistry that formed the initial solids in the solar system. It is part of the planet theory and primitive meteorites investigation categories, and is relevant to studies of “the formation of planets, satellites, and minor bodies, including dust, and to the early history of these bodies”, as highlighted within the Emerging Worlds call.

PI Name : Matthew Pasek	NASA Proposal Number 17-EW17_2-0024
Organization Name : University Of South Florida, Tampa	

Proposal Title : **Phosphorus mineral cosmochemistry in the emerging solar system**

SECTION VIII - Other Project Information

Proprietary Information

Is proprietary/privileged information included in this application?

Yes

International Collaboration

Does this project involve activities outside the U.S. or partnership with International Collaborators?

No

Principal Investigator No	Co-Investigator No	Collaborator No	Equipment No	Facilities No
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Explanation :

NASA Civil Servant Project Personnel

Are NASA civil servant personnel participating as team members on this project (include funded and unfunded)?

No

Fiscal Year	Fiscal Year	Fiscal Year	Fiscal Year	Fiscal Year	Fiscal Year
Number of FTEs	Number of FTEs	Number of FTEs	Number of FTEs	Number of FTEs	Number of FTEs

PI Name : Matthew Pasek	NASA Proposal Number
Organization Name : University Of South Florida, Tampa	17-EW17_2-0024
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system	

SECTION VIII - Other Project Information

Environmental Impact

Does this project have an actual or potential impact on the environment? No	Has an exemption been authorized or an environmental assessment (EA) or an environmental impact statement (EIS) been performed? No
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Environmental Impact Explanation:

Exemption/EA/EIS Explanation:

PI Name : Matthew Pasek	NASA Proposal Number
Organization Name : University Of South Florida, Tampa	17-EW17_2-0024
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system	

SECTION VIII - Other Project Information

Historical Site/Object Impact

Does this project have the potential to affect historic, archeological, or traditional cultural sites (such as Native American burial or ceremonial grounds) or historic objects (such as an historic aircraft or spacecraft)?

No

Explanation:

PI Name : Matthew Pasek	NASA Proposal Number
Organization Name : University Of South Florida, Tampa	17-EW17_2-0024
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system	

SECTION IX - Program Specific Data

Question 1 : Short Title:

Answer: Phosphorus Cosmochemistry

Question 2 : Type of institution:

Answer: Educational Organization

Question 3 : Will any funding be provided to a federal government organization including NASA Centers, JPL, other Federal agencies, government laboratories, or Federally Funded Research and Development Centers (FFRDCs)?

Answer: No

Question 4 : Is this Federal government organization a different organization from the proposing (PI) organization?

Answer: N/A

Question 5 : Does this proposal include the use of NASA-provided high end computing (HEC)?

Answer: No

Question 6 : HEC Request Number

Answer:

Question 7 : Research Category:

Answer: 3) Laboratory investigations of interest to Earth and Space Science (including sample analysis, physical simulations, and determination of physical parameters)

Question 8 : Flight Services

Answer: No

Question 9 : Do you understand that a Data Management Plan (DMP) is REQUIRED, and must be placed in a special section of the proposal, immediately following the References and Citations for the Scientific/Technical/Management portion of the proposal, as explained in ROSES-2016 Appendix C.1, section 3.5? If you don't understand this requirement, please read section 3.5 before you submit your proposal.

Answer: YES, I understand the requirement for DMPs

Question 10 : Team Members Missing From Cover Page:

Answer:

Christopher Mehta (USF Grad student)Carolyn Lang (USF Grad student)

Question 11 : This proposal contains information and/or data that are subject to U.S. export control laws and regulations including Export Administration Regulations (EAR) and International Traffic in Arms Regulations (ITAR).

Answer: No

Question 12 : I have identified the export-controlled material in this proposal.

Answer: N/A

Question 13 : I acknowledge that the inclusion of such material in this proposal may complicate the government's ability to evaluate the proposal.

Answer: N/A

Question 14 : Does the proposed work include any involvement with collaborators in China or with Chinese organizations, or does the proposed work include activities in China?

Answer: No

Question 15 : Are you planning for undergraduate students to be involved in the conduct of the proposed investigation?

Answer: No

Question 16 : What is the total number of student-months of involvement for all undergraduate students over the life of the proposed investigation?

Answer: 0

Question 17 : If yes, how many different undergraduate students?

Answer:

Question 18 : Provide the names and current year (1,2,3,4) for any undergraduate students that have already been identified.

Answer:

NA

Question 19 : Are you planning for graduate students to be involved in the conduct of the proposed investigation?

Answer: Yes

Question 20 : If yes, how many different graduate students?

Answer: 2

Question 21 : What is the total number of student-months of involvement for all graduate students over the life of the proposed investigation?

Answer: 72

Question 22 : Provide the names and current year (1,2,3,4, etc.) for any graduate students that have already been identified.

Answer:

Carolyn Lang (entering 3rd year)Chris Mehta (entering 3rd year)

Question 23 : Investigation Category

Answers :

Primitive Meteorites

Dust

Organics and volatiles (including ices)

Question 24 : Other Category Explanation

Answer:

Question 25 : Type of study

Answers :

Theoretical/Modeling

Laboratory experiments

Sample analysis

Question 26 : Other Type Explanation

Answer:

Question 27 : Methodology

Answer:

Microprobe, Raman, XRD, NMR, thermodynamic equilibrium modeling, disk diffusion and kinetics modeling

Question 28 : Facilities Request

Answers :

Question 29 : Type of PME

Answer: Not Applicable

Question 30 : Category of Equipment

Answer:

Question 31 : Geologic Map Production

Answer: No

PI Name : Matthew Pasek				NASA Proposal Number	
Organization Name : University Of South Florida, Tampa				17-EW17_2-0024	
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system					
SECTION X - Budget					
Cumulative Budget					
Budget Cost Category	Funds Requested (\$)				
	Year 1 (\$)	Year 2 (\$)	Year 3 (\$)	Year 4 (\$)	Total Project (\$)
A. Direct Labor - Key Personnel	11,148.00	11,482.00	11,827.00	0.00	34,457.00
B. Direct Labor - Other Personnel	50,872.00	52,276.00	53,722.00	0.00	156,870.00
Total Number Other Personnel	2	2	2	0	6
Total Direct Labor Costs (A+B)	62,020.00	63,758.00	65,549.00	0.00	191,327.00
C. Direct Costs - Equipment	7,000.00	0.00	0.00	0.00	7,000.00
D. Direct Costs - Travel	4,100.00	5,100.00	5,100.00	0.00	14,300.00
Domestic Travel	4,100.00	2,100.00	2,100.00	0.00	8,300.00
Foreign Travel	0.00	3,000.00	3,000.00	0.00	6,000.00
E. Direct Costs - Participant/Trainee Support Costs	0.00	0.00	0.00	0.00	0.00
Tuition/Fees/Health Insurance	0.00	0.00	0.00	0.00	0.00
Stipends	0.00	0.00	0.00	0.00	0.00
Travel	0.00	0.00	0.00	0.00	0.00
Subsistence	0.00	0.00	0.00	0.00	0.00
Other	0.00	0.00	0.00	0.00	0.00
Number of Participants/Trainees					0
F. Other Direct Costs	28,209.00	27,709.00	26,209.00	0.00	82,127.00
Materials and Supplies	6,000.00	4,000.00	4,000.00	0.00	14,000.00
Publication Costs	1,500.00	3,000.00	1,500.00	0.00	6,000.00
Consultant Services	0.00	0.00	0.00	0.00	0.00
ADP/Computer Services	0.00	0.00	0.00	0.00	0.00
Subawards/Consortium/Contractual Costs	0.00	0.00	0.00	0.00	0.00
Equipment or Facility Rental/User Fees	0.00	0.00	0.00	0.00	0.00
Alterations and Renovations	0.00	0.00	0.00	0.00	0.00
Other	20,709.00	20,709.00	20,709.00	0.00	62,127.00
G. Total Direct Costs (A+B+C+D+E+F)	101,329.00	96,567.00	96,858.00	0.00	294,754.00
H. Indirect Costs	36,442.00	37,550.00	37,694.00	0.00	111,686.00
I. Total Direct and Indirect Costs (G+H)	137,771.00	134,117.00	134,552.00	0.00	406,440.00
J. Fee	0.00	0.00	0.00	0.00	0.00
K. Total Cost (I+J)	137,771.00	134,117.00	134,552.00	0.00	406,440.00
Total Cumulative Budget					406,440.00

PI Name : Matthew Pasek						NASA Proposal Number		
Organization Name : University Of South Florida, Tampa						17-EW17_2-0024		
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system								
SECTION X - Budget								
Start Date : 05 / 01 / 2018		End Date : 04 / 30 / 2019		Budget Type : Project		Budget Period : 1		
A. Direct Labor - Key Personnel								
Name	Project Role	Base Salary (\$)	Cal. Months	Acad. Months	Summ. Months	Requested Salary (\$)	Fringe Benefits (\$)	Funds Requested (\$)
Pasek, Matthew	PI_TYPE	85,206.00			1	9,466.00	1,682.00	11,148.00
Total Key Personnel Costs								11,148.00
B. Direct Labor - Other Personnel								
Number of Personnel	Project Role	Cal. Months	Acad. Months	Summ. Months	Requested Salary (\$)	Fringe Benefits (\$)	Funds Requested (\$)	
2	Graduate Students	12			46,666.00	4,206.00	50,872.00	
2	Total Number Other Personnel	Total Other Personnel Costs					50,872.00	
Total Direct Labor Costs (Salary, Wages, Fringe Benefits) (A+B)								62,020.00

PI Name : Matthew Pasek		NASA Proposal Number	
Organization Name : University Of South Florida, Tampa		17-EW17_2-0024	
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system			
SECTION X - Budget			
Start Date : 05 / 01 / 2018	End Date : 04 / 30 / 2019	Budget Type : Project	Budget Period : 1
C. Direct Costs - Equipment			
Item No.	Equipment Item Description	Funds Requested (\$)	
1	Second tube furnace	7,000.00	
Total Equipment Costs		7,000.00	
D. Direct Costs - Travel			
		Funds Requested (\$)	
1. Domestic Travel (Including Canada, Mexico, and U.S. Possessions)		4,100.00	
2. Foreign Travel		0.00	
Total Travel Costs		4,100.00	
E. Direct Costs - Participant/Trainee Support Costs			
		Funds Requested (\$)	
1. Tuition/Fees/Health Insurance		0.00	
2. Stipends		0.00	
3. Travel		0.00	
4. Subsistence		0.00	
Number of Participants/Trainees:	Total Participant/Trainee Support Costs		0.00

PI Name : Matthew Pasek		NASA Proposal Number	
Organization Name : University Of South Florida, Tampa		17-EW17_2-0024	
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system			
SECTION X - Budget			
Start Date : 05 / 01 / 2018	End Date : 04 / 30 / 2019	Budget Type : Project	Budget Period : 1
F. Other Direct Costs			
			Funds Requested (\$)
1. Materials and Supplies			6,000.00
2. Publication Costs			1,500.00
3. Consultant Services			0.00
4. ADP/Computer Services			0.00
5. Subawards/Consortium/Contractual Costs			0.00
6. Equipment or Facility Rental/User Fees			0.00
7. Alterations and Renovations			0.00
8. Other: Tuition			20,709.00
9. Other:			0.00
10. Other:			0.00
Total Other Direct Costs			28,209.00
G. Total Direct Costs			
			Funds Requested (\$)
Total Direct Costs (A+B+C+D+E+F)			101,329.00
H. Indirect Costs			
	Indirect Cost Rate (%)	Indirect Cost Base (\$)	Funds Requested (\$)
Indirect Costs (F&A)	49.50	73,620.00	36,442.00
Cognizant Federal Agency: DHHS, Darryl Mayes, 301-492-4855.	Total Indirect Costs		36,442.00
I. Direct and Indirect Costs			
			Funds Requested (\$)
Total Direct and Indirect Costs (G+H)			137,771.00
J. Fee			
			Funds Requested (\$)
Fee			0.00
K. Total Cost			
			Funds Requested (\$)
Total Cost with Fee (I+J)			137,771.00

PI Name : Matthew Pasek						NASA Proposal Number			
Organization Name : University Of South Florida, Tampa						17-EW17_2-0024			
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system									
SECTION X - Budget									
Start Date : 05 / 01 / 2019		End Date : 04 / 30 / 2020		Budget Type : Project		Budget Period : 2			
A. Direct Labor - Key Personnel									
Name		Project Role	Base Salary (\$)	Cal. Months	Acad. Months	Summ. Months	Requested Salary (\$)	Fringe Benefits (\$)	Funds Requested (\$)
Pasek, Matthew		PI_TYPE	87,762.00			1	9,750.00	1,732.00	11,482.00
Total Key Personnel Costs								11,482.00	
B. Direct Labor - Other Personnel									
Number of Personnel	Project Role		Cal. Months	Acad. Months	Summ. Months	Requested Salary (\$)	Fringe Benefits (\$)	Funds Requested (\$)	
2	Graduate Students		12			48,066.00	4,210.00	52,276.00	
2	Total Number Other Personnel							Total Other Personnel Costs	
								52,276.00	
Total Direct Labor Costs (Salary, Wages, Fringe Benefits) (A+B)								63,758.00	

PI Name : Matthew Pasek		NASA Proposal Number	
Organization Name : University Of South Florida, Tampa		17-EW17_2-0024	
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system			
SECTION X - Budget			
Start Date : 05 / 01 / 2019	End Date : 04 / 30 / 2020	Budget Type : Project	Budget Period : 2
C. Direct Costs - Equipment			
Item No.	Equipment Item Description	Funds Requested (\$)	
		Total Equipment Costs	0.00
D. Direct Costs - Travel			
		Funds Requested (\$)	
1. Domestic Travel (Including Canada, Mexico, and U.S. Possessions)		2,100.00	
2. Foreign Travel		3,000.00	
		Total Travel Costs	5,100.00
E. Direct Costs - Participant/Trainee Support Costs			
		Funds Requested (\$)	
1. Tuition/Fees/Health Insurance		0.00	
2. Stipends		0.00	
3. Travel		0.00	
4. Subsistence		0.00	
Number of Participants/Trainees:	Total Participant/Trainee Support Costs		0.00

PI Name : Matthew Pasek		NASA Proposal Number	
Organization Name : University Of South Florida, Tampa		17-EW17_2-0024	
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system			
SECTION X - Budget			
Start Date : 05 / 01 / 2019	End Date : 04 / 30 / 2020	Budget Type : Project	Budget Period : 2
F. Other Direct Costs			
			Funds Requested (\$)
1. Materials and Supplies			4,000.00
2. Publication Costs			3,000.00
3. Consultant Services			0.00
4. ADP/Computer Services			0.00
5. Subawards/Consortium/Contractual Costs			0.00
6. Equipment or Facility Rental/User Fees			0.00
7. Alterations and Renovations			0.00
8. Other: Tuition			20,709.00
9. Other:			0.00
10. Other:			0.00
Total Other Direct Costs			27,709.00
G. Total Direct Costs			
			Funds Requested (\$)
Total Direct Costs (A+B+C+D+E+F)			96,567.00
H. Indirect Costs			
	Indirect Cost Rate (%)	Indirect Cost Base (\$)	Funds Requested (\$)
Indirect Costs (F&A)	49.50	75,858.00	37,550.00
Cognizant Federal Agency: DHHS, Darryl Mayes, 301-492-4855.	Total Indirect Costs		37,550.00
I. Direct and Indirect Costs			
			Funds Requested (\$)
Total Direct and Indirect Costs (G+H)			134,117.00
J. Fee			
			Funds Requested (\$)
Fee			0.00
K. Total Cost			
			Funds Requested (\$)
Total Cost with Fee (I+J)			134,117.00

PI Name : Matthew Pasek						NASA Proposal Number		
Organization Name : University Of South Florida, Tampa						17-EW17_2-0024		
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system								
SECTION X - Budget								
Start Date : 05 / 01 / 2020		End Date : 04 / 30 / 2021		Budget Type : Project		Budget Period : 3		
A. Direct Labor - Key Personnel								
Name	Project Role	Base Salary (\$)	Cal. Months	Acad. Months	Summ. Months	Requested Salary (\$)	Fringe Benefits (\$)	Funds Requested (\$)
Pasek, Matthew	PI_TYPE	90,395.00			1	10,043.00	1,784.00	11,827.00
Total Key Personnel Costs								11,827.00
B. Direct Labor - Other Personnel								
Number of Personnel	Project Role	Cal. Months	Acad. Months	Summ. Months	Requested Salary (\$)	Fringe Benefits (\$)	Funds Requested (\$)	
2	Graduate Students	12			49,508.00	4,214.00	53,722.00	
2	Total Number Other Personnel	Total Other Personnel Costs					53,722.00	
Total Direct Labor Costs (Salary, Wages, Fringe Benefits) (A+B)								65,549.00

PI Name : Matthew Pasek		NASA Proposal Number	
Organization Name : University Of South Florida, Tampa		17-EW17_2-0024	
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system			
SECTION X - Budget			
Start Date : 05 / 01 / 2020	End Date : 04 / 30 / 2021	Budget Type : Project	Budget Period : 3
C. Direct Costs - Equipment			
Item No.	Equipment Item Description		Funds Requested (\$)
		Total Equipment Costs	0.00
D. Direct Costs - Travel			
			Funds Requested (\$)
1. Domestic Travel (Including Canada, Mexico, and U.S. Possessions)			2,100.00
2. Foreign Travel			3,000.00
		Total Travel Costs	5,100.00
E. Direct Costs - Participant/Trainee Support Costs			
			Funds Requested (\$)
1. Tuition/Fees/Health Insurance			0.00
2. Stipends			0.00
3. Travel			0.00
4. Subsistence			0.00
Number of Participants/Trainees:		Total Participant/Trainee Support Costs	0.00

PI Name : Matthew Pasek		NASA Proposal Number	
Organization Name : University Of South Florida, Tampa		17-EW17_2-0024	
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system			
SECTION X - Budget			
Start Date : 05 / 01 / 2020	End Date : 04 / 30 / 2021	Budget Type : Project	Budget Period : 3
F. Other Direct Costs			
			Funds Requested (\$)
1. Materials and Supplies			4,000.00
2. Publication Costs			1,500.00
3. Consultant Services			0.00
4. ADP/Computer Services			0.00
5. Subawards/Consortium/Contractual Costs			0.00
6. Equipment or Facility Rental/User Fees			0.00
7. Alterations and Renovations			0.00
8. Other: Tuition			20,709.00
9. Other:			0.00
10. Other:			0.00
Total Other Direct Costs			26,209.00
G. Total Direct Costs			
			Funds Requested (\$)
Total Direct Costs (A+B+C+D+E+F)			96,858.00
H. Indirect Costs			
	Indirect Cost Rate (%)	Indirect Cost Base (\$)	Funds Requested (\$)
Indirect Costs (F&A)	49.50	76,149.00	37,694.00
Cognizant Federal Agency: DHHS, Darryl Mayes, 301-492-4855.	Total Indirect Costs		37,694.00
I. Direct and Indirect Costs			
			Funds Requested (\$)
Total Direct and Indirect Costs (G+H)			134,552.00
J. Fee			
			Funds Requested (\$)
Fee			0.00
K. Total Cost			
			Funds Requested (\$)
Total Cost with Fee (I+J)			134,552.00

PI Name : Matthew Pasek						NASA Proposal Number			
Organization Name : University Of South Florida, Tampa						17-EW17_2-0024			
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system									
SECTION X - Budget									
Start Date : 05 / 01 / 2010		End Date : 04 / 30 / 2021		Budget Type : Project		Budget Period : 4			
A. Direct Labor - Key Personnel									
Name		Project Role	Base Salary (\$)	Cal. Months	Acad. Months	Summ. Months	Requested Salary (\$)	Fringe Benefits (\$)	Funds Requested (\$)
Total Key Personnel Costs								0.00	
B. Direct Labor - Other Personnel									
Number of Personnel	Project Role		Cal. Months	Acad. Months	Summ. Months	Requested Salary (\$)	Fringe Benefits (\$)	Funds Requested (\$)	
0	Total Number Other Personnel		Total Other Personnel Costs					0.00	
Total Direct Labor Costs (Salary, Wages, Fringe Benefits) (A+B)								0.00	

PI Name : Matthew Pasek		NASA Proposal Number	
Organization Name : University Of South Florida, Tampa		17-EW17_2-0024	
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system			
SECTION X - Budget			
Start Date : 05 / 01 / 2010	End Date : 04 / 30 / 2021	Budget Type : Project	Budget Period : 4
C. Direct Costs - Equipment			
Item No.	Equipment Item Description		Funds Requested (\$)
		Total Equipment Costs	0.00
D. Direct Costs - Travel			
			Funds Requested (\$)
1. Domestic Travel (Including Canada, Mexico, and U.S. Possessions)			0.00
2. Foreign Travel			0.00
		Total Travel Costs	0.00
E. Direct Costs - Participant/Trainee Support Costs			
			Funds Requested (\$)
1. Tuition/Fees/Health Insurance			0.00
2. Stipends			0.00
3. Travel			0.00
4. Subsistence			0.00
Number of Participants/Trainees:		Total Participant/Trainee Support Costs	0.00

PI Name : Matthew Pasek		NASA Proposal Number	
Organization Name : University Of South Florida, Tampa		17-EW17_2-0024	
Proposal Title : Phosphorus mineral cosmochemistry in the emerging solar system			
SECTION X - Budget			
Start Date : 05 / 01 / 2010	End Date : 04 / 30 / 2021	Budget Type : Project	Budget Period : 4
F. Other Direct Costs			
			Funds Requested (\$)
1. Materials and Supplies			0.00
2. Publication Costs			0.00
3. Consultant Services			0.00
4. ADP/Computer Services			0.00
5. Subawards/Consortium/Contractual Costs			0.00
6. Equipment or Facility Rental/User Fees			0.00
7. Alterations and Renovations			0.00
8. Other:			0.00
9. Other:			0.00
10. Other:			0.00
Total Other Direct Costs			0.00
G. Total Direct Costs			
			Funds Requested (\$)
Total Direct Costs (A+B+C+D+E+F)			0.00
H. Indirect Costs			
	Indirect Cost Rate (%)	Indirect Cost Base (\$)	Funds Requested (\$)
	0.00	0.00	0.00
	0.00	0.00	0.00
	0.00	0.00	0.00
	0.00	0.00	0.00
	0.00	0.00	0.00
	0.00	0.00	0.00
	0.00	0.00	0.00
	0.00	0.00	0.00
	0.00	0.00	0.00
Cognizant Federal Agency:		Total Indirect Costs	0.00
I. Direct and Indirect Costs			
			Funds Requested (\$)
Total Direct and Indirect Costs (G+H)			0.00
J. Fee			
			Funds Requested (\$)
Fee			0.00
K. Total Cost			
			Funds Requested (\$)
Total Cost with Fee (I+J)			0.00

Phosphorus mineral Cosmochemistry in the Emerging Solar System

PI: Matthew A. Pasek

School of Geoscience

University of South Florida

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1. Scientific and Technical Management

1.1 Objectives and Significance

The element phosphorus (P) has a cosmic abundance of about 0.007 P atoms for every Si atom (Anders and Grevesse 1989). For this reason, phosphorus is generally classified as a minor or trace element in cosmochemical samples. However, despite its relative scarcity in the Solar System, phosphorus has received a significant amount of attention from the cosmochemical community, due both to its role in capturing volatiles in phosphate mineral crystal lattices, and in the astrobiological implications of phosphorus to the development of life on the earth (e.g., Pasek 2017). Despite the role of phosphorus in cosmochemical evolution, several facets of phosphorus cosmochemistry remain unclear, including 1) the extent of volatile forms of phosphorus present within the early Solar System, including the gas phosphine (PH_3), 2) the oxidation of siderophilic (metal-loving) P minerals such as schreibersite $(\text{Fe,Ni})_3\text{P}$ to form lithophilic (silicate rock-loving) phosphate minerals, and 3) the stability of phosphate minerals that may have formed by fluid-rock interactions on meteorite parent bodies (e.g., struvite) to those more common to anhydrous planetary bodies (e.g., merrillite). We propose to investigate key aspects of phosphorus cosmochemical behavior to better constrain the phases and forms that govern the distribution of this key element in our Solar System. This objective will be accomplished by experiments and sample analysis, with results fed into Solar System and planet chemistry models.

The experimental work will involve laboratory measurement of the rates of phosphidation of metals, specifically Fe metal, to determine how well metals “scrubbed” phosphorus from the early Solar System nebula. We shall also characterize how phosphides might oxidize to form phosphates, and will use this data to constrain the kinetics of equilibration in meteorite parent bodies, and will then apply these results to understand primary planetary metamorphism and the distribution of phosphorus. Finally, we shall determine the stability of minerals that may have formed by fluid-rock interactions, to see how well fluids may have altered the primary mineralogy of planetesimals, and the extent that this may have been preserved over 4.5 billion years. We will primarily use microprobe analysis as well as XRD and Raman to identify minerals formed in experiments, and NMR to identify P speciation. Models will include Solar System equilibrium chemistry models, and kinetic modeling of gas-solid reactions and gas transport.

1.2 Relevance

The proposed research is highly relevant to the objectives of NASA and the Emerging Worlds Program. Our work is particularly relevant to the areas of research emphasis outlined in ROSES as follows: large-scale chemical and isotopic fractionation processes, chemical and physical processing of gas, dust, and ice, and early thermal and chemical processes occurring on small bodies regardless of whether or when they differentiated. This research will attempt to constrain the bulk speciation of the element phosphorus, linking the P species to various meteoroid and Solar System environments. Results from these experiments and models will

detail the key phosphorus phases and minerals occurring within the early Solar System. In doing so, this study will strengthen our conceptual understanding of how phosphorus is distributed throughout the Solar System, and how this distribution affected emerging planetary systems from comets to rocks.

This proposal is fairly singular with its focus almost exclusively on the element phosphorus. We justify this approach as our lab may be especially suited to make a significant amount of progress in the area of phosphorus cosmochemistry, and this subject is relevant to the field of cosmochemistry as a whole for the roles P plays in meteorite and planetary mineralogy, as well as astrobiology. This study also provides a comprehensive look at P cosmochemistry, and covers temperatures from early condensation (~900°C) to temperatures of low-temperature alteration (25°C).

1.3 Results of Prior Work

Most of our research specifically investigates the potential reactions that arise when meteoritic schreibersite reacts with water, and with organic solutes within the water (e.g., Pasek and Lauretta 2005, Pasek *et al.* 2007, Bryant *et al.* 2009, Pech *et al.* 2011, Pasek *et al.* 2013, La Cruz *et al.* 2016, Pasek 2017). We have demonstrated that schreibersite is capable of spontaneously making nucleotides out of nucleosides, a key step in the synthesis of RNA (Gull *et al.* 2015). We have further shown that phosphorus participates in redox reactions both on the early earth (Pasek *et al.* 2013) and on the modern earth (Pasek *et al.* 2014), with both studies appearing in PNAS.

The experiments and work proposed here are a natural extension of our research funded previously by NASA Exobiology. Over the course of these investigations, we have identified several open questions in phosphorus cosmochemistry. These questions have included, “What volatile forms of phosphorus existed in the early solar system, and how important were they?”, “How might the production of phosphates from phosphides come about?”, and “How might phosphate mineral diversity have been altered by fluid-rock interactions and volatilization on meteorite parent bodies?”

We have had a total of 30 publications on P mineralogy and cosmochemistry, and five master’s students have graduated with theses coming from this work (Pasek and Block 2009, Pasek *et al.* 2012, 2014, La Cruz *et al.* 2016). In the past ~10 years we have made several breakthroughs in the study of P chemistry in the origin of life. During a suite of extraction experiments of meteoritic minerals, we encountered an unusual assortment of aqueous P compounds formed during the reaction of synthetic iron phosphide (Fe₃P) with water. The iron phosphide served as a proxy for meteoritic schreibersite, (Fe,Ni)₃P, an ubiquitous mineral in meteorites, and especially iron meteorites (Pasek and Lauretta 2008). Phosphide corrosion in de-ionized water results in a metastable mixture of mixed-valence, P-bearing ions including phosphate, hypophosphite, and phosphite, (Pasek and Lauretta 2005), and even some organophosphorus compounds (Pasek *et al.* 2007). The corrosion process leading to these species is now moderately well understood (Pasek *et al.* 2007, 2015 Bryant *et al.* 2009, 2010, 2013).

Recently we have focused on cosmochemical aspects of phosphorus chemistry. These include the chemistry resulting on the surface of schreibersite, as a set up for oxidation reactions (e.g., Bryant *et al.* 2013, Pirim *et al.* 2014, La Cruz *et al.* 2016). We have also investigated routes to the formation of schreibersite, both via impact reduction (Pasek 2015, 2017), and from phosphidation of metals (La Cruz *et al.* 2016). Notably, our lab is also able to produce synthetic schreibersite, with a formula of Fe_2NiP (La Cruz *et al.* 2016), and we can make schreibersite with many variations on this formulation. This research was performed originally to provide material for prebiotic chemical reactions, however, with modifications to the design, the setup can provide key data on reactions of interest to the early Solar System.

The PI is an associate professor of geoscience at the University of South Florida. We have presented our results at the *Gordon Conferences on the Origin of Life*, the *Goldschmidt Conference*, *AbSciCon*, and the *Geological Society of America Meeting*. Historically we have produced 2-4 papers for each major grant each year, and anticipate the proposed research will have a similar yield.

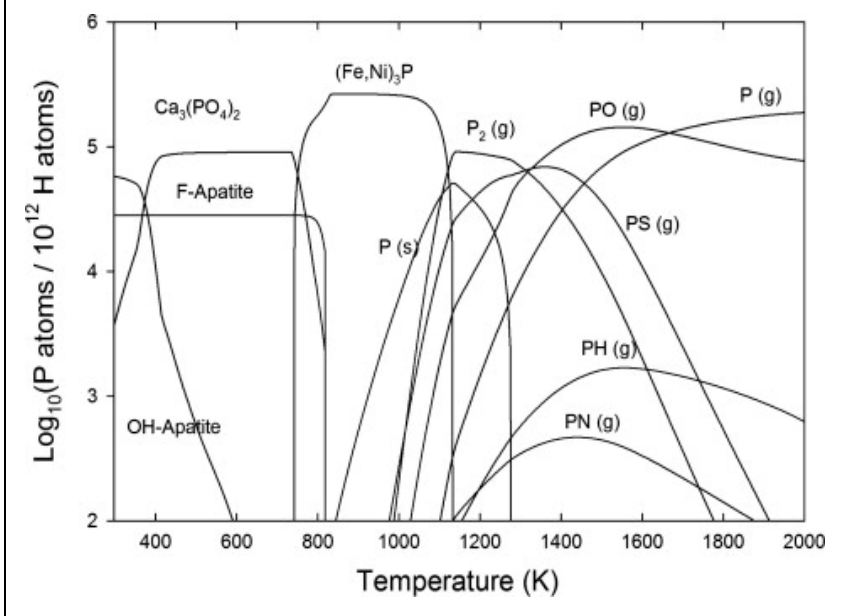
1.4 Background

Phosphorus is a minor element, occurring at about 0.007 atoms per Si atom in standard tables of Solar System abundances. The condensation sequence of phosphorus is given as Figure 1.

1.4.1 Phosphorus in the Cosmochemical Condensation Sequence

Phosphorus is typically considered to be a moderately volatile element (Figure 1), in that it forms its main solid (schreibersite, $\sim\text{Fe}_2\text{NiP}$) at temperatures lower than the condensation temperature of iron metal but higher than the condensation temperature of sulfur as troilite. The temperature at which P forms its first solids (~ 1250 K) is actually not much lower than the temperature at which iron first condenses (~ 1300 K at 10^{-4} atm, Palme and Fegley 1990). This means that phosphorus is unusual amongst the biogenic elements (C, N, H, O, S), which are all considered to be volatile ($T_{\text{condensation}} \sim 750\text{K}$) to highly volatile ($T_{\text{condensation}} < 300$ K).

Figure 1. Phosphorus condensation sequence in a nominal Solar System nebula, at 10^{-4} atm, with solar elemental abundances. From Pirim *et al.* (2014)



In addition to some ambiguity in the “volatile” classification of phosphorus, the geochemical classification of P is also temperature dependent. Under reducing Solar System conditions, phosphorus behaves as both a lithophile and a siderophile. At high temperature (700-1200K) P is in phosphide minerals, primarily the mineral schreibersite. At lower temperatures, P is in phosphate minerals, primarily Ca-phosphates. These calculations are confirmed by studies of undifferentiated meteorites, where P is in both forms, indicative of both a siderophile and lithophile P mineralogy (Zanda *et al.* 1994). To this end, during differentiation, P has the potential to be both in core material and in mantle material. The ultimate fate of P is dependent on the oxygen fugacity of the system, and the exact tipping point for fractionating most planetary P into a core is not clear (Scott *et al.* 2007). However, if the mantle abundance of P can be accurately measured from presumed mantle-derived clasts, then the earth’s core contains a majority of the earth’s phosphorus, and presumably the cores of other planets and differentiated asteroids would similarly bear most of their P in metallic minerals (McDonough and Sun 1995).

The condensation sequence also demonstrates that P forms its first solids via gas-metal reactions. Such reactions, akin to the formation of troilite ($\text{Fe} + \text{H}_2\text{S} = \text{FeS} + \text{H}_2$), are controlled by surface-gas reaction kinetics. Thus far, metal-phosphorus reactions (which are important in semi-conductor and catalyst technology) demonstrate that under reducing conditions P will readily react with metals (Wang *et al.* 2008). Few studies have focused on the phosphidation of iron, with Sasaki (1985) providing most of the data for iron and, separately, nickel phosphidation. Based on thermodynamic constraints, nickel phosphidation should occur more readily as Ni_3P formation is more exergonic than Fe_3P . The rate of these reactions under more Solar System-like conditions is unclear. *A goal of this proposal will be to determine the rates of Solar System-relevant metal phosphidation by P gases.*

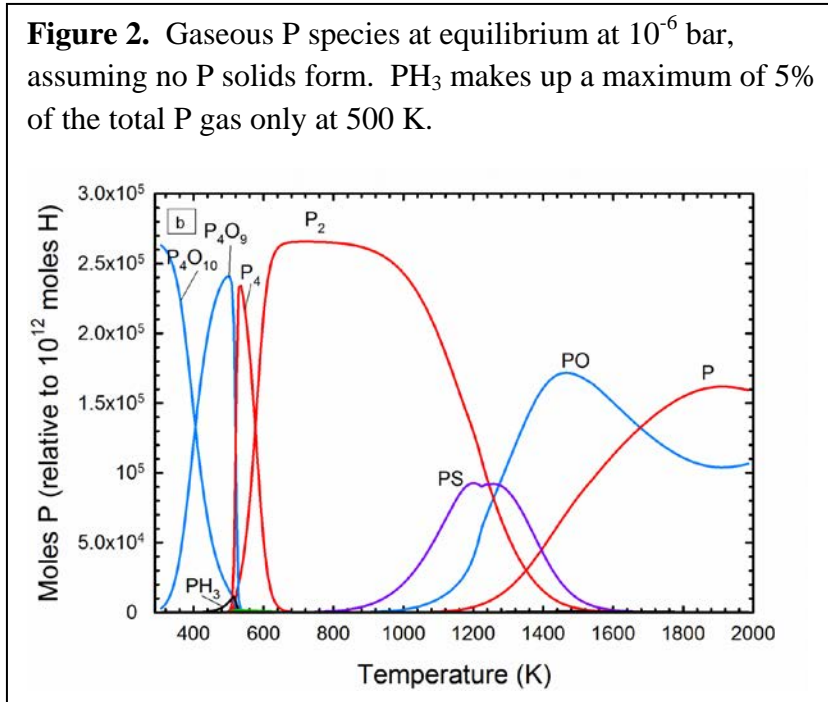
1.4.2 Volatile forms of Phosphorus

Elements can remain in the gas form if they do not form solids efficiently over Solar System formation timescales. Eventually, as temperatures decrease, volatile elements will form ices. Phosphorus is known to have some volatile forms, including, most prominently, the gas phosphine (PH_3). This gas is the likely sink for P on the gas giant planets (Borunov *et al.* 1995), and might be important for comets (Agundez *et al.* 2014). A common assumption in the comet community is that phosphorus is in PH_3 ices on comets (e.g., Altwegg *et al.* 2016). However, recent work (Pasek 2017, in review at *Icarus*) has suggested that gaseous PH_3 is never the most abundant P gas under any nominal solar system conditions (Figure 2), and that at lower temperatures, P_xO_y gases dominate instead, with P in an oxidation state opposite that of phosphine.

From the equilibrium thermodynamic calculations of Solar System chemistry above, P condenses by reaction of P gases with iron-nickel metal. This reaction is constrained by the kinetics of the gas-solid reaction. The rates of reactions between gases and solids are typically faster at higher temperature, and hence solids can pull out specific gases or elements from the surrounding environment when they are closer to the Sun, decreasing their relative abundance. As a consequence, metal might “scrub” phosphorus, removing it from the nebula gas near the

Sun. The preliminary data of Sasaki (1985) suggest that the rate of P gas removal is efficient, especially at high temperatures (800-1200 K), potentially even to lower temperatures (500-700 K). Furthermore, recent model data from Pasek (2017, in review) also demonstrates that metal phosphidation is very efficient at removing volatile P from the solar nebula, with loss of nearly 100% of the P over large swaths of the solar nebula, depending on reaction kinetics.

Assuming the nebular model is correct (Pasek 2017, in review) and the Sasaki (1985) kinetics are sufficient for Solar System modeling, all P gas could have been removed quickly (<10000 years), creating a P depleted region in the early Solar System nebula from 3-14 AU. As



a result of this chemical depletion, P gas from outside this region will diffuse to the depleted zone, resulting in decreased P throughout the nebula. The speed of this radial diffusion will determine how much P is left within the Solar System as the Solar System cooled. Such a process has been hypothesized to occur as part of the snow line (Ciesla and Cuzzi 2006), depleting oxygen, and likely affected sulfur (Pasek *et al.* 2005) in a

similar way.

A consequence of this P gas depletion is that there might have been extremely little P gas present within the early Solar System to get trapped into cometary material or migrate to form ices. Mousis *et al.* (2010) and Pasek *et al.* (2011) proposed PH_3 clathrates may have formed in water ice and been a source material for P in the outer Solar System, including comets. Indeed, a recent detection of elemental phosphorus in 67P/Churyumov-Gerasimenko was attributed to phosphine (Altwegg *et al.* 2016). However, this detection thus far is based solely on identification of elemental P, and the molecular form is yet unclear with $\text{PH}/\text{PH}_2/\text{PH}_3$ not detected. It is possible that depletion of phosphorus by solid-gas reactions could have prevented P ices from forming, suggesting little volatile P in comets.

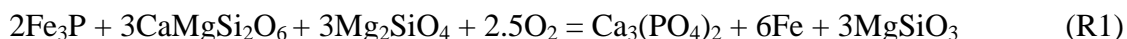
Table 1. Phosphorus gases detected in the extrasolar environment.

Gas	Reference
PN	Ziurys 1987
CP	Guelin et al. 1990
HCP	Guelin et al. 1990
PO	Tenenbaum et al. 2007
PH_3	Agundez et al. 2008
CCP	Halfen et al. 2008

Some confirmation of this hypothesis comes from discoveries of volatile P gases using radio telescopes. A total of six gases have been identified (Table 1). Thus far, these occur in the hot envelopes of stars. Indeed, P appears to be depleted in the cool ISM (Turner *et al.* 1990). It is possible that phosphorus is closer in chemistry to silicon than sulfur, and thus ices bearing volatile phosphorus compounds might be exceedingly rare. *A goal of this proposal will be to use experimental data to determine the effectiveness of removal of volatile P by iron-nickel metal in models of the early Solar System.*

1.4.3 Phosphide oxidation and distribution within chondrites

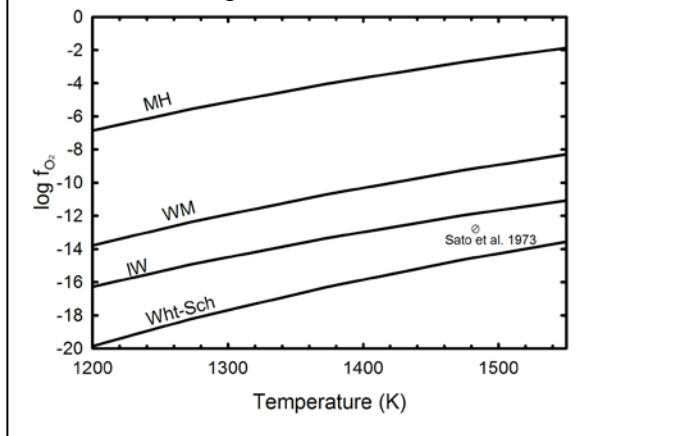
Equilibrium chemistry predicts phosphorus will remain primarily in phosphides under reducing conditions and in phosphates under oxidizing conditions. The oxidation of phosphide is given as the schreibersite-calcium phosphate oxygen fugacity buffer:



Conditions defined by this buffer are necessarily extremely reducing, and well below typical earth mantle conditions (Fig. 3).

The oxidation of schreibersite must ultimately have occurred on meteorite parent bodies, and is predicted to commence at about 800 K. This reaction is mainly a solid-solid reaction between a calcium silicate (likely $\text{CaMgSi}_2\text{O}_6$), schreibersite, and olivine, though water may provide the oxygen, with H_2 , iron metal, MgSiO_3 , and calcium phosphate (akin to whitlockite) as products.

Figure 3. Oxygen fugacity buffers magnetite-hematite (MH), wüstite-magnetite (WM), and iron-wüstite (IW), and schreibersite-whitlockite (wht-sch). Image from Pasek (2015).



Phosphorus within ordinary chondrites is highly dependent on equilibrium chemistry. Those chondrites that have equilibrated at higher temperature (4 to 6 petrographic grade) tend to possess only phosphates, whereas those chondrites that experienced less thermal metamorphism but perhaps more aqueous alteration (3-3.1) bear much of their P in metal, including schreibersite (Zanda *et al.* 1994, Kimura *et al.* 2008). The rate of oxidation of phosphides is unclear as Harlow *et al.* (1980) argued for very long timescales at low temperature, whereas Rambaldi and Wasson (1981)

propose short timescales with appreciable Ca and Mg silicate minerals.

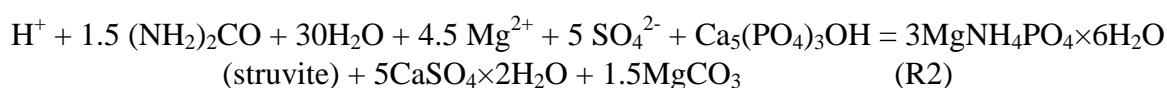
A goal of the proposed work is to determine the rate of phosphide oxidation that occurs in chondritic meteorites. In doing so, we will establish whether phosphorus might be able to elucidate meteorite parent body thermal histories. If the rate of phosphide oxidation is suitably

slow, it may be possible to estimate the timescale of metamorphism or the T-t path of chondrites and other meteorites.

1.4.4 Fluid-rock Phosphorus Chemistry: new phosphates?

Chondritic meteorites are dominated by calcium-phosphates such as merrillite and the apatite mineral group with respect to P mineralogy. Iron meteorites and pallasites do have other P minerals, primarily expected as a result of phosphide oxidation with counterbalancing cations (Na, Fe, Mg).

Recently we demonstrated that phosphate minerals may be susceptible to alteration by ammonia- and MgSO₄-bearing fluid, forming new minerals (Burcar *et al.* 2016). This reaction is summarized as:



and was reported as the alteration of apatite by urea-rich fluids. However, in these experiments, urea served only as a source of ammonium, and replicates with ammonium-rich fluids instead of urea have also shown transformation of apatite to the new phosphate mineral struvite.

The organic inventory of many meteorites is also characterized by high ammonia content of up to a few percent with respect to carbon (Pizzarello *et al.* 2011, Pizzarello and Williams 2012), or 100s of ppm with respect to total mass. Under these conditions, fluid alteration of meteorite parent bodies should result in the formation of ammoniacal minerals such as struvite from apatite. To date no ammonium minerals, including struvite and the ammonium feldspar buddingtonite, have been found in meteorites. We believe this may be due to the low pressure loss of ammonia and transformation of these minerals to Mg-phosphates and then to Ca,Mg-phosphates. To this end, a goal of this proposed work is to *explore the stability of ammonium phosphate and Mg-phosphate minerals under low pressure to determine if these minerals will be lost prior to the meteorite falling to the earth.*

1.5 Proposed Work

We propose three major projects or modules: **(1)** Determination of phosphidation rates of iron metal and iron-nickel alloys. Data from these experiments will then be used to verify/dismiss the hypothesis that metals were efficient sinks of P in the early solar nebula, and hence the early Solar System did not have significant sources of volatile phosphorus that could subsequently be caught in cometary ices. Data from comets thus far has born this out, as P in Wild 2 samples is in schreibersite (Brownlee *et al.* 2012) and phosphates (Rotundi *et al.* 2014). **(2)** Investigating phosphide oxidation rates under plausible meteorite parent body mineralogy. Data from these experiments will be used to elucidate temperature-time requirements for the establishment of P equilibrium chemistry, to see if the phosphides oxidize quickly (~days) or take significantly longer (~years). These data will be compared to P mineralogy of ordinary chondrites (mostly petrographic types 3.0 to 4.0). **(3)** Quantifying the possibility of new phosphate minerals

forming by fluid-rock interactions, specifically ammoniacal phosphates such as struvite. These phosphate minerals are significantly more water-soluble than calcium phosphates, and their formation would imply greater mobility for P on meteorite parent bodies than is expected. We anticipate that these minerals, were they to have formed, would have lost ammonia as a result of being under low pressure, and that this reaction would have occurred under relatively short timescales.

1.5.1 Rates of metal phosphidation

Metal phosphidation is the reaction of phosphorus with metal to make a metal phosphide, analogous to metal sulfidation to make a metal sulfide. Metal sulfidation has been well studied in the cosmochemical context (Lauretta and Fegley 1994, Lauretta *et al.* 1996, 1997). The proposed work will attempt to provide a first estimate of the efficiency of phosphidation in the removal of phosphorus from the early Solar System nebula, building on these sulfidation techniques. The experimental suite will not be as rigorous as these prior sulfidation experiments due to available time and facilities, and will likely constitute only a chapter of the dissertation of grad student Carolyn Lang, but will be focused on obtaining the key data necessary to address the questions posed. These experiments leverage existing equipment and techniques (Pasek 2015, La Cruz *et al.* 2016) to address questions on the rates of phosphorus reacting with metals.

Phosphidation experiments will be done in a tube furnace under a controlled temperature and gas composition. We have used this setup previously to synthesize schreibersite from elemental iron, nickel, and phosphorus (red) powders (La Cruz *et al.* 2016). Experiments will be performed under atmospheric pressure, under varying temperatures that are below the Fe-P eutectic (1048 °C), from 600 to 1000°C in 100°C increments.

Table 2. Reaction conditions. Values in parentheses will be done as time permits.

Metals	Surface Area (mm ²)	Partial Pressure (atm)	Temp. (°C)	Time (days)
Iron	22.5	10 ⁻⁴	(600)	1
(Nickel)	(70)	10 ⁻³	700	3
(Campo)	240	10 ⁻²	800	(6)
	1380	(10 ⁻¹)	900	10
			(1000)	(30)

In these experiments, a piece of iron metal foil (and, if time allows, Ni foil and a piece of the Campo del Cielo (IAB) iron meteorite) will be placed in an open crucible at the peak temperature point of the tube furnace (where the temperature is equal to the temperature set point). The metal will be suspended using a small platinum wire (unreactive towards P) to allow phosphidation on both sides of the foil. A small quantity of red phosphorus will be placed ~3 cm away from the metal, still inside the crucible, where it will be heated at a lower temperature, but still well above its boiling point (300°C). The tube will then be vacuum purged and filled with argon gas 3 times, and then temperature raised to the temperature set point (Table 2). As the temperature passes 300°C, the red P will vaporize, giving a partial pressure of P that can be calculated from the mass added to the tube initially (an alternative to this route presented in 1.7). For our 1.5 inch diameter tube, this equates to about 7×10^{-4} atm per mg of P added. We should

be able to create partial pressures of phosphorus that range between 10^{-4} atm to 0.1 atm with this methodology. Although the partial pressure of P gas expected in the early solar nebula should be about 10^{-9} atm, we will extend these data points to reach possible P pressures by assuming a linear rate of reactivity with respect to log fugacity (rate $\propto P_P^{0.15}$), an assumption found valid for Sasaki (1985) and to be confirmed here.

Metals and the Campo del Cielo meteorite are available commercially. The Campo meteorite has been chosen specifically because it lacks large schreibersite grains. We have chosen to use Ar as the carrier gas instead of H_2 as we intend to avoid production of PH_3 within our lab setup. PH_3 is not predicted to have been a major gas leading to phosphidation at any of the temperatures being examined here (Fig. 2), hence running these phosphidation experiments does not impact applicability to solar system chemistry. The major phosphidation gases are P gases (P , P_2 , P_4), and these are the gases formed in Sasaki's phosphidation experiments (1985). After reaction for a day to over a week, the tube will be cooled and the sample removed for analysis. From prior work the rate of reaction is fast (~ 1 hour), meaning that we may not need to do the long term experiments (30 days). Table 2 shows reaction conditions to be explored. Each variable will be compared to the "default" experiment consisting of iron foil with a surface area of 240 mm^2 , at 800°C , with a P partial pressure of 10^{-2} atm. About 7 critical experiments with three runs each, requiring 98 days of run time are planned in table 2. If time is available or more resolution is needed, an additional 4 experiments can be performed, and with a fourth time sample taken (6 days), a total of 220 days of run time will be needed.

The principal issue with Sasaki's (1985) experiments was that the metal foil used was a substantial portion ($\sim 5\%$) of the total surface area (metal + tube interior) of these experiments. In our proposed setup, the surface area will be between 0.03% and 2% of the total interior. In exploring the effect of surface area as a variable, we intend to determine the relationship between reaction rate and metal surface area, to see if we can extend the results of these phosphidation experiments to the solar nebula, where the available metal surface area would be about 10^{-6} that of Sasaki's (1985) experiments, assuming metal spheres $1 \text{ }\mu\text{m}$ in diameter (Pasek 2017, in review).

Microprobe Analysis

Half of each sample will be analyzed by XRD and Raman and the other half mounted and analyzed by microprobe to determine the extent of metal phosphidation, and the stoichiometry of the phosphide (metal phosphides range from M_4P to MP_2). Sasaki (1985) reported phosphidation that produced FeP and NiP solids, as opposed to Fe_3P or Ni_3P , and this was likely due to reacting these solids within vapor consisting only of P gas. Metal phosphides are approximately the same density of iron metal, so the surface of the metal should expand during phosphidation as mass is gained, and hence an accurate measurement of thickness before and after phosphidation will be made using calipers accurate to $10 \text{ }\mu\text{m}$. Samples will also be massed before and after phosphidation to determine the mass gain.

We will use a microprobe located at Florida International University to determine the P minerals present on the surface and extent of phosphidation. From this, we shall attempt to calculate individual parabolic rate constants for metal phosphidation based on the amount of phosphide created, and arrive at an activation energy for phosphidation to allow for extensibility to different temperatures. These parabolic rate constants can then be used with the Deal-Grove (1965) corrosion model to determine the relationship between temperature, pressure, and metal surface area per mass necessary to generate models of how quickly P reacts with metal.

Modeling

Ultimately this data will be used to predict P gas abundance in the early Solar System. This is done as a function of time, temperature, pressure, and reactive metal grain size. Effectively, from this data we can calculate K, the parabolic rate constant as a function of temperature and pressure. By multiplying this by a reaction timescale t , the amount of phosphide reacted is \sqrt{Kt} , in units of mass per surface area. Then, based on the size of metal grains (typically assumed to be spheres), the amount of P that reacts is dependent on the surface area per unit mass ($\frac{3}{\rho r}$ where ρ is the density of metal, and r is the radius).

The modeling to be done here will incorporate diffusive transport of gas (e.g., Ciesla 2007) with a zone of P removal where the kinetics of phosphidation are fast. This region had a width of about 1 AU in the analogous model of Pasek *et al.* (2005) for sulfur, and given the kinetics of phosphidation appear to be even faster for P than for S, and appear to operate over a larger temperature range, this region is larger, and hence the removal of P should have been much more extensive. As a result, we hypothesize that there will be little to no available P left over to make volatile P gases and ices (such as PH₃), and hence cometary P will be limited to P minerals such as phosphides and phosphates.

1.5.2 Phosphide oxidation chemistry

A set of experiments related to the above phosphidation experiments will be performed to investigate the oxidation rate of phosphides. In these experiments, mixtures of olivine (Mg₂SiO₄) and diopside (CaMgSi₂O₆), will be added to Fe₃P (all reagents commercially available) in a 10:10:1 ratio (compare to the above stoichiometry of 3:3:2 in R1) as powders (2 g total mass, 10 μ m grain size). These powders will be mixed and pressed into a pellet to minimize pore space (as per La Cruz *et al.* 2016). These pellets will be placed within a crucible, then covered with a second smaller crucible (Fig. 4) with a gap allowing for the transfer of gas. The larger crucible shall than be filled with a mineral redox buffer, such as iron-wüstite (Fe/FeO) or quartz-iron-fayalite (QIF). These buffers should control the oxygen fugacity within the crucible, including within the sample. We will focus initially on iron-wüstite and QIF buffers as these are closer to the redox state of chondrites, but may also attempt highly reducing (Si-SiO₂) and more oxidizing (FeO-Fe₃O₄, or WM). The buffers will be used in excess of the reaction material, by a factor of 10 with respect to mass.

Samples will be placed within a tube-furnace, which will be purged with vacuum and filled with argon three times. After the final purge of the chamber at room temperature, the sample will be heated to a set temperature from 200-600°C. The samples will remain at the peak temperature for up to one day as we anticipate oxidation will be rapid, especially at higher temperatures. If one day is insufficient for oxidation, experiments will be extended, especially the low temperature experiments.

We acknowledge that argon gas may have some quantity of O₂ as Ar is prepared by fractional distillation of air, hence we have attempted to minimize oxidation by trace O₂ by surrounding the sample chamber with the redox buffer, which also provides a measurement of f_{O₂} as a function of temperature. We have on hand corundum and graphite crucibles, and have access to a platinum crucible, and have budgeted purchase of a SiC crucible. In our schreibersite synthesis (La Cruz *et al.* 2016), the samples were prepared in a corundum crucible in Ar at temperatures of ~1000°C with no AlPO₄ forming, suggesting little unintentional oxidation in experimental samples with this setup.

Figure 4. Sample setup. The inner crucible (gray) holds the sample pellet (green), which is surrounded in the outer crucible by the redox buffer (pink).



After heating, the samples will be removed from the furnace, and mounted in epoxy and

Table 3. Reaction conditions. Values in parentheses will be done as time permits.

Minerals	Temp (°C)	Redox Buffers	Time (days)
Fe ₃ P + CaMgSi ₂ O ₆ + Mg ₂ SiO ₄	200	IW	0.25
	300	QIF	0.5
	400	Si-SiO ₂	1
	500	WM	5
	600		(10)

polished for analysis by microprobe, specifically looking for the formation of phosphate minerals from Fe₃P. XRD and Raman will also be used to identify mineralogy. In addition, a portion of each reaction pellet (0.1-0.2 g) shall be extracted with an EDTA solution (as per Pasek and Laurretta 2005, Pasek *et al.* 2007) and analyzed by ³¹P NMR to determine P speciation. We have found this to be an effective way of measuring P redox state: phosphate is visible clearly as HPO₄²⁻, whereas Fe₃P corrodes to produce phosphite (HPO₃²⁻) and phosphate (HPO₄²⁻) in a 1:1 ratio. The suite of experiments to be investigated is given as table 3. A total of eight experiments will be performed, each requiring 6.75 days for completion (54 total days). If necessary, each experiment can be run for 10 days to add a fourth time point for oxidation. We are requesting a second tube furnace in our budget so that we might run these oxidation experiments simultaneously with the phosphidation experiments.

In addition to the experimental work, several meteorites will be analyzed to determine how distributed P chemistry is with respect to petrographic type. Using EMPA elemental mapping we will analyze a suite of NWA meteorites (already on hand, table 4) and others to determine

how much P resides within metal, compared to P within Ca-phosphates. Although using NWA meteorites may seem to be problematic due to weathering, NWA meteorites are 1) readily accessible in case more samples need to be acquired, and 2) phosphorus has been shown to not redistribute during weathering unless that weathering is extensive (W3-W4, see Pirim *et al.* 2014). Schreibersite weathers after iron metal due to nickel (Bryant *et al.* 2009), hence W0-W2 chondrites should not have altered phosphides.

The goal of this work will be to identify the timescale and temperature requirements of phosphide mineral oxidation. The experiments will relate phosphide mineral oxidation to peak temperatures, which should be applicable to meteorite thermal histories, as petrographic type relates to metamorphic temperature (see Huss *et al.* 2006). Using our experimental data, we should be able to make some assessment of the time required to equilibrate P at a given peak temperature, and this data will be useful for meteorite studies. This project correlates well to project 1 above, which will analyze the timescale of phosphide mineral formation. As such these two projects connect nebular processes to small body processes wherein P is further redistributed from its primary mineral condensate.

1.5.3 Alteration of Phosphates by Fluids

This module of the proposed research will determine how fluid-rock interactions might alter phosphate mineralogy, ultimately relating these to minerals that should be present on meteorite parent bodies. Notably, of the ordinary chondrites, those meteorites with phosphides (3.0-3.1 petrographic types) also have evidence of aqueous alteration, hence some of their phosphate mineralogy may show alteration. We base this module on our recent research on the transformation of apatite to the mineral struvite (R2 above). This reaction proceeds under low water activity at 65-85°C, in fluids with high MgSO₄ and ammonia content (Burcar *et al.* 2016). Carbonaceous chondrite parent bodies, especially CI, are rife with sulfate minerals presumably formed by aqueous alteration. Although some have proposed that these sulfates formed instead by weathering (Gounelle and Zolensky 2001), that these minerals are present at all does appear to implicate mobility of Mg²⁺ and may indicate some sulfate was present on the parent body (Fredriksson and Kerridge 1988).

The transformation of apatite to struvite reported in Burcar *et al.* (2016) was surprising in its speed and robustness. To this end, we expect fluids bearing ammonia (Pizzarello and Williams 2012) and carrying dissolved MgSO₄ (Fredriksson and Kerridge 1988) should effect changes to

Table 4. Meteorites to be investigated, with weathering and shock grades. Note that some types have not been given types beyond 3, and will be identified using matrix and chondrule olivine Fa%.

Name	Type	W type	Shck
Bovedy	L3	W0	
NWA 10213	L6	W1	S4
NWA 10218	L4	W1	S2
NWA 11025	H3	W1	
NWA 4860	L4	W1	S6
NWA 4910	LL3.1	W1	S2
NWA 5060	L3	W1	
NWA 5477	L3	W1	S2
NWA 5701	L3	W0/1	S2
NWA 7676	LL3	W1	
SAH 02500	L3	W1	
Vicencia	LL3.2	W0	

calcium phosphate minerals known to be present on chondrites. Minerals we would expect to form from such reactions include struvite $\text{MgNH}_4\text{PO}_4 \times 6\text{H}_2\text{O}$, dittmarite $\text{MgNH}_4\text{PO}_4 \times \text{H}_2\text{O}$, and newberyite $\text{MgHPO}_4 \times 3\text{H}_2\text{O}$. However, thus far no phosphate minerals bearing either acid phosphate (HPO_4^{2-}) or ammonium have been discovered in meteorites. Did such minerals ever appear? Are they stable over the long term on meteorite parent bodies? Could there be evidence of these minerals in meteorites?

We will attempt to address these questions by investigating the stability of hydrous Mg and Mg/NH₄ minerals under heat and vacuum. We anticipate that ammoniacal and hydrous phosphate minerals may be susceptible to loss of volatiles over short time periods, leading to their ultimate metamorphism back to Ca,Mg-phosphates. This hypothesis will be tested by examining the mineralogy of phosphate minerals under vacuum at changing temperatures. Such research follows work done by wastewater treatment scientists (Bhuiyan *et al.* 2008, Babic-Ivancic *et al.* 2006), who report transformation of struvite to newberyite in high Mg²⁺ environments, and from struvite to ditmarrite or bobierrite under high temperature, and transformation ultimately to MgHPO₄ (amorphous) or Mg₂P₂O₇ under dry air. These reactions are reported to be fast (<24 hours) suggesting our experimental setup should be sufficient for experimental completion. Note that some of these reactions can be modeled via thermodynamic equilibrium modeling (see Gull and Pasek 2013, Burcar *et al.* 2016), however thermodynamic data of these species remains poorly constrained especially at higher temperatures (>70°C).

Reactions will be performed in glass containers heated with hot plates and attached to a vacuum manifold (1 Pa minimum pressure with current setup). The stability of struvite (synthesized in house via Gull and Pasek 2013), and newberyite (synthesized via Burcar *et al.* 2016) will be examined as a function of time and temperature. We anticipate dehydration reactions and loss of ammonia will dominate this chemistry, with formation of Mg-phosphates and possibly Mg₂P₂O₇ on reaction completion. We will also add powdered Ca minerals to subsequent experiments to see if the reverse reaction—change back to apatite—can also occur at temperatures of 200°C.

Sample products will be analyzed by a combination of Raman and XRD, and possibly

Table 5. Reaction conditions. Values in parentheses will be done as time permits.

Minerals	Temp (°C)	Time (days)
Struvite	25	0.25
Newberyite	70	0.5
(+ calcite)	130	1
(+ gypsum)	200	5
		10

microprobe when appropriate (namely to arrive at Mg/P ratios when the mineral identification is ambiguous). These minerals are all resolvable with unique diffractograms and different Raman spectra. Added to these analyses is ³¹P NMR of EDTA extracts, which will be primarily helpful when examining reactions for production of the phosphate dimer P₂O₇⁴⁻, which separates significantly from phosphate with respect to its NMR peak location (Pasek *et al.* 2008). Reaction conditions are outlined as table 5. These experiments are not performed in tube furnaces, and consist of 8 to 24

experiments (differing minerals, differing temperatures), with 10 days required for each

experiment, for a total of up to 240 days to run this suite. A suite of experiments will be run simultaneously under air to determine if pressure plays any role in loss of volatiles from these minerals as a control.

Meteorite Analysis

A goal of this work will be to compare this data with meteorite analysis. The low petrographic grade meteorites (table 4) will have small powdered samples (0.2 g) extracted by EDTA solution (Pasek and Lauretta 2005) and will be analyzed by ^{31}P NMR. If $\text{P}_2\text{O}_7^{4-}$ is present in the extracts and can be shown to be not due to Fe_3P corrosion (i.e., extracts lack phosphite), then the experiments above may show a route to forming this ion by aqueous alteration of phosphates and subsequent volatilization and heating to form diphosphate.

In doing so, this connects module 3 with general meteorite phosphorus chemistry. We can show that pyrophosphate is formed by aqueous chemistry, coupled to loss of volatiles, and as long as water activity remains low, pyrophosphate may persist within meteorite matrices. By demonstrating a route to pyrophosphate, and showing the presence of this anion in meteorites, we will be able to connect fluid alteration on meteorite parent bodies to our experiments, and provide new constraints on the fate of aqueous alteration volatiles, including constraints on water activity, and solubility of phosphate.

1.6 Impact to the Field

The proposed work will investigate the cosmochemistry of phosphorus from the gas phase, to its primary condensates, to its stable oxidation products, and finally to its (potentially unstable) fluid alteration products. The connecting theme between these experiments is that phosphorus reactions are proposed to occur rapidly: its reaction with metal, its oxidation from phosphides to phosphates, and the loss of temporary phosphate minerals formed by fluid alteration. This is not necessarily true, as some reactions may be considerably slower (for instance, low temperature oxidation of phosphides). Each module also operates on a guiding hypothesis:

- 1) P is minimally volatile at low temperature in the early solar system. A majority of phosphorus would have been trapped in siderophile phases such as schreibersite, removing P by both phosphidation and subsequent migration via diffusion of P-bearing gases.
- 2) Phosphide minerals are not stable when chondritic meteorites equilibrate, instead these phosphides oxidize to form phosphates. We will attempt to establish the temperature and rate at which this equilibration happens for phosphorus.
- 3) Finally the aqueous alteration products of phosphate minerals are likely not present on meteorite parent bodies, and are likely not even stable over short timescales. The ultimate reaction products will be determined in this module, and, if possible, some of these phases (pyrophosphate) will be searched for in chondrites investigated in module 2.

This proposal is designed to be thorough, as it covers a large temperature range of P bearing solids (25-900°C). It covers a range of potential solids, and will attempt to determine the data

that may be key to understanding meteorite parent body processes, from condensation, to equilibration, to fluid alteration, to subsequent loss of volatiles.

1.7 Potential Areas of Uncertainty

Potential sources of error or uncertainty in this work include constraints on P gas chemistry. In Sasaki (1985), red phosphorus was boiled to provide reactive P gas. In this setup, we expect no PH_3 to be formed, as the carrier gas will be argon. Based on thermodynamic models of gas phase P chemistry, phosphine is never the major P gas at the temperatures being studied here (Figure 2). Additionally, if P volatilization ends up being problematic, or if it is difficult to maintain an adequate P partial pressure, we will modify the reaction setup to connect the tube with a chamber of liquid red P heated at constant temperature, which has vapor pressures that are well-known as a function of temperature (Melville and Gray 1936).

We do not have an accurate method of measuring oxygen fugacity in the heated experiments. To this end, we have chosen instead to surround our experimental samples with mineral redox buffers. Using these redox buffers we can help ensure that whatever oxygen gets in to the tube furnace, either from small leaks in the setup or trace O_2 in the argon don't impact the samples significantly. In our prior work (La Cruz *et al.* 2016), schreibersite was synthesized without issue and without oxidation, implying these oxidation sources are generally negligible. Our crucibles may be reactive towards some of these phosphate minerals, especially the ones composed of Al_2O_3 (forming AlPO_4). Our prior work did not show AlPO_4 formation (La Cruz *et al.* 2016), but we also have graphite and Pt crucibles available, and will purchase SiC crucibles.

1.8 Management Plan

All research proposed here will be directed by Matthew Pasek, who will also lead experimental design, analytical procedures, and modeling. He has extensive research experience in these areas. The metal phosphidation reaction kinetics will be set up and pursued by graduate student Lang as part of her dissertation project. Carolyn, a third year grad student, has worked thus far on the chemistry of awaruite (Ni_3Fe), and has used microprobe as an analytical tool. She will spend years 1 and 2 running and analyzing phosphidation and oxidation experiments. We anticipate both sets of experiments will take about one year to run, and can run simultaneously if we acquire a second tube furnace. These will form two chapters of her dissertation. Secondly, Chris Mehta will build models of phosphidation within the solar system (project 1), and will perform the aqueous chemistry experiments of project 3 (over 1 year of experimental time). Chris is a third year student, and has been working thus far on examining meteorite ablation models, so he has experience in modeling techniques. Results from this work will be presented at the GSA, ACS, and related workshops over the course of the project. Publications resulting from this project will be submitted to journals such as *Icarus*, *Geochimica et Cosmochimica Acta*, and *Meteoritics & Planetary Science*. Historically we have generated 4-8 publications over the course of each grant.

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3. Data Management Plan

1. Introduction

The research project described in this data management plan involves the production of data from experiments and models of how phosphorus reacts with metals and in aqueous solution.

2. Data Types and Storage

This types of data generated and/or used in this project include 1) microprobe images, maps, and individual data point measurements, 2) Raman spectra of individual points with photos of the accompanying points, 3) x-ray diffractograms of minerals formed in phosphidation experiments, and 4) NMR fid spectra of aqueous solutions. In addition laboratory data such as sample preparation and foil thickness will also be acquired. Prepared samples will include metal phosphides and solutions.

Most of this data is stored as tabulated .csv format or .txt format files. Such files are generally accessible to excel for opening, graphing, and manipulating. Data will be documented with the date of collection, and experimental details of the data, and the type of data collected (organized by module).

3. Data Organization, Documentation and Metadata

The plan for organizing, these data include storing all of the data on university servers (scholarcommons.usf.edu) and select, publication-prudent data on researchgate, where the data will ultimately be open access to interested researchers. In addition, supplemental data will be stored in association with published work. Data will be stored according to module, experiment number, and date acquired.

4. Data Access and Intellectual Property

The data have the following access and ownership concerns: data that become thesis-material for grad students Lang and Mehta will not be made available until after publication of their work. This is to allow these students the time to write and go through peer-review of their work.

We have historically produced a few patents from NASA-funded work (see CV), and will follow university guidelines for publication there (usually delaying publication until an appropriate provisional patent has been filed).

Data will be made accessible by the PI by posting to the open access site scholarcommons.usf.edu and researchgate.net. No personal data or high-security data will be stored or generated by this project.

5. Data Sharing and Reuse

The data will be released for sharing on the scholarcommons.usf.edu website, and on researchgate. Scholar Commons is globally accessible by anyone with access to the Internet. Generally, only members of the USF academic community may upload content. Likewise, Researchgate is accessible to anyone with access to the internet. However, Researchgate is more targeted as the immediate peers of our research group have access to our newsfeed and when new data is uploaded. Data will be shared with a required file that states acknowledgement should be given to NASA Emerging Worlds.

6. Data Preservation and Archiving

The data will be preserved and archived in the following ways: Scholar Commons uses a Berkeley Electronic Press (Bepress) platform that features a multi-tiered disaster recovery plan utilizing fail-over servers and regular on-site and off-site backups. They make copies of repository content available for institutional back-ups, and support LOCKSS, an OAIS-compliant preservation strategy that provides tools for libraries to back up each other's content.

Data will be archived permanently, as the files will consist primarily of txt files, csv files, and less than 100 1-5 MB tifs.

7. Roles and Responsibilities

Grad students Mehta and Lang will be in charge of uploading their data as it is generated, and PI Pasek will ensure data uploading is timely (every 3 months) and done systematically.

4. CV

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College of William and Mary
University of Arizona

Geology & Chemistry
Planetary Science

B.S. 2002
Ph.D. 2006

Ph.D. Advisor: Dante Lauretta

Appointments:

Associate Professor University of South Florida, 08/15-present

Assistant Professor, University of South Florida, 08/10-08/15

Visiting Assistant Professor, University of South Florida 01/09-05/10

NASA Astrobiology Institute Postdoctoral Fellow, University of Arizona, 1/07-12/08

Research Goals:

- 1) To understand the role of meteorites in the origin of life from the perspective phosphorus redox biogeochemistry
- 2) To constrain the aqueous redox geochemistry of phosphorus
- 3) To determine the effects of lightning on geologic samples
- 4) To detail chemical processes occurring in the solar system

10 Most Relevant Peer- Reviewed Publications (out of 34)

Burcar, B., Pasek, M.A., Gull, M., Cafferty, B.J., Velasco, F., Hud, N.V., and Menor-Salván, C. 2016. Darwin's warm little pond: a one-pot reaction for prebiotic phosphorylation and the mobilization of phosphate from minerals in a urea-based solvent. *Angewandte Chemie International Edition* **55**, 13249-13253

La Cruz, N.L., Qasim, D., Abbott-Lyon, H., Pirim, C., McKee, A.D., Orlando, T., Gull, M., Lindsay, D., and Pasek, M.A., 2016. The evolution of the surface of the mineral schreibersite in prebiotic chemistry. *Physical Chemistry Chemical Physics*, **18**, 20160-20167.

Gull, M., Mojica, M., Fernandez, F.M., Gaul, D., Orlando, T., Liotta, C., and Pasek, M.A., 2015, Nucleoside phosphorylation by the mineral schreibersite. *Scientific Reports* **5**, 17198.

Pasek, M.A., Herschy B., and Kee, T.P., 2015. Phosphorus: a case for mineral-organic reactions in prebiotic chemistry. *Origins of Life and Evolution of Biospheres* **45**, 207-218.

Pasek, M.A. 2015. Phosphorus as a Lunar volatile. *Icarus* **255**, 18-23.

Pirim, C., Pasek, M.A., Sokolov, D.A., Sidorov, A.N., Gann, R., and Orlando, T.M., 2014. Investigation of schreibersite and intrinsic oxidation products from Sikhote-Alin, Seymchan, and Odessa meteorites and Fe₃P and Fe₂NiP synthetic surrogates. *Geochimica et Cosmochimica Acta* **140**, 259-274.

Pasek, M.A., Harnmeijer, J., Buick, R., Maheen, G. and Atlas, Z., 2013, Evidence for reactive

phosphorus species in the early Archean ocean. *Proceedings of the National Academy of Science USA*, in press.

- Bryant, D.E., Greenfield, D., Walshaw, R.D., Johnson, B.R.G., Herschy, B., Smith, C., Pasek, M.A., Telford, R., Scowen, I., Munshi, T., Edwards, H.G.M., Cousins, C.R., Crawford, I., and Kee, T.P., 2013. Hydrothermal modification of Siphonite-Alin under low pH geothermal environments. A plausible prebiotic route to activated phosphorus on the early earth. *Geochimica et Cosmochimica Acta* **109**, 90-112.
- Pasek, M.A., Dworkin, J.P., and Lauretta, D.S., 2007, A radical pathway for organic phosphorylation during schreibersite corrosion with implications for the origin of life. *Geochimica et Cosmochimica Acta* **71**, 1721-1736.
- Pasek, M.A. and Lauretta, D.S., 2005, Aqueous corrosion of phosphide minerals from iron meteorites: a highly reactive source of prebiotic phosphorus on the surface of the early Earth. *Astrobiology* **5**, 515-535.

Patents

- Provisional Patent (December 2015). Recovery of atmospheric phosphine as a sustainable source of phosphorus.
- Provisional Patent (April 2012). Phosphorylation in deep eutectic solvents.

Awards and Scholarships

- | | |
|------------|--|
| 10/15 | Faculty Outstanding Research Achievement Award (USF) |
| 07/14 | Miller Fellow of the International Society for the Study of the Origin of Life |
| 01/14 | Elected Chair of GRC Origins of Life Conference (2018) |
| 10/07 | Sagan/Haskin NASA Fellow |
| 11/06 | NASA Astrobiology Postdoctoral Fellow |
| 7/06 | Gordon Origins of Life Conference Young Researcher Poster Award |
| 4/06 | Galileo Scholar at University of Arizona, Astrobiology |
| 9/05 | Received NASA Cosmochemistry travel grant for Meteoritical Society meeting |
| 4/05 | Galileo Scholar at University of Arizona, Theoretical Astrophysics Program |
| 12/04 | Research named one of the top 100 science stories of 2004, Discover Magazine |
| 9/04 | Recipient of NASA Graduate Student Research Proposal award |
| 6/04, 6/05 | Full tuition scholarship at University of Arizona |
| 4/04 | Galileo Scholar at University of Arizona, Department of Planetary Sciences |
| 5/02 | Highest Honors Thesis at College of William and Mary |
| 12/01 | Recipient of Gerry Johnson Phi Beta Kappa Award |
| 12/01 | Phi Beta Kappa at College of William and Mary |
| 8/98-5/02 | Dean's list at College of William and Mary |
| 8/98-5/02 | Dow Scholar at College of William and Mary |
| 8/98-5/02 | Monroe Scholar at College of William and Mary |

5. Summary of Work Effort

Name	Effort	Title	Year 1	Year 2	Year 3
M. A. Pasek	0.083	P. I.	8.3%	8.3%	8.3%
C. Mehta	1.00	Graduate Student	100 %	100%	100%
C. Lang	1.00	Graduate Student	100%	100%	100%

6. Current and Pending

Current

PI: Matthew Pasek

Title: *Schreibersite as the prebiotic phosphorus source*

Agency: NSF Center for Chemical Innovation, Center for Chemical Evolution

Purpose: Analyze prebiotic phosphorus reactions.

Training: Post-doc + Undergrad

Total Amount Funded: \$1,000,000

Support: 1 Summer month

Dates: 10/01/2015-09/30/2020

Pending

PI: Matthew Pasek

Title: *The Interplay of Nitrogen and Phosphorus Minerals in Planetary Habitability*

Agency: NASA Habitable Worlds

Purpose: Analyze nitrogen mineral chemistry.

Training: Grad (2)

Total Amount Requested: \$400,000

Support: 1 Summer month

Dates: 10/01/2017-09/30/2020

7. Budget and Budget Justification

Equipment:

Funding Request:	Year 1	Year 2	Year 3	Total
Costs per year:	\$7,000	\$0	\$0	\$7,000

Funds are requested in year 1 to purchase a tube furnace as capital equipment (estimated at \$7000). This will allow for the running of phosphidation and phosphide oxidation experiments simultaneously. This cost is based on the cost of purchasing the first tube furnace (in 2013) from Fisher Scientific. We will acquire a similar instrument also from Fisher to allow for comparability of data collected. This equipment will be used exclusively for the proposed research activities.

Direct Costs:

Funding Request:	Year 1	Year 2	Year 3	Total
Materials	\$3,000	\$1,000	\$1,000	\$5,000
Analyses	\$3,000	\$3,000	\$3,000	\$9,000
Publication Fees	\$1,500	\$3,000	\$1,500	\$6,000
Tuition	\$20,709	\$20,709	\$20,709	\$62,127
Costs per year:	\$28,209	\$27,709	\$26,209	\$82,127

Materials and Supplies:

During the first year of the proposal start-up expenses of \$3,000 for metal samples (Fe, Ni, and Campo foils ~\$400), SiC crucibles (~\$200), Argon gas (~\$400), metal oxides for buffers (\$300) and minerals (diopside, olivine, gypsum, \$300), Fe₃P (\$400), glassware (\$500), and D₂O (\$300), as well as thick section preparation materials (\$200). Replacement costs in years 2 & 3 are estimated at \$1000, and consists of glassware (\$300), D₂O (\$300), and gas replenishment (\$400).

Sampling Analyses

Costs per year are based on the following:

Microprobe \$3,000 per year (8 days @ \$375/day)

Total: \$3,000 per year

We have a long-term contract to use NMR with unlimited time at USF through our CCE grant. We also have access to Raman and XRD in the lab.

Publication Fees

Funding of \$1500/year is requested for years one and three for publication and open-access fees (estimated from the fees at *Scientific Reports*). Funding of \$3000 is requested in year 2 to cover instant online access for any publications appearing in the journals *PNAS*, *Nature Communications*, or *Scientific Advances*.

Tuition.

Tuition for students Lang and Mehta costs \$431 per credit hour with 24 credit hours required for a full-time student appointment.

Travel:

Funding Request:	Year 1	Year 2	Year 3	Total
Domestic	\$4,100	\$2,100	\$2,100	\$8,300
International		\$3,000	\$3,000	\$6,000
Costs per year:	\$4,100	\$5,100	\$5,100	\$14,300

Funds are requested for all three years of the proposal for the P.I. and one graduate student to travel to at least one scientific conference per year. The domestic trip cost is based on an average length of 5 days at a cost of \$2,050 (\$500 roundtrip airfare, and per diem of \$250/day for hotels, ground transportation and meals, and \$300 for conference registration). In year 1 these will be domestic trips. In years 2 & 3, these will include one international trip. An international trip is expected to cost \$3000 (\$1000 for airfare, and a per diem of \$300/day with a \$500 conference registration fee over 5 days).

8. Facilities and Equipment

7.1 USF Geology MS Facilities

The University of South Florida Geology department operates an open MS facility which is housed in the. MS instruments include:

1. Perkin Elmer Elan II DRC Quadrupole ICP-MS

More than 70 elements can be detected simultaneously at trace levels by inductively coupled plasma-mass spectrometry (ICP-MS). The Perkin Elmer Elan II DRC employs both standard and dynamic reaction cell (DRC) modes to analyze nearly all elements from Sc to U with high precision. DRC mode offers users the ability to analyze those elements with known mass interferences (e.g., As, Sb, Fe, etc.) with high precision to very low concentrations (< 1 ppb (ug/L)).

2. High Performance Liquid Chromatography (HPLC)

The elements As, Te, Bi, Pb, Sb and Se are routinely analyzed to levels as low as 1 -5 ppb (ug/L). Elements easily converted into hydrides (e.g., AsH₃) can be readily analyzed by Atomic Fluorescence Spectrometry (AFS). In addition to the determination of total concentrations we also provide speciation of arsenic (arsenite, arsenate, MMA and DMA) and of selenium (selenite and selenate). This is done via species separation in an ion exchange column prior. Detection limits are in the 1 ppb (µg/L) range.

Note that this equipment has been broken for one year. We have just hired Perkin Elmer to do the needed repairs.

3. High Temperature Equipment

A Thermo Scientific Lindberg blue M tube furnace is present in Pasek's laboratory. This equipment is capable of temperatures of 1100°C with the currently installed quartz tube. We can replace this tube with an alumina tube to achieve temperatures of 1200°C.

A Centrotech closed-atmosphere furnace is also available for use by Pasek's group. This furnace can reach temperatures of 1700°C.

4. USF Geochemistry Laboratories

The department of geology houses a sample preparation laboratory available for full use by the PI, which includes laboratory space, access to a fume hood, deionized water, and thermal equipment for these studies. The lab operates a state-of-the-art water analysis laboratory to prepare waters from around the world for analysis.

Water purification is achieved using a Barnstead NANOpure® Diamond Analytical combined reverse osmosis-deionization system. The lab is equipped with a variety of other equipment including hotplates, a recirculating water chiller, analytical balances, chemical fume

hoods, and a desiccator cabinet for storage of experimental samples.

5. USF NMR Facility

The University of South Florida operates an open NMR facility, which is housed in the Chemistry Department. NMR Instruments available:

1. Unity Inova 400 spectrometer. The Inova400 is a two-channel instrument with liquid and solid-state capabilities and a single axis gradient amplifier. It's primarily used for routine walk-ons 1D and 2D experiments and overnight acquisition. There are 3 probes associated with this instrument: 5 mm Quad ($^1\text{H}/^{19}\text{F}/^{13}\text{C}/^{31}\text{P}$)-Z, 5 mm ID Indirect Detection probe, and a 7 mm CPMAS Cross Polarization and Magic Angle Spinning probe for solids, Nano Probe for samples behaving in a semisolid semi-liquid state. The instrument is also equipped with a rotor synchronizer. A nine-sample carousel can be use for multi sample runs.

All instruments are available for "hands on" use after appropriate training is completed.

6. USF Raman and XRD Facility

The Pasek Lab has a $\mu\text{Sense-I/L}$ high performance EnWave Raman spectrometer. The Raman operates a 785 nm Laser and has a resolution of about 1 cm^{-1} . The Raman spectrometer is presently attached to a Leica microscope but can be readily detached for these experiments. Raman spectra are interpreted using the Crystal Sleuth freeware program.

The Pasek lab also has an Olympus benchtop XRD for analyzing samples with a $\text{Cu-}\alpha$ x-ray tube. We also have remote access to a Cobalt x-ray tube for other mineral ID.

7. USF Office

The PI is provided with a full-time Budget Analyst to aid in financial aspects of contract administration including budget preparation, proposal submission, monitoring and projecting expenses for existing grants and contracts. Administrative services are provided and include items such as document preparation/compilation, purchasing items as budgeted, faxing, filing, copying, and mailing of business correspondence as related to grant work. Additionally, the Department of Research is comprised of several full-time employees who oversee proposal submission, contract requirements, financial monitoring, purchasing polices, and account closeout.

8. FIU Microprobe Lab

The FIU microprobe lab features a JEOL 8900R Superprobe with 5-2 crystal WDS spectrometers, An EDS-UTW detector, Both PC and Mac remote operation, and capability of analyzing from Boron to Uranium. Several standards are available for metals and minerals, and the equipment is capable of high accuracy quantitative analysis, in addition to high accuracy analysis of light elements. The facility also has CL and SEI/BEI detector capabilities, and Remote access worldwide.

9. Budget Detail:

Budget Detail

	Year 1	Year 2	Year 3	TOTAL
D. Equipment	7,000	0	0	7,000
E. Travel				
1. Domestic	4,100	2,100	2,100	8,300
2. Foreign	0	3,000	3,000	6,000
G. Other Direct Costs				
1. Materials and Supplies	6,000	4,000	4,000	14,000
2. Publication Costs	1,500	3,000	1,500	6,000
3. Consultant Services	0	0	0	0
4. Computer Services	0	0	0	0
5. Subawards	0	0	0	0
6. Other		0	0	0
7. Non F&A Other	0	0	0	0
(tuition)	20,709	20,709	20,709	62,127
Total Costs minus salary + F&A	39,309	32,809	31,309	\$103,427

Total budget document.

Justification

Labor and Fringe Benefits:

Funding Request:	Year 1	Year 2	Year 3	Total
Costs per year:	\$62,020	\$63,758	\$65,549	\$191,327

Funds for all three years are requested for the P. I. at 8.3% FTE in the amounts of \$9,466 (based on a 9-month salary of \$85,206 for 1 summer month) and a cost of living increase of 3% in years two and three. The fringe benefit rate for the PI is 17.73%.

Funds are requested for all three years for two full time Ph. D. graduate students (Carolyn Lang and Chris Mehta) at 100% FTE based on an annual salary of \$23,333. The fringe benefit rate for graduate students is 0.3%. Health insurance for both students is \$1990 annually, each.

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ground transportation and meals, and \$300 for conference registration). In year 1 these will be domestic trips. In years 2 & 3, these will include one international trip. An international trip is expected to cost \$3000 (\$1000 for airfare, and a per diem of \$300/day with a \$500 conference registration fee over 5 days).

F & A Costs:

Funding Request:	Year 1	Year 2	Year 3	Total
Costs per year:	\$36,442	\$37,550	\$37,694	\$111,685

The F & A rate for each of the three years will be applied at 49.5% to the MTDC base, less the graduate student tuition remission and capital equipment.

Cognizant Agency:

DHHS,

Division of Cost Allocation,

330 Independence Avenue,

S.W., Washington.

Representative: Darryl Mayes, 301-492-4855.

Total Estimated Costs:

Funding Request:	Year 1	Year 2	Year 3	Total
Costs per year:	\$137,771	\$134,117	\$134,552	\$406,439