JSC Mars-1 Martian Soil Simulant: Melting Experiments and Electron Microprobe Studies

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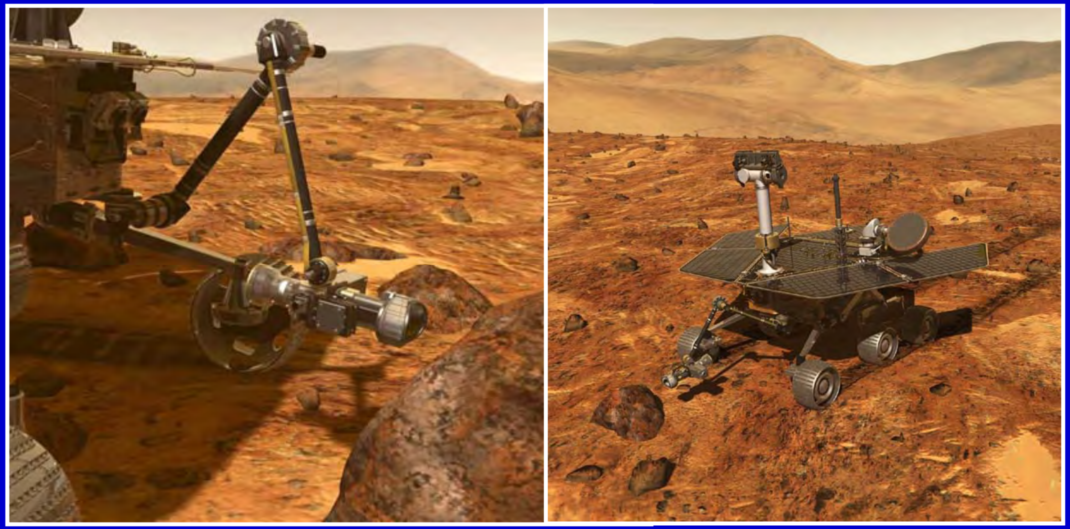
In Situ Resource Utilization

- Extraction of oxygen, metals from soil and rock
- Building materials from soil
- Radiation shielding
- Propellant for vehicle return / transportation, energy systems
- Materials fabrication and processing, rapid prototyping
- Repair, recycling

Mars Rock and Soil Chemistry / Geology

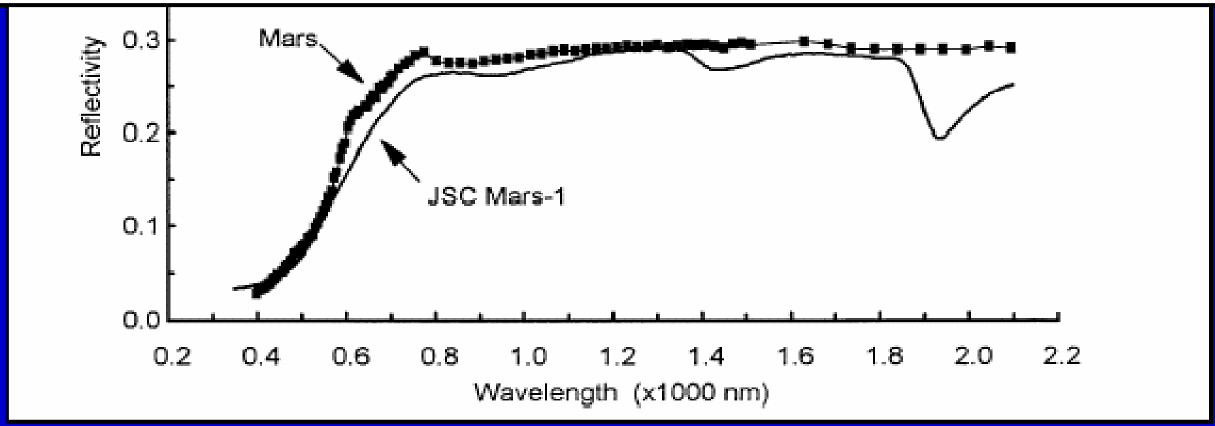


- Martian meteorites (28 found to date)
  SNC, ALH84001: peridotites, pyroxenites, basaltic rocks (ol, cpx, opx, plag)
- Viking 1 and Viking 2 landers (1976)
  XRFS, GCMS, NMS, Magnetic: soil chemistry, organics, magnetic minerals
- Mars Global Surveyor
  Global imaging calibrated using lander and rover data
- Pathfinder (1997), Spirit, Opportunity (Jan 2004)
  Panoramic Camera: High resolution imaging
  Thermal Emission Spectrometer: Mineral identification, test for H_2O, OH
  Mossbauer Spectrometer (Co^{57} source): Fe oxidation state
  APXS (Cm^{244}) Alpha Proton X-ray Spectrometer: Major element rock analysis
  Microscopic Imager: Fine scale imaging of grains

JSC Mars-1 Simulant

- "JSC Mars-1" is the < 1 mm size fraction of a palagonitic tephra of basaltic composition from Pu'u Nene cinder cone on the Island of Hawaii (Mauna Kea, ~ 1 m tephra layer beneath organic layer).
- Hawaii: Fresh tephra is altered to palagonite via dissolution, oxidation and addition of water. Passive enrichment, no transport.
  Removal of SiO_2, MgO, CaO, Na_2O, and K_2O
  Enrichment in TiO_2, Al_2O_3, Fe_2O_3, MnO, P_2O_5, and H_2O
- Mars-1 simulant used for terrestrial studies that aim to evaluate the suitability of Martian soil for materials processing.

Mars-1 has similar optical reflectance spectra to Martian surface (OH^- in Mars-1)



Mars-1 vs. Martian Soil

- Chemistry:
  Similar SiO_2, Fe_2O_3, and CaO.
  Mars-1: higher Al_2O_3, TiO_2, and H_2O
  Martian soil: higher MgO, SO_3, Cl
- Mineralogy:
  Mars-1: hawaiite glass, plagioclase, Ti-magnetite, olivine, Ca-pyroxene
  Martian soil: hematite, nanophase goethite, low-Ca pyroxene, high Ca-pyroxene and/or olivine, magnetic Fe-Ti spinel
  Mars-1 coarser fractions, Martian soil has < 100 μm component.
- Oxidation state of Fe:
  Mars-1: FeO 3.2, Fe_2O_3 11.8, $Fe^{3+}/Fe^{2+} \sim 3.2$
  Martian soil Fe^{3+}/Fe^{2+} 3 – 20, Fe_2O_3 21.2 (APXS oxygen budget)
  Martian rocks Fe^{3+}/Fe^{2+} 0.7 – 3
- Martian rocks modeled using meteorites. Soil-free rock calculated by deconvolving soil draped signal from Pathfinder APXS data.
- Mars: Andesitic rock (low MgO, SO_3) and global basaltic soil with high MgO, SO_3
- (Data in part from Morris et al., JGR 2000)

JSC Mars-1 Compared to Martian Soil / Rock

- Mars-1 Simulant
  XRF norm volatile free
  Fe_2O_3* 15.6
  Fe^{3+}/Fe^{2+} ~ 3.2
- Pathfinder Soil
  APXS A-2 Deploy
- Pathfinder SFR
  Soil-free rock
- Viking Lander 1
  XRF norm volatile free
  (Total 89%), avg 3, Fe_2O_3*
- Shergotty meteorite
  INAA
- Yellow: Mars-1 differs from Soil / SFR
- Blue: Soil differs from SFR

	Mars-1	Soil	SFR	VL-1	Sher
SiO_2	43.5	40.9	57.7 ± 1.5	48.4	51.36
TiO_2	3.8	0.7	0.5 ± 0.15	0.74	0.87
Al_2O_3	23.3	10.4	12.3 ± 0.7	8.2	7.06
Cr_2O_3		0.3			
Fe_2O_3	15.6	21.2		20.8	
FeO			14.2 ± 0.8		19.41
MnO	0.3	0.5			0.52
MgO	3.4	8.7	0.8 ± 0.8	6.7	9.28
CaO	6.2	6.1	6.7 ± 0.5	6.6	10
Na_2O	2.4	3.2	4.2 ± 0.6		1.29
K_2O	0.6	0.5	1.2 ± 0.08	< 0.17	0.16
P_2O_5	0.9	0.9	0.4 ± 0.2		0.8
SO_3		6.0	0.1 ± 0.04 S	7.4	0.13 S
Cl		0.7	0.4 ± 0.1	0.8	0.01
LOI	(22)				
Total	(100)	100.1	98.5	(100)	100.9

CIPW Normative Analysis

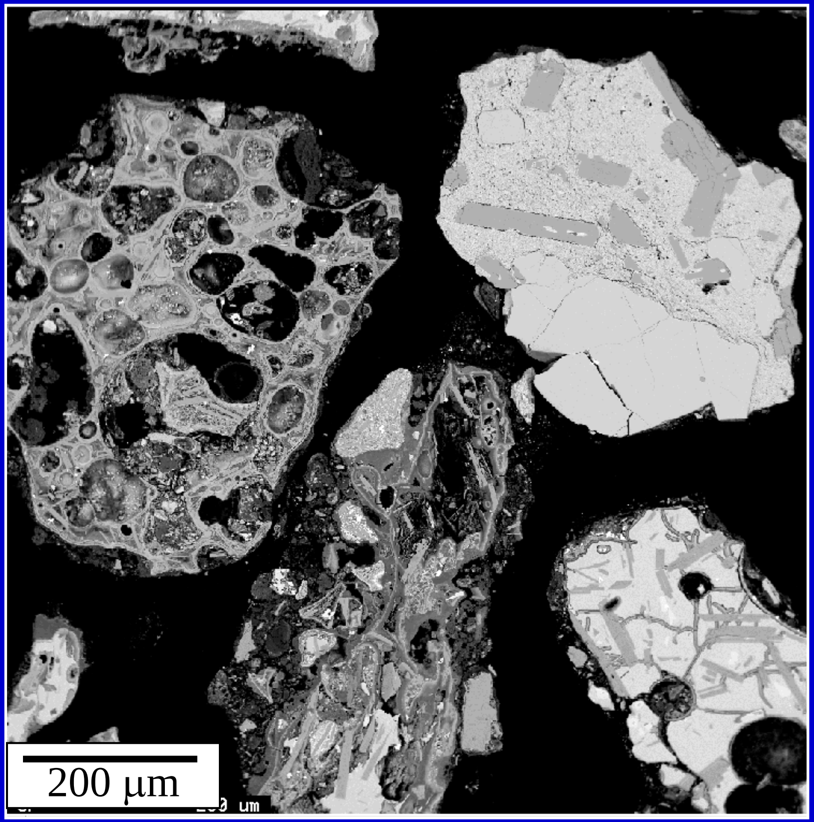
- Normative calculation allows mineral equivalent comparison for different geological environments
- Mars-1 Simulant
- Pathfinder Soil APXS A-2 Deploy
- Pathfinder SFR Soil-free rock
- Viking Lander 1
- Shergotty meteorite INAA

	Mars-1	Soil	SFR	VL-1	Sher
Quartz	2.4		8.8	12.2	1.6
Corundum	9.7	1.0			
Orthoclase	3.6	3.1	7.2	1.1	0.9
Albite	20.6		32.3		9.9
Anorthite	25.3	25.6	13.2	24.4	13.4
Halite		1.2			0.02
Thenardite		6.2			0.23
Diopside			15.6	10.3	25.7
Hypersthene	28.9	58.1	20.1	50.4	44.6
Olivine		0.6			
Magnetite	0.07	0.07	0.07	0.05	0.08
Chromite		0.46			0.20
Ilmenite	7.3	1.4	0.96	1.6	1.6
Apatite	2.1	2.2	0.94		1.8
Mg / Mg + Fe	0.36	0.45	0.09	0.40	0.47

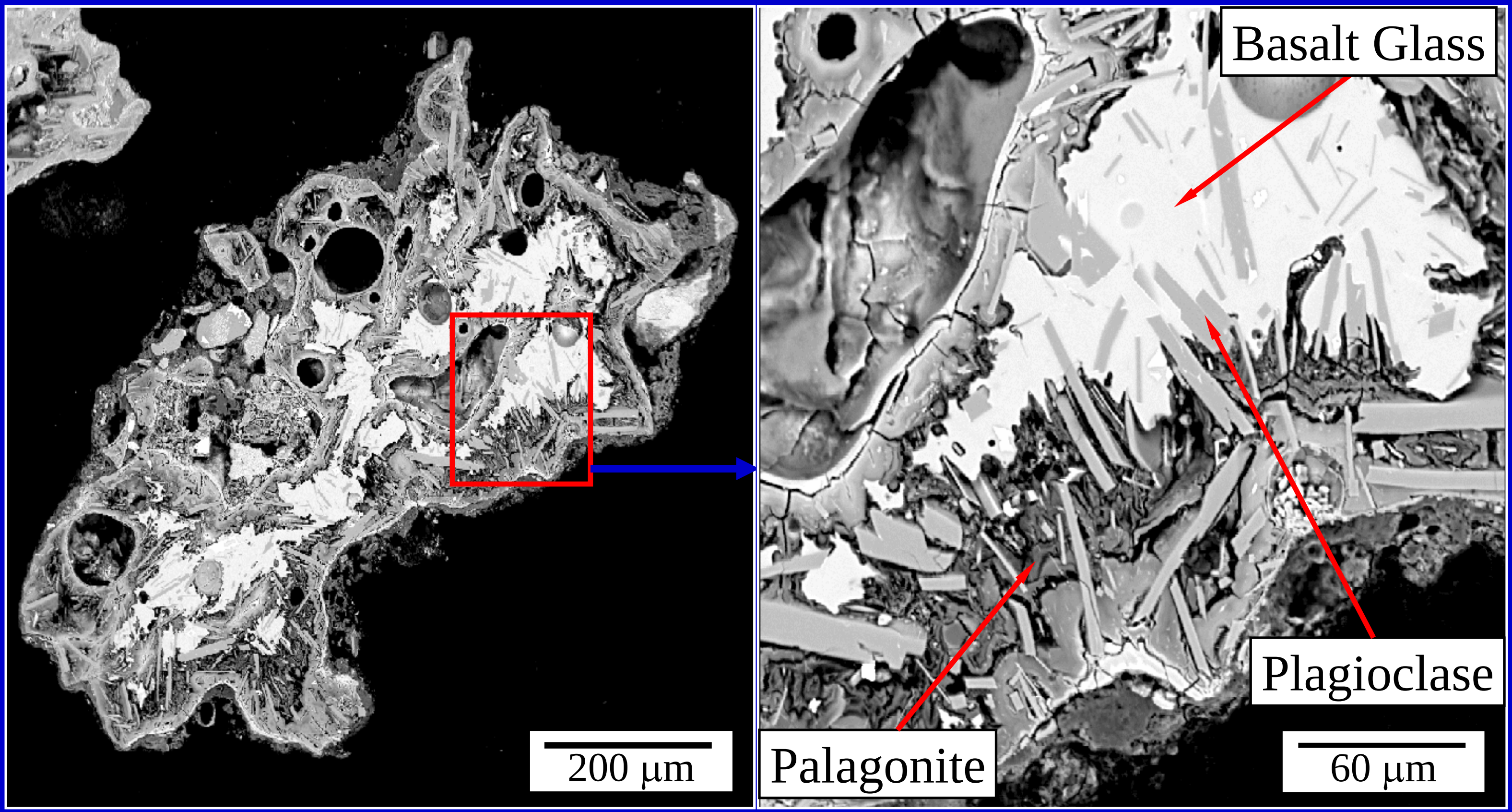
Quartz SiO_2 Corundum Al_2O_3
Orthoclase $KAlSi_3O_8$ Albite $NaAlSi_3O_8$ Anorthite $CaAl_2Si_2O_8$ Halite NaCl Thenardite Na_2SO_4
Diopside $Ca(Mg,Fe)Si_2O_6$ Hypersthene $(Mg,Fe)SiO_3$ Olivine $(Mg,Fe)_2SiO_4$ Magnetite Fe_3O_4
Chromite $FeCr_2O_4$ Ilmenite $FeTiO_3$ Apatite $Ca_5(PO_4)_3(Cl)$

JSC Mars-1 Mineralogy

- Coarse fraction ~ 0.5 mm
- Lithic and glassy fragments present
- Relatively fresh rock fragments
- Chemically weathered grains, typically porous
  Glass → Palagonite
- Mineralogy
  Glass, plagioclase, augite, olivine, Ti-magnetite, palagonite



JSC-1 Typical Grain



- Rock fragment with glass, plagioclase, augite, Ti-magnetite, palagonite alteration.

Fe Reduction Experiments

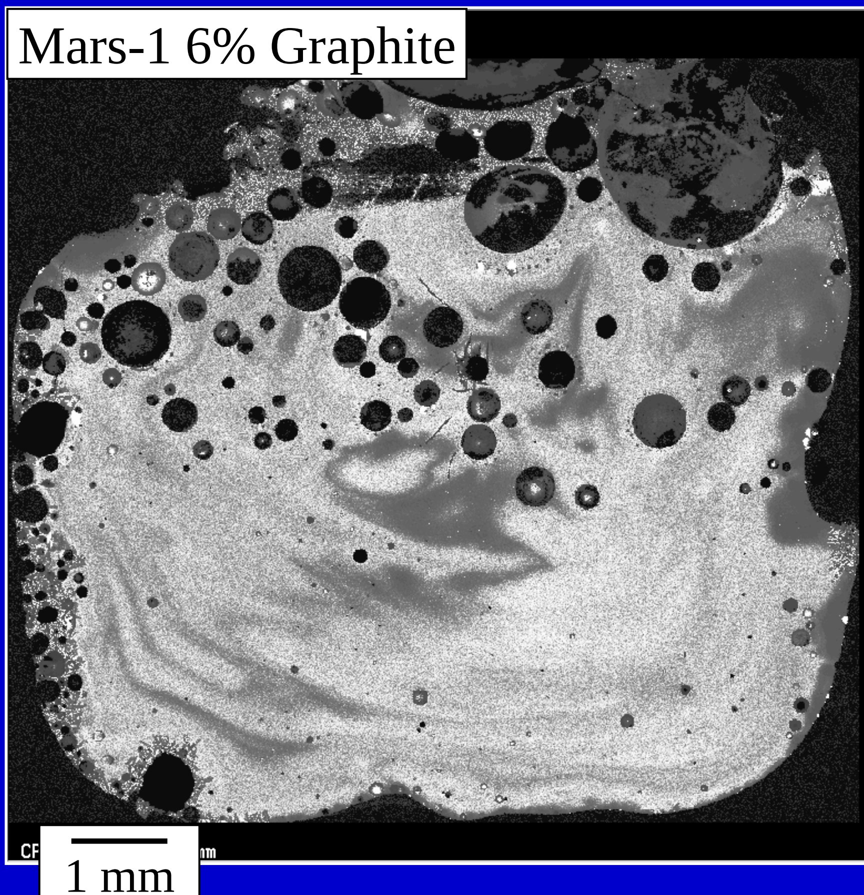
- Carbothermal reduction of Fe in 2.4 GHz conventional microwave oven.
  Graphite excellent susceptor due to resistive heating by microwaves.
  Magnetite Fe_3O_4 better microwave susceptor than hematite Fe_2O_3.
  $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$
  $Fe_3O_4 + CO \rightarrow 3FeO + CO_2$
  $FeO + CO \rightarrow Fe + CO_2$

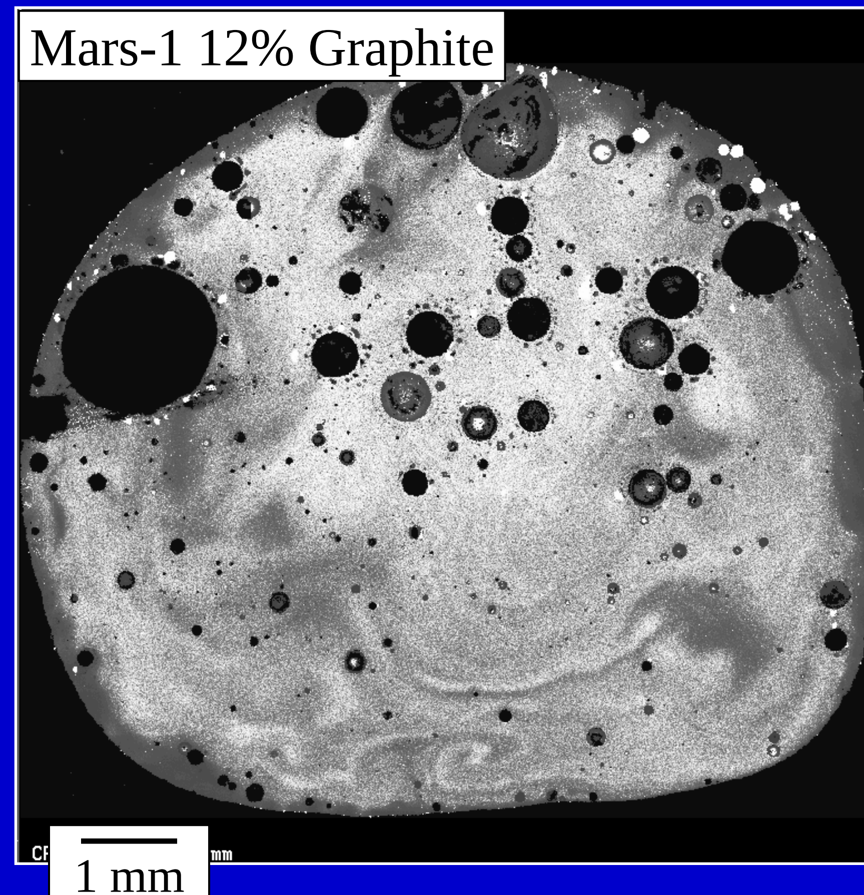
- 1 g quantity of unsieved Mars-1 with 6, 8, 10, and 12 % graphite added by weight, placed in Al_2O_3 crucibles.
  6% sample: magnetic soil fraction used (300-500 Gauss)
  12% sample: non-magnetic soil fraction used
- Microwave run times of 8 minutes:
  0 ~ 2 minutes: Vigorous ejection of material
  2 ~ 5 minutes: Melting complete
  5 ~ 8 minutes: T decrease due to loss of carbon?

Microwave Melting of Mars-1

- Video of Mars-1 microwave melting experiment.
  10% graphite, Al_2O_3 crucible
- Left: 0:15 – 0:25 sec ET
  Ejection of material – devolatilization of Mars-1 ~ 20% LOI
- Right: 1:15 – 1:55 sec ET
  Incadescence, melting, sparking, CO / CO_2 gas burnoff

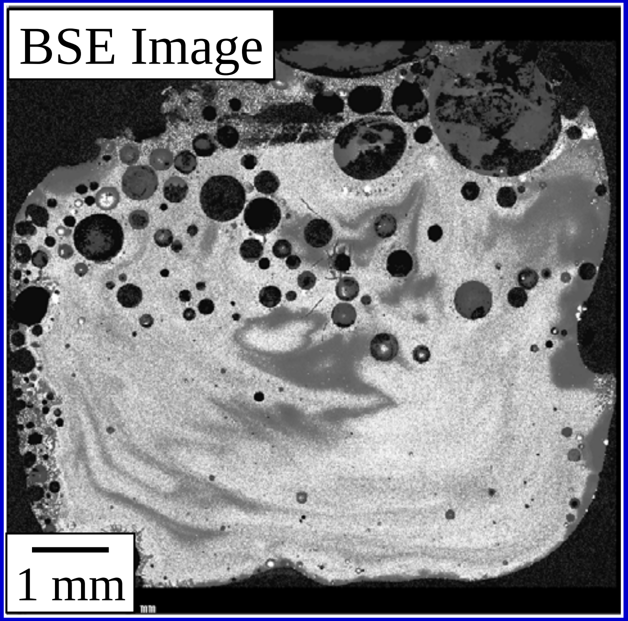
Mars-1 Microwave Processed Samples
6% magnetic – 12% non-magnetic

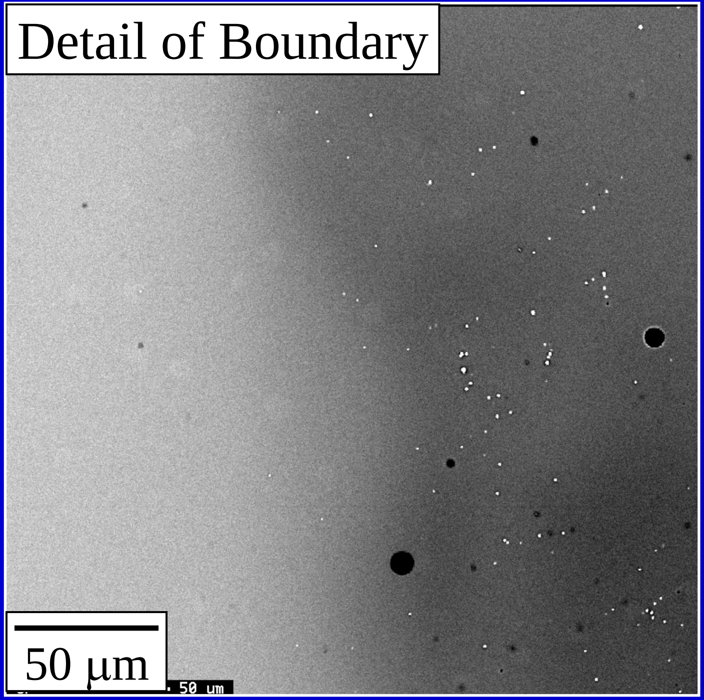




Backscattered-electron stage maps

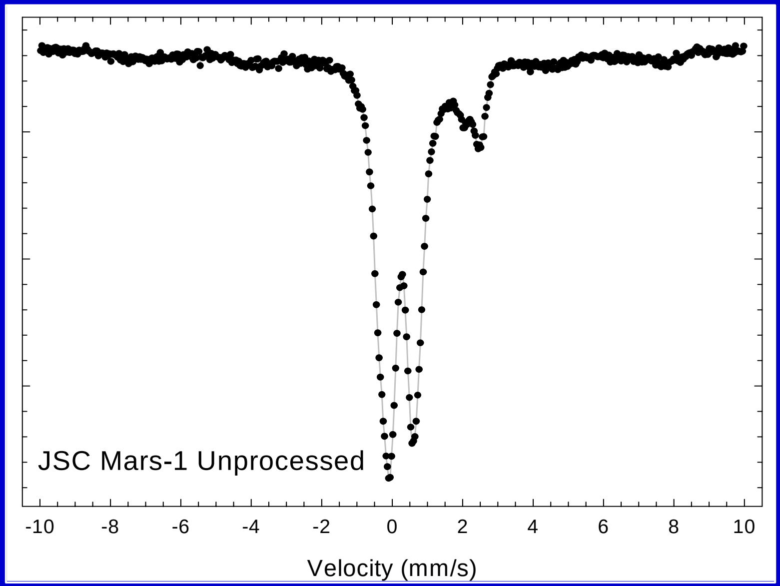
Fe Grain Detail

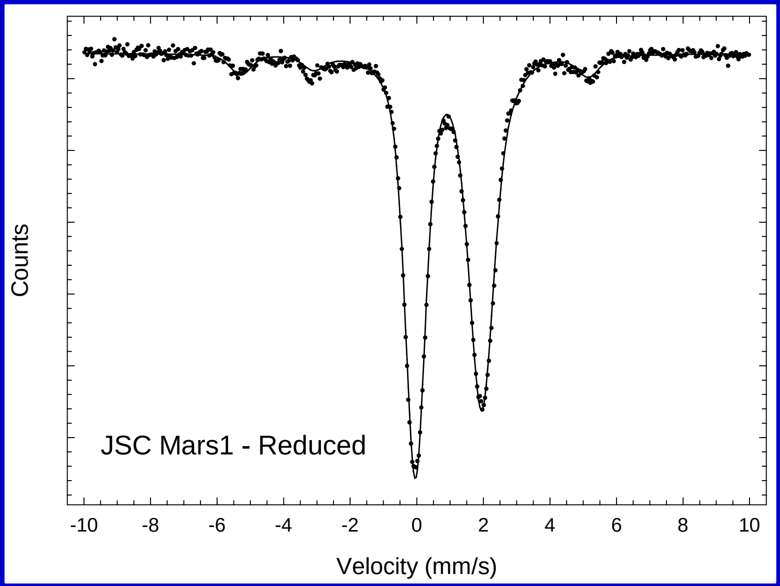




- Fe grains form by unmixing of silicate melt in liquid immiscibility reaction.
- Bright BSE region unreacted, dark BSE region contains Fe grains.
- Fe grains observed adjacent to olivine grains with Fe melt enrichment.

Mars-1 Mössbauer spectra

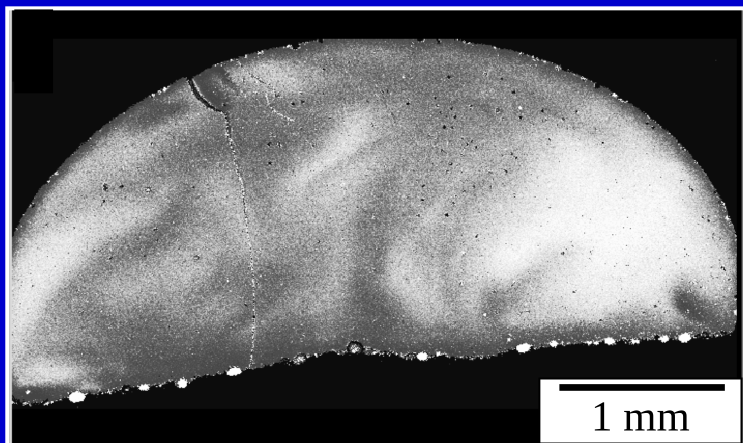


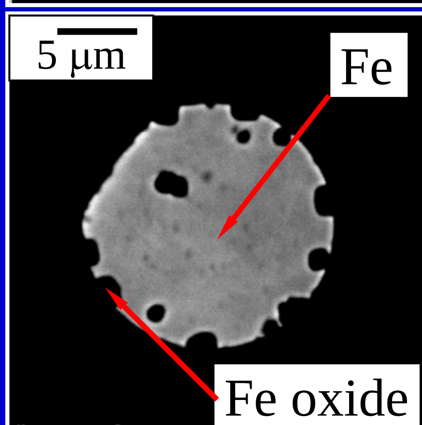


- Preliminary Mössbauer analysis of unprocessed and processed Mars-1
- Elimination of Fe^{3+} , conversion to Fe^{2+} and Fe^{0}
- Proportions indicated 9% α-Fe, 91% ferrous glass, peak fitting of profiles
- David Agresti, University of Alabama at Birmingham

Mars-1 Furnace Isothermal Melting Experiment

- BN crucible, 1-Atm furnace, Ar purge, no graphite, T 1250-1300 deg. C
- Internal Fe/Fe-oxide grains, gravitationally settled 2 and 4-phase Fe-Si-P grains
- 2 phase grain is coexisting Fe-P solid & melt at ~1280 deg. C





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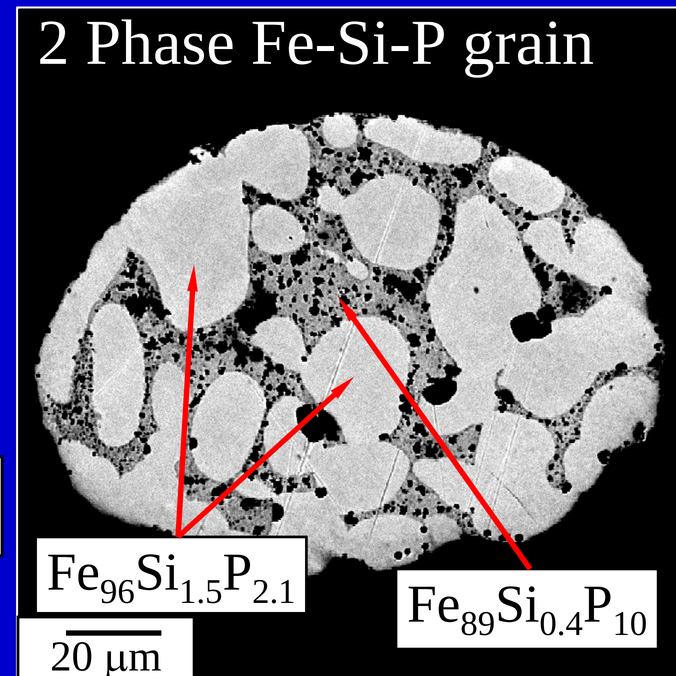
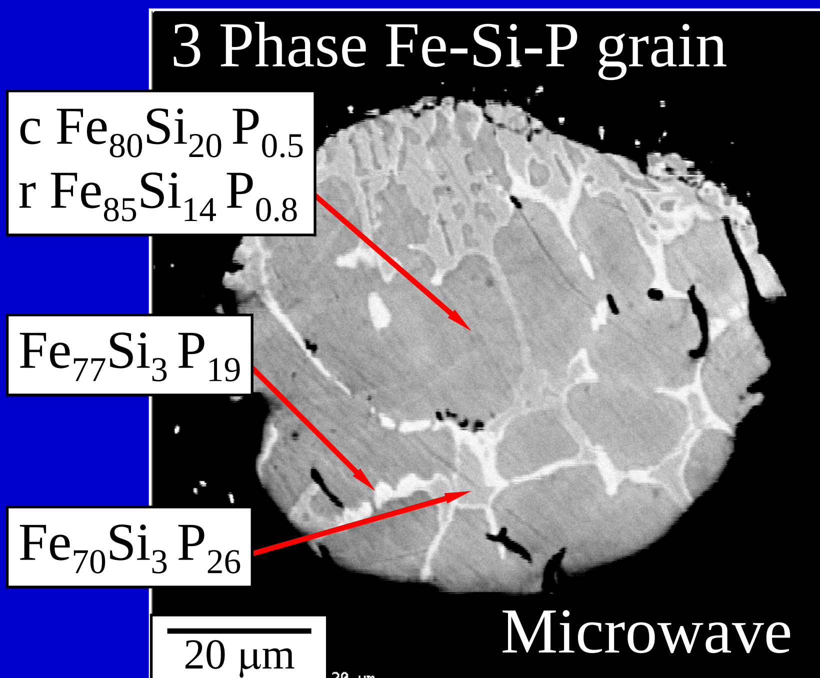
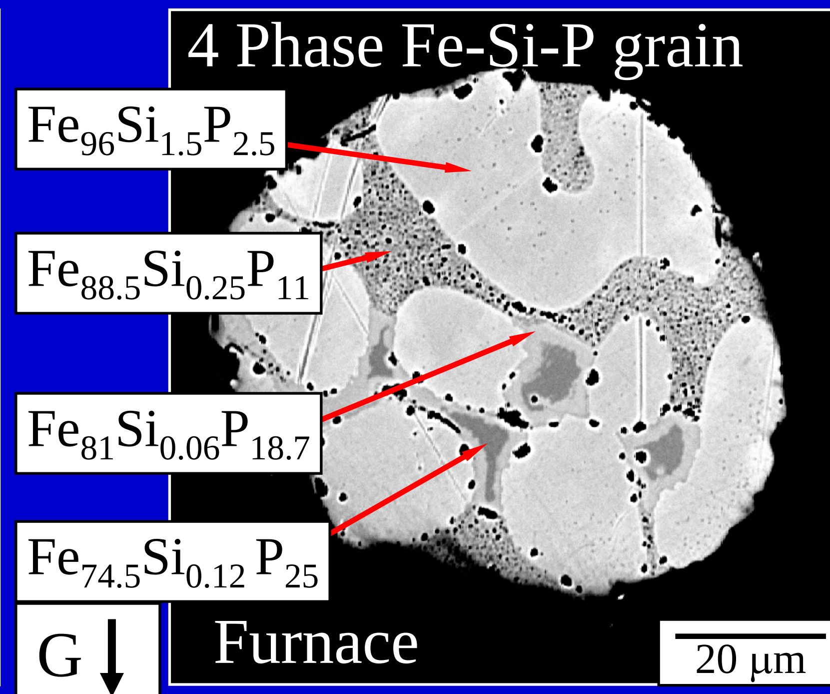


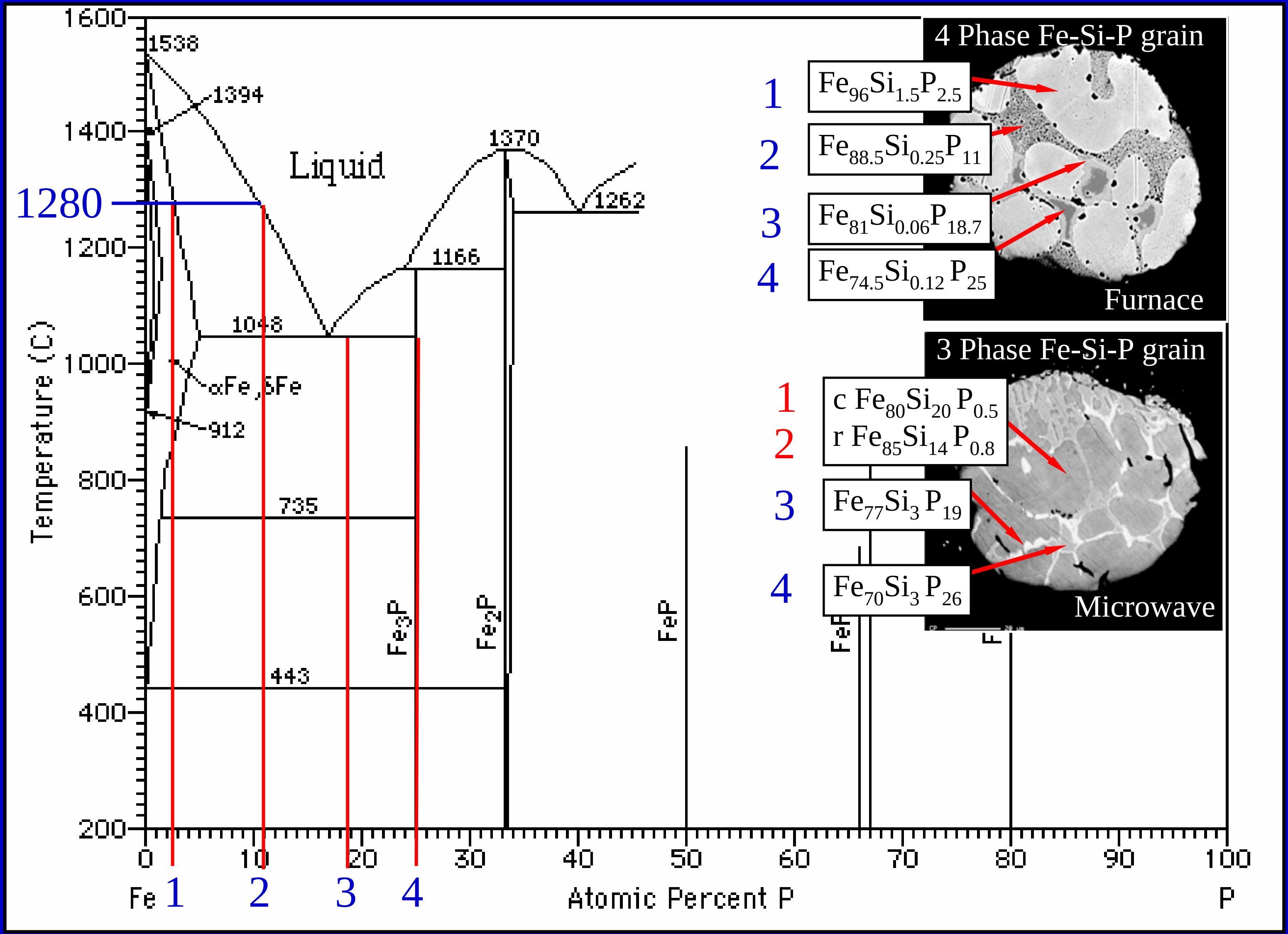
Mars-1 Fe-Si-P Grains: Microwave vs. Furnace

- Microwave:
  $Fe_{80}Si_{20}$ core composition: T ~ 1280 deg C
  Decreasing fO_2 causes Si/SiO_2 to decrease, result is Si-poor rim.
  Cooling, fractionation trend passes Fe-P eutectic ($Fe_{83}P_{17}$), final melt → Fe_3P.
- Furnace:
  Equilibrium at T ~ 1280 deg C: solid $Fe_{96}Si_{1.5}P_{2.5}$ -- melt $Fe_{88.5}Si_{0.25}P_{11}$.
  Quench, fractionation trend also passes Fe-P eutectic, final melt → Fe_3P.
- Trend of γFe → Fe_3P.
- Scavenging of P, Si, V, Cr from melt.

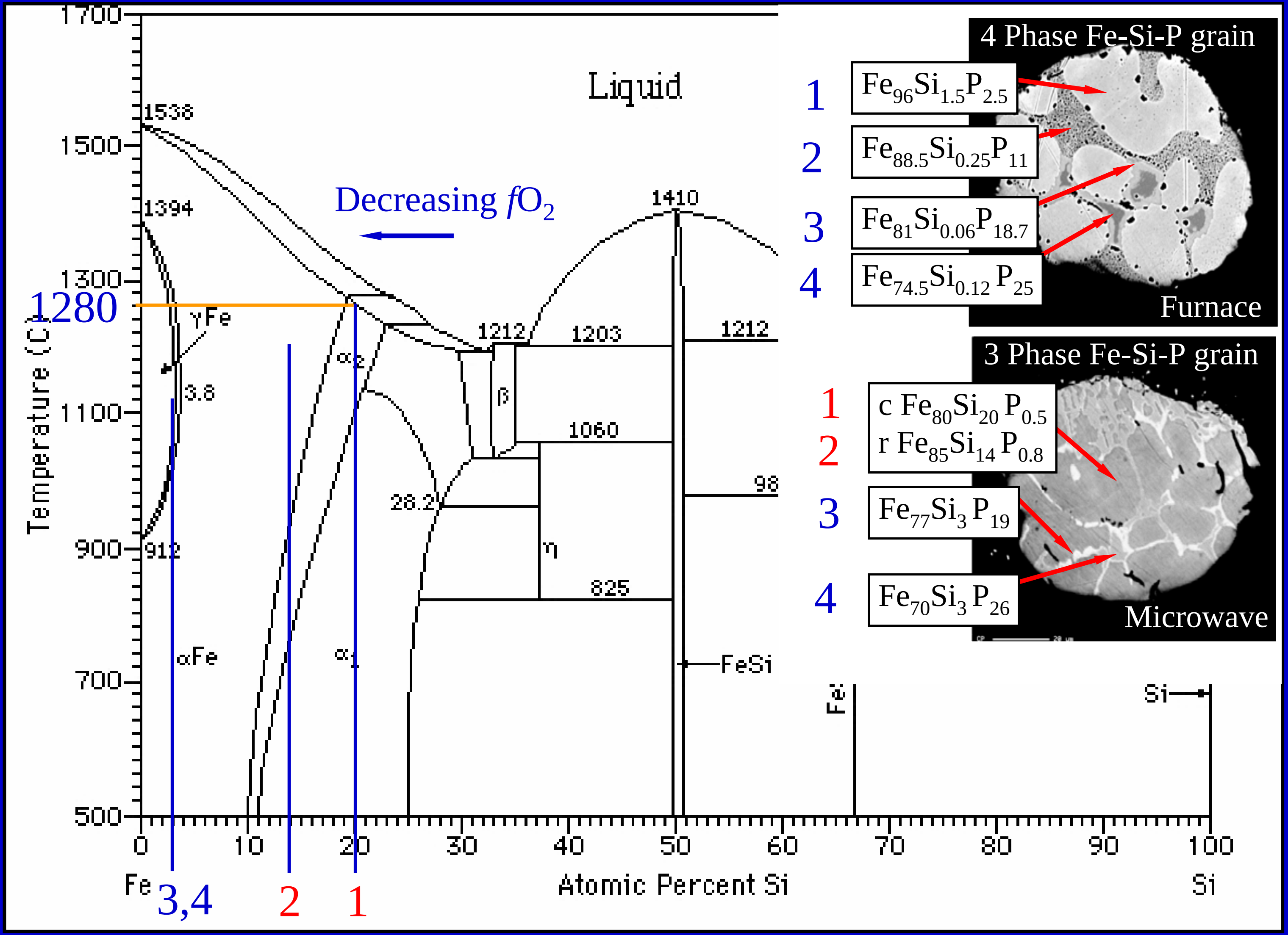




Fe-P Binary Phase Diagram

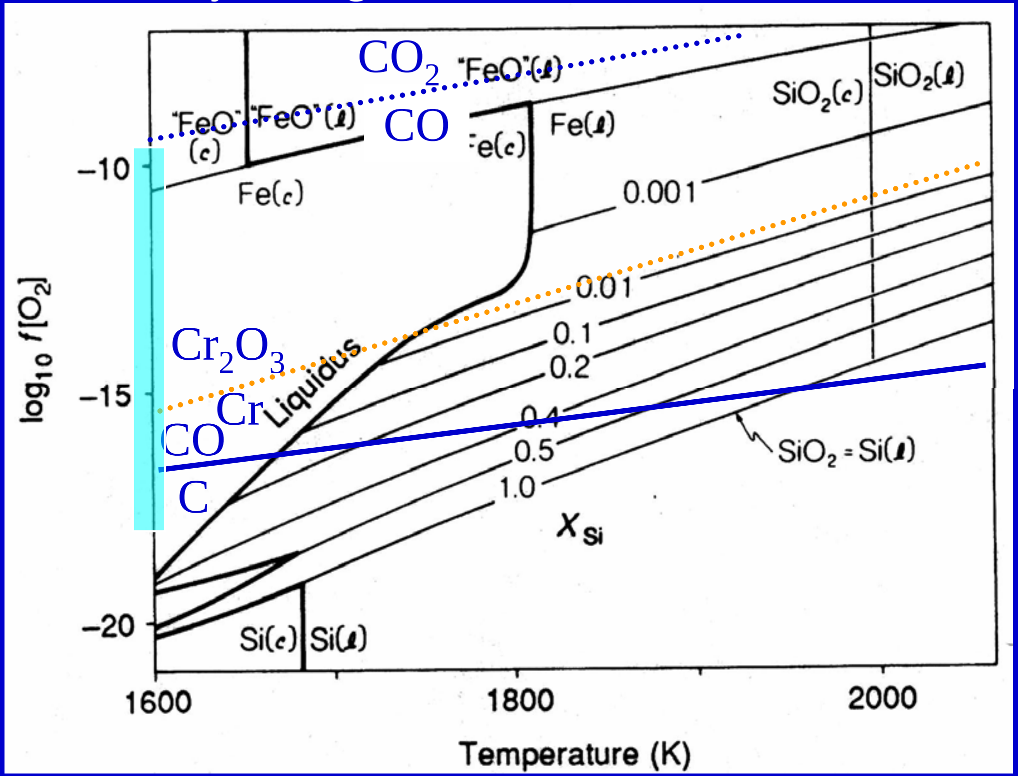


Fe-Si Binary Phase Diagram

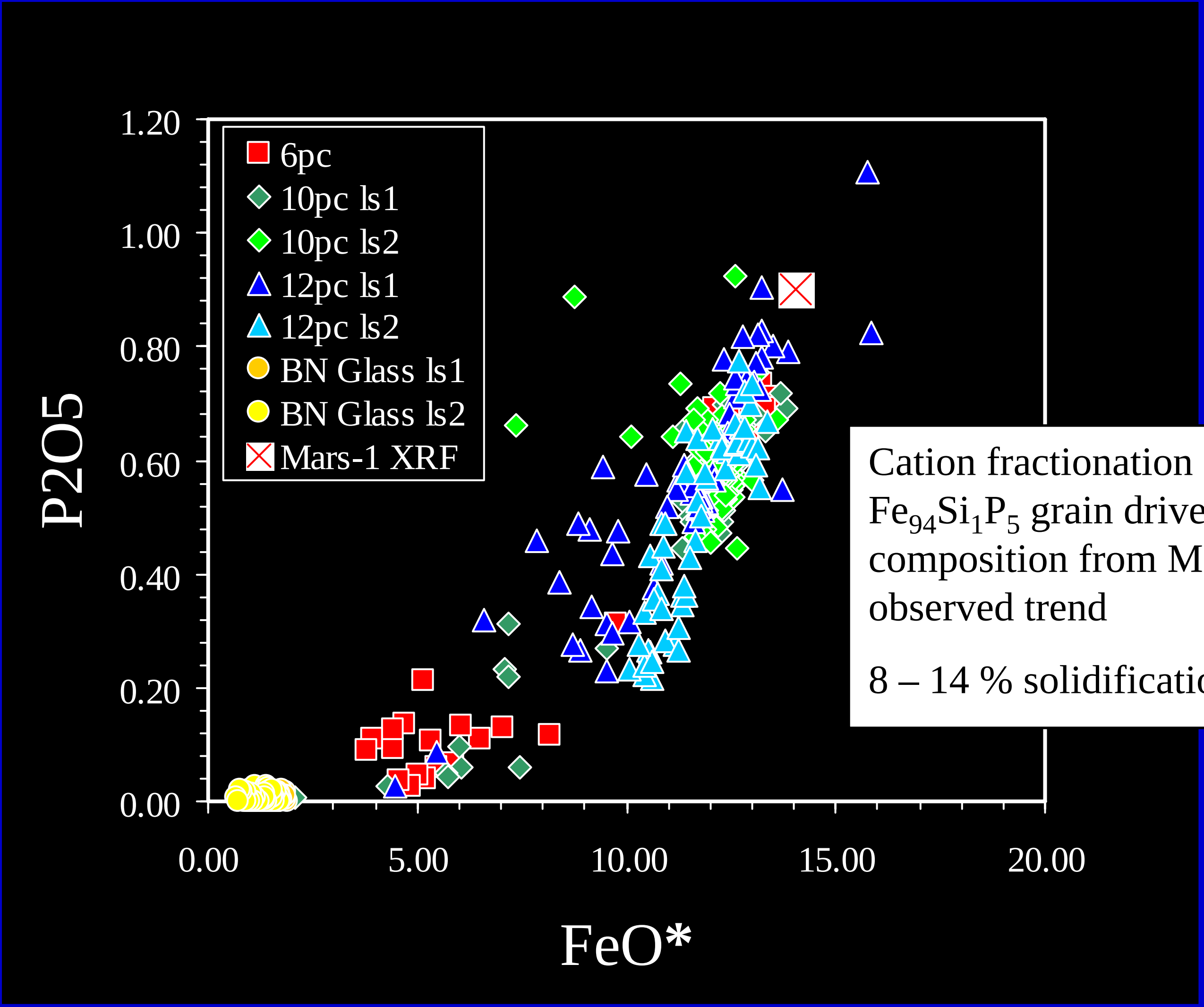


Fulgarites – Lightning Strike Glasses

- Fe/FeO grains: higher $fO_2 \sim 10^{-9}$ @ 1575 degrees K
- 2, 3 and 4-phase Fe-Si-P (Cr, Ti) grains: intermediate fO_2
- $Fe_{80}Si_{20}$ indicates $fO_2 \sim 10^{-17}$ @ 1575 degrees K, reaction with graphite?
- Decreasing fO_2 with time explains decrease in Si of Fe-Si-P grains as Si → SiO_2
- Graphite breakdown to CO limits extent of reduction, but better mixing with CO
- Indicated fO_2 range 10^{-9} to 10^{-17} @ 1575 degrees K
- Data from Essene study of Fulgarites



EPMA of Mars-1 Glasses



Cation fractionation of average $Fe_{94}Si_1P_5$ grain drives melt composition from Mars-1 bulk to observed trend

8 – 14 % solidification of FeSiP

CIPW Normative Analysis: Mars-1 vs. Processed Mars-1

- Least reacted differs from Mars-1
  Orange:
  Olivine → Quartz normative
  Olivine tholeiite → Quartz tholeiite
- Yellow: Decrease in normative:
  Corundum Al_2O_3
  Hypersthene $(Mg,Fe)SiO_3$
  Magnetite Fe_3O_4
  Apatite $Ca_5(PO_4)_3(Cl)$
- Blue: Increase in normative:
  Quartz SiO_2
  Orthoclase $KAlSi_3O_8$
  Albite $NaAlSi_3O_8$
  Anorthite $CaAl_2Si_2O_8$
  Ilmenite? $FeTiO_3$
  Mg/Mg+Fe

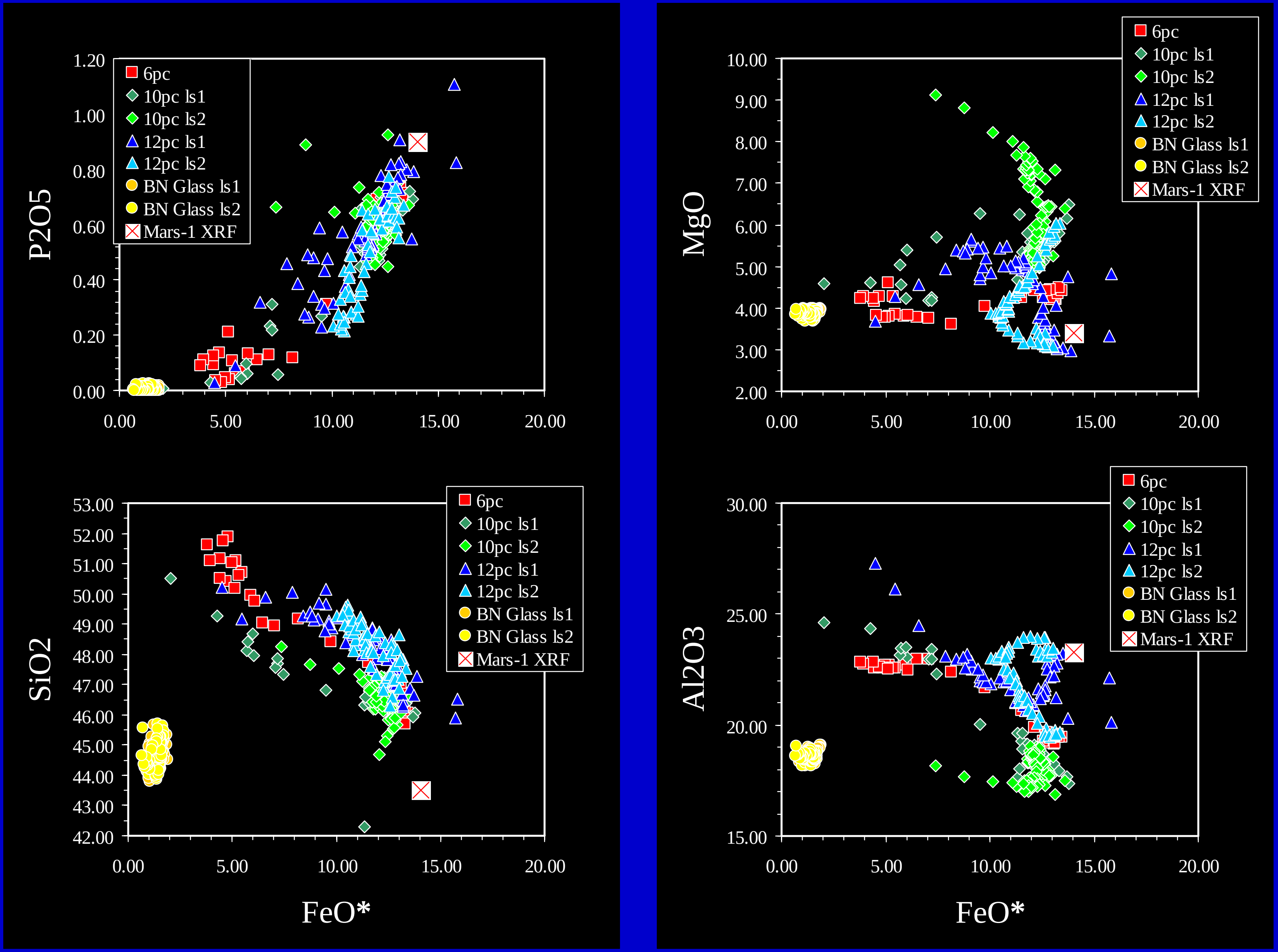
	Mars-1	6pc Bright	6pc Dark
Quartz	2.4		6.7
Corundum	9.7	3	4.5
Orthoclase	3.6	5.5	6.4
Albite	20.6	28	31
Anorthite	25.3	28	32
Diopside			
Hypersthene	28.9	18	12
Olivine		9	
Magnetite	0.07	0.05	0.01
Chromite		0.01	0.01
Ilmenite	7.3	6.5	7.6
Apatite	2.1	1.6	0.2
Mg / Mg+Fe	0.36	0.43	0.93

Conclusions

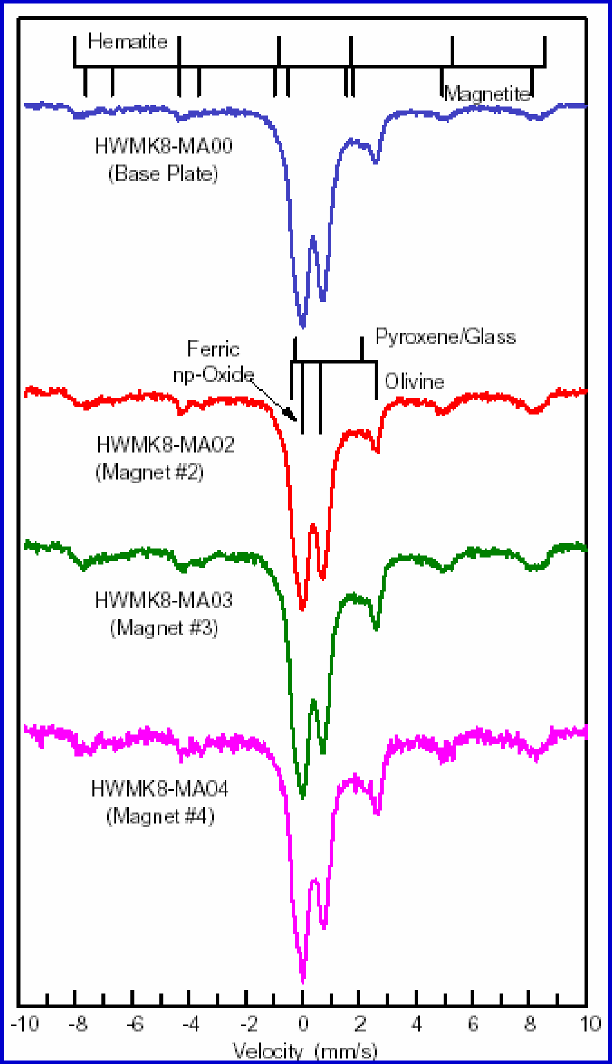
- Fe reduction experiments on JSC Mars-1 produced Fe, Fe-oxide, 2, 3, and 4-phase Fe-Si-P grains.
- 9 – 14 % yield estimates derived from EPMA and Mössbauer measurements.
- Microwave/graphite melting runs more reducing, but transient fO_2 compared to furnace experiments with Ar purge.
- Deduced conditions: T ~ 1280 deg C, fO_2 range 10^{-9} to 10^{-17}.
- Further work on miniaturized online reactor using microwave, laser, CO stream, soil agitation and active separation processing.
- Effect of compositional differences between Mars-1 and Martian soil (Al_2O_3, SO_3, etc) on materials processing needs to be evaluated.
- Application to study of fractionation from olivine tholeiite to quartz tholeiite: petrology, geochemistry.
- Simulation of fulgarites possible with higher T and lower fO_2.

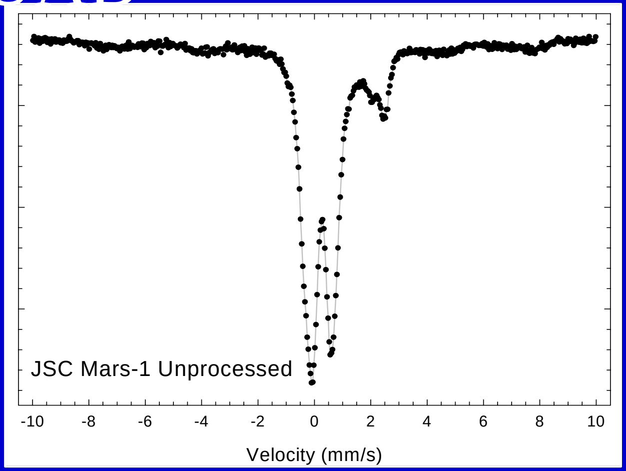
Additional Material

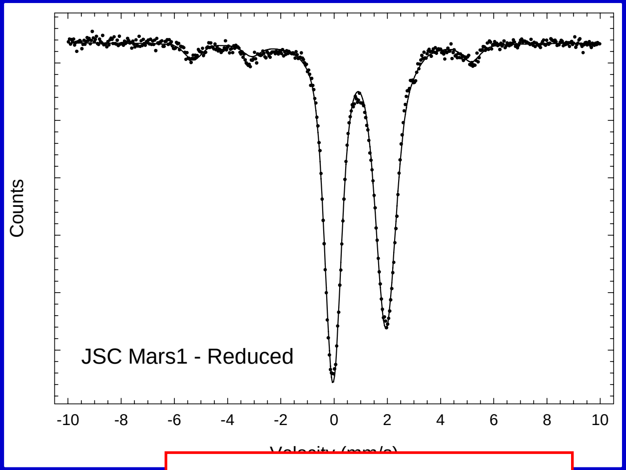
Mars-1 Variation Diagrams



Mössbauer spectra
David Agresti, UAB

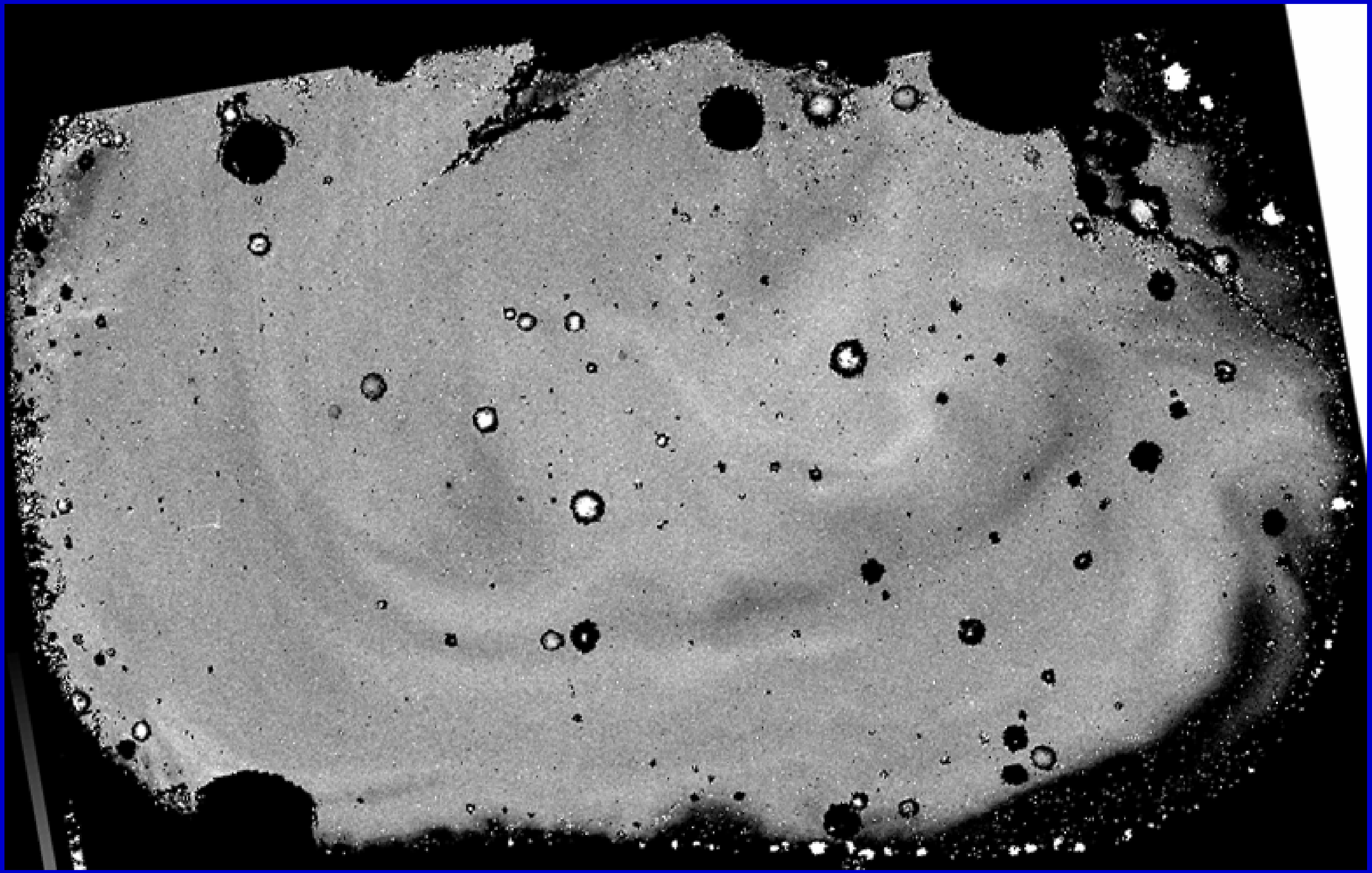




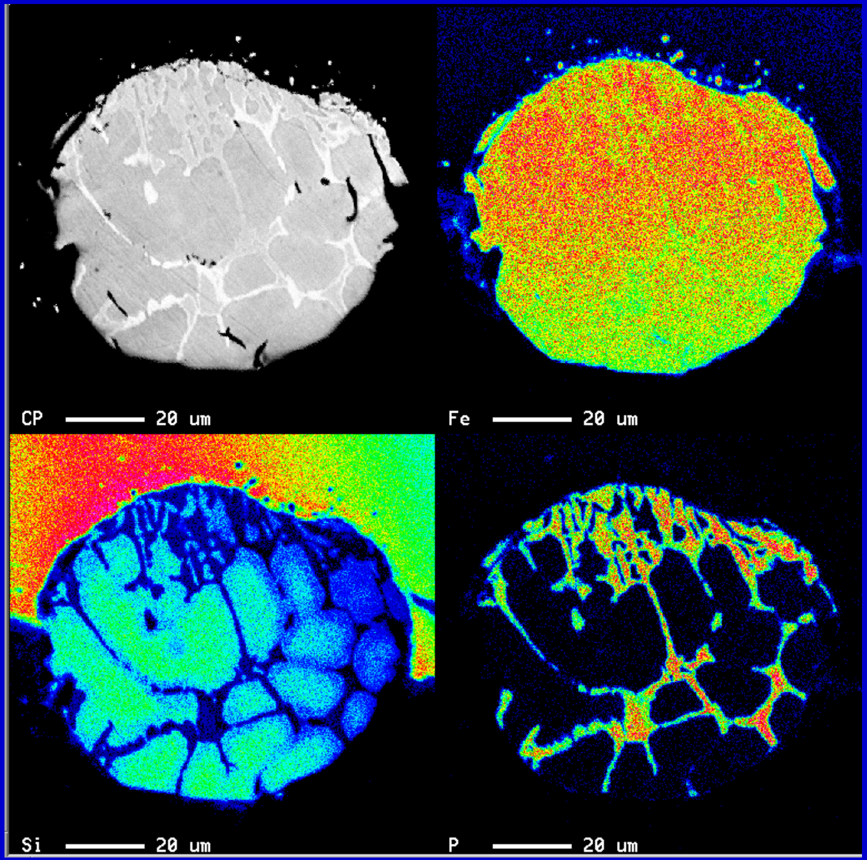


9% α-Fe
91% Ferrous Glass
Uncorrected

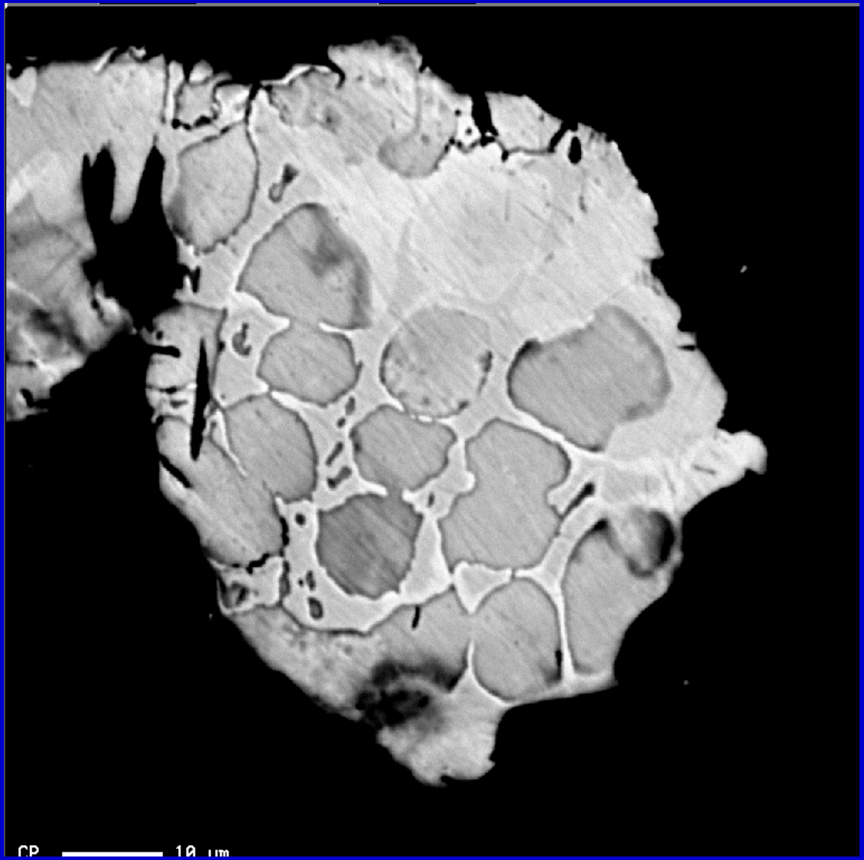
Mars-1 with 10% Graphite

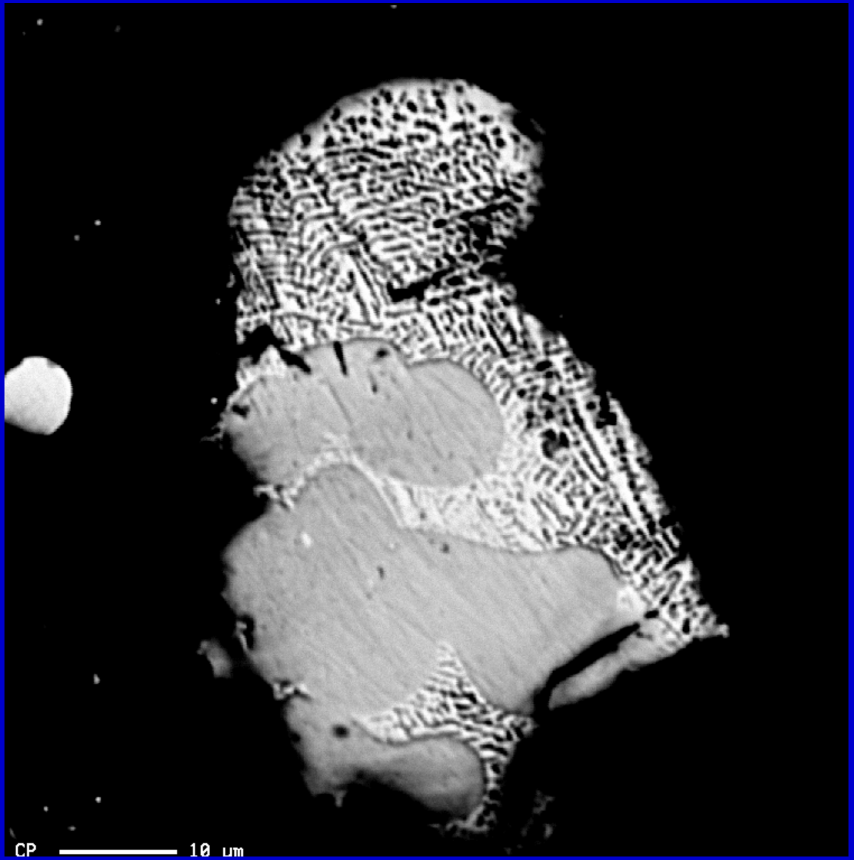


Mars-1 with 10% Graphite
Fe grains

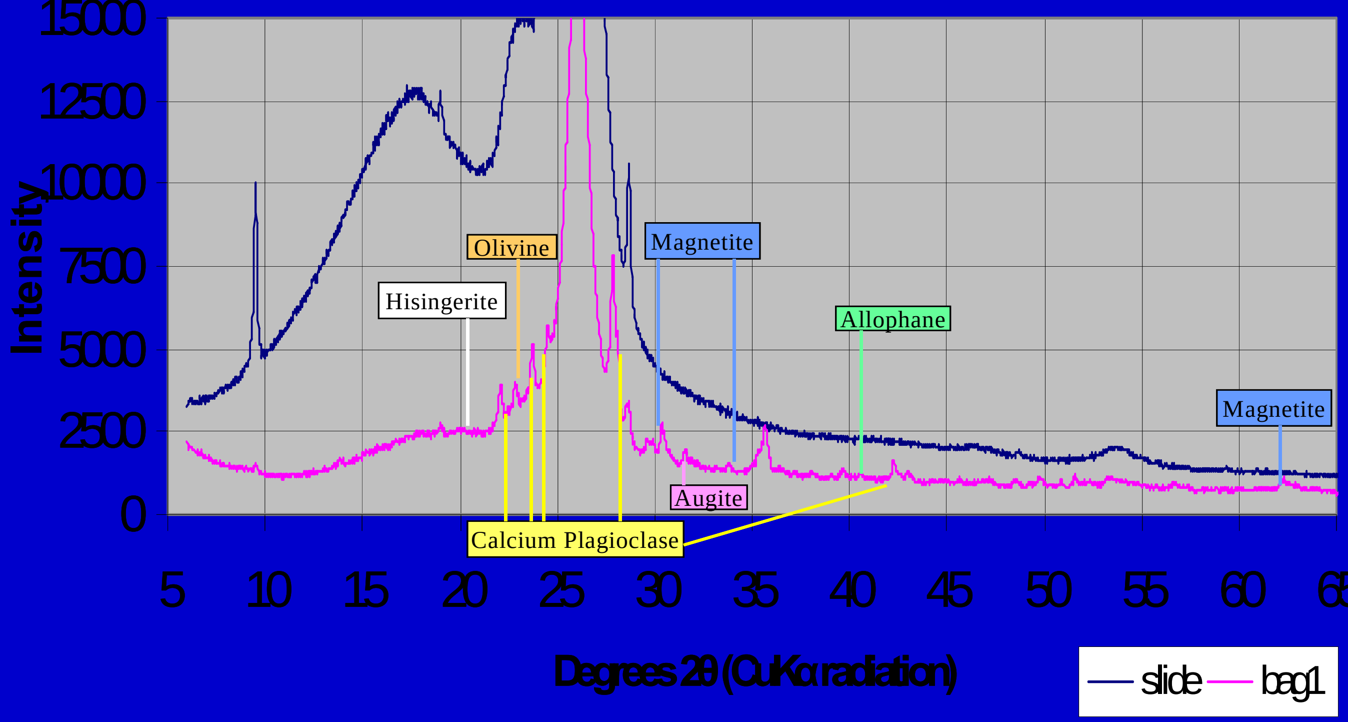


Mars-1 with 10% Graphite
Fe grains

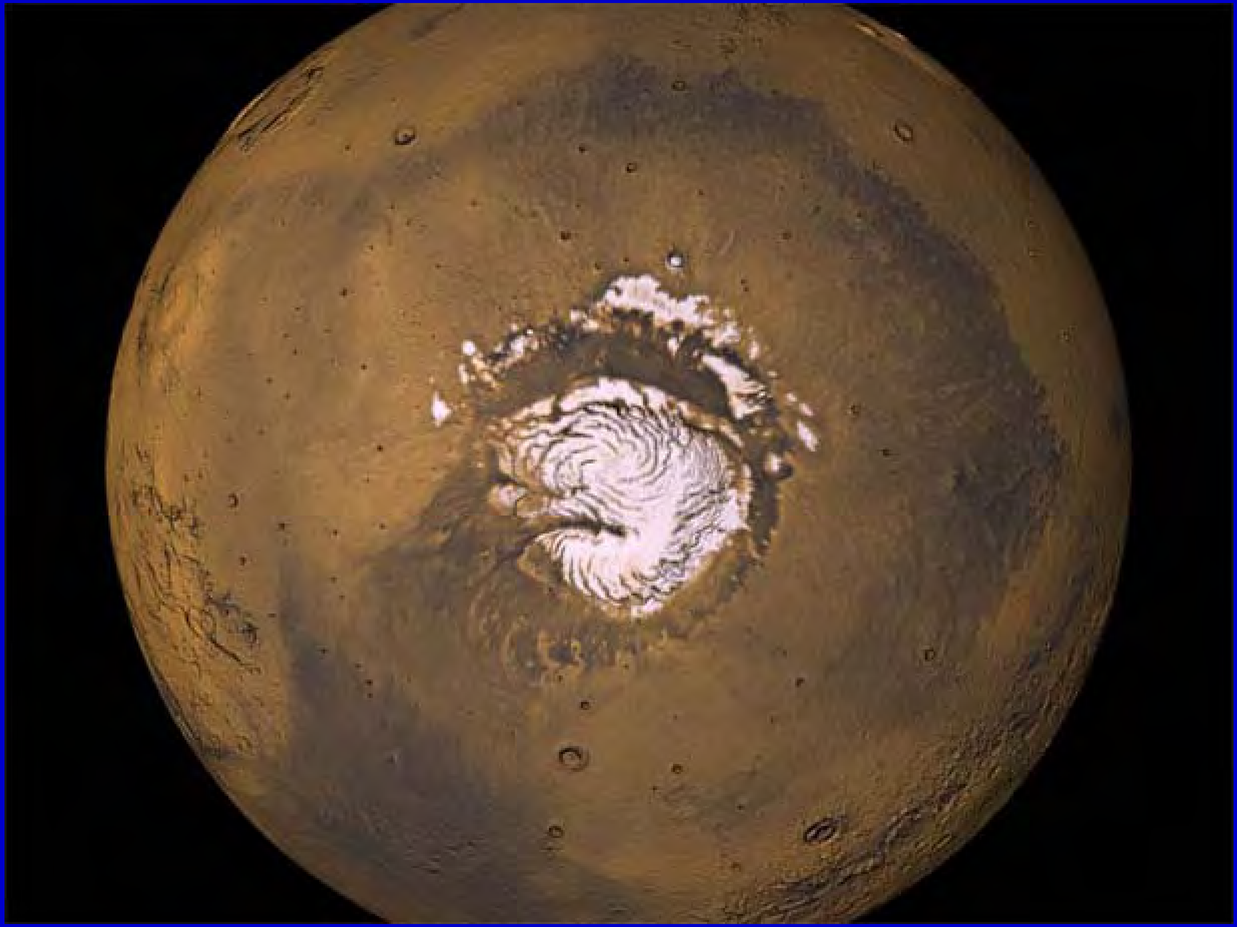




XRD Scans JSC-1



Mars Northern Polar Region



Water Ice Revealed as Dry Ice Dissapates