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Study of extraterrestrial materials aims to answer fundamental questions, for example:

- How did the Universe begin and what is its ultimate fate?
- How do planetary systems form and evolve?
- What processes take place in extreme environments?
- How is the evolution of life linked to planetary evolution and to cosmic phenomena?
- How might humans inhabit other worlds?

Origin of the Solar System

- Our Solar System formed from a vast rotating cloud of gas and dust.
- First the Sun formed at the center by gravitational accretion.
- Then dust condensation and accretion built up large bodies -the planets, asteroids, etc. orbiting the Sun.
- The solar nebula is believed to have been hot near the Sun, with the temperature decreasing with heliocentric distance.



Henize 1357 • Stingray Nebula
PRC98-15 • ST Scl OPO • April 2, 1998
M. Bobrowsky (Orbital Sciences Corp.) and NASA

HST • WFPC2

Probing the Solar Nebula with Extraterrestrial Materials

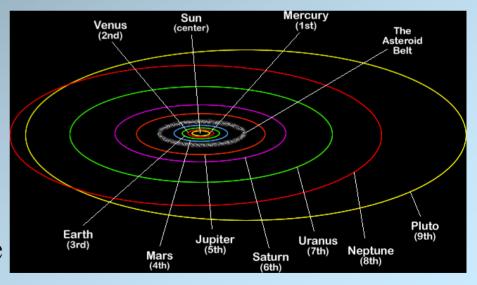
- Detailed examination of material that condensed at different heliocentric distances probes condensation conditions -- temperature, composition, oxygen fugacity, etc.
- Terrestrial samples are highly altered by geologic processing.
- Various collections provide samples from:

Moon (1 AU)

Mars (1.4 AU)

Asteroid Belt (2 to 4 AU).

• But only recently have we obtained samples from large heliocentric distances



Extraterrestrial Materials

Samples Discovered and Collected on Earth





Sample Return Space Missions

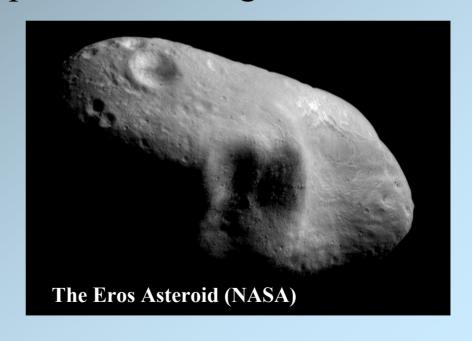
Samples Discovered and Collected on Earth

Meteorites

- Rocks from Asteroids, Moon, Mars, etc.
- Antarctica is a special place for finding meteorites

Stratospheric Particles

- Interplanetary Dust
- Asteroids
- Comets
- Interstellar Grains



Meteorite Categories and Percentage of Falls

Stony Chondrites (85.7%)

- Ordinary
- Carbonaceous
- Enstatite

Achondrites (7.1%)

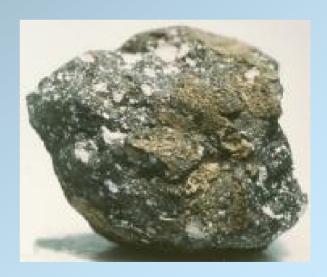
- HED group
- Martian
- Aubrites
- Ureilites
- Lunar

Stony irons (1.5%)
Pallasites

Irons (5.7%)

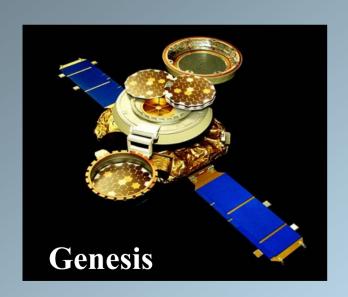
Mesosiderites

Lunar meteorite

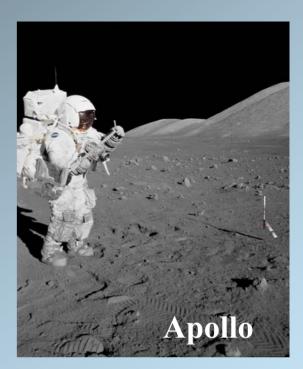


Sample Return Space Missions

- Apollo and Luna Programs (Moon)
- Genesis (Sun Solar Wind)
- Stardust (Comet Wild-2)







Extraterrestrial Materials — Total Masses Collected

- Meteorite Collections (asteroids): $> 10^7$ g (2 m)
- Apollo and Luna Missions (lunar): $\sim 10^5$ g (0.6 m)
- Genesis (solar wind): $\sim 10^{-3}$ g (1 mm)
- Stardust (comet): $\sim 10^{-6}$ g (100 microns)



Why Sample Return?

High-Quality Analyses

Spacecraft instruments and their measurements are severely limited by the weight requirements imposed on the missions.

Permanent Resource

NASA continues to receive requests for Lunar samples almost 4 decades after they were returned from the Moon.

New Analytical Techniques

Years after collection the samples can be analyzed by techniques not envisioned at the time of their collection.

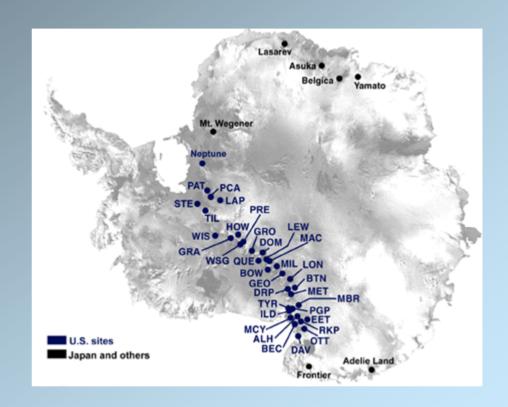


Some instruments are too heavy to launch into space ... cheaply.

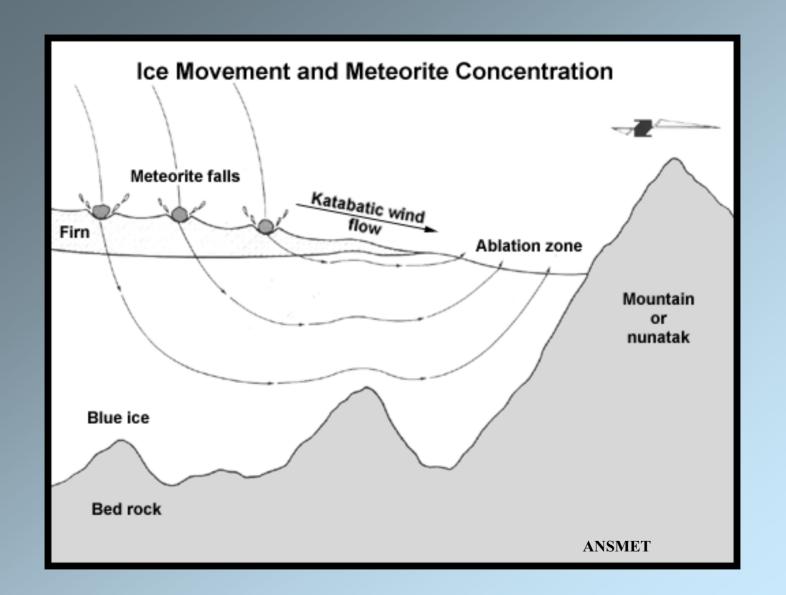
Harvesting Meteorites in Antarctica

Antarctica is a unique place to find meteorites:

- 1) The natural movement and sublimation of ice sheets concentrates meteorites in particular locations.
- 2) Meteorites are easy to identify; anything that's dark is likely to be a meteorite (fusion crust).



The U. S. Antarctic Search for Meteorites (ANSMET) program is a collaborative effort of the NSF, NASA, and the Smithsonian Institution.



Value of the Antarctic Meteorite Collection

- Large number of samples collected (>30,000)
- New types of meteorites and rare meteorites have been found including rocks from the Moon and Mars
- The larger collection of meteorites allows a better understanding of the abundance of meteorite types in the solar system.

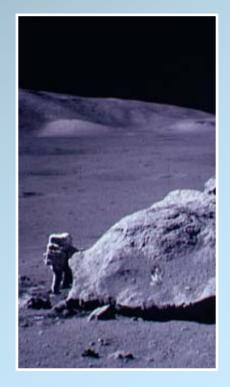


- The old terrestrial age of some meteorites (>100,000 years) allows a look back into time to see what the abundances were millions of years ago and to study the behavior of the Sun
- The cleanliness of the samples allows studies that previously were difficult or impossible with available samples.

Discoveries of the Apollo Program

- The Moon is an evolved body with internal zoning similar to that of Earth.
- The Moon is ancient and still preserves an early history (the first billion years) that must be common to all terrestrial planets.
- The youngest Moon rocks are virtually as old as the oldest Earth rocks.
- The Moon is lifeless; it contains no living organisms, fossils, or native organic compounds.
- All Moon rocks originated through high-temperature processes with little or no involvement with water.
- Early in its history, the Moon was melted to great depths to form a "magma ocean." The lunar highlands contain the remnants of early, low density rocks that floated to the surface of the magma ocean.
- The Moon and Earth are genetically related and formed from different proportions of a common reservoir of materials.





Oxygen Barometry of Igneous Materials using Vanadium Valence

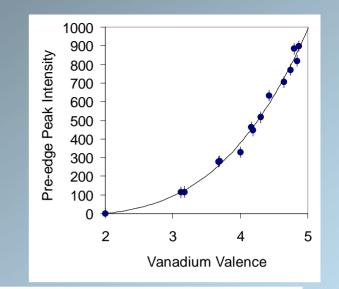
- Oxygen activity in silicate melts controls mineral crystallization
- Method based on x-ray absorption
 spectroscopy of vanadium using synchrotron
 x-ray microprobe
- Vanadium is attractive; ubiquitous and multiple valences (V⁵⁺, V⁴⁺, V³⁺, V²⁺?)
- ...large potential redox dynamic range!
- Method is calibrated using glasses and minerals produced under controlled conditions (fO_2, T, X) ... valence states determined independently by optical spectrometry, in some cases.

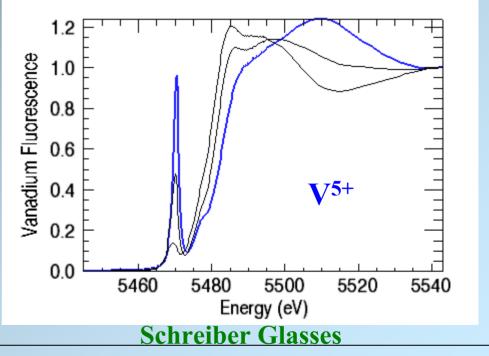


Apollo 17 orange volcanic glass (1 mm field; G. Ryder, Lunar and Planetary Institue)

Vanadium XANES Spectra: Pre-edge Peak

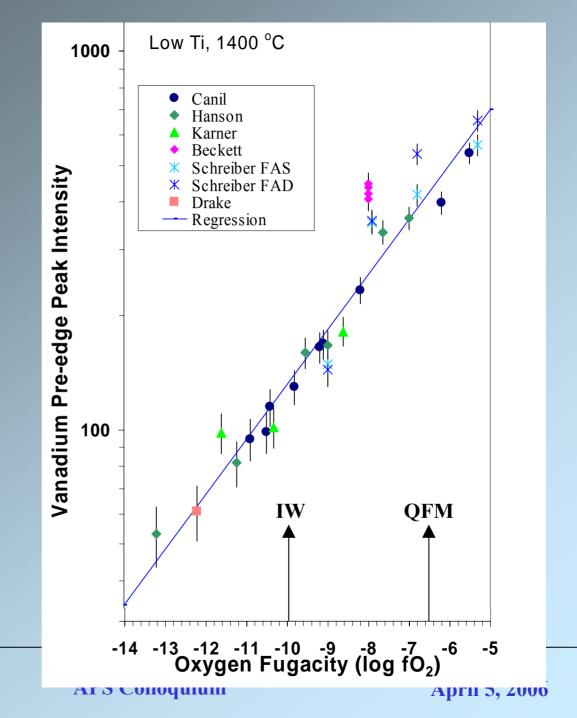
- Pre-edge peak: Bound state electronic transition from 1s to 3d
- Transition probability decreases systematically with outer shell filling $(V^{5+} \rightarrow V^{3+})$.
- •Pre-edge peak intensity shows well-defined trend versus valence for standards (100-fold variation)





"Intensity-Oxygen Fugacity" Calibration

 Calibration curve for each liquidus temperature



Inferred fO2 Results for Natural Glasses

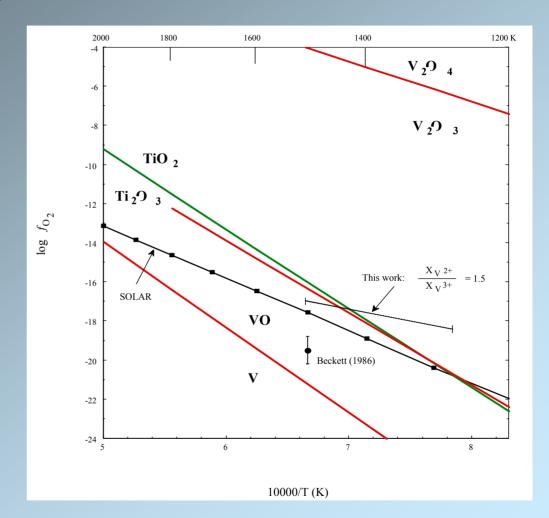
	Oxygen Fugacity rel. IW (log fO ₂)	Oxygen Fugacity (log fO ₂)	Temp.	Pre-edge Peak Intensity	Energy (eV)	Valence
Lunar Pyroclastic Glasses						
Green (15318, 15425, 15426)	-1.8 (0.2)	-11.7 (0.2)	1400	73 (11)	5468.1 (0.1)	2.87 (0.07)
Yellow (15318, 15425)	-1.7 (0.3)	-11.6 (0.3)	1400	75 (11)	5468.1 (0.1)	2.88 (0.07)
Very Low Titanium (VLT; 79315)	-1.0 (0.2)	-10.9 (0.2)	1400	96 (12)	5468.2 (0.1)	3.02 (0.08)
Orange (74220)	-1.9 (0.2)	-12.2 (0.2)	1365	70 (11)	5468.3 (0.1)	2.85 (0.08)
Lunar Mean	-1.6 (0.1)	-11.6 (0.1)		78 (11)	5468.2 (0.1)	2.90 (0.08)
Martian Impact Glass						
EETA79001-lith C	0.0 (0.5)	-9.9 (0.5)	1400	135 (14)	5469.2 (0.1)	3.21 (0.07)
Terrestrial Basaltic Glasses						
Kilauea Iki	2.9 (0.2)	-9.2 (0.2)	1190	278 (21)	5469.5 (0.1)	3.74 (0.06)
Makaopuhi Lava Lake (22-18)	3.8 (0.2)	-9.5 (0.2)	1100	300 (22)	5469.5 (0.1)	3.81 (0.06)
Makaopuhi Lava Lake (22)	3.6 (0.3)	-8.9 (0.3)	1160	328 (23)	5469.5 (0.1)	3.88 (0.06)
Mid-Atlantic Ridge (ocean floor)	3.8 (0.1)	-7.4 (0.1)	1270	429 (28)	5469.8 (0.1)	4.11 (0.06)
Cerro Negro inclusions	4.0 (0.2)	-8.0 (0.2)	1200	403 (27)	5469.7 (0.1)	4.06 (0.07)

Sutton, S. R., et al. (2005) Geochim. Cosmochim. Acta 69/9, 2333-2348



Evidence for Highly Reducing Conditions in the Early Solar Nebula

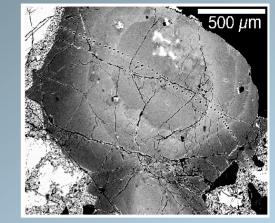
- Fassaite (Ti-rich pyroxene) in refractory inclusions shows radial zonation and spikes in Ti and V concentration (Simon et al.)...redox control?
- Ti³⁺ shown (EMP stoichiometry) to be negatively correlated with Ti content (Grossman et al.)
- V oxidation state by microXANES (2.4 ± 0.1)...consistent with crystallization under solar nebula conditions



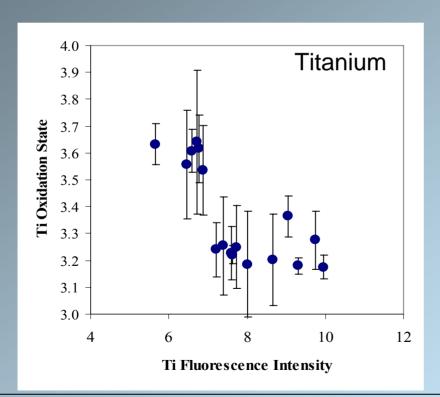
Sutton, S.R., et al. (2002) Lunar Planet. Sci. XXXIII, 1907.

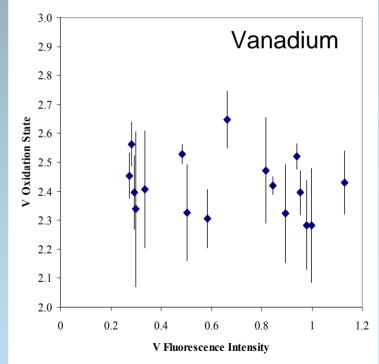


- MicroXANES shows Ti³⁺ variations qualitatively consistent with EMP results.
- V oxidation state ~constant and independent of V content.
- Oxidation state specific partitioning effect?



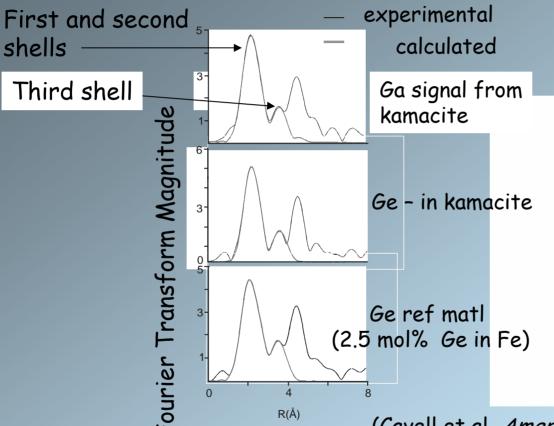




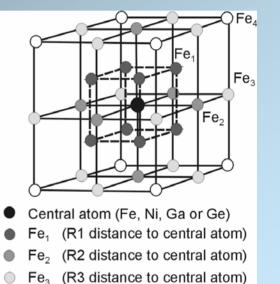


EXAFS Analysis of Ga and Ge in Canyon Diablo

(kamacite has BCC structure)



(Model - 8 BCC cubes assembled into unit, one unique atom, X, in center of assembly. Fit with FEFF)



Fe₄ (distance to central atom not

calculated)





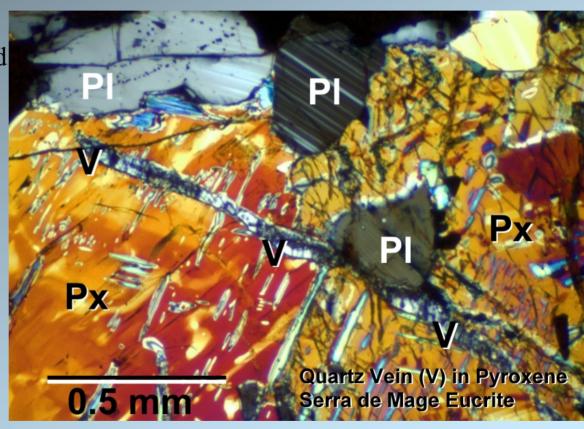






Ancient Water on the Vesta Asteroid?: Identification of α -Quartz in the Serra de Magé meteorite

- Quartz veinlets in the Serra de Magé meteorite (associated with Vesta asteroid by pyroxene signature)
- Identical to 'crack-seal' quartz veinlets in terrestrial rocks which are known to precipitate from liquid water
- Identified by synchrotron microXRD (NSLS X26A) as α -quartz
- Supports hydrothermal deposition



Treiman, A. et al. (2004) Earth and Planet. Sci. Lett., 219, 189-199

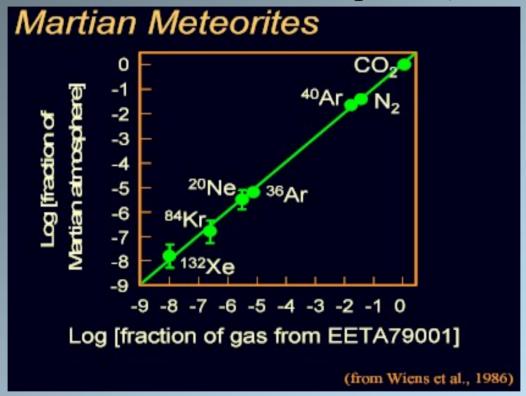
Martian Meteorites

- 31 of the 10,000s of meteorites are from Mars
- Four are witnessed falls (Shergotty, Nakhla Chassigny, and more recently Zagami); so-called SNC meteorites
- How do we know these are from Mars?
 - Fusion crust > not terrestrial
 - Relatively young igneous rocks > "recently" active planet
 - Trapped gases match martian atmosphere measurements by Viking.



Antarctic meteorite . . . an 8-kilogram (17 lb) piece of Mars!? Remains of dark fusion crust, created during high speed entry through Earth's atmosphere, are visible.

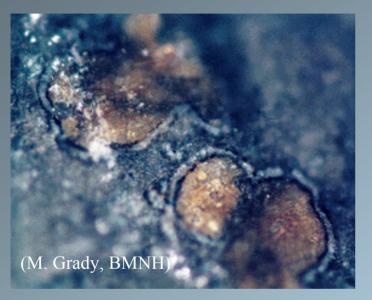
Comparison of Gases Trapped in Martian Meteorites and Mars Atmosphere (Viking)



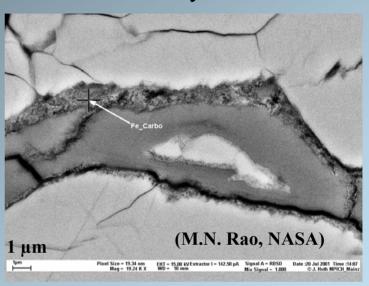
Points on the graph fall on the straight line from lower left to upper right indicating the gas from the martian meteorites is identical to the martian atmosphere.

Secondary Minerals Produced by Liquid Water

ALH84001 Carbonates



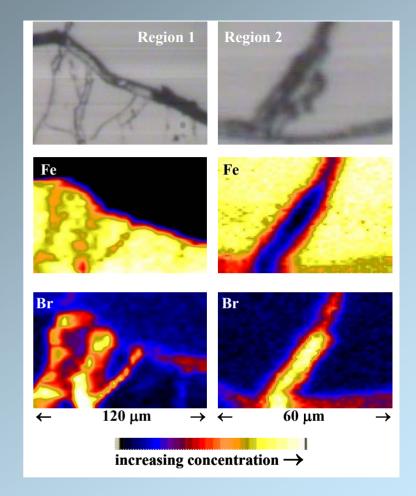
Nakhla Secondary Mineral Vein



- The formation of carbonates and hydrous minerals in the rock fractures indicates the presence of liquid water.
- Dated at a few **billion** years, the carbonates were formed on Mars, before the rock's ejection into space.
- Some secondary mineral assemblages contain carbonate-sulfatehalite (e.g., Nakhla) while others lack halite (e.g., Lafayette)

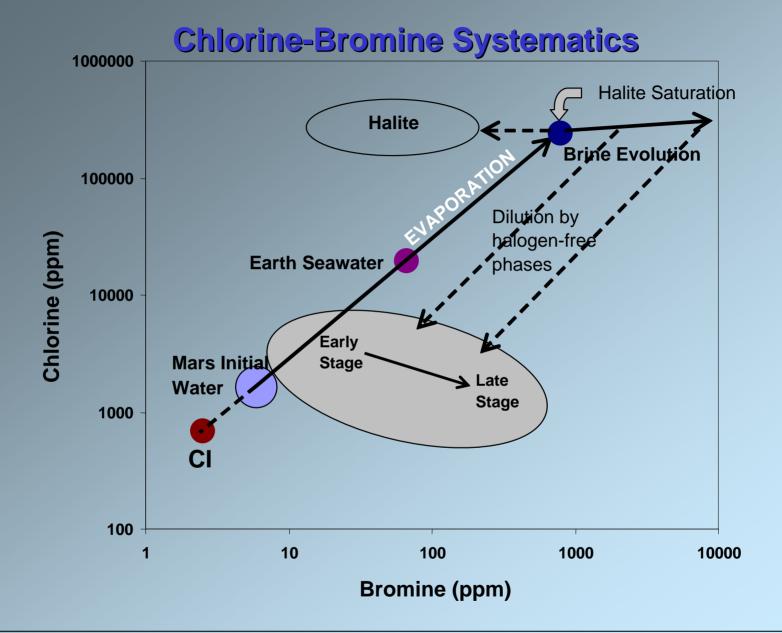
Evaporative Evolution Of Martian Brines

- Use halogen ratios to follow evaporative evolution of martian brines.
- Compare results on meteorites with those from Rover analyses
- Cl and Br abundances determined by APS X-ray Microprobe and EMPA analyses of secondary aqueous minerals in Nakhla veins.



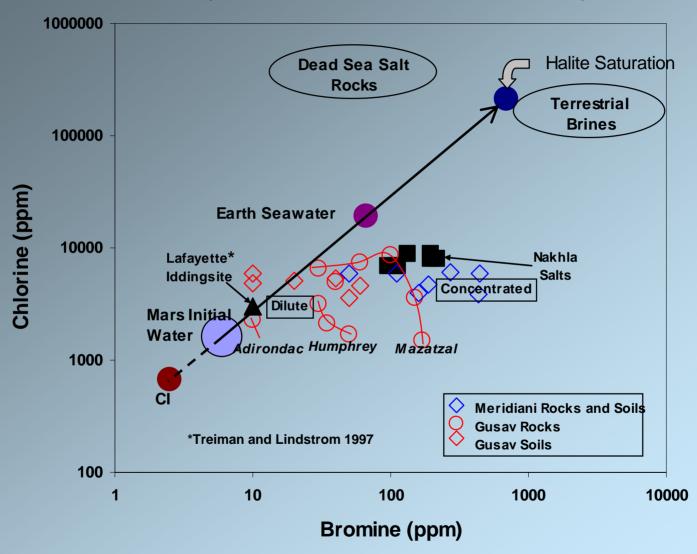
Optical images (top) and x-ray microprobe maps of two Nakhla regions. Br only occurs in the fracture filling material.

Rao, M. N., et al. (2005) JGR-Planets 110, E12S06.





Chlorine-Bromine Martian Meteorite Secondary Minerals and Rover Analyses



Fluid Evolution Summary

- Cl and Br concentrations in solutions prior to halite saturation evolved by evaporation retaining initial Cl/Br ratios.
- Samples inundated with these fluids produced secondary mineral assemblages lacking halite (dilute fluids; e.g., Lafayette iddingsite)
- Onset of halite saturation led to halite precipitation and enrichment in Br relative to Cl in brines
- Samples inundated with these fluids produced secondary mineral assemblages containing halite (concentrated fluids; e.g., Nakhla veinlets).
- Rapid dessication led to "closed-system" precipitation retaining Cl/Br of the parent brine.

Genesis: Solar Wind Sample Return

- Mission of collect solar wind ions by implantation in ultrapure substrates (sapphire, silicon, diamond)
- Goal is to obtained more precise determinations of solar elemental and isotopic abundances
- Launched in August 2001; spent 29 months at Lagrangian 1 point; returned to Earth Sept. 2004
- Non-nominal landing
- Collectors (mostly fragmented) retrieved and analyses in progress.
- Much effort in learning how to deal with terrestrial contamination.

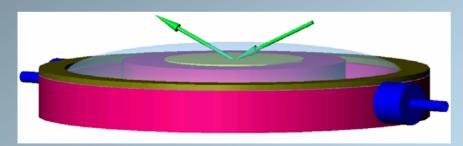




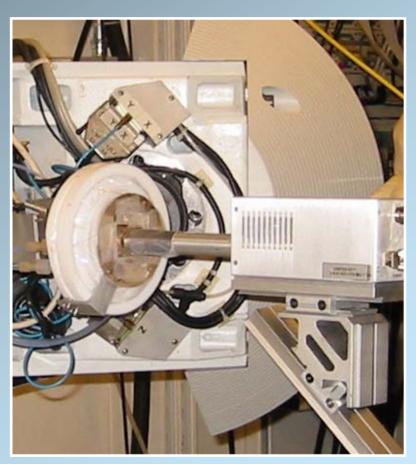


Grazing Incidence X-ray Fluorescence

- GIXRF allows XRF analysis of near surface regions (e.g., ion implants)
- Yield curves (XRF intensity vs. sample angle) can distinguish between surface contamination, implant and bulk impurities

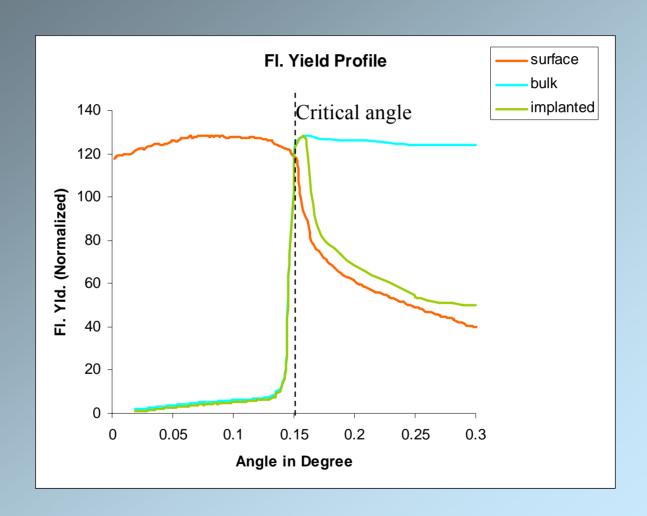


GIXRF analysis geometry



13-ID-C Diffractometer

Fluorescence Yield Profiles vs. Element Depth Distribution

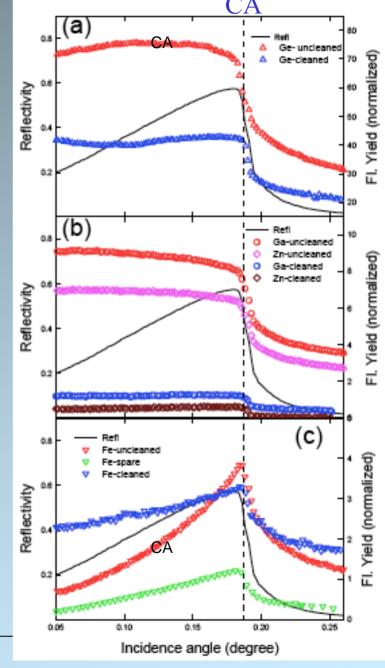


Fluorescence Yield Profiles for Genesis Flight Sapphire

- Surficial contamination profile: Flat below the critical angle (CA), sharp drop at CA and low signal above the CA. Ga, Zn and Ge yield curves have the same shape and typify this type of profile.
- Near surface and/or shallow implant profile: In contrast, the Fe is peaked near the CA suggesting an implanted component.

K. Kitts et al. (2006) LPSC, 1451





Inferred Solar Wind Fe Abundance

- The Fe bulk abundance was calculated using the highest angle yield value and normalizing to that measured for a Geimplanted silica standard (1 keV/nucleon; 5 x 10¹⁴/cm²).
- Fe abundance of an unflown sapphire spare was subtracted off.
- Solar wind abundance thus derived was 8×10^{12} /cm² compared to predicted value of 2×10^{12} /cm²
- Should be considered an upper limit at this point as some Fe may still be from surface microparticles.
- Profile modeling, surface cleaning procedures and studies of additional samples are expected to eventually allow a full separation of surface and implant signals.

Interplanetary Dust Particles

- Many tons of dust grains, including samples of asteroids and comets, fall from space onto the Earth's atmosphere each day.
- High flying aircraft with special sticky collectors capture this dust ($\sim 1-30~\mu m$) as it falls through the stratosphere, before it becomes mixed with Earth dust.

Stratospheric Collection



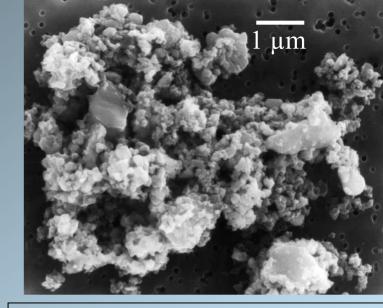
•A ultra-clean laboratory at NASA-JSC curates over 2000 cosmic dust particles and distributes samples to investigators all over the world.

Why are IDPs of Interest?

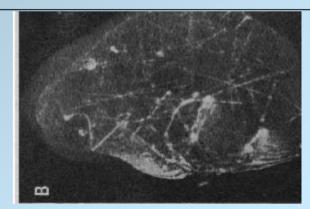
- Potentially most primitive solar system solids
- Meteoritic material least altered by atmospheric entry
- Hosts of interstellar grains

IDP Mineralogy

- Two basic types: porous and compact
- Porous: contain mainly anhydrous silicates (olivine, pyroxene) >> cometary?
- Compact: contain hydrous layered silicates (clay minerals)



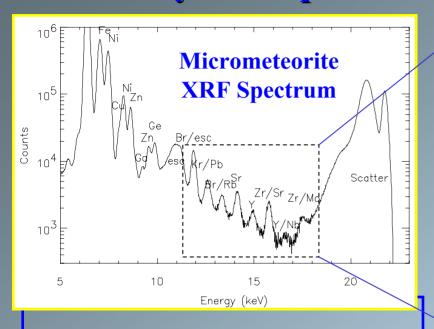
How do we know they're extraterrestrial? They contain solar flare tracks.



Solar flare tracks in olivine (Mg,Fe)₂SiO₄ From Bradley et al. (1984) Science, 1432



IDPs: X-ray Microprobe Analyses



- Total mass ~ 30 picogram (3μm)
- Trace element concentrations

$$Sr = 4.6 \text{ ppm } (CI=7.9 \text{ ppm})$$

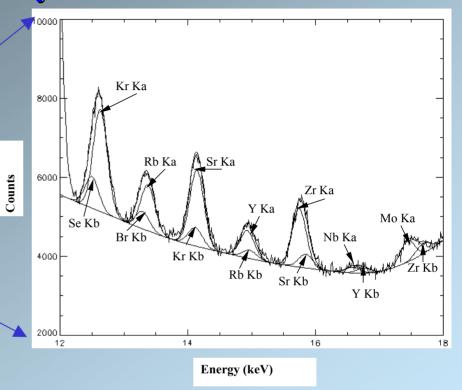
$$Y = 1.4 \text{ ppm } (CI=1.5 \text{ ppm})$$

$$Zr = 2.5 \text{ ppm } (CI=3.7 \text{ ppm})$$

$$Nb = 0.2 \text{ ppm } (CI=0.3 \text{ ppm})$$

$$Mo = 1.3 \text{ ppm } (CI=0.9 \text{ ppm})$$

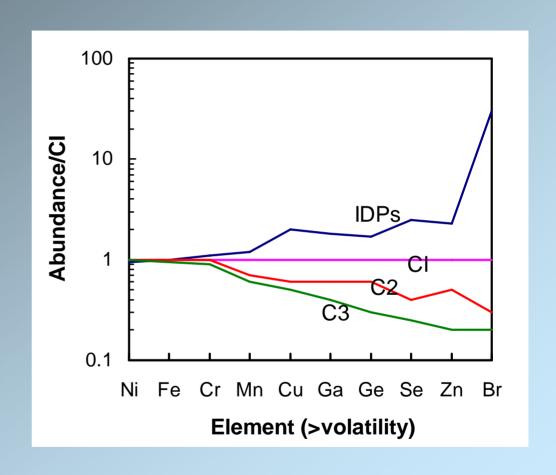
• 1 ppm \approx 30 ag



• Evidence of odd-even abundance pattern expected for a primitive solar composition

IDPs: X-ray Microprobe Results

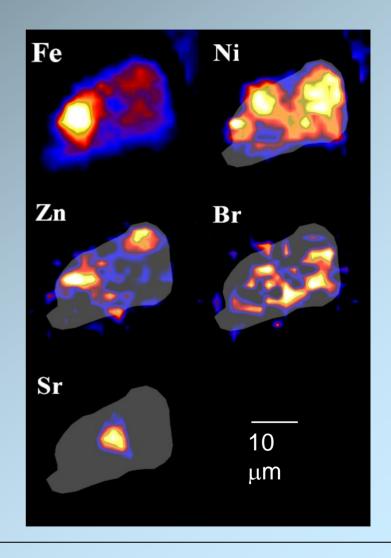
- Volatile element enrichments
- Complementary abundance patterns to carbonaceous meteorites
- Particles derive from parent bodies more primitive than carbonaceous meteorites
- Possible there is a sampling bias in the IDP collection.



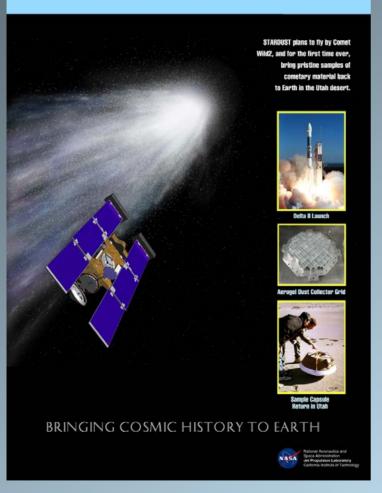
IDPs: Fluorescence Microtomography

- Are the volatile element enrichments indigenous or stratospheric contamination?
- Fluorescence tomography images show that volatile elements (Zn and Br) are not strongly surface-correlated, suggesting that these elements are primarily indigenous rather than from atmospheric contamination
- Information on the host phases of trace elements (e.g., Zn, the first element lost during entry heating, is isolated in a few spots, probably ZnS identified by TEM in IDPs; Sr in carbonate)

Sutton, S.R., et al. (2000) Lunar Planet. Sci. XXXI,1857.

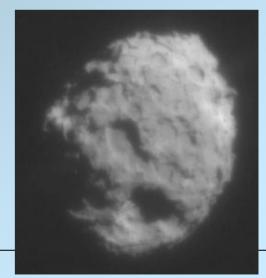


STARDUST



- "Fly-by" mission to collect dust particles from a comet and return samples to Earth
- Innovative aerogel collectors
- Launched, February 1999
- Fly-by of Comet Wild-2 on January 2, 2004
- Returned to Earth, January 15,
 2006 (nominal landing)
- Wild-2: only 5 solar passes; right place at right time

Comet Wild-2 photographed by Stardust



Comets as Sources of Primitive Dust from Our Solar System

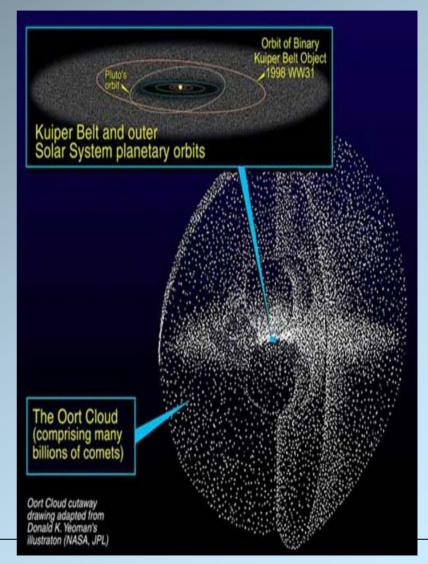
- The detection of CO₂ gas emission when comets are near the Sun indicates the comets have preserved CO₂ ice since Solar System formation.
- This indicates that comets formed in a region of the Solar System cold enough for CO₂ to condense.
- Further, it suggests that comets have preserved in "cold storage" the dust that was trapped within the ice since the time of comet formation.
- Thus, comets are expected to contain pristine samples of the dust from their formation region.

Comet Hale Bopp



Comet Formation and Storage Regions

- Comets are believed to reside in the Oort Cloud and in the Kuiper Belt.
- The Oort Cloud is a spherical cloud of comets situated about 50,000 to 100,000 AU from the Sun.
- The most widely-accepted idea is that Oort cloud objects formed much closer to the Sun, as part of the process that formed the planets and asteroids, but gravitational interaction with Jupiter ejected them into extremely long elliptical orbits.
- The Kuiper belt, confined to the plane of the ecliptic, is believed to be the source of most short period comets entering the inner solar system.
- Kuiper Belt comets are believed to have formed in place at >30 AU (~ distance of Pluto)



Intact Capture with Aerogel

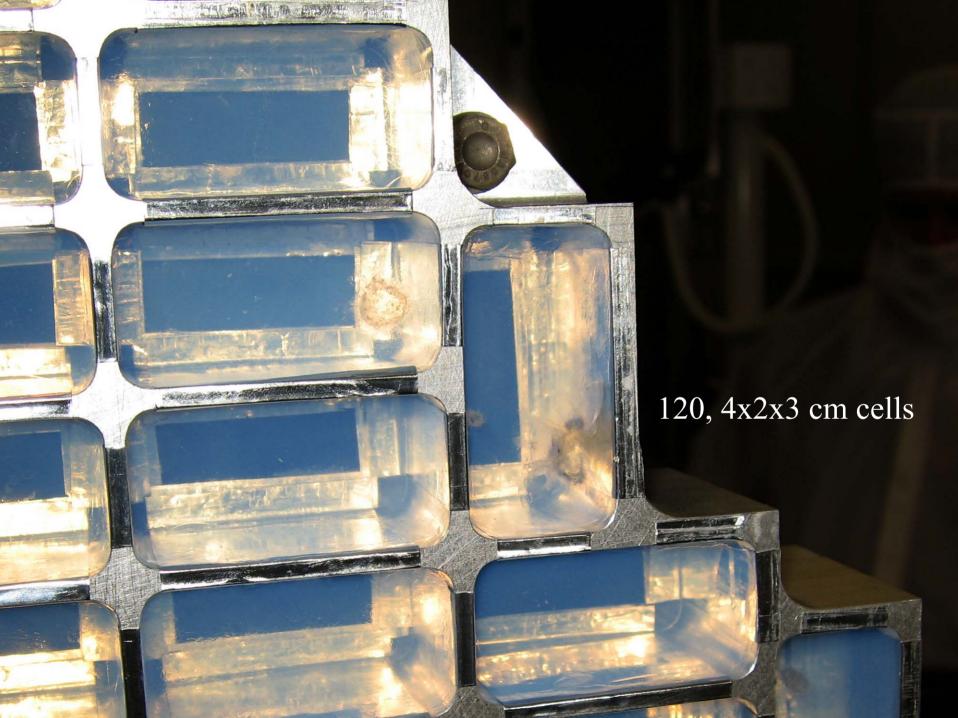
- Silica aerogel is a silicon-based solid with a porous, sponge-like structure in which 99.8 percent of the volume is empty space (density ~ 0.02 g cm⁻³; developed by P. Tsou, JPL)
- When a particle hits the aerogel, it buries itself in the material, creating a carrot-shaped track up to >100 times its own length.
- This slows the particle down and brings it to a relatively gradual stop.
- Intact capture allows comet dust to be collected at high speed, without using fuel to slow down, collect samples, then speed up for return to Earth.

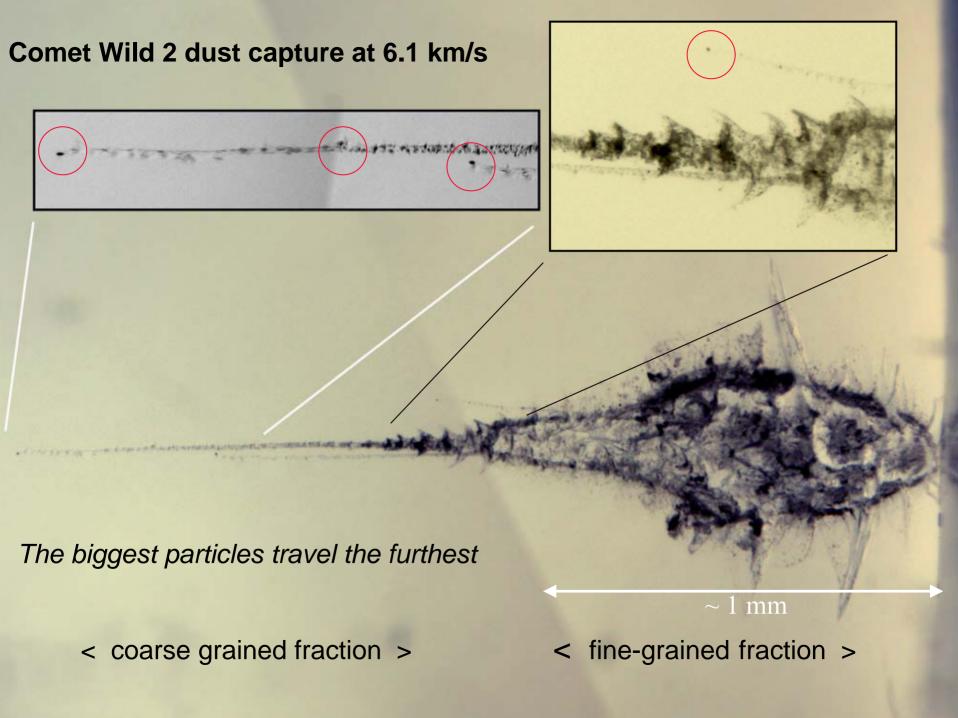
Hypervelocity particle captured in aerogel (lab experiment)

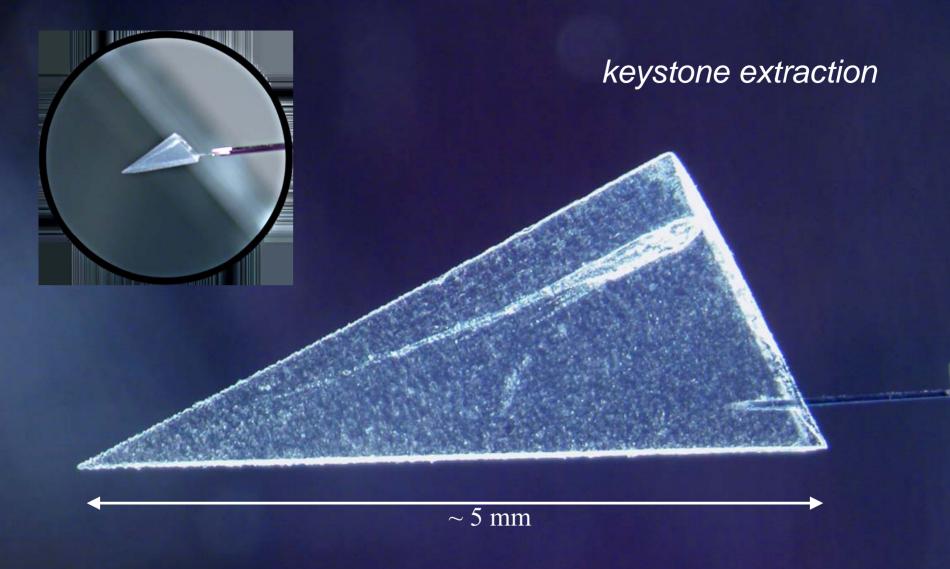




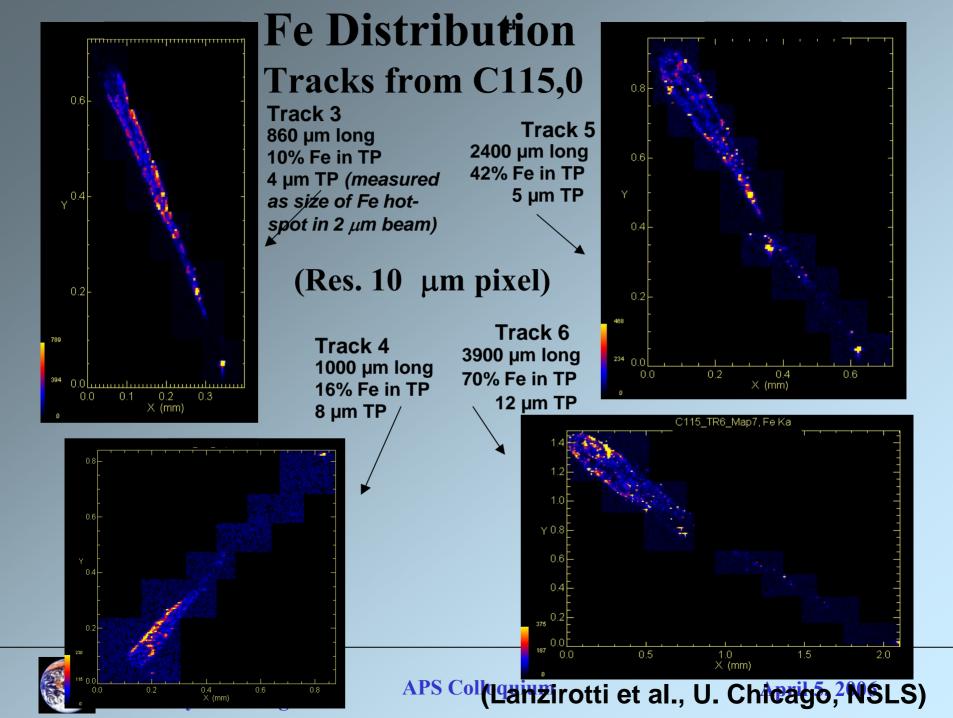




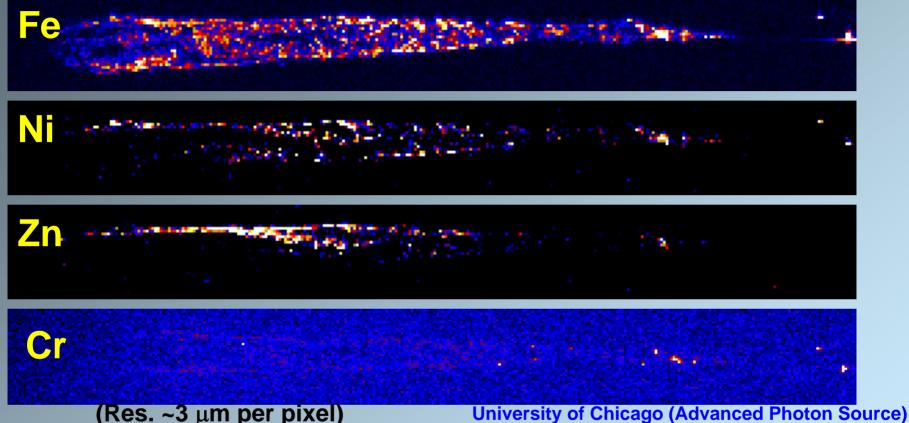




Keystoners- Westphal, Snead, Nakamura/Messenger



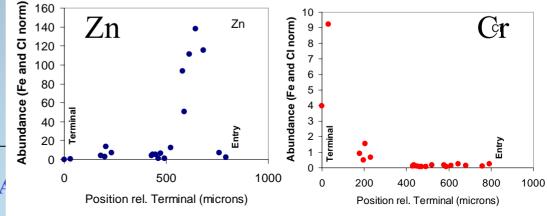
Element Distribution Along Track 3



(Res. ~3 μm per pixel) Elements are heterogeneous

along the track, with Zn occurring near the entry, with low Zn in the terminal particle, while Cr occurs near the terminal

160 Zn Cr 140

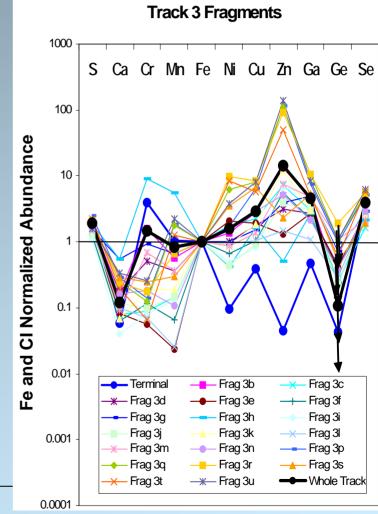


enc **GeoSoilEnviroCARS University of Chicago**

Composition of Fragments Along Track 3

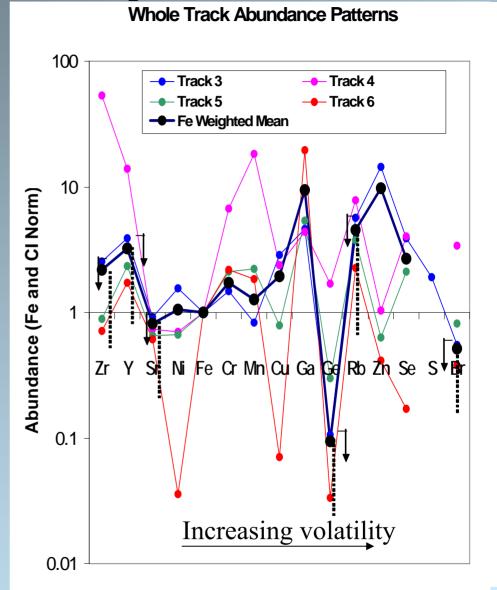
Track 3 (860 μm; 10% of Fe in TP; 4 μm TP)

- The 20 most intense Fe-hot spots were reanalyzed for a much longer time.
- The spot to spot variation is significant -- $>10^3$ for Zn, $>10^2$ for Ni.
- A "whole track composition" was determined by averaging these long spectra of the 20 most intense spots in the Fe map, and at hot spots in other element maps (e.g., Ni, Zn).
- This "whole track composition" (black) differs significantly from that of the terminal particle (blue), e.g. Ni/Fe ~CI in "whole track" but <0.1xCI in the TP and Cu, Zn, Ga and Se are >CI in the whole track but <<CI in the TP.



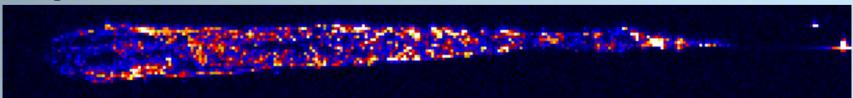
"Whole Track" Compositions

- The alternative -- summing all point spectra in a map yields fewer elements in the "whole track" since many elements are concentrated in a few spots (e.g., Cr).
- Averaging the ~20 most intense spots in Fe and other maps (including the TP) yields 15 elements in 3 of the 4 tracks.
- All but Tr. 6 show ~CI Ni/Fe.
- The four track Fe-weighted average (black line) overlaps CI for most refractory elements, but all moderately volatile elements measured are >CI except Ge and Br.

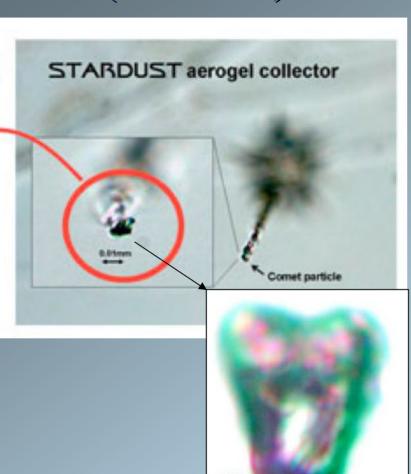


First Bulk Composition Results

- Terminal particles (TP) frequently contain much less than 50% of the total Fe along the track suggesting the comet dust is very weakly held together.
- The size-scale for compositional heterogeneity in Wild-2 is at least 12 μm (based on the Track 6 TP), much larger than in porous IDPs.
- Many elements (notably, K, Ca, Ti, Cr, Ni, Ga, Ge, & Ba) vary widely from particle to particle.
- Ni and several moderately-volatile elements (e.g., Zn) are frequently found to be concentrated in the entry region of tracks.
- The composition of TPs is generally not representative of the particle that struck the aerogel, but the composition of the original particle can be inferred by mapping elements over the whole track.
- Preliminary data suggests CI-like refractory elements with hints of an enrichment of moderately volatile elements.
- Analyzing and integrating whole tracks is essential for determining the bulk composition of Wild-2



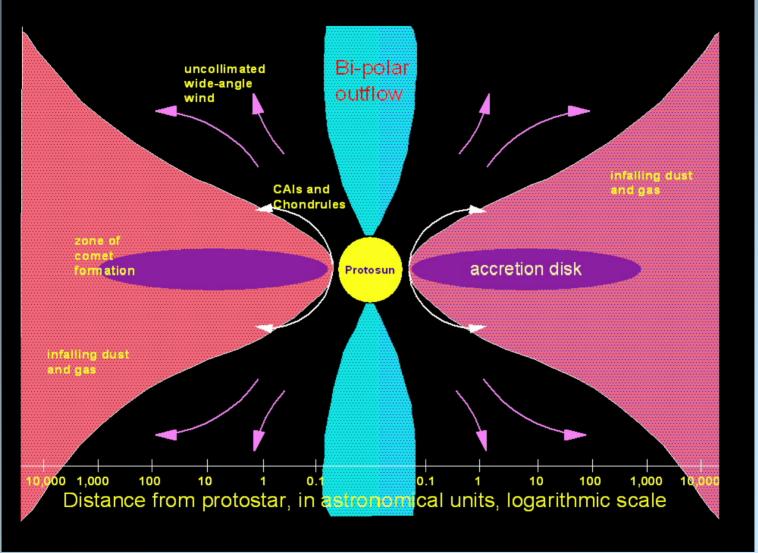
First Stardust Results (continued)



- Essentially all impacts contain analyzable material
- Large (1-10µm) grains of forsterite, enstatite, pyrrhotite and perhaps CAI-like minerals appear to be common
- No hydrated silicates, carbonates, magnetite seen (yet)
- The presence of refractory forsteritic olivine (CaO>0.5wt %) implies that Wild 2 is distinct from CI chondrites
- Wild 2 contains abundant "high temperature" minerals!

Courtesy: Stardust Science Team

Presence of refractory grains in comets is a prediction of the "X-wind" model



F. H. Shu, S. Hsien, T. Lee, Science 271, 1545 (1996)

Other SR Applications to ET Materials

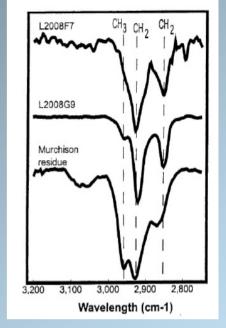
Organic Matter

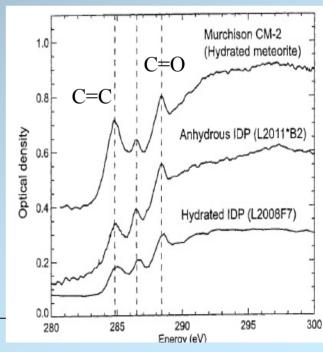
- Infrared and XANES (C, O) on anhydrous IDPs show that water is not essential for producing some prebiotic organic matter in meteorites
- D/H enrichments in some of these organic phases suggests they are presolar

Flynn, SUNY-Plattsburgh)

C XANES spectra of IDPs and the organic residue from the Murchison meteorite (G.

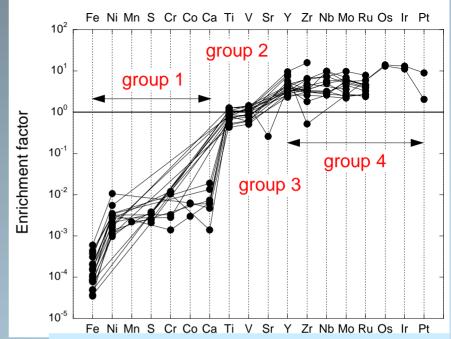
IR spectra of IDPs and the organic residue from the Murchison meteorite (G. Flynn, SUNY-Plattsburgh)



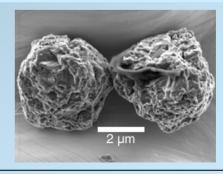


Presolar Grains

- Trace element abundance patterns can be used to constrain nucleosynthesis and condensation processes
- Patterns for mainstream grains (right) agree well with theoretical predictions for sprocess (slow, neutron capture); depleted in non-sprocess elements (group 1).
- Zr/Nb systematics suggest radioactive 93 Zr ($t_{1/2}$ = 1.5×10^6 y) was live at the time SiC grains condensed (further tying them to AGB stars). Y. Kashiv et al. (2006) LPSC.

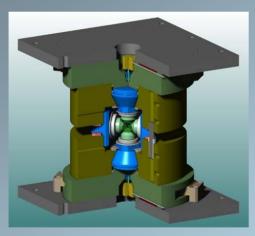


Element Abundances in presolar SiC grains (Y. Kashiv; U. Chicago; Sector 2). SEM image by A. Davis; U. Chicago.



High Pressure/High Temperature Studies

- Meteorites can be used as starting materials for high PT synchrotron experiments
- Radiography of formation processes
- Element partitioning (silicate/melt) at high PT



Large Volume Press: 1000 ton force; ~30 GPa; mm³ sample volume; external heating to several thousand degrees



Diamond Anvil Cell: ~ 100 μm sample chamber; ~ 300 GPa; laser heating to several thousand degrees

Summary

Synchrotron radiation is allowing extraterrestrial materials to be examined in new ways to help to answer key questions:

- Chemical histories of presolar matter
- Origin(s) of primitive Solar System materials providing constraints on events in the early solar nebula
- Oxidation states of magmas on bodies in the inner Solar System
- Occurrence and evolution of fluids on Solar System bodies
- Origin(s) of organic matter and potentially its role in the origin of life

Future Sample Return Missions

Asteroids

• Hayabusa (Japan): Collected samples from the surface of near-Earth asteroid, Itokawa. Return to Earth in 2010.

Mars

• Robotic sample return missions under consideration for >2009

Moon

• Humans return to the Moon < 2018



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