

# NANO-SYNCHROTRON XRF AND XRD: A POWERFUL NON-DESTRUCTIVE TECHNIQUE FOR IN-SITU CHEMICAL AND STRUCTURAL ANALYSES OF PRESOLAR GRAINS

M. Jadhav<sup>1</sup> (manavi@higp.hawaii.edu), S. Schmitz<sup>2</sup>, T. K. Croat<sup>3</sup>, F. E. Brenker<sup>2</sup>, M. Schmitt<sup>2</sup>, B. Vekemans<sup>4</sup>, L. Vincze<sup>4</sup>, T. Schoonjans<sup>4</sup>, G. Wellenreuther<sup>5</sup>, B. De Samber<sup>5</sup>, G. Falkenberg<sup>5</sup>, M. Burghammer<sup>6</sup>, G. R. Huss<sup>1</sup>

<sup>1</sup>University of Hawai'i at Mānoa, Hawai'i Institute of Geophysics and Planetology, Honolulu, USA; <sup>2</sup>Goethe University, Dept. of Geosciences, Frankfurt/M., Germany; <sup>3</sup>Laboratory for Space Sciences, Washington University, USA; <sup>4</sup>Gent University, Dept. Anal. Chemistry, Gent, Belgium; <sup>5</sup>DESY, Hamburg, Germany; <sup>6</sup>ESRF, Grenoble Cedex 9, France.

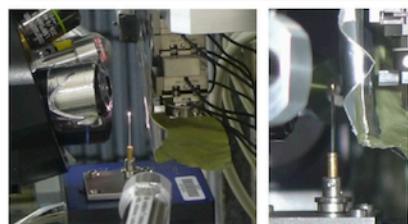
## Introduction

- ❖ Multi-technique, correlated analyses of individual presolar grains
- ❖ Most of the techniques used to study presolar grains (SIMS, TEM, RIMS) are destructive that lead to the loss of precious stardust material
- ❖ Here we demonstrate some of the powerful capabilities of **nano-Synchrotron X-ray Fluorescence and Diffraction (SXRF & SXRD)** to study presolar grains
- ❖ **High resolution** measurements were carried out with the new generation synchrotron sources at

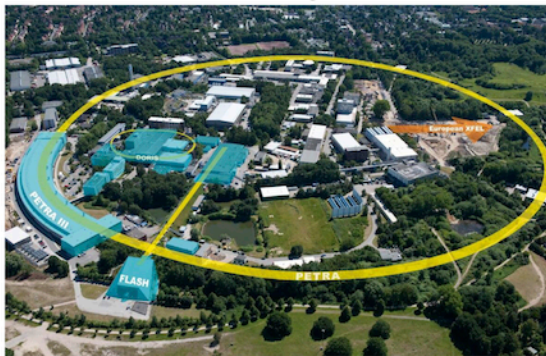
### European Synchrotron Radiation Facility (ESRF)



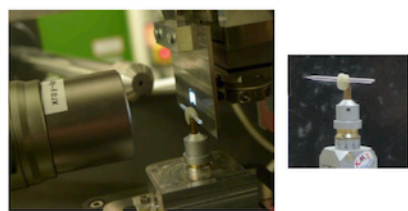
Beamline: Microfocus ID13  
Beam size: 200 nm (H) × 150 nm (V)  
Beam energy = 13 keV  
Beam intensity =  $3 \times 10^9$  photons/s



### Deutsches Elektronen-Synchrotron (DESY)



Beamline: PETRA III  
Beam size: 139 nm (H) × 127 nm (V)  
Beam energy = 13 keV  
Beam intensity =  $1.8 \times 10^7$  photons/s



See Schmitz et al. (2012) for more experimental details

## Nano-SXRF & SXRD capabilities – FUTURE PLANS

- ❖ **Quantitative results**
  - Trace element abundances of the graphites AND the subgrains
  - Diffraction data on the host grain AND the subgrains
  - Rare earth elemental (REE) patterns for micron sized subgrains
- ❖ **3d stereographic projections**
  - Chemistry vs radial distance (= time)
    - e.g., obtain Ti/V ratios per pixel (Croat et. al. 2003)
  - Sub-grain size vs time
- ❖ **Contamination on/in grains**

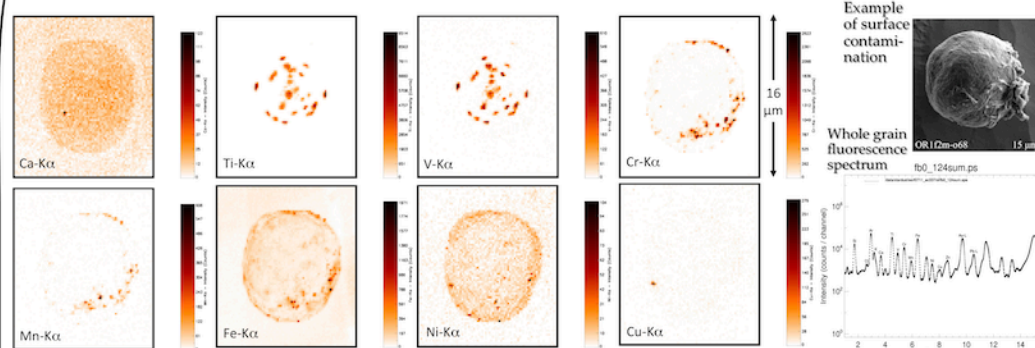
**Chemical, structural, and tomographic information on host grains and their nm-sized refractory subgrains (TiC, SiC, Fe-Ni metals, etc.) will provide a wealth of information on the physical and chemical conditions in the circumstellar environments where these grains condensed. Such in situ measurements can reconstruct temporal evolution of the physical, chemical and isotopic properties of the circumstellar environment**

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References

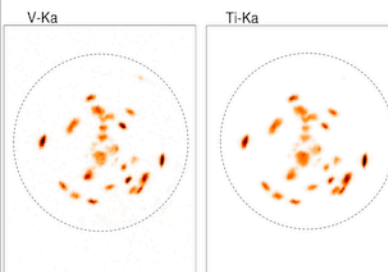
- Schmitz S. et al. (2012) *Meteoritics & Planet. Sci.*, 75, #5215  
Croat T. K. et al. (2003) *Geochim. Cosmochim. Acta*, 67, 591-595  
Bernatowicz T. J., et al. (1996) *Astrophys. J.*, 472, 760-782  
Croat T. K., et al. (2011) *LPS XLII*, #1533  
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## Presolar graphites are ideal candidates because of large grain sizes (1 – 17 μm)

Orgueil low-density graphite #1 (diameter = 11 μm); measured at ESRF

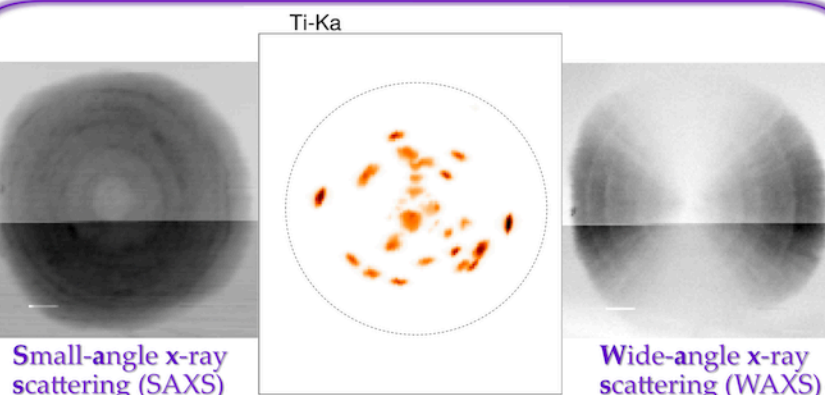


### Correlated Ti & V signals



### Low-density #1

- ❖ 50-100 TiC subgrains a few hundred nm in size; 10-20 subgrains up to a micron in size
  - Ti and V contents are correlated
  - Ti & V exist in the form of (Ti,V)C – previously observed by Croat et al. (2003) etc.
  - Central core of tiny TiCs < beam size – 3-d view confirms this
  - Grain size of TiCs increases with distance
  - Outer shells have no TiCs
  - TiCs appear platy and aligned flat on shells
- ❖ Cr, Mn, Fe, Ni- rich grains on surface
  - Are chromites and kamacites seen previously extrinsic?
- ❖ Diffraction measurements identify well-graphitized carbon with a **d<sub>002</sub> spacing = 3.35** → unexpected for low-density graphite

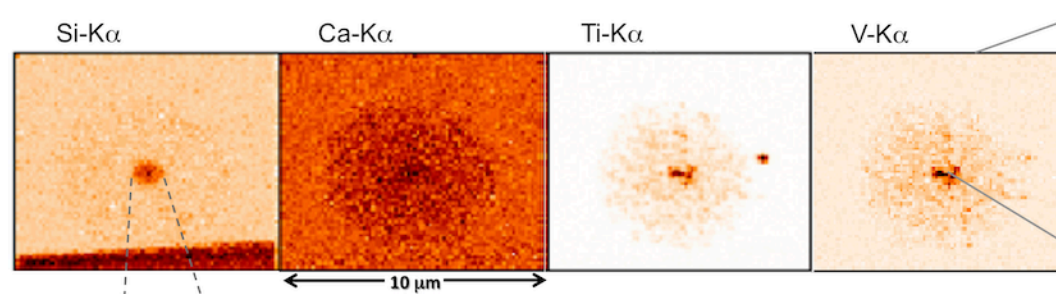


Small-angle x-ray scattering (SAXS)

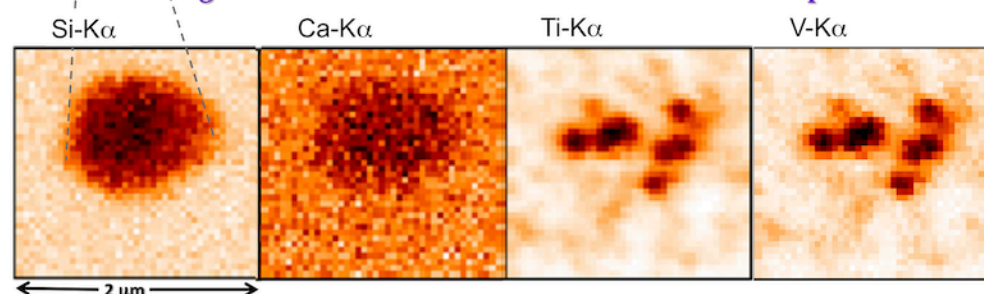
Wide-angle x-ray scattering (WAXS)

- ❖ Low-density core (SAXS) coincides with smallest carbides in center. Similar to nanocrystalline core observed in Murchison onion graphites (Bernatowicz et al. 1996)
- ❖ Shell-like structure (SAXS) indicative of sequential growth
- ❖ Variable degrees of crystallinity (WAXS) suggest crystallization in phases

Orgueil low-density graphite #2 (diameter ~ 7 μm); measured at DESY



### High resolution measurement of central Si-Ca-rich phase



### Low-density #2

- ❖ Si-Ca-rich phase (~ 1 μm) was nucleation site for the host grain
- ❖ Ti & V hotspots → (Ti,V)C subgrains condensed on pre-existing Si-Ca-rich phase
- ❖ **Interesting Si-Ca-rich phase** could represent one of the following scenarios:
  1. **Supernova TiC:** Condensed as a <sup>44</sup>TiC grain with material from Si/S zone → <sup>44</sup>Ti decayed to <sup>44</sup>Ca (τ<sub>1/2</sub> = 60 a) in the subgrain → Source of the strong Ca signal; Si/S zone also contains almost pure <sup>28</sup>Si → correlated Si and Ca signals
    - ✓ Isotopic measurements on the subgrain should yield simultaneous <sup>28</sup>Si and <sup>44</sup>Ca excesses, similar to those found in SiC-X and other SN graphite grains
  2. **SiC-X inclusion:** Previously found in LD Orgueil graphites (Croat et al. 2011) → <sup>28</sup>Si and <sup>44</sup>Ti from the Si/S zone → Ca signal due to decay of <sup>44</sup>Ti to <sup>44</sup>Ca
    - Scenario 1 & 2 could be an **IN SITU VIEW OF CORRELATED <sup>28</sup>Si and EXTINCT <sup>44</sup>Ti** from the Si/S zone of a SN !!
  3. **SiC central subgrain:** Croat et al. (2010) recently found rare SiC inclusions within high-density Murchison graphite grains with large <sup>29,30</sup>Si excesses → Contains material from O-rich zones of a SN enriched in <sup>29,30</sup>Si → Zones also enriched in <sup>42,43</sup>Ca.
    - ✓ Large <sup>29,30</sup>Si excesses from SIMS analysis can verify this case