XRF nano-analysis of stellar condensates trapped in presolar carbon microspheres

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Introduction

More than 4.5Ga ago, our solar system was formed from a mixture of gas and dust. This dust was inherited by our parent molecular cloud from the interstellar medium and from cooling stellar outflows or explosions. Most of the primary chemical information was lost due to the mixing and homogenization of the gas and dust within the interstellar medium (ISM), in the molecular cloud or during planet formation. However, some pristine matter survived the destructive processing in the early solar system and was identified on the basis of nucleosynthetic isotopic signatures [e.g. Refs. 1,2]. These so-called presolar grains can be found in pristine cometary and asteroidal matter and in interplanetary dust particles (IDPs) [see Ref.3 for a complete review]. The most pristine meteorites identified so far contain a tiny portion (several 100 ppm) of nearly undisturbed stellar material formed in the outer shells of dying stars more than 4.56 Ga ago. All the presolar graphite grains from meteorites are in the form of spherules [4]. Isotopic analyses of these grains, as with other presolar grains, suggest a number of stellar sources including several different AGB stars, novae, supernovae and possibly Wolf Rayet stars and planetary nebulae ([5] and refs therein). The grains range in size from 0.8-28µm in diameter and have a range of densities from 1.6g/cm^3 to 2.2g/cm^3.
In this project the chemical composition and 2D/3D distribution of trapped metal carbides (e.g. (Si-,Ti- and V Carbide) in circumstellar carbon spheres were studied by scanning nano-XRF. The nanoscale spatial resolution of the P06 nanoprobe allows for the first time the analysis of the chemical and structural composition of presolar 'onion type' graphite spheres, in-situ and without potentially destructive sample preparation.

Experimental

The grains were provided on an Au-foil and were mounted on glass capillaries using a *Kleindiek* nano-manipulator set-up. The individual graphite grains were attached to glass capillaries with a tip of ~1µm using only electrostatic forces.
During two beamtimes, two different C-spheres were measured: (1) a low density (SN3) and (2) a high density (OR1) grain [6]. Due to mounting issues, during the second beamtime, only particle SN3 was found back in the optical image, so measurements were focused on that particle. Due to the limited space in the set-up, the capillaries were mounted horizontally on a brass pins, attached to standard goniometer heads.
During our first experiment at the nanoprobe end-station of PETRA-III P06 a beam size of 139nm (H) × 127nm (V) was used with an energy of 15keV and intensity of ~1.8×10^7 photons/s. The intensity was slightly higher during the second beamtime, reaching 4.7×10^7 - 5.7×10^7 photons/s.

Results

Two C-spheres were measured during the first experiment, OR1 and SN3, in order to explore the two-dimensional elemental distributions within these unique particles on the sub-micron resolution level. Due to the relatively low count rates, the measuring time for obtaining detailed elemental maps was chosen between 8-10s/point (see larger overview maps, Fig1,2a) and 20-60 s/point (smaller detailed maps, Fig.1 inset, Fig.2b) yielding measuring times of several hours per 2D scan.

The high-density grain (OR1, size ~7µm) measured at P06 exhibits hotspots which are mainly rich in Fe and Cr, and are in most cases obviously located at the surface (Figure 1). To demonstrate the high spatial resolution obtained at P06, different regions were selected for detailed 2D XRF mappings (Figure 1, inset). The inset of Figure 1 clearly shows two distinct hotspots of Fe and Cr next to each other, associated with two different sub-micron particles.

The low-density grain (SN3, size ~7µm) shows an enhancement of Ti and V in a small number of nanoscopic hotspots (~100nm). These hotspots appear to be located close to the centre of the spherule, which was confirmed by stereoscopic measurements in a subsequent analysis. The W-L and signal most likely originates from the preparation process: a W-needle was used to position the spheres on the supporting Au-foil. Fe, Ni, Mn and Cr are mainly located at the rim of the sphere, representing probably contaminants. This was confirmed by extra (stereoscopic) measurements, during which two observation angles were employed to confirm the position of the hotspots (whether inside the sphere or along the rim).

The stereoscopic measurements were performed on particle SN3, using optimized detection conditions. Surprisingly, under optimized detection conditions, in the centre of the carbon-sphere an additional Si- and Ca-rich feature (~1.5µm) could be detected next to the Ti, V hotspots. The Ca, Si rich phase in the centre can be interpreted as a crystal nucleus, which accreted C on its surface. Rotation of 10° in the horizontal plane allows the characterization of which fragments are located inside the sphere and which are on the surface, and therefore most probably contaminants. **Figure 2a** shows the superimposed image of the XRF maps obtained under 0° and +10° observation angles. The Ti and V hotspots clearly stay in position indicating a location in the center of the sphere, whereas most of the Fe-rich hotspots change in position according to their location on the surface (most likely contamination or remnants of the original meteoritic material). **Figure 2b** shows high resolution XRF maps (50 nm/pixel) of the particle center with a Si-rich central nucleus and associated Ti, V-rich sub-grains.

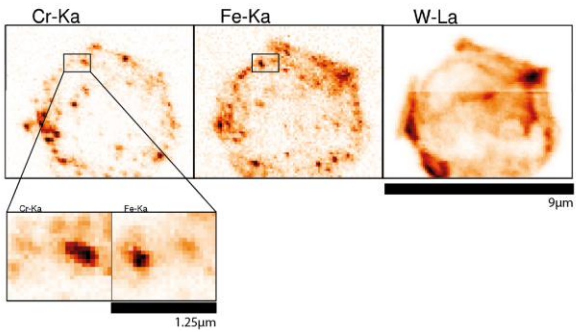

Figure 1: Overview map (Cr, Fe, W) of sphere OR1. The inset (below) demonstrates the high resolution of the set-up. Fe & Cr hotspots are most likely located on the surface.

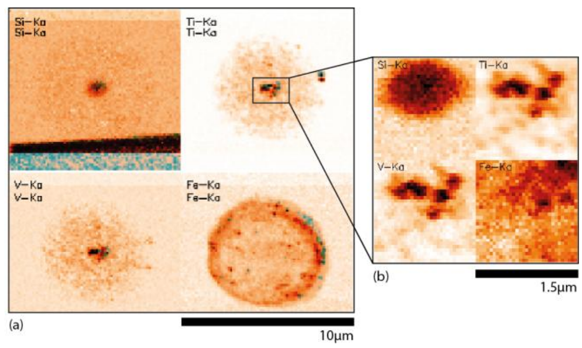

Figure 2: (a) Superimposed 2D XRF maps of particle SN3, obtained under two observation angles (Δθ=10°). Ti, V hotspots are located in the center of the particle, whereas the Fe hotspots are located on the surface. (b) Detailed maps of the central part of the sphere showing a Si-rich core with Ti,V hotspots of a few 100 nm.

References

[1] Vollmer, C., Hoppe, P. & Brenker, F.E. (2008) Si-isotopic composition of presolar silicate grains from Red Giant Stars and Supernovae. – The Astrophysical Journal 684, 611-617.

[2] Croat T. K., Jadhav M., Lebsack E., and Bernatowicz T. J. (2011) A unique supernoa graphite: contemporaneous condensation of all things carbonaceous. Lunar Planet. Sci. XLII, #1533.

[3] Zinner E. (2007) Presolar grains. In Treatise on Geochemistry Update 1 (eds. H. D. Holland and K. K. Turekian; vol. ed. A. M. Davis), Elsevier Ltd., Oxford, Online update only. Vol. 1.02 pp 1-33.

[4] E. Zinner, Space Sci. Rev. **56**(1-2), 147 (1991), [5] E. Anders & E. Zinner, Meteoritics **28**, 490 (1993).

[6] M. Jadhav et al., New Astron. Rev. **50**(7-8), 591 (2006).