

Analysis of extraterrestrial particles using monochromated electron energy-loss spectroscopy

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Abstract

A monochromated (scanning) transmission electron microscope was used to analyze individual sub-micron grains within interplanetary dust particles (IDP). Using low-loss and core-loss electron energy-loss spectroscopy, we analyzed fluid and gas inclusions within vesiculated aluminosilicate grains. It is shown that nanometer-sized vesicles contain predominantly molecular oxygen (O₂) beside a small fraction of H₂O. Low-loss spectra reveal the Schumann–Runge continuum peaking at 8.6 eV and absorption bands reflecting vibrational excitation states of O₂ molecules between the first (12.1 eV) and second (16.1 eV) ionization energy. The presence of oxygen gas is supported by the corresponding oxygen K-edge fine structure. The valence state of Fe in iron-oxide within the IDP was also studied. Low-loss spectra provide qualitative information about the oxidation state of iron consistent with the Fe²⁺/Fe³⁺ ratio quantitatively derived from the Fe L_{2,3} edge. Published by Elsevier Ltd.

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1. Introduction

1.1. Techniques

Valence electron energy-loss spectroscopy (VEELS) and core-loss electron energy-loss spectroscopy (EELS) are widely used in (scanning) transmission electron microscopy to probe the electronic structure of materials (see, e.g. Howie and Milne, 1985; Dorneich et al., 1998; French et al., 1998; Rafferty and Brown, 1998; Muller et al., 1999; Jiang et al., 2003; Allen et al., 2003; Rez et al., 1995). Both, the energy-loss near edge structure (ELNES) and the fine structure in VEEL spectra, contain specific information about the electronic structure of a material, i.e. about its density of unoccupied electron states. The information accessible with these techniques is, however, not identical.

The near edge fine structure in core-loss spectroscopy reflects the symmetry-projected density of states, governed by dipole-allowed transitions and here particularly important, it is the *local* density of states, i.e. the density of states at the site the atom is being excited (see, e.g. Egerton, 1996).

VEELS maps the unoccupied electron states of a solid in a different way; the valence region of an EEL spectrum reflects energy losses caused by the excitation of outer shell (or valence) electrons to unoccupied states above the Fermi level. For semiconducting or insulating materials, an electron is excited from a valence band to a conduction band. The lowest potential energy loss a primary electron can undergo by inelastic electron–electron scattering corresponds to the energy gap between the highest occupied and the lowest unoccupied state, i.e. the band gap. Interband as well as intraband transitions can thus directly be accessed by VEELS (Van Benthem et al., 2001; Rafferty and Brown, 1998). In a simple approach, an electron state in an energy band (whether occupied or not) is intrinsic for the solid and can neither be attributed to a certain atomic species nor be localized within the solid. It is primarily information about

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the *non-localized, joint* density of states, i.e. about the band structure of the material, which is measured by VEELS.

Although the information provided by these two techniques is not fundamentally different, by combining ELNES spectroscopy and VEELS, the electronic structure of a material can be studied from different points of view. VEELS accesses inherent information about the band structure of a material (Van Benthem et al., 2001; Rafferty and Brown, 1998), whereas ELNES complementary provides the local density of states, which contains more explicit information about the bonding characteristics of a certain element (Egerton and Whelan, 1974; Muller et al., 1999). Although the combined ELNES and VEELS approach is promising, applications of simultaneously utilizing both techniques to study materials are rare (Guitérrez-Sosa et al., 2003; Schmid, 1995). Owing to a lack in energy resolution, broad tails of the zero-loss beam typically impact the signal to background ratio in the valence-loss region. Hence, it has been difficult to extract detailed information from the valence- or low-loss region of an EEL spectrum, particularly at energy losses below ~ 5 eV. Elaborate data processing techniques have been developed in order to expand the accessible energy range down to ~ 2 eV (Reed and Sarikaya, 2002). Here we use a monochromated (scanning) transmission electron microscope providing an energy resolution of ~ 0.2 eV to analyze two different grain types in interplanetary dust particles. Information obtained from core-loss and low-loss EEL spectra are combined to form a more complete picture of the particles. Besides the improved energy resolution in core-loss edges and in the low-loss region, by maintaining a high signal to background ratio, low-loss spectra can directly be interpreted down to about 1 eV electron energy loss.

It has been proven that quantitative electronic structure information, i.e. the dielectric function, can be extracted from VEEL spectra of known compounds (French et al., 1998; Dorneich et al., 1998; Van Benthem et al., 2001). In the present work, the compound, its local defects and stoichiometry are not a priori known. In a first step, the low-loss region of an unknown compound can be compared with spectra of known standard samples. This allows for identifying certain absorption features as, e.g. the band gap and exciton states, and thus for describing the basic electronic characteristics of the material.

In addition to band structure information and low energy core-loss edges, low-loss EELS provides information about excitation states of single gas molecules. Similar information is commonly accessed via vacuum ultraviolet (VUV) (see, e.g. Patel et al., 2002) or low-energy electron energy-loss spectroscopy with a primary energy down to ~ 100 eV and an energy resolution of ~ 25 meV (Johnson and Kanik, 2001). Although the spectral resolution of EELS in a monochromated electron microscope (still) does not reach the spectral resolution of VUV and low-energy high-resolution EELS, the key advantage of EELS performed in scanning transmission mode is the spatial resolution.

Precise spectral information of materials on the (sub-)nanometer scale can be accessed.

1.2. Interplanetary dust particles

Interplanetary dust particles (IDPs) are a rare example of natural 'nano-materials'. They are collected in the stratosphere at ~ 20 km altitude using NASA ER2 aircraft and they consist of heterogeneous aggregates of submicrometer-sized silicate minerals, organic and inorganic carbon, implanted solar wind gases, and a variety of other nanometer-sized mineral inclusions such as FeNi metals and FeNi sulfides (Sandford, 1987; Bradley, 1994a,b; Flynn et al., 2004; Bradley, 2004). A single ~ 10 μm diameter IDP may contain $> 10^6$ mineral crystals mixed with (silicate) glass and carbonaceous matter. IDPs are from comets and asteroids and some of them are more cosmically primitive (unaltered) than even the most primitive meteorites. These IDPs carry a record of physiochemical conditions in the solar nebula and presolar interstellar and circumstellar environments (Flynn et al., 2004; Bradley, 2004; Bradley et al., 1999). The high spatial resolution of analytical transmission electron microscopy provides a means of accessing this record.

Although crystalline silicate minerals like forsterite (Mg_2SiO_4) and enstatite ($\text{Mg}_2\text{Si}_2\text{O}_6$) are found in IDPs, most of the silicates are amorphous with properties similar to those of common silicate glasses (see, e.g. Bradley, 2004; Henning, 1998). Since these glasses are sometimes non-stoichiometric they likely contain electronically active defects like dangling bonds. Pure magnesium silicates and aluminosilicates are the most common glasses in IDPs. Irradiation, hydration, oxygen excess, and oxygen deficiency may contribute to local chemical and local structural disorder within these glasses. Oxygen deficiency may lead to local defects of SiO_4 tetrahedra which results in electronically active defects such as E' centers. The variety of potential silicate defects is thus expectedly large. However, since the silicate glasses often contain a variety of nanometer-sized inclusions, the analysis of the silicate matrix phase is just one step in the characterization of a certain grain type.

During atmospheric entry, all IDPs are frictionally heated for a few seconds as they decelerate from cosmic velocity (≥ 10 km s^{-1}) at ~ 90 km altitude. The peak temperature depends primarily on the particle size, density, speed and entry angle (Love and Brownlee, 1996). Many IDPs contain solar flare tracks indicating that they were not heated above ~ 650 $^\circ\text{C}$ during atmospheric entry (Bradley et al., 1984). Others are heated above 1000 $^\circ\text{C}$ leading to loss of volatiles (e.g. S) and in some cases complete recrystallization (Sandford and Bradley, 1989; Germani et al., 1990). The IDP described in this study appears to have suffered intermediate heating (850 – 1000 $^\circ\text{C}$) as evidenced by erasure (annealing) of solar flare tracks, accumulation of submicrometer-sized vesicles within their glassy components,

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