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Laboratory X-ray microscopy for high-resolution imaging of environmental colloid structure

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ABSTRACT

Transmission X-ray microscopy is a uniquely suited technique for studies of environmental colloids since it allows imaging in aqueous media with high spatial resolution, presently down to the 20 nm range. Such nano-scale morphological description of these high-specific-surface-area compounds show promise for improved understanding of soils, sediments or groundwater aquifers. However, present high-quality X-ray microscopes are located at synchrotron radiation facilities resulting in limited applicability and accessibility for colloid scientists. Here we investigate the applicability of a laboratory-scale transmission X-ray microscope for studies of colloids of the environment. The microscope is based on a laser-plasma source in combination with multilayer and zone plate optics. Samples are held at atmospheric pressure in their natural wet state. We show images revealing the nano-scale morphology of the clay nontronite, soils such as chernozem and luvisol, and the mineral hematite, an iron oxide. Comparative studies of dried substances clearly show the need for imaging in the wet state. The image quality approaches that of synchrotron-based microscopes, albeit at longer exposure times. Stereo imaging is investigated as a means for giving 3D information with shorter exposure times than tomography requires. Finally the future development of the laboratory X-ray microscope is discussed, especially with regard to the reduction of exposure times.

1. Introduction

High-resolution imaging of environmental colloids is of central importance for the understanding of, e.g., soils, sediments, and aquatic systems. Transmission X-ray microscopy is especially suitable for this purpose since it allows morphological imaging on the nano-scale in the natural aqueous state. Unfortunately, present X-ray microscopes rely on large-scale synchrotron sources, thereby prohibiting their localization in the individual environmental colloid science laboratory as one tool among others. In the present paper we demonstrate laboratory-scale transmission X-ray microscopy of wet soil samples with synchrotron-like image quality.

The science of environmental colloids (Sumner, 2000; Senesi et al., 2009; Frimmel and Niessner, 2010) is highly interdisciplinary, spanning from microbiology over surface chemistry to reology and physics. Consequently, the environmental colloid laboratory requires a wide spectrum of advanced instrumentation, from biology to physics, and including imaging (Senesi et al., 2009; Frimmel and Niessner, 2010). However, soils and other environmental colloids present an unusually challenging nano-scale imaging problem. The mm to sub-μm porous soil structure determines the inner surface of a soil and effects important parameters and processes such as turnover of nutrients, adsorption of toxicants, bioavailability of substances, water storage capacity, and water flow. These micro pores are mainly built up by inorganic colloids such as clays, quartz particles, iron and aluminium oxides, or organic colloids as bacteria, fungi, or humic substances. Finally we note that nearly all chemical reactions and biological activity occur in the aqueous phase. Therefore nanometer-resolution imaging of the natural wet-state structure is of fundamental importance for the scientific understanding of soils. The properties of X-ray microscopy makes it uniquely suitable for morphological imaging in the aqueous state.

X-ray microscopy is an emerging technique for high-resolution imaging by exploiting the short wavelength of X-rays in combination with novel optics. Applications range from biology to materials. Susini et al. (2003), Aoki et al. (2006) and David et al. (2009) provide a good overview of the present status of the field. Transmission X-ray microscopy (TXM) in the water-window ($E = 284–540$ eV; $\lambda = 2.3–4.4$ nm) exploits the difference in absorption between the carbon and oxygen K-edges to obtain natural wet-state contrast between organic material and water (Attwood, 1999). The primary application field is in cell biology (Kirz et al., 1995; Uchida et al., 2009). The absorption coefficient of water is typically 0.1 μm^{-1}, thus, allowing approx. 10-μm-thick samples to be imaged. The absorption coefficient for organic soil material is typically 10× higher (and more for inorganic

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material), providing strong natural contrast (cf. Fig. 1). The resolution is presently approx. 25 nm (half period), i.e., an order of magnitude higher than competing methods for the wet-state imaging such as optical microscopy. TXM resolution is expected to improve since it is presently limited by the fabrication of the optics (so called zone plates) and not by fundamental issues such as in optical microscopy. Taken together these intrinsic properties give TXM a unique potential to become the high-resolution imaging tools of choice for wet-state science. In addition we note that scanning transmission X-ray microscopy (STXM) allows for chemical analysis with high spatial resolution (Thieme et al., 2010). Present X-ray microscopes, transmission as well as scanning, rely on the high brightness of large-scale synchrotron radiation sources. Consequently practically all XRM imaging on environmental colloids has been performed at these large-scale facilities (see, e.g., Thieme et al., 2007; Harutyunyan et al., 2009; Thieme et al., 2010). Unfortunately, the scale of this source prohibits the microscope to be co-localized with other instruments in the local environmental colloid science laboratory. This complicates interdisciplinary studies on the same samples with several methods.

The first sub-visible-resolution water-window laboratory transmission X-ray microscope (Berglund et al., 2000) was enabled by the development of the high-brightness liquid-jet laser-plasma source (Rymell and Hertz, 1993; Jansson et al., 2005). Present laboratory TXMs (Takman et al., 2007) are based on this source in combination with multilayers as condenser optics (Stollberg et al., 2006) and diffractive optics (Attwood, 1999; Holmberg et al., 2004) for the high-resolution imaging. These TXMs have demonstrated imaging of diatoms, cells, and colloids, recently with better than 25-nm half-period resolution using a special compound micro zone plate (von Hofsten et al., 2009). Alternative laboratory TXM configurations include discharge sources (Rudolph et al., 1994; Benk et al., 2008) and reflective optics (Hoshino and Aoki, 2008), both resulting in lower resolution and/or lower contrast.

In the present paper we apply laser-plasma-based laboratory X-ray microscopy to soil science and demonstrate laboratory XRM approaching synchrotron quality as regards contrast and resolution. Furthermore, and in recognition of the importance of 3D imaging, we demonstrate stereo imaging (Gleber et al., 2009) of soils with a simple arrangement. Although tomography (Bertilson et al., 2009) naturally provides more information, the shorter exposure time of stereo imaging is of special importance when operating laboratory XRM.

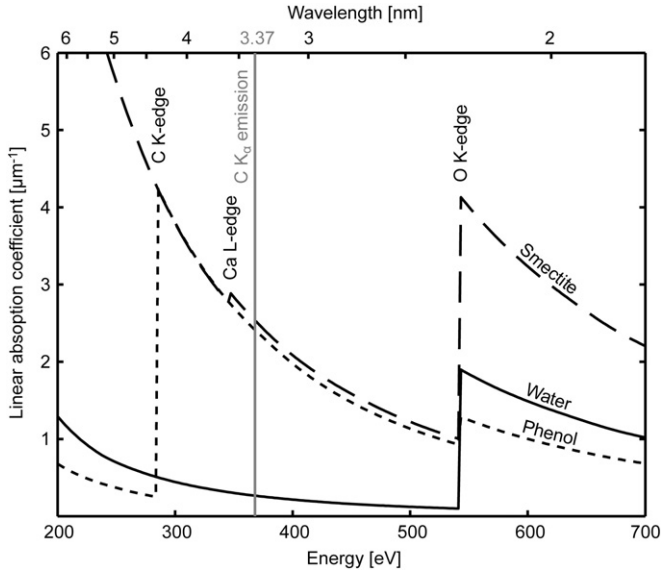

Fig. 1. Linear absorption cross-section μ_l of the mineral smectite, the organic substance phenol and water as a function of X-ray energy. The absorption edges of oxygen, calcium and carbon are indicated as well as the operation wavelengths of the laboratory X-ray microscope.

2. Laboratory X-ray microscopy for soil science

The transmission laboratory X-ray microscope operates in water-window. Fig. 1 compares the linear absorption coefficients μ_l (1/μm) for water, the inorganic clay mineral smectite and the organic substance phenol as a function of the X-ray energy. Smectite and phenol represent abundant classes of inorganic and organic matter, respectively. The large difference in absorption between water and organic or inorganic substances in this spectral region provides a natural contrast mechanism for specimens in an aqueous environment. These types of samples can therefore be imaged using an X-ray microscope without the need of drying, fixating or staining the sample. Depending on thickness of the samples to be studied, contrast can be improved by choosing the operating wavelength/energy of the microscope.

Fig. 2 shows the experimental arrangement of the laboratory X-ray microscope used for the soil studies. The major components are the regenerative liquid-jet laser-plasma source, a multilayer condenser mirror, a helium filled sample environment, a micro zone plate objective for the high-resolution imaging, and a back-illuminated soft X-ray-sensitive CCD detector. The microscope can be operated at two different wavelengths, $\lambda = 2.48$ nm and $\lambda = 3.37$ nm (501 eV and 368 eV, respectively) (Takman et al., 2007). Due to the thin samples studied in the present paper, all experiments were performed at $\lambda = 3.37$ nm, as indicated in Fig. 1. Consequently the description below focuses on this mode of operation.

The liquid-jet laser plasma (Rymell and Hertz, 1993) is a high-brightness soft X-ray source well suited for laboratory X-ray microscopy. The source is spatially well defined and stable, allows high-repetition-rate operation due to its regenerative target system, produces minimum debris and has narrow-bandwidth line emission (Wilhein et al., 1997) suitable for chromatic optics such as zone plates. The $\lambda = 3.37$ nm source used in the present experiments was generated by focusing the beam of a pulsed (100 Hz, ~3 ns), frequency-doubled Nd:YAG laser (Coherent Infinity 40–100) onto the laminar part of a ~10 μm diam methanol jet (de Groot et al., 2003). Pulse energies up to ~130 mJ, corresponding to focal intensities of $\sim 2.5 \times 10^{13}$ W/cm^2, were used. This produces a spectrum primarily consisting of helium and hydrogen-like carbon and oxygen with several lines in the 2–4 nm wavelength range. On average, the X-ray flux is $\sim 5.0 \times 10^{11}$ photons/(pulse × sr × line) and the source size is ~25 μm FWHM. For operation at $\lambda = 2.48$ nm a liquid jet of nitrogen is used, resulting in emission from hydrogen-like nitrogen (Jansson et al., 2005). This source concept also has applications in the EUV regime (Hansson and Hertz, 2004).

The condenser is a normal-incidence Cr/Sc multilayer mirror with approx. 3% reflectivity (Stollberg et al., 2006; Takman et al., 2007). This 0.064 numerical aperture (NA) optic images the plasma source onto the specimen (critical illumination). Due to the narrow reflectivity peak of the multilayer mirror, it acts as a monochromator selecting the $\lambda = 3.37$ nm emission line from the plasma. Furthermore, the intense laser light and other visual wavelengths are blocked by a 300 nm thick free-standing titanium filter.

The high-resolution imaging relies on nickel zone plates as objectives (Holmberg et al., 2004). These circular diffraction gratings were fabricated on silicon nitride membranes with an in house tri-level nanostructuring process including e-beam lithography, reactive ion etc. steps and nickel electro-plating. The resolution of zone plate imaging typically is equal to the outer zone width, dr_n. Images in the present paper were acquired using a zone plate with $dr_n = 25$ nm outer zone width, which means its numerical aperture is matched to the numerical aperture of the condenser illumination. The first-order efficiency of this zone plate is about ~8.5% at $\lambda = 3.37$ nm (Bertilson et al., 2007).