

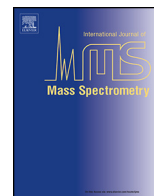


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The challenge of generating iron-sulfur clusters

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ABSTRACT

Free iron-sulfur cluster cations are generated by the sputtering of targets which are composed of a mixture of iron and sulfur powder and the produced cluster distributions are analyzed with a quadrupole mass spectrometer. As the iron powder is prone to the facile oxidation by air, a significant amount of oxygen in the targets is observed. Consequently, the determination of the exact cluster composition is impeded by the almost identical mass of S and O₂. Therefore, a series of targets with different material compositions have been investigated to assist the stoichiometric assignment of the produced cluster cations and to gain insight into the influence of oxygen on the production of iron-sulfur clusters. The generation of iron-chalcogenide clusters Fe_xO_yS_z⁺ (x = 2–4) is studied as a function of target composition and compared with the cluster generation by sputtering the mineral pyrite.

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1. Introduction

Small iron-sulfur clusters represent the central components of the naturally occurring iron-sulfur proteins and are thus of fundamental importance to all living organisms. Apart from their function as electron transfer media in biochemical redox reactions, iron-sulfur clusters also act as catalytically active centers in enzymes such as nitrogenase and hydrogenase [1,2]. In particular, their outstanding catalytic activity at mild reaction conditions renders them prototype systems for a 'green', i.e. environmentally friendly and sustainable catalysis.

Thus, the investigation of the electron transfer processes and catalytic reactions of iron-sulfur proteins is not only of importance with respect to the understanding of the naturally occurring processes but can also fundamentally assist the targeted development of industrial heterogeneous and homogeneous catalysts. Toward this goal we intend to pursue a completely new approach by mimicking the catalytically active centers of iron-sulfur proteins in the form of gas phase clusters and by studying their intrinsic redox activity and catalytic properties. Since both theoretical and experimental studies on the structure [3–7] and reactivity [8–14] of free iron-sulfur clusters are still scarce and have only been reported for selected systems, comprehensive investigations of the influence of cluster size, composition and charge on the cluster properties are of particular interest. This will allow to gain insight

into fundamental processes on a strictly molecular level and to develop general concepts.

The first step in this approach is of course the production of suitable gas phase model systems. In the literature three different methods for the generation of free iron-sulfur clusters are described: (1) the generation of iron clusters and subsequent reaction of those with C₂H₄S, COS, or CS₂ [12,15], (2) the generation of ligated iron-sulfur anions via electrospray ionization [5], and (3) the laser ablation of binary iron-sulfur targets [9,10,14,16–19]. These latter targets are typically fabricated by compressing a mixture of iron and sulfur powder of different compositions. However, iron and especially highly dispersed iron powder is easily oxidized at air which should lead to a considerable amount of oxygen in the target and thus in the produced clusters. Since one sulfur atom has almost the same mass as one oxygen molecule ($m(^{32}\text{S}) = 31.97 \text{ u}$ and $m(^{16}\text{O}_2) = 31.99 \text{ u}$) the unambiguous peak assignment in the produced cluster distributions is expected to be difficult. Surprisingly, this problem has not been addressed so far in the literature. Only Bernstein and coworkers mentioned the observation of oxygen containing clusters Fe_xO_yS_z⁺ due to trace amounts of oxygen impurities in the targets or the carrier gas [10].

In our experimental approach, iron-sulfur clusters are produced by sputtering of binary iron-sulfur targets with high energetic xenon ions. Recently, it has been shown that the sputtering of air pre-oxidized metal targets can lead to the production of a considerable amount of metal-oxide clusters in this sputter source [20,21]. Thus, it is essential to gain insight into the influence of oxygen on the production of iron-sulfur clusters and the degree of oxygen contamination.

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In this contribution, we present cluster ion distributions obtained by sputtering a series of targets with different Fe:S ratios compressed from iron and sulfur powder. The generated iron-chalcogenide cluster ($\text{Fe}_x\text{O}_y\text{S}_z^+$) distributions are compared with the cluster distribution generated by sputtering the mineral pyrite (FeS_2). This systematic study provides insight into the influence of the oxygen contamination on the iron-sulfur cluster generation and assists the unambiguous assignment of the stoichiometry of the pure iron-sulfur cluster cations.

2. Experimental method

2.1. Experimental setup

The production of small iron-chalcogenide clusters has been studied in a high vacuum setup consisting of a sputter source and a quadrupole mass spectrometer. The cluster source is composed of a high energy xenon ion source (CORDIS, Cold Reflex Discharge Ion Source) and a sputtering region [22,23,31]. An enlarged view of the source is shown in Fig. 1.

The CORDIS is filled with about 6×10^{-2} mbar xenon gas. This gas is ionized by electrons which are generated via six resistively heated tantalum filaments (about 170A/6V for tantalum wires with a diameter of 1 mm). To increase the ionization yield, the filaments are surrounded by 18 radially placed permanent cobalt-samarium steering magnets and an additional voltage of about 80 V is applied to the magnets.

The xenon cations Xe^+ are extracted, accelerated, and focused by a series of three cylindrical lenses. For this purpose a voltage of

about +10 kV is applied to the whole ion production region as well as the first lens. A voltage of up to -3 kV is applied to the second lens, and the third lens is grounded. These lenses are designed to allow for the extraction of four spatially separated xenon ion beams (indicated by red lines in Fig. 1) which are then focused onto four targets. The xenon ion current at the targets is on the order of several μA and the sputter yield is estimated to be on the order of 10^{-3} – 10^{-5} for cationic clusters independent of the target material used in this study.

The targets are attached to water cooled copper blocks in an angle of 60° with respect to the Xe^+ beam which is optimal for a large sputtering yield [24]. Furthermore, a repelling potential (typically about +40 to +70 V) is applied to the targets to release the ionic clusters (indicated by green lines in Fig. 1) more easily. Additionally, a water cooled copper repeller plate is located across from the targets in order to reverse the direction of the cluster motion (typical voltage of +60 to +90 V). After reflection of the charged particles, they are focused into a quadrupole ion guide via an electrostatic Einzel lens system (typical voltages of +40 to +60 V/ -120 to -180 V/+40 to +60 V are applied). The quadrupole ion guide is filled with helium (typically about 6×10^{-2} mbar) to collimate and cool down the cluster beam before entering the quadrupole mass spectrometer. The mass-selected ion current is subsequently recorded on a Faraday collector and monitored by a picoampere meter (Keithley 617).

2.2. Target production

To gain insight into the influence of oxygen on the production of iron-sulfur clusters, a series of home-made targets with different material compositions (molar ratios) have been investigated: Fe:Fe₂O₃ = 6:1, Fe, Fe:S = 3:1, Fe:S = 2:1, and Fe:S = 1:2. All targets were produced by compressing well-mixed powders of iron (purity $\geq 99\%$, Sigma Aldrich), iron(III) oxide (99.999%, Sigma Aldrich) and/or sulfur ($\geq 99.5\%$, Sigma Aldrich) in a screw press (force of 60 N). In this way disk shaped targets (2 cm diameter, 2–3 mm thickness) could be produced that are rigid enough to be mounted on the Cu blocks (target holders). However, with this method we did not succeed to produce stable iron-oxide-targets. To nevertheless gain information about the production of iron-oxide clusters the iron-oxide powder was implemented into a matrix of iron powder. For comparison, targets cut from naturally occurring pyrite stone (FeS_2) were studied.

3. Results and discussion

Fig. 2 (left column) displays photographs of the different targets used (the photographs were obtained after sputtering for some hours) as well as the corresponding detected cluster cation distributions (right column). In the current experiment, the quadrupole mass spectrometer has been operated in a constant resolution mode which leads to a broadening of the peaks at higher masses. Furthermore, the voltages applied to the target, repeller, and the lens system depend on the cluster size of interest. To compensate these effects as good as possible each of the shown mass spectra represents a compilation of two different mass spectra, one recorded after optimization of the cluster source as well as the lens and quadrupole systems for production and detection of very small di- and tri-iron clusters $\text{Fe}_x\text{O}_y\text{S}_z^+$ ($x=2, 3$) and one after optimization for the slightly larger tetra-iron clusters $\text{Fe}_x\text{O}_y\text{S}_z^+$ ($x=4$). Typical cluster ion currents obtained after optimization range between 2 and 30 pA.

Fig. 2a shows a photograph of the iron-oxide target (Fe:Fe₂O₃ = 6:1) which exhibits the typical rust-red color of the iron(III)-oxide Fe₂O₃. The corresponding cluster distribution is

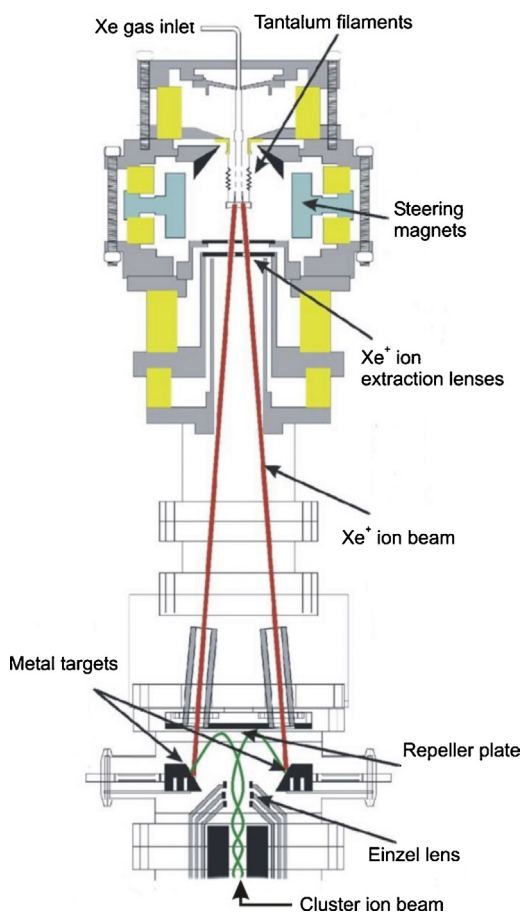


Fig. 1. Schematic drawing of the cold reflex discharge ion source (CORDIS) and the adjacent sputtering region. More details are given in the text.

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