

X-RAY ABSORPTION NEAR-EDGE SPECTROSCOPY (XANES) APPLIED to  
SELENIUM SPECIATION STUDY of INCRUSTATIONS from FOGO  
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## Introduction

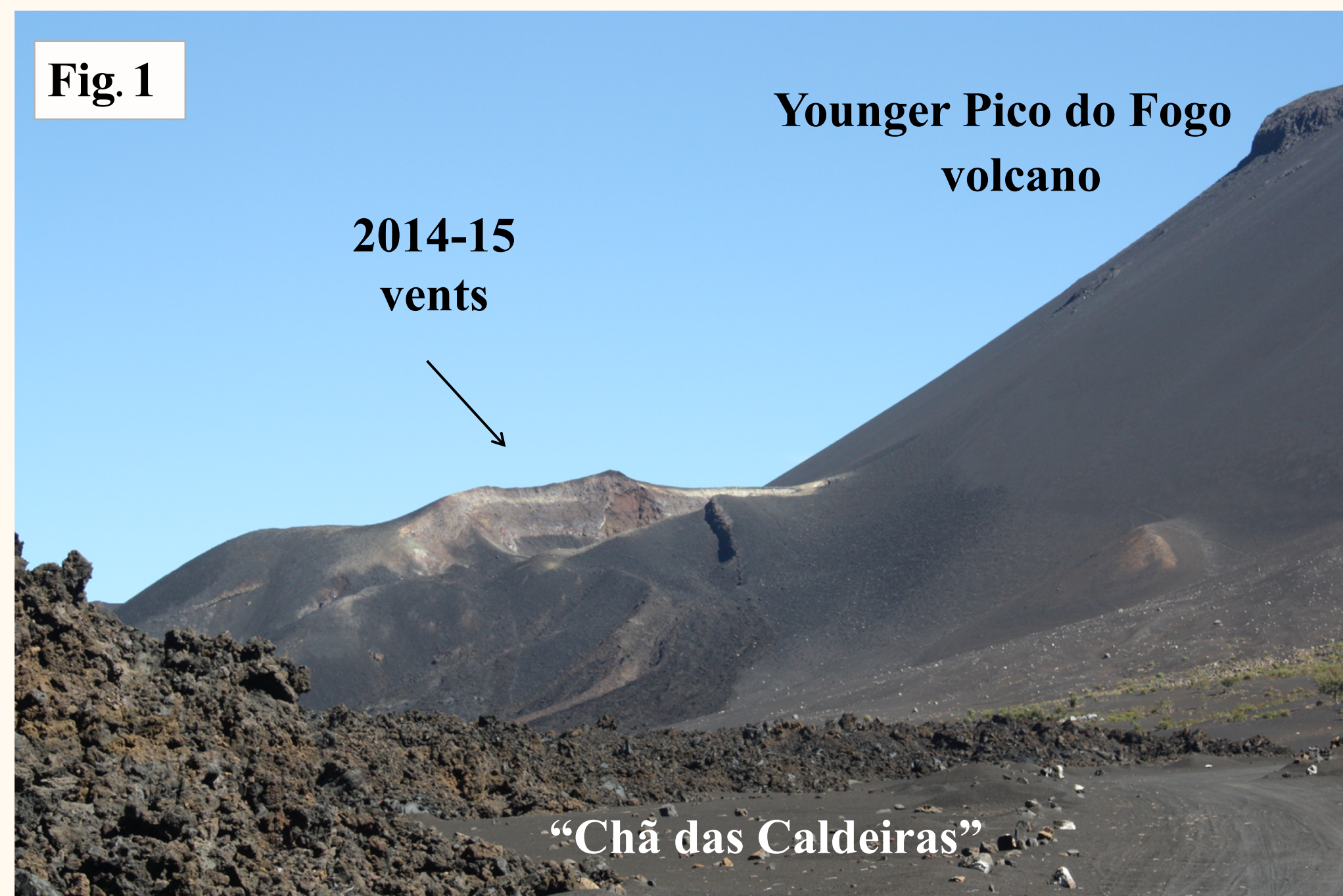
Selenium (Se), an element that usually substitutes sulphur, assumes a variable speciation state depending of the carrier mineral. This fact allied to the high concentration obtained for this element in fumarole incrustations samples from Fogo volcano (Fogo Island, Cape Verde archipelago) plays a major health hazard concern as local populations use sulphur and white materials as treatment for some diseases for themselves and for animals.

The most recent eruption of Fogo volcano, started on November 23, 2014 and lasted until February 7, 2015 (Fig. 1). Extensive lava flow fields (a'a and pahoehoe) were produced at "Chã das Caldeiras", that destroyed houses and agriculture (mainly vine and fruit plantations). The knowledge of the nature and range of heavy elements carried by gases emanating from active fumaroles after a volcanic eruption is vital, because frequently, such elements include metals, for example mercury, lead and the severely poisonous thallium [1].

Selenium is an essential nutrient for humans, but it becomes toxic at concentrations slightly above the nutritional levels. In the environment, Se can occur in several oxidation states ranging from selenide (Se<sup>2-</sup>) to elemental selenium (Se<sup>0</sup>), selenite (Se<sup>4+</sup>) and selenate (Se<sup>6+</sup>).

The main mineral phases present in incrustations resulting from the last eruption and potentially Se-carriers, were identified by X-ray diffraction: e.g. native sulphur (α-S), anhydrite (CaSO<sub>4</sub>), bassanite (CaSO<sub>4</sub>·1/2H<sub>2</sub>O), gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), thenardite (Na<sub>2</sub>SO<sub>4</sub>), ralstonite (Na<sub>x</sub>MgxAl<sub>2-x</sub>(F,OH)<sub>6</sub>·yH<sub>2</sub>O).

An X-ray absorption near-edge spectroscopy study (XANES) using synchrotron radiation was undertaken at Se K-edge (ESRF, beamline BM 25A), to clarify the speciation state of Se and the nature of Se-carrier phase(s), in fumarole incrustations samples from the last eruption.



## Materials and Methods

Two sampling campaigns were performed near the 2014-15 vents in November 2016 and in February 2017, and rocks (basaltic lava) plus incrustations were collected. Neighbouring to the principal vent, yellow (sulphur) and white materials (Fig. 2) were deposited on the field as well as orange-red coloured rocks.

The chemical characterization was achieved through X-ray Fluorescence Spectrometry with wavelength dispersive system (XRF-WDS) at the laboratory and through energy dispersive X-ray Fluorescence (EDXRF) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The experiments were performed with the instrumental set up of beamline BM 25A (Fig. 3), using an excitation energy of 20 keV (powdered samples and model compounds were placed between two Kapton foils, a pure adhesive tape). The EDXRF spectra collected during 300s for each sample were fitted using the PyMca software [2].

X-ray absorption near-edge spectra (XANES) were collected at the Se K-edge (12658 eV for elemental selenium) in fluorescence yield (FY) mode with an energy resolution of ΔE/E=1.5×10<sup>-4</sup> using a 13-element Si(Li) solid-state detector and a Si(111) monochromator. Pure lead metal foil was irradiated for energy calibration purposes.

Samples and Se-O model compounds (commercial products) were previously characterized by X-ray diffraction (XRD). Model compounds, were chosen to configure various formal valences and geometrical coordination of Se cations: Se<sup>4+</sup> in pyramidal coordination (selenite, SeO<sub>2</sub> and Na<sub>2</sub>SeO<sub>3</sub>) and Se<sup>6+</sup> in tetrahedral coordination (selenate, Na<sub>2</sub>SeO<sub>4</sub>).

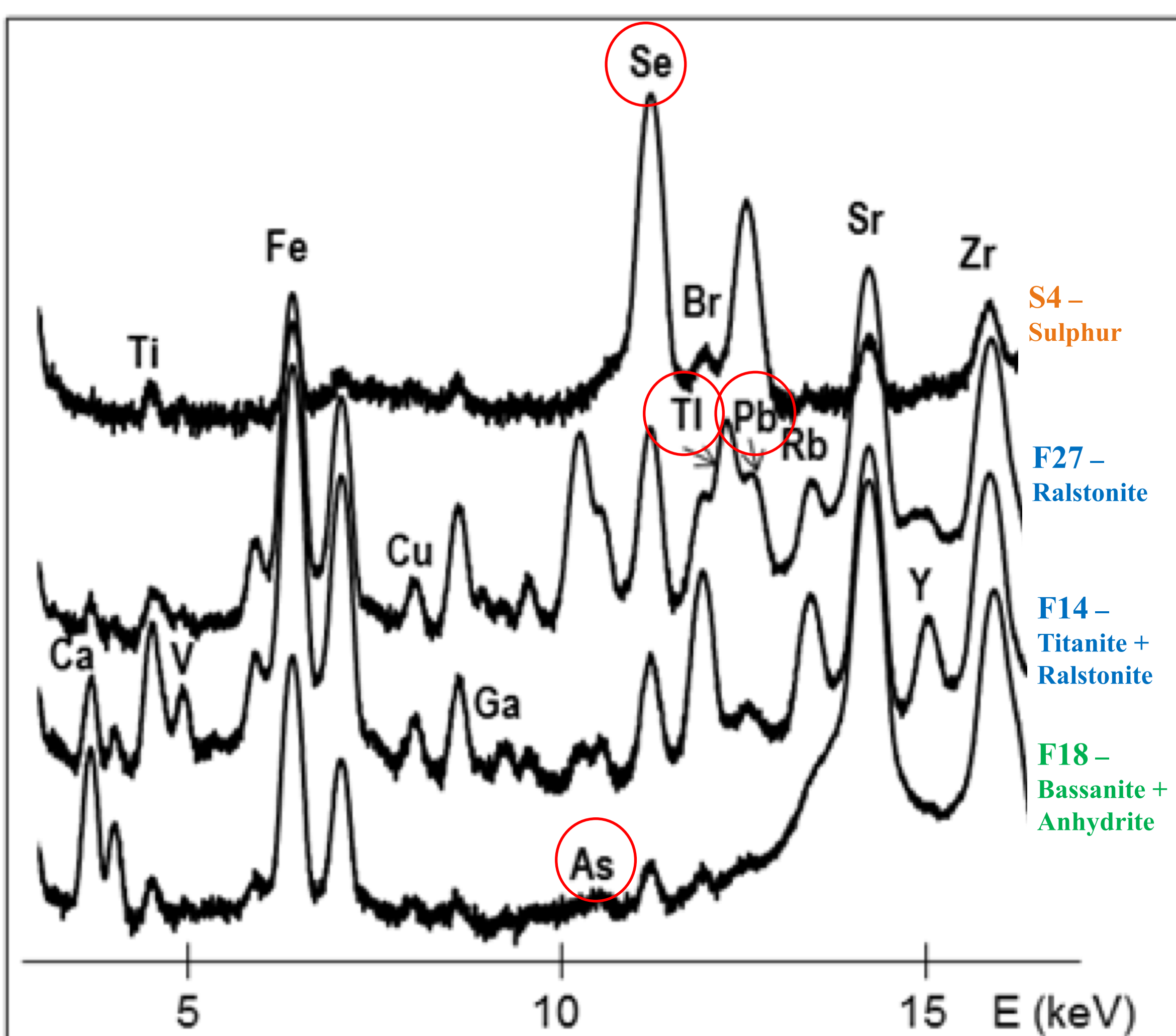


Fig. 4 – EDXRF spectra obtained for incrustations samples irradiated to collect the Se K-edge XANES spectra. Only the diagnosis line of each element is assigned [4].

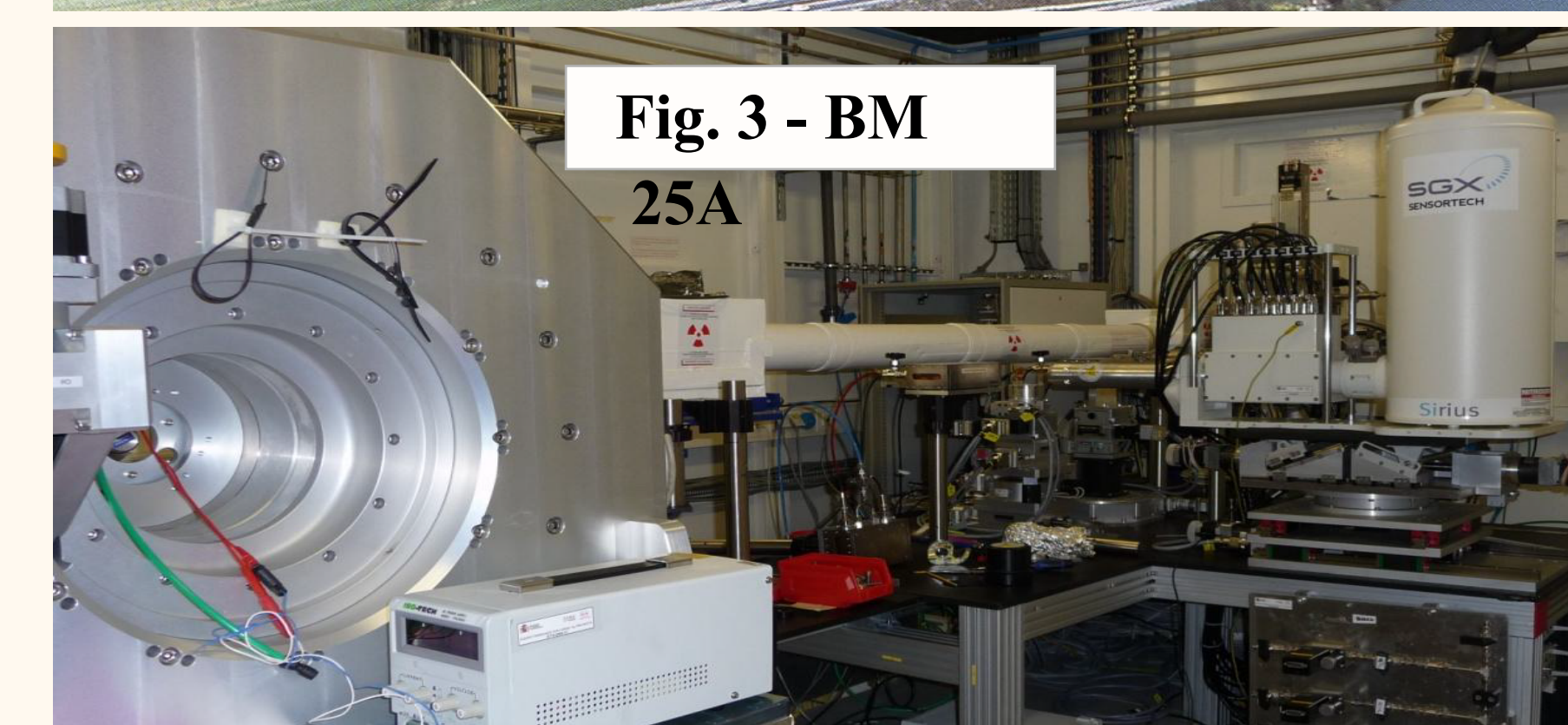
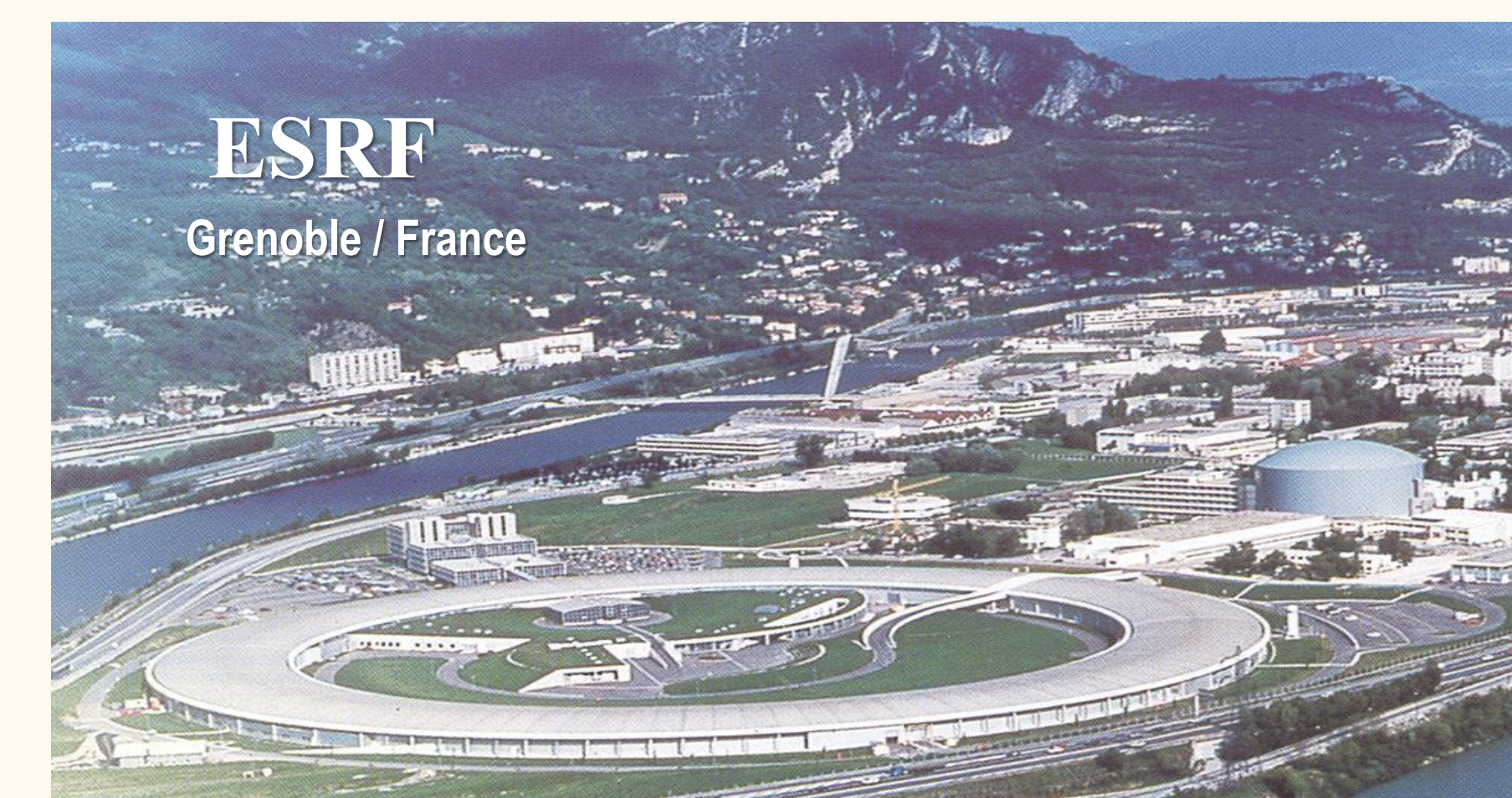
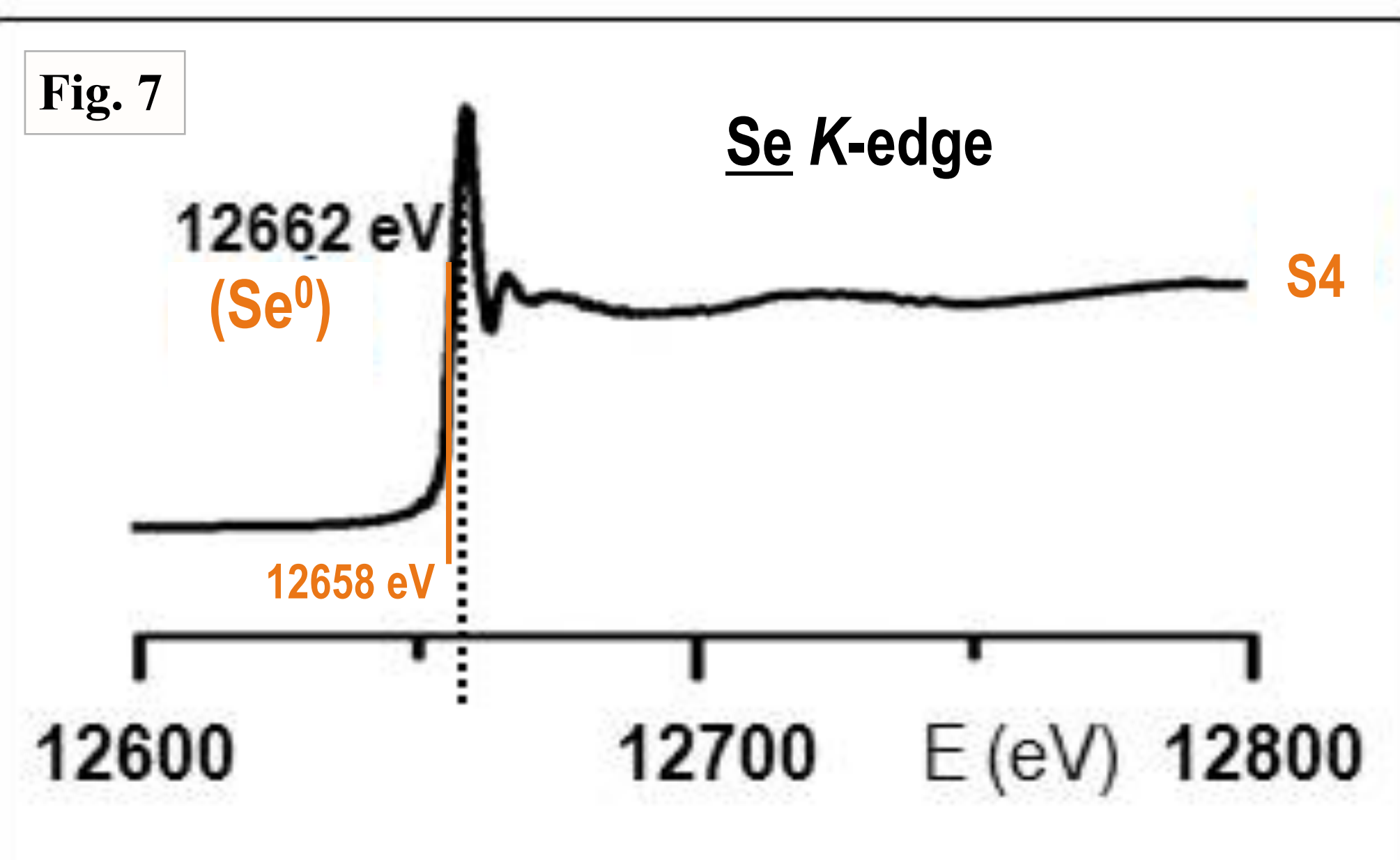
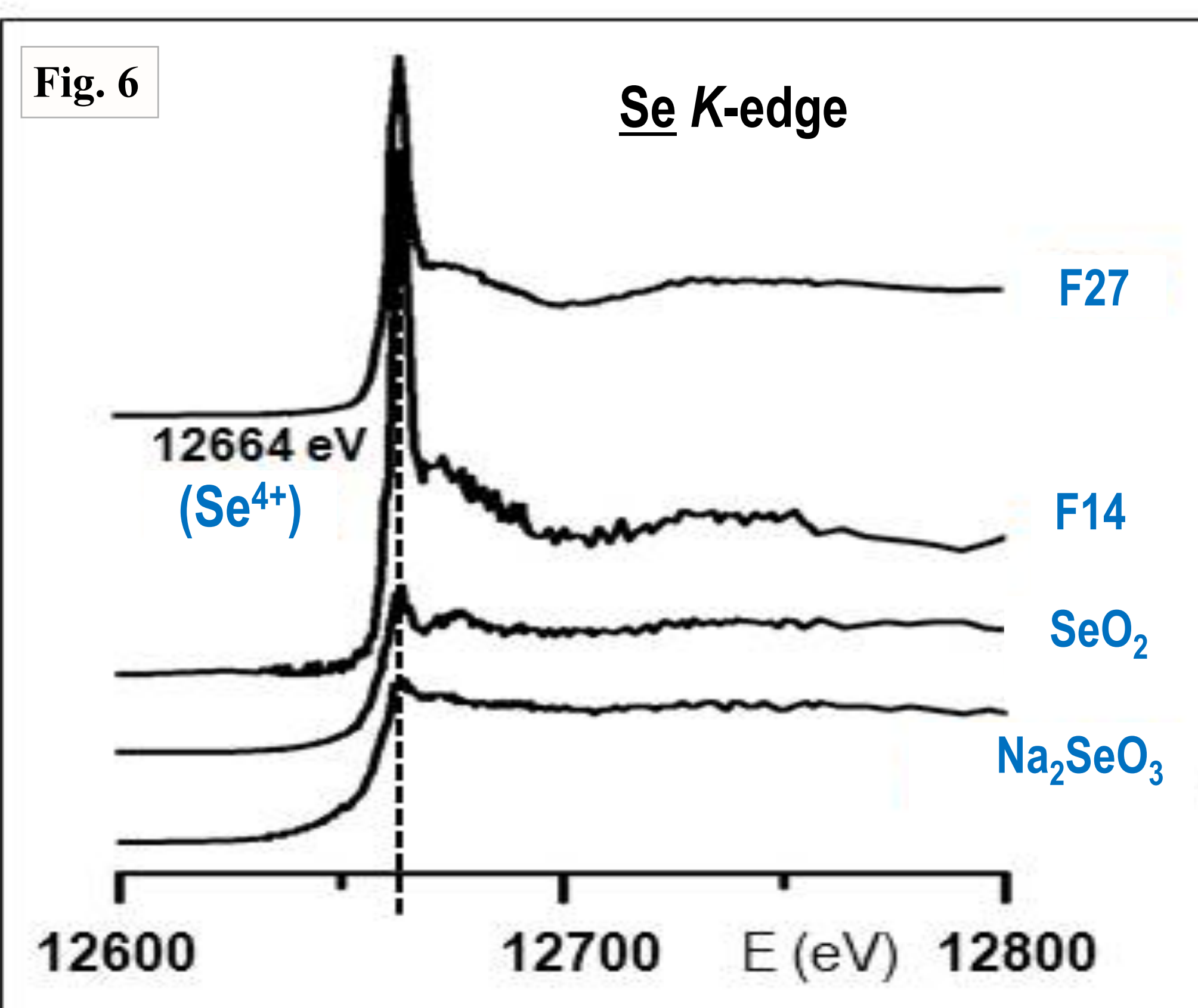
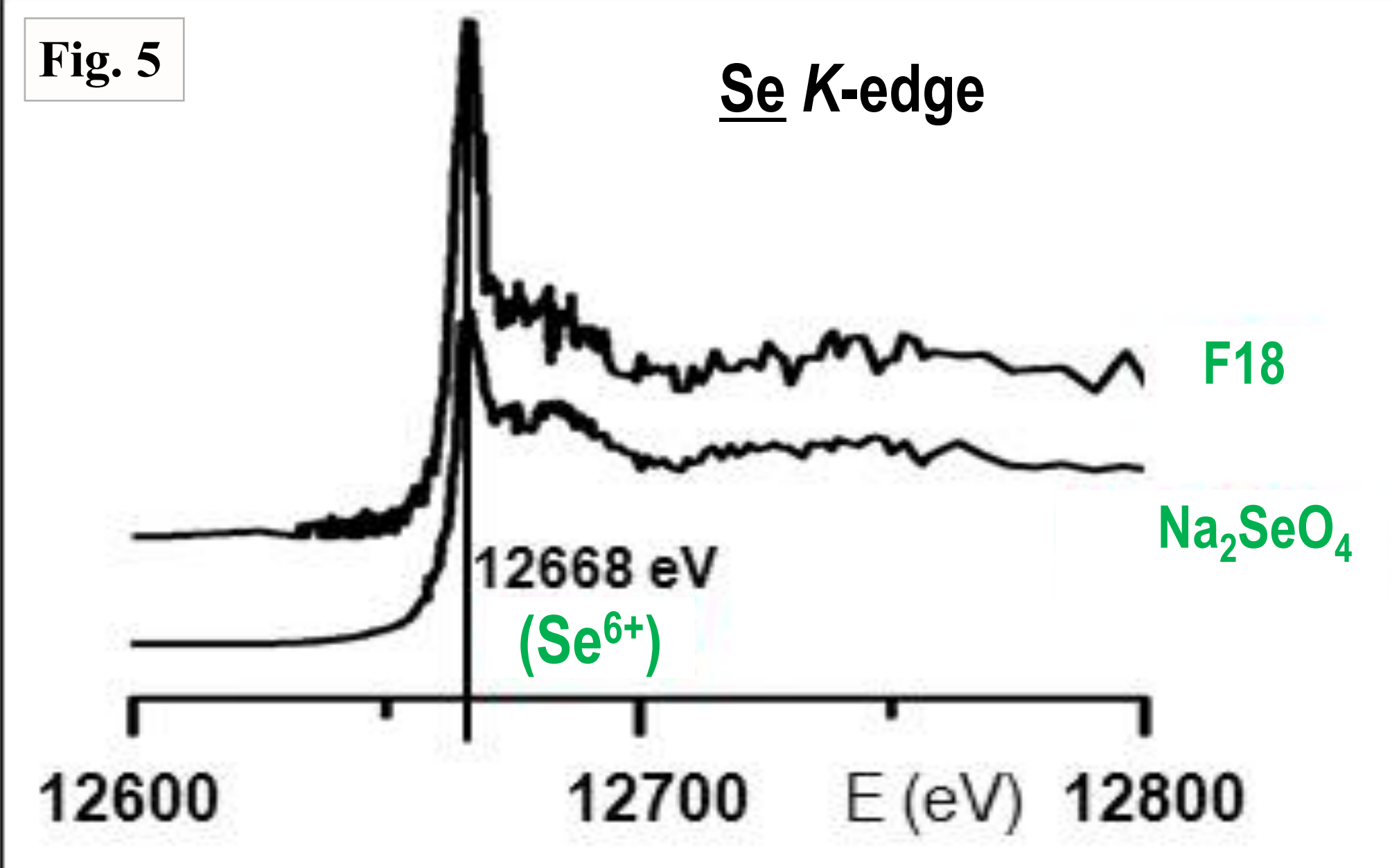
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## Results and Discussion

The highest content obtained for Se by XRF-WDS was 1000 ppm (1mg/g), being 0.3mg/day the tolerable upper intake level [3].

The EDXRF spectra (Fig. 4) showed that Se is mainly carried by sulphur (sample S4) but is also present in all samples. Ti and Pb are transported by ralstonite (F27 principally, but F14 as well) and As by the mixture of bassanite and anhydrite (F18). Sample F14, where bromine is well represented, is a mixture of titanite (CaTiSiO<sub>6</sub>) and ralstonite.

Different situations for Se speciation were observed through Se K-edge XANES spectra when comparing samples and model compounds: Se<sup>6+</sup> tetrahedral coordination in F18 sample (Fig. 5), due to replacement of S by Se in SO<sub>4</sub> tetrahedra that are linked to Ca atoms (anhydrite) or to Ca atoms and water molecules (bassanite); Se<sup>4+</sup> pyramidal coordination in F14 and F27 samples (Fig. 6) where selenium is probably linked to oxygen; and Se<sup>0</sup> in S4 sample (packing of S<sub>8</sub> ring molecules) due to diadochic replacement of S by Se (Fig. 7). The energy of the strong absorption maximum (white line) was highlighted, as well as the Se K-edge (12658 eV for Se<sup>0</sup>).

The high concentration plus the various oxidation states observed for Se, creates a great concern, because overexposure to Se in the diet, leads to gastrointestinal upsets, hair loss, white blotchy nails, fatigue, irritability, and mild nerve damage. A more complete chemical study by EDXRF and the ascertaining of the speciation state(s) of arsenic, thallium and lead (elements also present in incrustation samples and potentially toxic) are foreseen.