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Iron oxidation state variations in zoned micro-crystals measured using micro-XANES

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ABSTRACT

The determination of the oxidation state of transition metals at high spatial resolution is a crucial issue for many fields of science, including solid state physics, earth sciences, biology, bio-chemistry and catalysis. Among the other available analytical methods, micro-XANES allows to probe *in situ* the oxidation state with high lateral resolution, enabling an unprecedented level of description in heterogeneous samples. In geological samples the determination of the $Fe^{3+}/\Sigma Fe$ ratio is of particular interest since it can be used as an indicator of the oxygen fugacity (fO_2) at which a mineral formed. With this respect, we performed a micro-XANES experiment aiming to investigate the Fe-redox state variation across single-crystals of both garnet and omphacite exploiting the X-ray microprobe available at the ESRF ID22 beamline to reach a spot size of 1.7 μm × 5.3 μm. For garnet, the absolute Fe^{3+} content was determined in a space-resolved way. In the case of omphacite, the analysis of the XANES data is not straightforward owing to the presence of a significant dichroism effect and to the random orientation of the different grains in the mineral assemblage. The investigated samples are highly complex materials which represent a challenge for the micro-XANES technique. These zoned micro-crystals are therefore ideal systems to develop analytical procedures which can be subsequently generalized to other relevant fields of science such as the Fe speciation in a single cell or a single grain for life science and catalysis applications, respectively.

1. Introduction

The determination of the oxidation state of transition metals is a problem of primary importance for many fields of science, ranging from solid state physics to structural biology. X-ray Absorption Spectroscopy (XAS) is a powerful tool to address this issue since the analysis of the X-ray Absorption Near Edge Structure (XANES) region can simultaneously provide information on electronic and local structural properties.

Generally, XANES spectroscopy is performed using mm-sized X-ray beams, thus measuring absorption coefficients integrated over a relatively large volume [1]. However, in the last years the huge increase in the brightness of synchrotron radiation sources and the new developments in the X-rays focusing devices allowed to obtain intense (sub-)micron X-ray beams and to drastically improve the spatial resolution down to 10 nm [2]. The possibility to perform also XANES with high lateral resolution (micro-XANES) paved the way for a new level of description of heterogeneous samples or individual nanostructures [3,4]. For instance, micro-XANES is probably the unique analytical method available to probe *in situ* the oxidation state of trace elements within cell and subcellular compartments [5,6]. Interestingly, the two first studies that demonstrated the feasibility of micro-XANES on single cells were both devoted to the determination of Fe oxidation state [7,8].

Also in the field of heterogeneous catalysis probing the structural and electronic properties of materials *in situ* is of central importance and in many cases spatial variations in catalyst structure can be crucial as in the case of microstructured catalysts or integral catalytic reactors with prominent concentration and temperature profiles [9–15]. For instance, de Smit et al. studied the Fe-based Fischer Tropsch Synthesis (FTS) catalyst by imaging an individual catalyst particle at a resolution of 35 nm using chemical micro-spectroscopy [16,17]. Also Tada et al. investigated by Ni K-edge micro-XAS the oxidation state and local coordination structure of a single particle of a practical catalyst $NiO_x/Ce_2Zr_2O_y$

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using a 1.0 μm × 0.8 μm beam [18]. Another relevant example is the study of the spatial changes of the catalyst oxidation state in a fixed-bed microreactor as a function of temperature and velocity of the reaction mixture performed by Grunwaldt et al. [10,19]. The previously discussed studies adopted a scanning (sub-) micro-XAS mode: another possibility to obtain space resolved information on the element oxidation state is to use full-field transmission X-ray microscopy. This approach ensures larger field of views and faster acquisition times at sub-micrometric resolution, but cannot be used for trace elements detection and needs precise sample realignment after flat field acquisition [1,2,20,21]. The same Fe-based FTS catalyst studied by de Smit et al. [16] using a scanning approach was recently investigated also by full-field transmission X-ray microscopy allowing the *in situ* 3D characterization of an individual particle with nanometer spatial resolution and elemental sensitivity under realistic reaction conditions [22].

Finally, micro-XANES has been widely employed for the space-resolved determination of ferric iron contents on micrometric crystals without destroying their textural context [23–30]. In geological samples the determination of the $Fe^{3+}/\Sigma Fe$ ratio is of particular interest since it can be used as an indicator of the oxygen fugacity (fO_2) at which a mineral formed. In particular, micro-scale measurements of the $Fe^{3+}/\Sigma Fe$ ratio in zoned crystals are essential to understand the variations in the redox conditions experienced by the mineral during its progressive growth in different geodynamic contexts (*e.g.* during subduction at high- to ultra-high pressures [26,31] or at mantle depths [32]).

In this paper we present a micro-XANES study of the $Fe^{3+}/\Sigma Fe$ ratio spatial variations in two different minerals, garnet and omphacite, both occurring as strongly zoned micrometric crystals. The challenge of our investigation was threefold: (i) the $Fe^{3+}/\Sigma Fe$ variations across the zoned crystals are expected to be small (<10%), therefore a high spectral resolution is needed to appreciate the differences in the oxidation state; (ii) the spatial resolution has to be in the order of microns since the $Fe^{3+}/\Sigma Fe$ variations are expected to occur on a micrometric scale; (iii) for omphacite, which crystallizes in the monoclinic system, the effect of the X-ray beam polarization has to be considered, as it can result in X-ray dichroism effects.

From the above mentioned issues, it clearly emerges that the investigated samples are highly complex materials which represent a challenge for the micro-XANES technique. These zoned micro-crystals are therefore ideal systems to develop analytical procedures which can be subsequently employed also for different kinds of samples to measure *in situ* the iron oxidation state, relevant in the disciplines mentioned above: solid state physics, earth sciences, biology, bio-chemistry and catalysis.

2. Materials and methods

2.1. Samples description

The measured almandine ($Fe^{3+}/\Sigma Fe = 0$) and magnetite ($Fe^{3+}/\Sigma Fe = 2/3$) crystals are high purity reference standards for X-ray microanalysis (SPI Supplies – reference numbers: #AS1020-AB and #AS1210-AB), mounted in a 25 mm diameter, 6 mm thick non-magnetic stainless steel disk. The measured augite crystal ($Fe^{3+}/\Sigma Fe = 0$), well characterized at EMP-WDS (sample 5P104 [33]), belongs to a thin section of a marble from the Sesia Zone (western Alps), *ca.* 30 μm thick, mounted on a high chemical purity SiO_2 amorphous slide using Fe-free Araldit®-epoxy. The single crystal of aegirine ($Fe^{3+}/\Sigma Fe = 1$) characterized using micro-XANES is a high purity reference standard for X-ray microanalysis (sample H091 [33]) mounted in a 2 mm diameter, 10 mm thick non-magnetic stainless steel disk.

The investigated micro-crystals of garnet and omphacite belong to a fine-grained eclogite (from the Monviso meta-ophiolitic Massif, Italian western Alps), consisting of omphacite, garnet and rutile with minor blue amphibole and very minor lawsonite, talc and jadeite [34], petrologically interpreted by Groppo and Castelli [31]. The polished thin section (*ca.* 30 μm thick) is mounted on a high chemical purity SiO_2 amorphous slide using Fe-free Araldit®-epoxy. Garnet occurs as small idioblasts (up to 0.5 mm in diameter) set in a matrix mainly consisting of omphacite (up to 0.5–0.6 mm in length). Garnet cores are crowded of very small inclusions mostly of omphacite, whereas garnet rims are almost free of inclusions. Both SEM-EDS and EMP analytical techniques have been used to analyze the major element concentrations across garnet and omphacite crystals. The microphotographs of the analyzed garnet and omphacite micro-crystals are reported in Fig. 1.

Garnet is strongly zoned, showing an Mn and Ca decrease toward the rim, counterbalanced by a Fe and Mg increase. More in detail, the X_{Mn} decreases from 0.24 in the core to 0.00 in the rim and it is balanced by an increase in both X_{Mg} and X_{Fe} (X_{Mg} is 0.01–0.12, and X_{Fe} is 0.56 to 0.82 from core to rim, respectively). Ca zoning is more complex, slightly increasing from the inner core to the outer core and decreasing toward the rim (X_{Ca} varies from 0.21 to 0.27 and to 0.11 toward the rim [31]) [$X_{Mn} = Mn/(Ca + Mg + Fe^{2+} + Mn)$; $X_{Mg} = Mg/(Ca + Mg + Fe^{2+} + Mn)$; $X_{Ca} = Ca/(Ca + Mg + Fe^{2+} + Mn)$; $X_{Fe} = Fe^{2+}/(Ca + Mg + Fe^{2+} + Mn)$].

Omphacite in the rock matrix is also strongly zoned: the deep green omphacite core (Omp_c in Fig. 1c) has higher X_{Aeg} and lower X_{Jd} [$X_{Aeg} = 35 \rightarrow 28$; $X_{Jd} = 25 \rightarrow 35$; $X_{Mg}(Fe_{tot}) = 40–50$] than omphacite rim (Omp_r in Fig. 1c) [$X_{Aeg} = 24 \rightarrow 14$; $X_{Jd} = 35 \rightarrow 45$; $X_{Mg}(Fe_{tot}) = 52–66$] [$X_{Aeg} = Fe^{+3}/(Fe^{+3} + Al^{VI} + Fe^{+2} + Mg) \times 100$; $X_{Jd} = Al/(Fe^{+3} + Al^{VI} + Fe^{+2} + Mg) \times 100$; $X_{Mg}(Fe_{tot}) = Mg/(Mg + Fe)$] [31].

2.2. Micro-XANES spectroscopy

Fe K-edge XANES spectra were recorded at the ID22 beamline of the ESRF at Grenoble [35,36] which exploits the radiation produced by two different undulators: a standard linear undulator (U42), covering the energy range from 6 to 50 keV, and a second one (U23), which is a so-called in-vacuum linear undulator, inducing a much higher brilliance. Harmonic rejection is done by a flat horizontally deflecting Si mirror. A Kohzu fixed-exit double crystal monochromator with Si(3 1 1) crystals was employed in this work to ensure a better energy resolution (0.5 eV) compared to Si(1 1 1) crystals (1 eV).

The microprobe set-up is based on the Kirkpatrick-Baez (KB) mirrors [2], that allowed us to reach a beam size of 1.7 μm (vertical) × 5.3 μm (horizontal). The focused beam profiles were collected by means of knife-edge scans [37]. A gold cross deposited by electron beam lithography on an Si substrate is translated vertically and horizontally through the X-ray micro-beam using a well-calibrated piezo stage. Assuming a beam propagating with a Gaussian intensity profile, the beam sizes in both horizontal and vertical directions are estimated separately from the FWHM of the numerical derivative of the Au fluorescence intensity as a function of the position.

When the current on the ESRF ring is 200 mA, the KB mirrors, having an efficiency of approximately 70%, allow to obtain in the focal spot a photon flux of about 10^{12} photon/s at 13 keV. As visible in Fig. 2, different detectors such as a mini-ionization chamber and a Silicon Drift Detector are used to monitor the intensity of the incoming beam and the XRF signals. A video-microscope allows for the easy alignment of the sample and the microprobe set-up.

All XANES spectra were recorded in X-ray fluorescence mode. The samples were mounted at 45° with respect to both the incident beam and the Si drift detector (see Fig. 2c and d). XANES spectra