



	Experiment title: The binding state of rhenium in its natural carrier, molybdenite: a XANES study through the L-edges	Experiment number: CH-3421
Beamline: BM-23	Date of experiment: from: 20 September 2011 to: 23 September 2011	Date of report: 2011.11.15
Shifts: 9	Local contact(s): Dr. Carla Azimonte	<i>Received at ESRF:</i>
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Report:

Rhenium is a scarce metal occurring in Nature mainly associated to molybdenite (MoS_2) that occasionally may display a high content of both tungsten and rhenium [1]. Taking into account that the commercial route for molybdenum extraction involves the roasting of the molybdenite concentrate, much rhenium is expected to be lost under the form of gaseous Re_2O_7 , a molecular compound in which structure rhenium assumes both tetrahedral and octahedral coordination [2]. The formal valence of rhenium ranges from -1 to +7 and, due to the stability of this very high oxidation state, it has become technologically relevant in the production of catalysts, along with platinum. Nowadays it is applied in very distinctive areas, like the biomedical and nuclear fields, plus the electrical and aero-spatial industries, particularly for the production of super alloys [3]. Having in view the interest in exploring the mining residues of exhausted mines in various ore deposits in Europe aiming at a sustainable rhenium recover, the main purpose of the present experiment was to ascertain the binding state of Re in molybdenite, thus contributing to interpret the dominant hosting mechanism: diadochic/alleatory replacement of Mo or confined concentration under the form of specific nanophases.

XANES spectra from rhenium metal (for energy calibration) and well crystallized molybdenite fragments were collected in fluorescence yield (FY) mode. Molybdenite samples with different provenances were studied by scanning the L_3 -edges of Re at 10.535 keV and W at 10.207 keV (this element is commonly present in granite pegmatites and the interference with rhenium was checked): from the Merlin Zone of Mount Dore deposit in Australia (a molybdenum-rhenium porphyry deposit), from Aldfield Township in Quebec/Canada, from Bispberg iron mine in Sater/Sweden, from Climax/USA, from Borralha and Carris abandoned mines (Vila Real, northern Portugal), where molybdenite occurs in quartz veins within granite pegmatites and from Cubos plus Venturinha (Viseu, central Portugal).

Synthetic compounds were studied in transmission mode (powdered pellets with BN): the model sulphide WS_2 , as well as rhenium oxides figuring out various formal valences and coordination environments – octahedral in ReO_3 (perovskite type arrangement), octahedral plus tetrahedral in Re_2O_7 and exclusively tetrahedral in KReO_4 . These compounds (commercial products) were previously characterized by X-ray diffraction. A powder sample with a few ppm of rhenium, collected in the waste material of the ancient sulphur factory from S. Domingos abandoned mine (Iberian Pyrite Belt, southern Portugal) exploited for the extraction of copper and sulphur, was similarly studied.

A preliminary approach to the study of copper minerals was also initiated collecting XANES spectra at the Cu K-edge (8.979 keV) in FY mode.

From a total of about 120 registered scans, 16 good XANES and 2 EXAFS sum-spectra were obtained.

Fig. 1 illustrates the Re L_3 -edge XANES spectra collected from model compounds (rhenium oxides) and Fig. 2 reproduces the Re L_3 -edge XANES spectra obtained from two molybdenite (MoS_2) samples from Quebec and Australia compared with the spectrum collected at W L_3 -edge for the model sulphide (WS_2) displaying similar trends at the beginning of the spectra. Synthetic WS_2 has a structural arrangement identical to molybdenite with W^{4+} ions in prismatic coordination within [S-W-S] planar modules, that could explain the similarity.

Fig.1- Re L_3 -edge XANES spectra of model compounds.

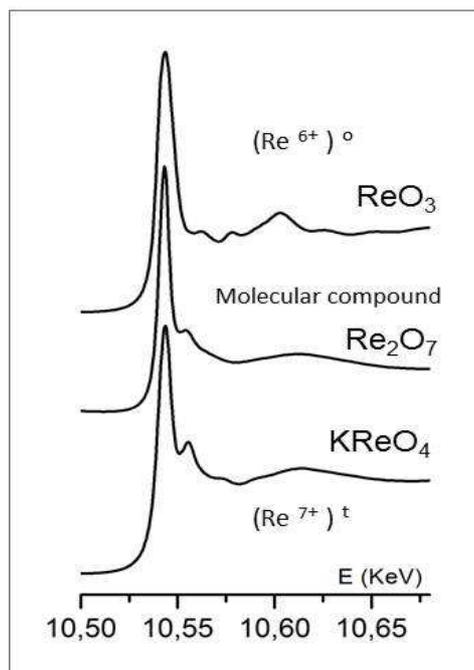
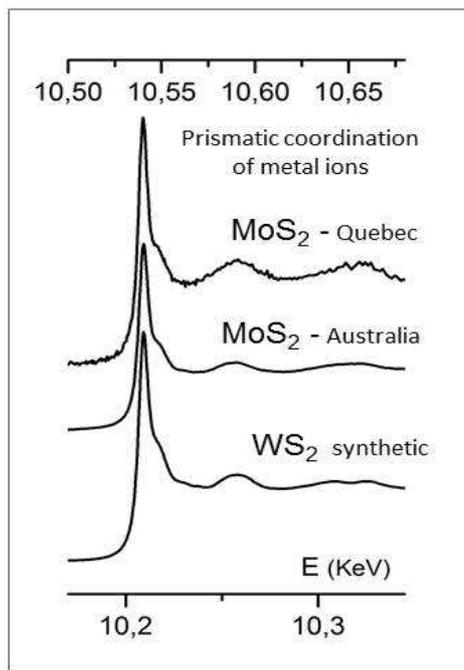


Fig.2- Re L_3 -edge XANES spectra of molybdenites and W L_3 -edge spectrum of synthetic WS_2 .



Between successive [S-Mo-S] layers, additional octahedral and tetrahedral interstices are available which are unfilled in molybdenite but which could be locally occupied by ions (namely Re) with other coordination requirements, giving rise to nanodomains of another phase. The results of this experiment will be used to clarify whether Re stands preferably in solid solution or within dispersed nanophases in molybdenite and to ascertain if Re-Re bonding occurs in the natural rhenium carrier. L_3 -edge XANES spectra will be theoretically modelled using a multiple scattering approach through the FEFF code [4]. Obtained results will be compared to published spectroscopic data (e.g. [5-7]).

- [1] A. BLERNARD, R.B. SYMONS & W.I. ROSE (1990) Volatile transport and deposition of Mo, W and Re in high temperature magmatic fluids. *Applied Geochem.* **5**, 317.
- [2] B. KREBS, A. MÜLLER & H. BEYE (1969) Crystal structure of rhenium (VII) oxide. *Inorg. Chem.* **8**, 436.
- [3] P. CARON & T. KHAN (1999) Evolution of Ni-based superalloys for single crystal gas turbine blade applications. *Aerosp. Sci. Technol.* **3**, 513.
- [4] A.L. ANKUDINOV, B. RAVEL & J.J. REHR (2000) Manual of FEFF8.10 Program. *The FEFF Project*, Dept. Physics, Univ. Washington, Seattle, USA, 62 pp.
- [5] A. KUZMIN, J. PURANS, M. BENFATTO & C.R. NATOLI (1992) *Ab initio* multiple-scattering calculations of the rhenium L_3 and L_1 edges XAFS in ReO_3 . *Japan J. Appl. Phys.*, **32**, suppl. 32-2, 46-48.
- [6] G. WITSCHKE, M. FRÖBA, H. FUESS & W. METZ (1994) XAS and XRD studies of rhenium-oxygen compounds. *Fresenius J. Anal. Chem.* **349**, 230.
- [7] M. FRÖBA, K. LOCHTE & W. METZ (1996) XANES study on Re L absorption edges of Re_2O_7 graphite intercalation compounds and of other rhenium-oxygen compounds. *J. Phys. Chem. Solids* **57**, 635.