ISIS@MACH ITALIA

Science and Technology Facilities Council
ISIS Neutron and Muon Source

Experiment Proposal

Experiment number GP2024037

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Experiment title	SEM-EDS INVESTIGATION, MICROMANIPULATION AND FIB MACHINING OF MICROSIZED BISMUTH SULPHATES
MRF Instrument	**FIB-SEM GAIA 3**
Access Route	Direct Access
Science Areas	Chemistry
Sponsored Grant	None
Grant Title	-
Start Date	-
Similar Submission?	-
Industrial Links	-

Days requested: 3
Previous GP Number: No
DOI: -
Sponsor: -
Grant Number: -
Finish Date: -

Non-Technical Abstract

Recently, three bismuth sulphates have been discovered at Alfenza Mine (Crodo, Ossola Italy), a rare one, cannonite [Bi2O(OH)2SO4], which has provided the first crystal structure refinement from a natural sample (before the structure was known only from a synthetic analogue), and two new minerals. All these bismuth sulphates occur together within the same hand specimen, often within the same millimetre sized geodes, and form micrometre sized crystals with different crystal habit. About the two new minerals, approximate crystal structure information has been obtained by TEM, but unfortunately not as sufficient as to make them accepted as new minerals. Confiding in the analytical and nanomachining capabilities of modern FIB-SEM instruments, this proposal aims to obtain the definite crystal structure of both new minerals.

Publications -

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E-platform: No

Instruments	**Days Requested:**
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Sample record sheet

Principal contact
MRF Instrument **FIB-SEM GAIA 3** **Days Requested:** 3
Special requirements:

SAMPLE

Material	Bi, O, S, Te, H, Si, Al, Fe, Ca, Na, K, Mg	-	-
Formula	-	-	-
Forms	Solid		
Volume	1 cc		
Weight	3 g		
Container or substrate	mineral rock	-	-
Storage Requirements	-	-	-

SAMPLE ENVIROMENT

Temperature Range	room temperature - K	-	-
Pressure Range	room pressure - mbar	-	-
Magnetic field range	- T	-	-
Standard equipment	None	-	-
Special equipment	standard mounts for single crystal XRD: brass cylinder 3 mm in diamter carrying a glassy fiber 0.2 mm in diameter. The whole mount is 1.5 cm long	-	-

SAFETY

Prep lab needed	Yes	-	-
Sample Prep Hazards	No	-	-
Special equip. reqs	Carbon coater	-	-
Sensitivity to air	No	-	-
Sensitivity to vapour	No	-	-
Experiment Hazards	No	-	-
Equipment Hazards	-	-	-
Biological hazards	no	-	-
Radioactive Hazards	no	-	-
Additional Hazards	-	-	-
Additional Details	-	-	-
Sample will be	Removed By User	-	-

ISIS@MACH ITALIA Experimental Proposal – SEM-EDS INVESTIGATION, MICROMANIPULATION AND FIB MACHINING OF MICROSIZED BISMUTH SULPHATES

1. Background and context

The mineralized quartz dikes of the Alfenza Mine (Crodo, Ossola, Italy) are renewed since the 17th century because of their content of auriferous pyrite. The Alfenza mineralization is just one of the various auriferous manifestations present in the Ossola region, which has been the most renowned region in Italy for the exploitation of gold. The Alfenza Mine, after several periods of exploitation followed by stops, was definitely abandoned in 1941. It has provided with time a rich variety of minerals, such as perfect crystals of bismuthinite (Roggiani 1940) the sulfosalt cosalite and native gold (Roggiani 1970). Recently, three bismuth sulphates have been discovered at Alfenza Mine (Capitani et al. 2014), a rare one, cannonite [$Bi_2O(OH)_2SO_4$], which has provided the first crystal structure refinement from a natural sample (Capitani et al. 2013) – before the structure was known only from a synthetic analogue – and two new minerals. All these bismuth sulphates occur together within the same hand specimen, often within the same millimetre sized geodes, and form micrometre sized crystals with different crystal habit. About the two new minerals, approximate crystal structure information has been obtained by TEM, but unfortunately not as sufficient as to make them accepted as new minerals. Confiding in the analytical and nanomachining capabilities of modern FIB-SEM instruments, this proposal aims to obtain the definite crystal structure of both new minerals.

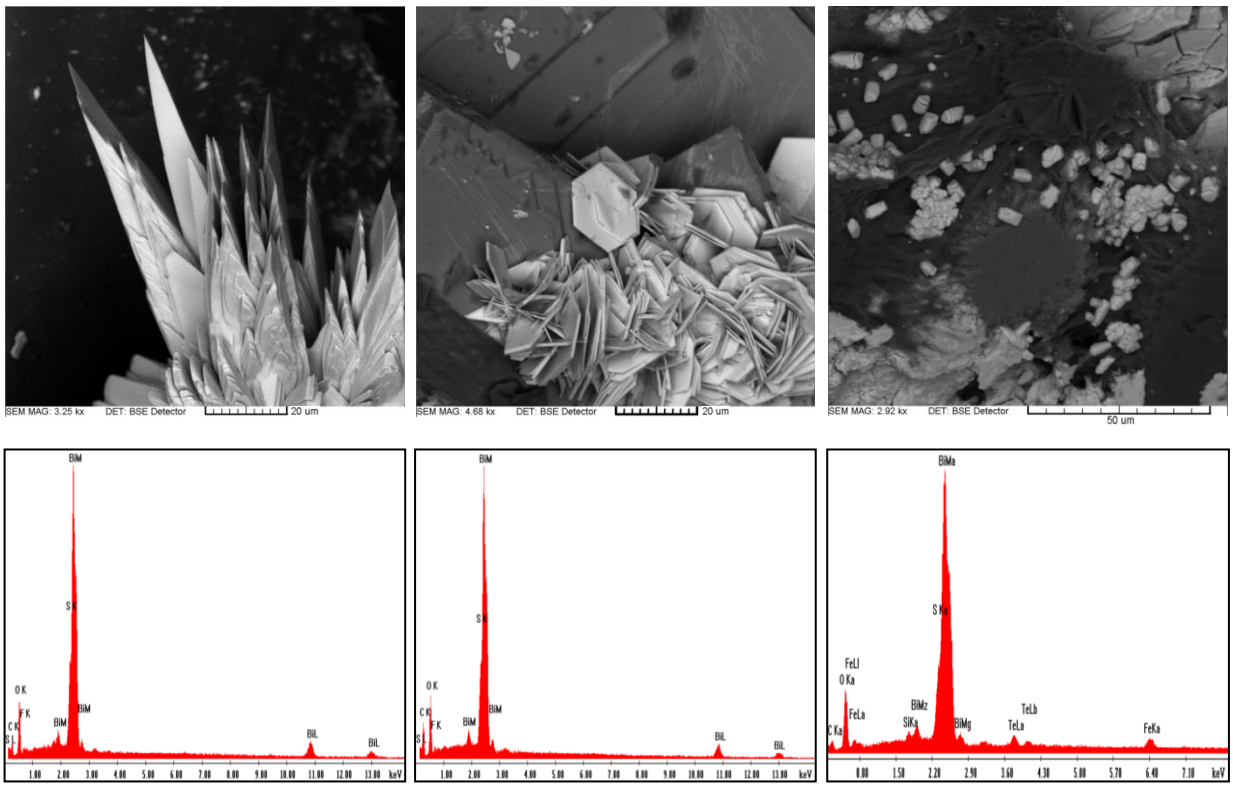

Figure 1. Upper row, from left to right: SEM images of bismuth sulphate cannonite, the new mineral 1 and the new mineral 2. Note how the three minerals have a distinguished crystal habit. Lower row, from left to right: EDS spectra of cannonite, the new mineral 1 and of the new mineral 2. Note how a small amount of Te distinguishes the latter from the former two bismuth sulphates, which are undistinguishable from the chemical point of view.

2. Proposed experiments

The proposed experiment is a step towards the achievement of the crystal structure of two new bismuth sulphates discovered in the Alfenza Mine mineralization. Because of the micrometer size

dimension of the new minerals, the first step is a SEM-EDS investigation of some new samples from the same locality. By coupling the characteristic morphology and chemical composition, it should not be too difficult to identify the new minerals within the complex mineral association they come with. Once located, the next step is to pick up some single crystals by a micromanipulator and to stick some of them on a TEM grid, for TEM analysis, and some at the top op of glassy fibers for single crystal XRD. These last mounts do not require any further preparation and are ready for single crystal synchrotron XRD. On the contrary, the sample on the TEM grid need to be ion milled with the FIB to make them electron transparent, for successive electron diffraction tomography (EDT) studies. Both EDT and single crystal synchrotron XRD will be done elsewhere, since not present within the facility offered by the ISIS@MACH ITALIA.

3. Summary of previous experimental proposals or characterisation

The proposal has never submitted before, however, similar samples from the same localities were previously investigated by optical microscopy, SEM-EDS and TEM. The new mineral 1 forming "hortensia-like" aggregates made of randomly oriented, ~20 microns wide, hexagonal platelets, have cell parameters: a = 20.4(6), b = 15.5(5), c = 14.7(4) Å, β = 102.9(1)°, *Pc* or *P2/c* symmetry and indicative composition $Bi_2SO_4(OH)_4$.

The new mineral 2 forming barrel-like crystals ~20 microns long has space group *P-62c*, cell parameters a = 9.5(2) Å, c = 15.4(3) and indicative composition $(S_2)_{1+x}[Bi_{9-x}Te_x(OH)_6O_8(SO_4)_2]_2$. These data identify both minerals as new minerals. Unfortunately, without a reliable crystal structure, they cannot be accepted as new minerals. This is the motivation of this proposal.

4. Justification of experimental proposals request

The proposed experiment is a step towards the achievement of the crystal structure of two new bismuth sulphates discovered in the Alfenza Mine mineralization, which will be chased by two parallel approaches: i) by single crystal synchrotron XRD and ii) by EDT, but first the sample need to be studied by SEM-EDS, the crystals picked up by a micromanipulator and ion milled with a FIB. All these operations can be done with the SEM-FIB Tescan Gaia3 available within the ISIS@MACH ITALIA consortium. Three days appears as a reasonable amount of time to prepare two TEM grids (with two crystals each) for each new mineral and three single crystal mounts for XRD for each new mineral.

From the side of the Fundamental Science, the finding of new minerals and the achievement of their structures are relevant results, since they enlarge our knowledge. Minerals have since the beginning of the human history represented the raw material for human manufactures and mineral properties are nowadays exploited in a number of technological and industrial applications. Bismuth is a heavy atom, close to Pb in the Periodic Table and often substituting for it in sulfosalts, but is comparatively less toxic and isotopically more stable. Sulfosalts have potential applications in innovative solar cells. Bismuth sulphate foils are used as sputtering targets and evaporation materials for uses such as solar energy materials and fuel cells.

Capitani, G., Catelani, T., Gentile, P., Lucotti, A., Zema, M., 2013. Cannonite [$Bi_2O(SO_4)(OH)_2$] from Alfenza (Crodo, Italy): Crystal structure and morphology. Mineralogical Magazine, 77(8), 3067–3079.

Capitani, G., Mugnaioli, E., Rius, J., Gentile, P., Catelani, T., Lucotti, A., Kolb, U., 2014. The Bi sulfates from the Alfenza Mine, Crodo, Italy: An automatic electron diffraction tomography (ADT) study. American Mineralogist, 99, 500–510.

Roggiani, A.G. (1940) Il regno minerale nell'Ossola. II° La bismutinite delle miniere aurifere di Crodo "Secondo ritrovamento". Tipografia C. Antonioli, Domodossola, 11 pp.

Roggiani, A.G. (1970) Appunti per una mineralogia dell'Ossola: Oro nativo e cosalite: due ulteriori conferme sulla validità scientifica dei giacimenti auriferi dell'Alfenza (Crodo). Illustrazione Ossolana, XII, 4, 104–112.