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Data Article

Linarite and connellite dataset from Calabria region (Southern Italy): First evidence

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ABSTRACT

This dataset article contains mineralogical and chemical data of linarite and connellite sulfate minerals. These minerals were found included in the oxidized zones of cupriferous sulfide ores in the Fiumarella Mine, in Calabria region (Southern Italy). Linarite is a basic sulfate of copper and lead with the formula of $\text{PbCuSO}_4(\text{OH})_2$ while connellite is a hydrated sulfate of copper with an ideal formula of $\text{Cu}_{36}\text{Cl}_6(\text{SO}_4)_2(\text{OH})_{62} \cdot 12\text{H}_2\text{O}$.

Recently, in the mine of Fiumarella, in addition to primary minerals such as barite, galena, cerussite, anglesite, fluorite and chalcocopyrite, wulfenite (PbMoO_4) was also detected. Linarite consists of a prismatic bright blue crystal with a vitreous luster of micrometric size implanted upon on a matrix made up of barite. Connellite includes micrometric acicular tuft crystals protruding from matrix. Methods for obtaining the datasets include optical microscopy, micro X-ray Fluorescence and micro-Raman spectroscopy.

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Subject area	Earth science
More specific subject area	Mineralogy
Type of data	Tables, figures
How data was acquired	Stereo binocular (Askania, GSZ 2T, Germany) fitted with a digital camera (Fuji X-E2, Japan). Elemental semiquantitative analysis of the mineral was performed using an M4 Tornado μ XRF spectrometer (Bruker Nano GmbH, Berlin, Germany) equipped with a Rh tube and a polycapillary optic (50 kV, 600 μ A, 30 W, 25 μ m of spot size), and with two XFlash [®] silicon drift detectors having 30 mm ² of active area and a resolution lower than 140 eV (Mn-K α). Analyses were carried out under vacuum (20 mbar) and 120 s live time was adopted. Finally, only one detector was used for the quantitative analysis while the second one was employed to detect ambiguous peaks, ascribable to diffraction phenomena. Spectrum deconvolution and quantification were performed using the M4 Tornado analysis software. Micro-Raman analyses were performed using a Thermo Fisher DXR Raman microscope (Waltham, MA, USA), equipped with OMNICxi Raman Imaging software 1.0, an objective of 50 \times , a grating of 900 ln/mm (full width at half maximum, FWHM), and an electron multiplying charge-coupled device (EMCCD). The 532.0-nm line (solid state laser) was used at an incident power output at 6 mW. The spatial resolution of the laser beam was about 3–5 μ m.
Data format	Raw and Analyzed
Experimental factors	Samples were investigated non-destructively without any modification
Experimental features	Crystals were recovered under optical microscope; micro X-ray Fluorescence and micro-Raman spectrometer without pretreatment.
Data source location	38°55'19.19" N, 16°34'25.71" E, Fiumarella mine, Catanzaro province, Calabria Region, Italy
Data accessibility	All raw data are available within this article

Value of the data

- For the first time, linarite and connellite crystals have been detected and characterized from Calabria region (Italy) for both local and global comparisons.
- Linarite crystals could be of used in industry for their good physical performance.
- The dataset can be used to valorize the location of Fiumarella, according to the Convention on the Protection of World, Cultural and Natural Heritage, adopted by UNESCO in 1972.
- The data presented here may be used by other authors to compare composition, morphological features and Micro-Raman bands of other linarite and connellite crystals discovered in other parts of the world.
- The data can be compared with those obtained from similar geologic environments and motivate studies on rare sulfate minerals in the future.

1. Data

This data article contains mineralogical and chemical data of linarite $\text{PbCuSO}_4(\text{OH})_2$ and connellite $\text{Cu}_3\text{Cl}_6(\text{SO}_4)_2(\text{OH})_{62} \cdot 12\text{H}_2\text{O}$ both sampled from the barite mine of Fiumarella in Calabria Region (Southern Italy) (Fig. 1) [1,2]. The crystals of linarite and connellite were identified and characterized by optical microscopy, micro-Raman spectroscopy and micro X-ray fluorescence spectroscopy. Linarite occurs as a secondary mineral in the oxidized parts of deposits originally containing lead and copper sulfides and it is of widespread distribution but almost always detected in small amounts [3,4]. Connellite is a rare mineral, and similar to linarite it is found in oxidized zones of base metal ore bodies such as Cu [5].

Linarite and connellite colour and morphology are shown in Figs 2 and 3. Chemical analysis of linarite and connellite crystals are given in Figs 4 and 5, respectively. The Raman spectrum of the linarite and connellite and their typical bands are shown in Fig. 6 and Fig. 7 respectively and in Table 1.

2. Experimental design, materials and methods

2.1. Study area description

The Fiumarella mine (38°55'19.19" N; 16°34'25.71" E) is located in the western part of Catanzaro town, along Fiumarella Creek, in location Molino Masticarro (Fig. 1). The area has been intensively

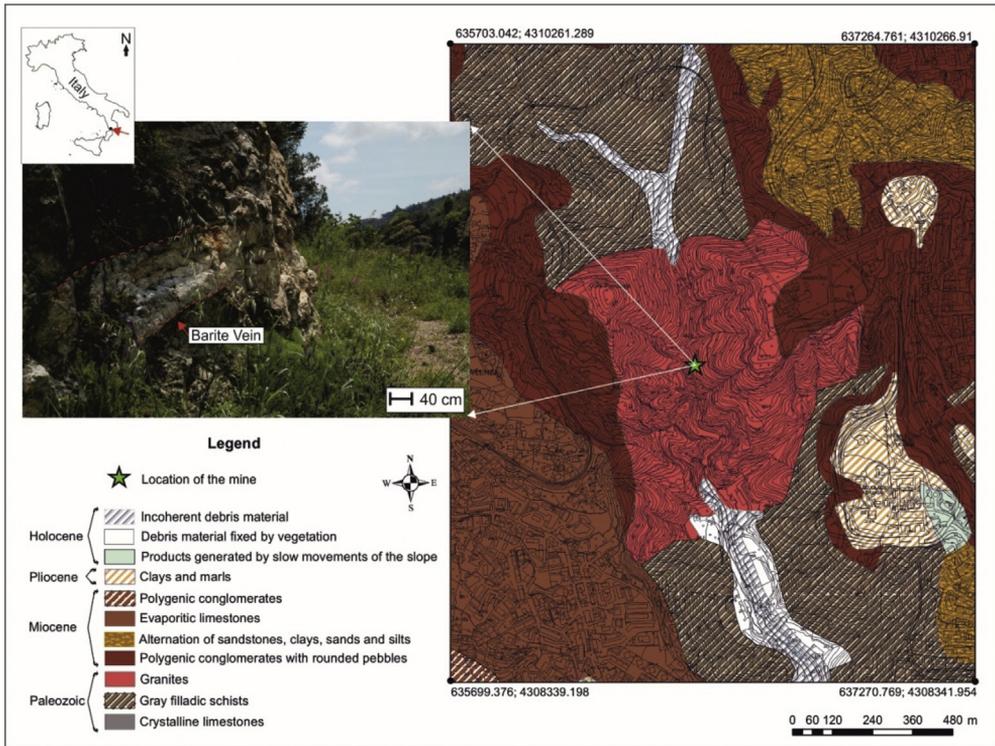


Fig. 1. Location of the Fiumarella mine and geological map of the area (After [6]). The barite vein where the linarite and connellite crystals were found is indicated by the red arrow.

exploited till the end of the eighties and about 5000 m of galleries have been excavated mainly to extract barite, fluorite, galena and chalcopyrite [1,2]. Recently wulfenite crystals have also been identified in the Fiumarella mine [6].

2.2. Optical microscopy

Samples were investigated using a stereo binocular microscope (Askania, GSZ 2T, Germany) and images of the linarite and connellite crystals were acquired using a digital camera (Fuji X-E2, Japan). Linarite crystals occur as overgrowth on a matrix containing white-milk granular massive barite and green malachite. All the linarite crystals are blue in colour, translucent with a vitreous luster (Fig. 2). These brilliant blue individual crystals can reach 200 μm in width and 1 mm in length. Linarite crystallizes in a monoclinic lattice (2/m) [7], in prismatic shape elongated along [010] (Fig. 2), this morphology is similar to that found in Arizona deposits [8,9]. Linarite crystals in small amounts have also been detected in other Italian regions such as Lombardy, Tuscany, Veneto and Sardinia [4].

Connellite occurs as small acicular tufts, often forming small spherical aggregates (Fig. 3). The single acicular crystals were light blue in colour and showed a maximum length of 50 μm , and a width of few micrometer (Fig. 3). Connellite is a relatively rare mineral [10]. In Italy it was found in Tuscany and in Sardinia.

2.3. Micro X-ray fluorescence (μXRF) data

Elemental semiquantitative analysis of the minerals were performed using an M4 Tornado spectrometer (Bruker Nano GmbH, Berlin, Germany). Linarite is a basic sulfate of copper and lead with the formula of $\text{PbCuSO}_4(\text{OH})_2$ which has shown to have peculiar physical properties [11]. In the crystals of

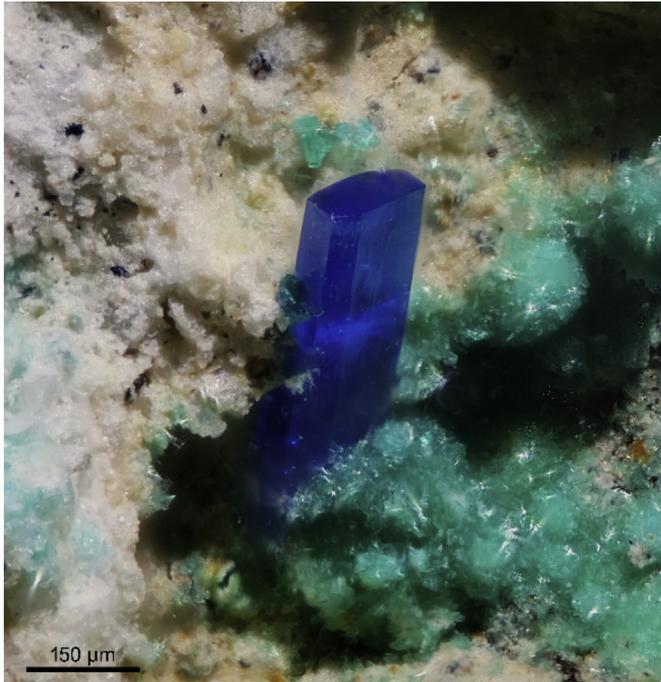


Fig. 2. Optical image of a well-developed blue linarite single crystal from Fiumarella mine (Southern Italy).

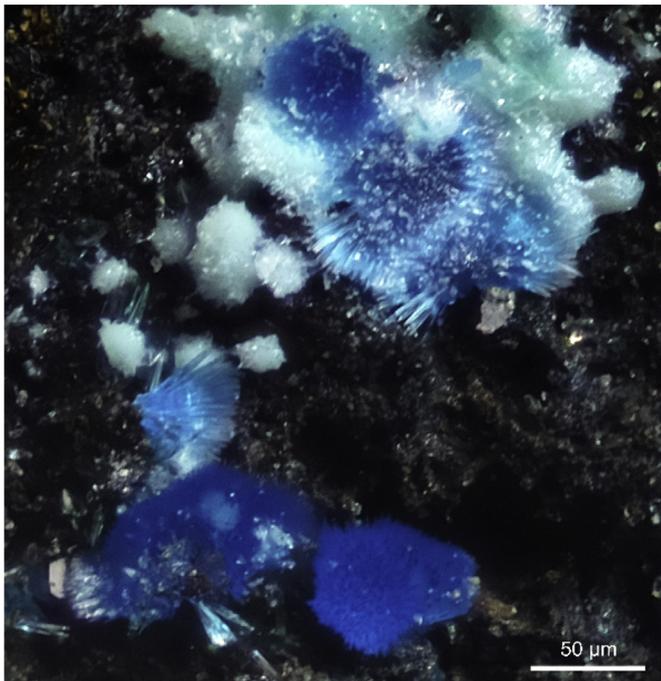


Fig. 3. Optical image showing aggregates of acicular tufts of connellite with a light blue colour from Fiumarella mine (Southern Italy).

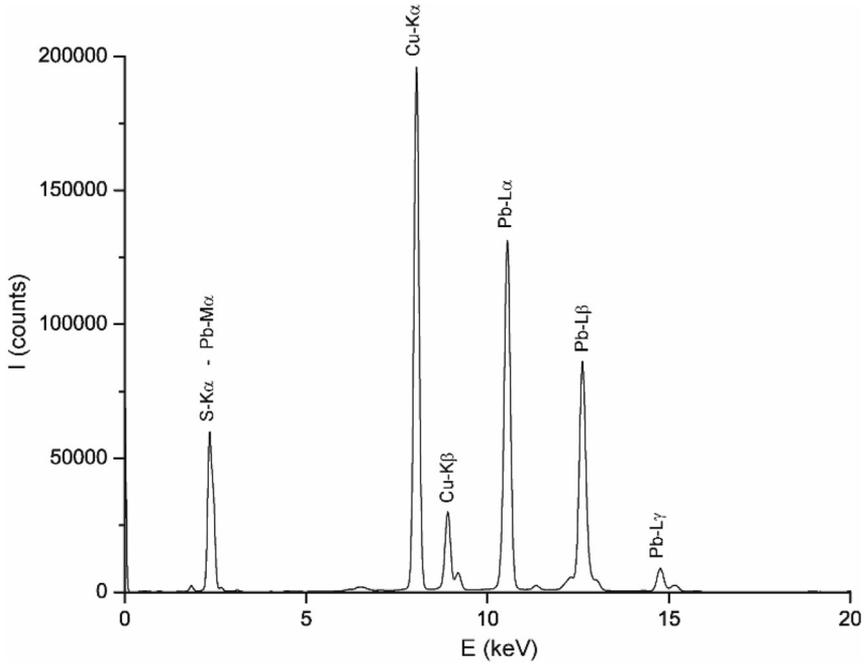


Fig. 4. Micro X-ray fluorescence (μ XRF) spectrum of the linarite mineral from the Fiumarella mine (Catanzaro - Southern Italy).

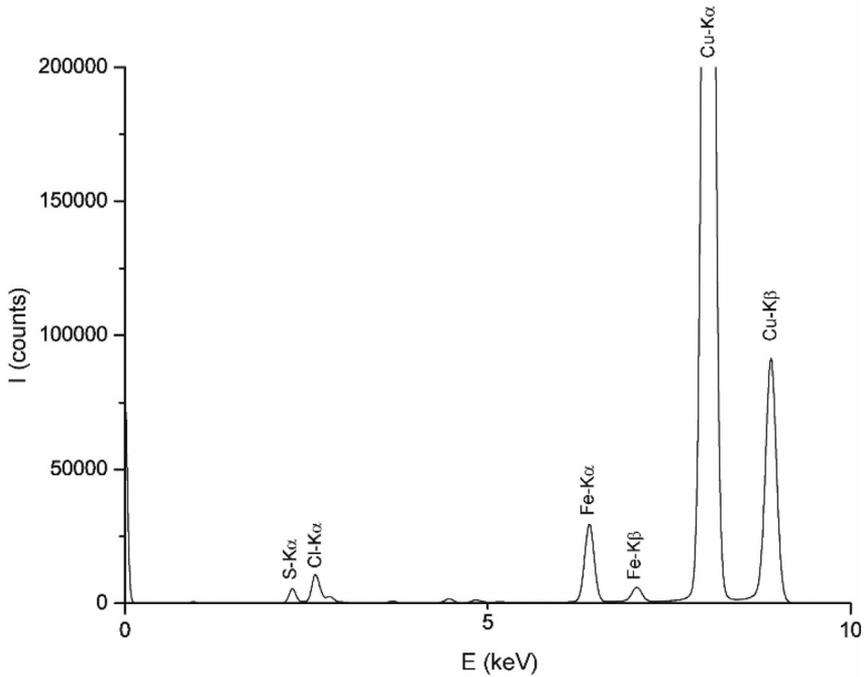


Fig. 5. Micro X-ray fluorescence (μ XRF) spectrum of connellite mineral from the Fiumarella mine (Catanzaro - Southern Italy).

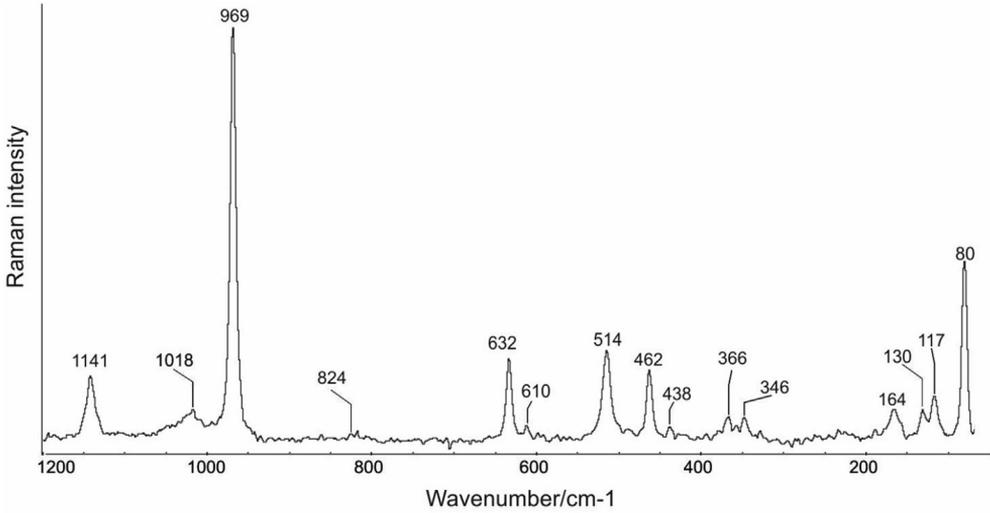


Fig. 6. Raman spectrum of the linarite mineral coming from the Fiumarella mine (Catanzaro - Southern Italy).

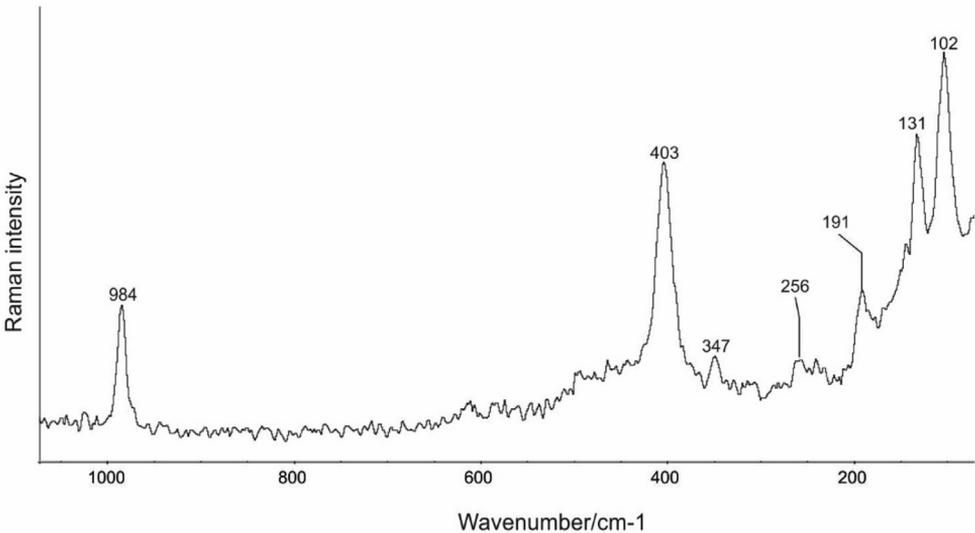


Fig. 7. Raman spectrum of the connellite mineral from the Fiumarella mine (Catanzaro - Southern Italy).

linarite, the following average amounts of oxides (as calculated on seven analyzed points) was determined: $\text{Cu}_2\text{O} = 19.97$ wt%, $\text{PbO} = 61.13$ wt% and $\text{SO}_3 = 18.90$ wt%, and graphically reported in Fig. 4. This finding is in agreement with the existing literature data [4,8,9,11].

As regards the chemical composition of connellite, the major elements include Cu, S, Cl and Fe (Fig. 3), consistent with connellite composition. In the crystals of connellite, the following average amounts of oxides (as calculated on seven analyzed points) was determined: $\text{CuO} = 88.9$ wt%, $\text{SO}_3 = 6.82$ wt%, $\text{Cl} = 4.28$ wt%. The chemical composition of connellite was generally close to that of its stoichiometric formula. Slight deviations from the theoretical chemical composition are due to the presence of impurities such as Fe. The connellite minerals investigated had quite the same size of the

Table 1Micro-Raman Band wavenumber/cm⁻¹ for linarite and connellite crystals from Fiumarella mine (Catanzaro - Southern Italy).

Mineral's name	Bands wavenumber/cm ⁻¹ according with references [10–14] and RRUFF database	Assignments
Linarite	80, 117, 130	Lattice modes
	164, 346, 366	Cu–OH/Pb–OH
	438, 462, 514	$\nu_2(\text{SO}_4)$
	610, 632	$\nu_4(\text{SO}_4)$
	824	OH bending
	969	$\nu_1(\text{SO}_4)$
	1018, 1141	$\nu_3(\text{SO}_4)$
	Connellite	102, 131, 191
	256	CuCl bands
	347, 403	CuO stretch
	984	SO symmetric stretching

primary X-ray beam, and for this reason, a contribution from the surrounding area cannot not be excluded. Moreover, as reported in the literature [12], the stoichiometric complexity of connellite makes the determination of its exact composition difficult with conventional analytical techniques. For this reason, in this paper we have also used Raman spectroscopy to confirm the identification of this mineral. Indeed, it is worth remembering that Raman spectroscopy readily lends itself to the analysis of these types of phases [12].

2.4. Micro-Raman spectroscopy data

Micro-Raman analyses were performed using a Thermo Fisher DXR Raman microscope (Waltham, MA, USA). Fig. 6 shows the Raman spectrum of the linarite crystals with typical bands at 80, 117, 130, 164, 346, 366, 438, 462, 514, 610, 632, 969, 1018 and 1141 cm⁻¹ in agreement with the spectrum present in the RRUFF database named “R060472”. Table 1 lists assignments for the observed Raman bands, according to literature data [13,14]. Fig. 7 shows the Raman spectrum of connellite crystals with typical bands at 102, 131, 191, 256, 347, 403 and 984 cm⁻¹ in agreement with the spectrum present in the RRUFF database named “R060503”. Table 1 lists assignments for the observed Raman bands, according to literature data [12,13].

Acknowledgments

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] I.J. Buchanan, B. De Vivo, A.K. Kramer, A. Lima, Fluid inclusion study of the Fiumarella barite deposit (Catanzaro S. Italy), *Miner. Depos.* 16 (2) (1981) 215–226.
- [2] L. Dattola, La miniera di barite del Torrente Fiumarella presso catanzaro: i minerali, *Riv. Mineral. Ital.* 20 (3) (1996) 289–292.
- [3] R.B. Cook, Linarite mammoth-St. Anthony mine, tiger, pinal county, Arizona, *Rocks Miner.* 81 (3) (2006) 208–213.
- [4] P. Orlandi, E. Bonaccorsi, Montetrisaite, a new hydroxy-hydrated copper sulfate species from Monte Trisa, Vicenza, Italy, *Can. Mineral.* 47 (1) (2009) 143–151.

- [5] A.M. Pollard, R.G. Thomas, P.A. Williams, Connellite: stability relationships with other secondary copper minerals, *Mineral. Mag.* 54 (376) (1990) 425–430.
- [6] A. Bloise, L. Dattola, I. Allegretta, R. Terzano, M. Taranto, D. Miriello, First evidence of wulfenite in Calabria region (Southern Italy), *Data in Brief* 19 (2018) 687–692.
- [7] P.F. Schofield, C.C. Wilson, K.S. Knight, C.A. Kirk, Proton location and hydrogen bonding in the hydrous lead copper sulfates linarite, $\text{PbCu}(\text{SO}_4)(\text{OH})_2$, and caledonite, $\text{Pb}_5\text{Cu}_2(\text{SO}_4)_3\text{CO}_3(\text{OH})_6$, *Can. Mineral.* 47 (3) (2009) 649–662.
- [8] J.W. Anthony, S.A. Williams, R.A. Bideaux, R.W. Grant, *Mineralogy of Arizona*, University of Arizona Press, Tucson, 1995.
- [9] R.A. Bideaux, Famous mineral localities: tiger, Arizona, *Mineral. Rec.* 11 (1980) 155–181.
- [10] D.E. Hibbs, P. Leverett, P.A. Williams, Buttgenbachite from Bisbee, Arizona, USA: a single crystal X-ray study, *Neues Jahrb. Mineral. Monatshefte* 5 (2002) 225–240.
- [11] M. Schäpers, A.U.B. Wolter, S.-L. Drechsler, S. Nishimoto, K.-H. Müller, M. Abdel-Hafez, W. Schottenhamel, B. Büchner, J. Richter, B. Ouladdiaf, M. Uhlarz, R. Beyer, Y. Skourski, J. Wosnitza, K.C. Rule, H. Ryll, B. Klemke, K. Kiefer, M. Reehuis, B. Willenberg, S. Süllow, Thermodynamic properties of the anisotropic frustrated spin-chain compound linarite $\text{PbCu-SO}_4(\text{OH})_2$, *Phys. Rev. B* 88 (18) (2013) 184410.
- [12] R.L. Frost, P.A. Williams, W. Martens, J.T. Kloprogge, Raman spectroscopy of the polyanionic copper (II) minerals buttgenbachite and connellite: implications for studies of ancient copper objects and bronzes, *J. Raman Spectrosc.* 33 (9) (2002) 752–757.
- [13] M. Bouchard, D.C. Smith, Catalogue of 45 reference Raman spectra of minerals concerning research in art history or archaeology, especially on corroded metals and coloured glass, *Spectrochim. Acta A* 59 (2003) 2247–2266.
- [14] N. Buzgar, A. Buzatu, I.V. Sanislav, The Raman study on certain sulfates, *Analele Stiintifice ale Universitatii Al. I. Cuza* 55 (2009) 5–23.