Luminescence and compositional studies for the identification of "fire-setting" features at prehistoric mine La Turquesa (Catalonia, Spain)

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Abstract

Modern mining activities often leads to destruction of archaeological records, making difficult to date the contexts and tools. In this work, a prehistoric mine with "fire-setting" techniques evidence was used to demonstrate the relevance of luminescence protocols to identify and date ancient mining activities. Chemical and mineralogical studies complemented the dosimetric ones by means of luminescence protocols. One of the samples shows lower absorbed dose suggesting heating procedures, like "fire-setting" and its luminescence age, determined by SAROSL, points to copper exploitation during the Middle/Late Bronze Age at La Turquesa mine, in accordance with archaeological records.

Keywords

Prehistoric mining, "Fire-setting", Luminescence protocols, Luminescence dating, Geochemistry

Introduction

"Fire-setting" is well recognized as one of the oldest mining techniques for breaking up hard rocks and extract the ore, mostly in open mines of northern Europe, and was identified since prehistoric times up to the 19th century [1, 2]. Fires were set against a rock face to heat it; it was then doused with liquid, usually water, causing the rock to weaken and fracture due to the thermal shock. The technique is usually associated with mechanical methods (hammering, picking, wedging, etc.). The use of "fire-setting" in European prehistoric copper mines was clearly identified in mining districts of France (Cabrières and Faravel), Austria (Mitterberg and Tyrol), Ireland (Mt. Gabriel mines), Wales, former Yugoslavia (Rudna Glava) and Spain (Aramo mine in Asturias) [2–7]. The main evidence of the use of "fire-setting" in ore exploitation is the presence of meter-sized spherical or sub-spherical cavities, sometimes spaced along the same vertical line in an ore seam, together with charcoal and traces of fire. The wood fire, generally associated to this technique, lead to a range of temperatures between 100 °C to 600 °C with different effects in the parent material [2].

The few existing studies regarding exploitation techniques in prehistoric mines are mainly focused on mineralogical and chemical alterations of the rock, the used fuel, the achieved temperatures, the gradient temperature inside the rock, the procedures, the study of tools and charcoal finds, as well as experimental simulation [2, 5, 8, 9]. A different approach was applied to the prehistoric mines of the French and Austrian Alps, including anthracological and dendrochronological analysis of wood remains, in order to evaluate the chronology of the exploitation and the impact of the mining economy in the region [5–7, 10].

There is a lack of chronological data for this type of archaeological context, particularly related with the moment of the technological event, relevant to ancient mining and metallurgy activities. When organic materials are available in mining contexts, such as wooden tools, mining tools, or firewood and charcoal, ^{14}C dating is usually used [5, 11, 12]. However, these materials are rare in mines and their contexts were disturbed by the alternated periods of exploitation *vs* abandonment. In addition, a complex stratigraphy and diverse reuses over time are associated with these mining contexts, making the absolute dating difficult[13]. Nevertheless, working techniques remains and associated inorganic materials can be studied by using luminescence techniques [14]. A few dating attempts of the last heating of feldspars and quartz (e.g. in slags or in rocks) have been done in mining contexts with “fire-setting” evidence [4]. Studies applying luminescence protocols on quartz, polymineralic and alkali feldspars fractions from burnt rocks, heated flint and fire-cracked rocks of prehistoric human occupations are well described [15–19]. Luminescence was also used to assess the reached temperature on fired rock surfaces and dating fires on historical buildings [20].

Recent archaeological work in La Turquesa mine (also known with the name of Mas de les Moreres mine), Cornudella de Montsant, Catalonia, Spain (coordinates: ETRS89: UTM31N, 323884.605/4566667.437), where secondary copper ores were exploited, reveals sub-elliptical or sub-spherical cavities on the rock, pointing to the use of “fire-setting” techniques during pre-industrial mining activities [21]. La Turquesa mine is located on the south-western sector of the Pre-Litoral Range, containing the southernmost outcrops of Palaeozoic rocks in the Catalan Coastal Ranges. Based on a previous work developed on rock samples from a similar archaeological site [14], the authors performed a preliminary study, in which a thermoluminescence protocol was applied [22]. This first approach points to the use of heating processes against the rock surface.

In this work, an innovative and detailed study is performed, with the main goal of testing luminescence techniques as a reliable tool to confirm the practice of "fire-setting", and aiming to better establish the use of "fire-setting" techniques in ancient mining activities. In order to complement the luminescence analysis, a more detailed characterization of La Turquesa mine is done with the determination of the chemical composition of rock fragments from two mining shafts and geological background, and the correlation with the mineralogical composition of the materials.

Geo-archaeological context

La Turquesa mine has morphological features and archaeological remains usually associated to the use of "fire-setting" during pre-industrial mining activities [21]. This mine is located at the southwestern sector of the Pre-Litoral Range, where the southernmost outcrops of Palaeozoic rocks in the Catalan Coastal Ranges are observed. Outcrops of sedimentary materials from the Upper Devonian and the Carboniferous also occur. These series were deformed by the Hercynian orogeny, and affected by contact metamorphism produced by granite intrusions. The Mesozoic series uncomfortably overlies the above materials and are covered in a discordant manner, by detrital series from the Tertiary Period. The ensemble had been compartmented by faults from the Alpine Period [23]. The deposit of La Turquesa mine was formed following a vein structure related to the main Cornudella fault and has a NNW-SSE direction. The veins are hosted by chert metasedimentary units of Tournaisian age that have millimeter-thick apatite beds interbedded. The primary minerals are chalcopyrite and pyrite disseminated in milky quartz. The supergene alteration produced a gossan zone with goethite, malachite, azurite and cuprian crandallite. The gossan evolves at 3 m in depth, to a supergenic enrichment zone with Cu-rich sulphides as chalcocite, which replaces the primary chalcopyrite. La Turquesa mine was opened to exploit secondary copper ores, located in the upper part of a vein zone with pyrite and primary chalcopyrite that, due to supergene alteration, results in a gossan with crandallite and malachite, accompanied by minerals of the alunite group, and a zone of supergenic enrichment with chalcocite. The indicated paragenesis has its remote origin in the simultaneous meteorisation of pyrite and apatite in the hosting rocks, in one hand, and of the chalcopyrite veinlets, on other hand [23].

Three excavation campaigns occurred in 2012, 2013 and 2015 in La Turquesa mine. These campaigns allowed documenting more than a hundred mining stone tools, as well as, the main copper mineralization, a mining shaft (L1), and the remains of two more mine shafts (L2 and L3).

The chronological records established up to now for La Turquesa mine are: (i) a prehistoric horizon including lithic mining prehistoric tools (picks, picks/percussors and percussors), and mining working without any evidence of the use of metal-tools intervention (thus excluding a post-Roman chronology); (ii) radiometric dates obtained from the infill sediment of the mining shaft L1, providing a date *ante quem*, corresponding to the early Middle Ages; and (iii) the consistency of isotopic signature of the mine with archaeological materials, attributed to the Late Chalcolithic and to the Early-Middle Bronze Age (2800-1300 cal BC) [24].

Samples

At La Turquesa mine, samples were taken from the remains of two mining shafts, L2 and L3, located in the centre of the mine close to the mined Cu-vein, with evidence of pre-industrial mining (Fig. 1). In addition, two representative samples from geological background and one from a non-exploited section of the copper vein were collected. In shaft L2, four rock fragments were sampled, corresponding to the references MT1_1, MT1_2, MT1_3 and MT1_4. In shaft L3, one sediment (MT2_1) and three rock fragments were collected, corresponding to the references MT2_2, MT2_3 and MT2_4 (Fig. 1). The selected rock fragments are poorly indurated and break apart easily by hand, especially fragment MT1_1. The sediment MT2_1 was removed using a stainless-steel tube, according to the conventional sampling protocol for luminescence dating [25]. Two samples from the bedrock surrounding the mine (MT3 and MT4), and one sample in the copper vein (MT5) were also selected for this study (Fig. 1 and Fig.). The MT3 and MT4 samples were collected on the exploitation limit that corresponds to the 19th century mining activities, on the western and eastern edge of the mining shaft respectively. In opposition, the MT5 sample was taken on the southern edge of the Cu-vein (N-S) where no evidence of mining activities was observed. The MT3, MT4 and MT5 rock fragments were collected to be used as references for the luminescence signal boundaries, since it is expectable that they preserve the geological signal, without consequences of heating during mining processes. The MT2_1 sample, corresponding to the sediment accumulated at the shaft L3 after the last mining activity, is expected to have a lower luminescence signal. This sample was also used as luminescence signal boundary, but with the opposite purpose, of representing the material with geological signal bleached by recent sun exposure.

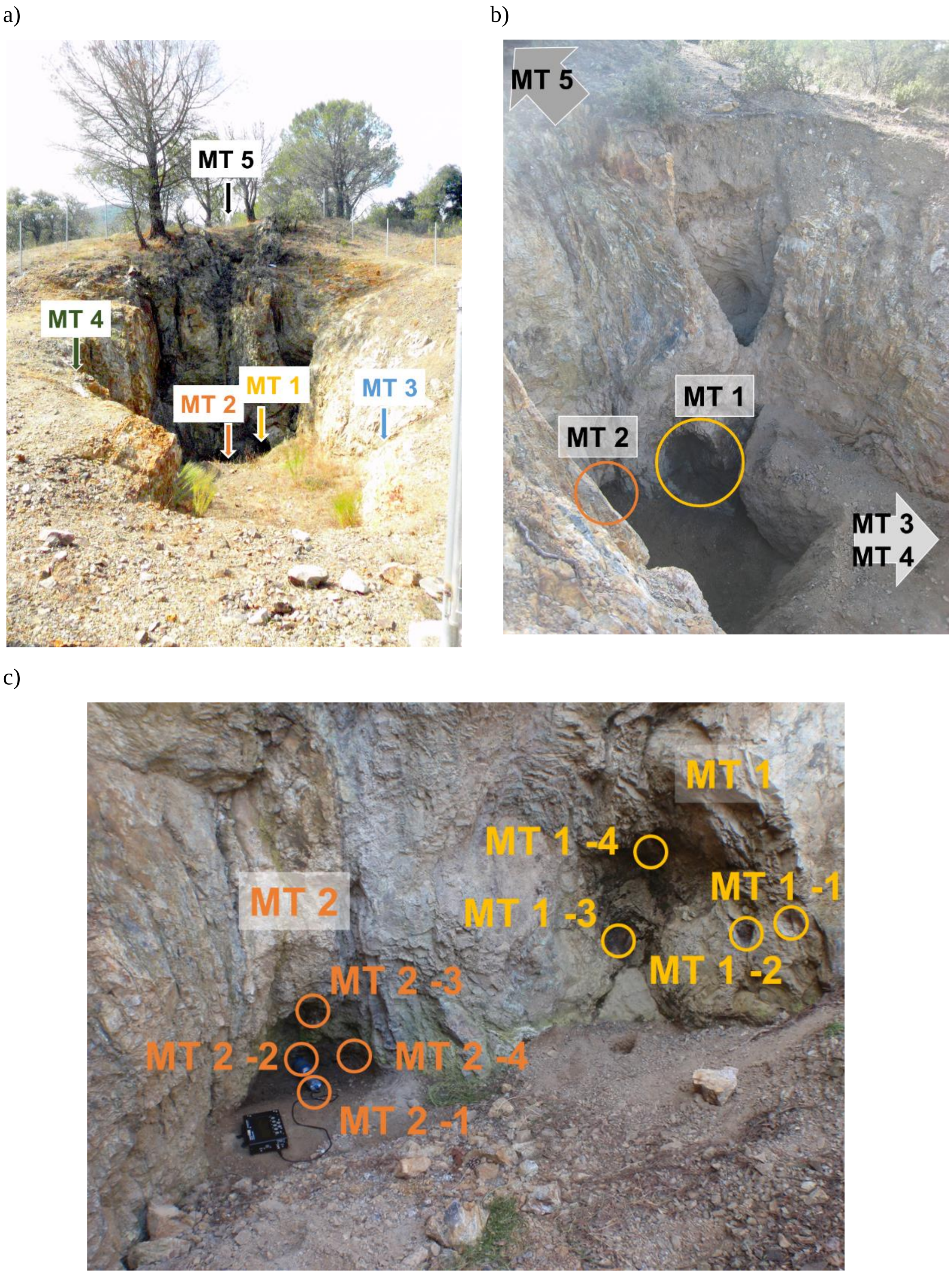

Fig. 1 Photographs of samples location at La Turquesa mine, Cornudella de Montsant (Catalonia, Spain): a) overview of the mine with identification of the sampling points (MT1, MT2, MT3, MT4, and MT5); b) view of the mine entrance with the identification of the sampling points MT1 and MT2; and c) detailed view of the shafts L2 (sampling point MT1) and L3 (sampling point MT2) and the respective samples (MT1_1, MT1_2, MT1_3, MT1_4; MT2_1, MT2_2, MT2_3, MT2_4).

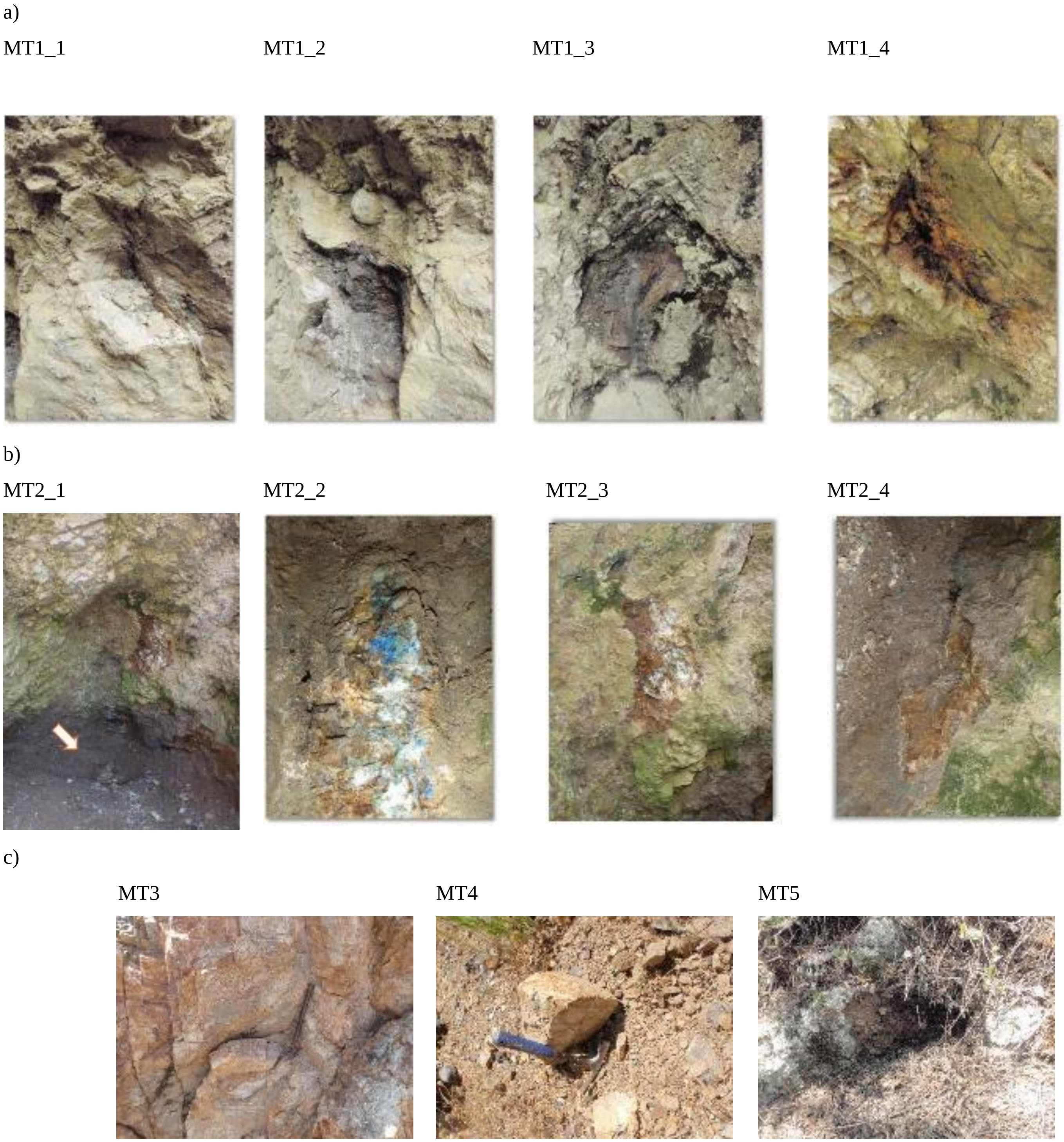

Fig. 2 Details of the La Turquesa mine, Cornudella de Montsant (Catalonia, Spain) samples: a) shaft L2, sampling point MT1 (samples from 1 to 4); b) shaft L3, sampling point MT2 (samples from 1 to 4); and c) sampling points MT3, MT4 and MT5.

Methodological approach

The first step in the sample preparation is the removal of the outer part of the rock fragments and the external part of the material collected using the stainless-steel tubes. This material was used for the chemical and mineralogical analyses, being first powdered in an agate mortar. The inner part of the samples was selected for luminescence analyses, avoiding the analysis of grains exposed to sunlight.

The mineralogical composition of rock and sediment samples [22] was achieved by means of X-ray diffraction (XRD), using a Philips Pro-Analytical spectrometer with a Cu-Kα source. Semi-quantitative analysis of mineral assemblages was undertaken by measuring the principal peak areas with intensities correction, using the recommended weighting factors [26–36].

The chemical analyses were performed at Activation Laboratories Ltd. (Actlabs) (Ontario, Canada). Chemical contents of Sc, Cr, Co, As, Br, Rb, Mo, Sb, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Th and U were obtained by instrumental neutron activation analysis (INAA) and the chemical content of Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, V_2O_5, MnO, $Fe_2O_{3(Total)}$ and CuO by X ray fluorescence (XRF).

An enriched quartz coarse grains fraction of rock and sediment samples was obtained by manual disaggregation using an agate mortar. From this material, the 180-250 µm fraction was separated by dry sieving. A conventional laboratory procedure was applied to isolate the quartz grains, by etching the samples with HCl 10 % and H_2O_2 to remove carbonates and organic matter. The resulting material was washed with distilled water and a density separation process with heavy liquid LST was applied to obtain the fraction between 2.61 gcm^{-3} and 2.70 gcm^{-3}. A final cleaning process of the quartz grains was performed by using a chemical treatment with HF 40 % and HCl 10 % solutions. After washing with distilled water, the enriched quartz coarse grains fraction was dried at 50 °C. To proceed to the luminescence measurements, monolayers of quartz grains were fixed on stainless steel discs using silicone oil (aliquots).

To confirm the use of “fire-setting” techniques, the evidence of heating was tested in the enriched quartz coarse grains fraction by two luminescence protocols. The first one was based on a previous work [14] and performed by the authors as slightly more complex thermoluminescence (TL) measurements protocol for coarse quartz grains, instead of a simple TL protocol applied to polymineralic samples [22]. Normally, TL measurements applied to quartz enable a distinction between non-heated samples and samples heated to above 300 °C, which have lower intensity in the TL signal. Thermoluminescence measurements were performed according to a sequence already described in [22]. In that work, for all the aliquots of each sample, the natural thermoluminescence curves (TLn) were measured, and subsequently groups of four aliquots of each sample were irradiated during 100, 400 and 800 s, respectively. After a pause of 12 hours, regenerative thermoluminescence (TLr) curves were obtained (TLr100, TLr400 and TLr800) [22].

The second procedure proposed in the present work is commonly used as a semi-quantitative protocol with high stratigraphic resolution in profiling studies [4, 37–40] to solve chronological issues and will be applied for the first time in the identification of ancient mining activities. In addition, a quantitative luminescence protocol is applied to refine/confirm the chronology of the copper exploitation in this mine. Due to the heterogeneous heating of the rock and the complexity of the associated protocols, this approach is a challenge, with particular emphasis on the preparation of the mineral grains for analysis (difficult in desegregating the rock for isolate and purify a quartz fraction). The semi-quantitative luminescence protocol, using five aliquots of each sample, comprising multi-signal measurements (TL, OSL and IRSL), is given in Table 1. This protocol enables the evaluation of dominant luminescence signals to guide subsequent quantitative analysis, and provides indications if the material has been heated or not [4], and efficiently produces semi-quantitative estimations of absorbed dose (apparent absorbed dose) for luminescence dating [4, 25, 38, 39, 41]. In the semi-quantitative luminescence protocol, signals that resulted from a single regenerative dose in the quasi-linear region of the sample's dose response are used. The extrapolation of the quasi-linear calibration dose response would tend to overestimate the signal that resulted from doses in the range of 10–200 Gy, in which the effects of saturation in the dose response. So, to allow the comparison between all results, the apparent absorbed doses obtained were estimated by using a common saturating exponential dose response characteristic (DRC). It was defined by using the average of the standardised post- IR OSL responses to 50 sβ, with test dose of 10 sβ used in all analyses. The DRC is described by a single saturating exponential function, $I = I\infty(1 - \exp(-D/D)$ using a signal at saturation ($I\infty$) equal to the average dose of signal saturation (D) [42]. For each sample, the average of the five apparent absorbed dose and the respective uncertainty was calculated.

Table 1 Sequence for semi-quantitative luminescence protocol, using a Riso TL/OSL automatic reader with a ^{90}Sr/^{90}Y beta. Beta irradiators giving 0,0842 (± 0,0009) Gys^{-1}.

Sequence	Two cycles	
	Natural	After irradiation (5 Gy)
Preheat TL	240 °C, 5 °C/s	
IRSL	125 s, 50 °C	
OSL	125 s, 125 °C	
Test Dose	1 Gy	
Preheat TL	160 °C, 5 °C/s	
IRSL	125 s, 50 °C	
OSL	125 s, 125 °C	
TL	500 °C, 5 °C/s	

The application of quantitative luminescence protocols to attain the proposed objectives is mainly supported by the known response of quartz grains to the thermal and optical stimulation [43]. Those protocols can provide information about heating temperatures and detect the amount of time elapsed from the last heating. The latter is correlated with the emitted light intensity (Equivalent Dose, De) taking into account the dose rate (Dr) in the studied material and its environment and enables to obtain the luminescence age (De/Dr) [43]. For the chronological assessment, the luminescence approaches include the quantitative analyses to obtain the absorbed dose. Before these analyses, the quartz purity check [44] and the dose recovery test [45] were performed. For the quantitative determination of the absorbed dose, a SAR-OSL protocol with an internal pre-heat test was applied to the enriched coarse quartz grains fraction [46]. Twenty-four aliquots were measured and the sequence of regenerative calibration doses is shown on Table 2.

Table 2 Calibration doses (in seconds) used in SAR-OSL sequences for luminescence dating of heated material collected at La Turquesa prehistoric mine (sample MT1_1, shaft L2). OSL was measured at 125 °C for 125 s. Beta irradiators giving 0,120 (± 0,002) Gys^{-1}. The sequence includes a pre-heat test with temperatures between 180 °C and 280 °C and the cut heat temperature was 160 °C.

Sequence	Time of irradiation (s)	Aliquots	Pre-heat temperature (°C)
Natural	-	1-4	180
β	40	5-8	200
Z	0		
β/4	10	9-12	220
β/2	20		
2β	80	13-16	240
4β	160		
Zero (R)	0	17-20	260
β (R)	40		
β (IR)	40	21-24	280
β test	7		

where R indicates a repeat point and IR indicates a repeat point where OSL response was measured following infrared exposure to test the presence of other minerals than quartz.

Signals were obtained by subtracting the average count rate in the last 5 s of measurement from that in the first 5 s, which included the majority of the rapidly decaying OSL. Signals normalized to subsequent test dose responses were fitted with linear curves, and the absorbed dose was interpolated. Based on Luminescence Analyst software [47], results were accepted when: (i) the relative uncertainty of the natural test dose signal σTn was < 10 %; (ii) the recycling ratio was consistent with unity at 2σ; (iii) the OSL IRSL depletion ratio [44] was consistent with unity at 2σ; and (iv) the sensitivity corrected recuperation signal (i.e., the OSL signal in response to a zero Gy regenerative dose) was consistent with zero at 2σ. The accepted results were statistically analysed to estimate the absorbed dose for the sample using the robust mean and the respective uncertainty calculated by Robust Statistics V1.0 [48].

Dose rate estimation was obtained combining cosmic, beta, and gamma dose rates. The cosmic dose rate was calculated considering the density of the studied materials [49, 50], and attenuation factors were applied [51]. The evaluation of the material dose rate was made considering the chemical content of K, Rb, Th and U, obtained by INAA. The environment dose rate was determined in situ measurements using a field gamma-ray spectrometer (FGS) at each sampling location, using a 3''x 3'' NaI probe with an HPI Rainbow MCA. Stripped counts in the windows 1380–1530 keV, 1690–1840 keV, and 2550–2760 keV (designed to obtain signals dominated by ^{40}K, ^{214}Bi and ^{208}Tl respectively), were calibrated relative to previous measurements in the Oxford and the Gif-sur-Yvette blocks [52, 53], to obtain apparent parent element concentrations, assuming equilibrium in the ^{232}Th and ^{238}U series. The estimation of beta and gamma radiation was obtained from elemental concentrations of K, Rb, Th and U using conversion factors [51] and was corrected for water content [54], assuming 5% of water content. For the dose rate estimation, 83% of beta dose obtained from INAA results and 21% of gamma dose from INAA results added to 79% from FGS results were considered.

Results and discussion

Compositional studies

In order to achieve a more detailed characterization of La Turquesa mine, a compositional study was performed to complement the luminescence analysis. In this way, the mineralogical assemblage [22] and the chemical composition of the two mining shafts and geological background was made. The XRD analyses performed showed that quartz is the main mineral in all samples. Phyllosilicates, particularly micas, and traces of hematite and cuprite (Table 3) occur. Azurite was detected in trace amounts in the Cu vein and on samples MT2_1 and MT2_2, and the highest proportion of phyllosilicates was found in the sediment. All these results are in accordance with the mineralogical associations obtained earlier for the mineralised zones and the host rock [23] of this area. Despite the high temperatures, which can promote the production of new formed minerals [32, 55–57], no mineral phases resulting from this process were observed [22]. However, in La Turquesa mine "fire-setting" cannot be excluded, and was previously discussed [22].

The chemical results obtained by INAA and XRF for La Turquesa mine samples show that all samples are mainly composed by SiO_2 (Table 3), which is in accordance with the mineralogical assemblage found. Some chemical variations are observed in the studied samples: (i) despite the low amounts of CuO in samples, the higher contents were detected in the samples collected nearest to the copper vein, as expected, in each shaft (MT1_3, MT1_4, MT2_2, and MT2_3) particularly in sample MT2_2, where an intense blue colour (Fig.) was observed during the sampling process, nevertheless only traces of azurite and cuprite were identified by XRD in these samples; (ii) the highest contents of Na_2O, MgO, Al_2O_3, K_2O, TiO_2, Rb, Cs, Ce and Th were detected in the sediment (MT2_1) collected at the shaft L3, where the higher proportions of phyllosilicates were detected; (iii) the lowest contents of P_2O_5, CaO, V_2O_5, Fe_2O_3, CuO, Cr, Mo, Sb, heavy rare earth elements (HREE) and U, and the highest content of Si_2O occur on the samples of geological background (MT3 and MT4), in accordance with the higher amounts of quartz; and (iv) the highest contents of P_2O_5, CaO, MnO, and Co were found in sample MT1_4. Higher contents of rare earth elements (REE) are found on shaft L3, except for sample MT2_2. Samples MT3 and MT4 show positive Ce anomalies and, in general, L2 samples show lower fractionation of REE.

In general, the high proportions of quartz present in samples may difficult the identification of other mineral phases, existing in smaller amounts, and which may incorporate some of the chemical elements such as Co, Mn or As. It should be noted that other techniques should be applied to identify these mineral phases that could include carbonates, iron oxy-hydroxides or heavy minerals.

Despite the heterogeneity observed in the chemical composition of the samples collected in the shafts, a cluster analysis using chemical elements as variables, and unweighted pair-group average rule and the Pearson correlation coefficient, suggests the existence of three clusters. One of the clusters comprises the rock samples (MT3 and MT4) and the sediment (MT2_1) suggesting that this sample collected on the shaft L3 may be derived from the weathering of the bedrock surrounding. It should be mention that this sediment was deposited at the shaft L3 after the last mining activities.

Table 3 Chemical composition obtained by INAA and XRF; semi-quantification of mineralogical assemblage obtained by XRD for the samples collected at shafts L2 and L3 from La Turquesa prehistoric mine (nd – not detected; * - including micas; traces - < 5%).

		L2				L3				Bedrock		Cu vein
		MT1_1	**MT1_2**	**MT1_3**	**MT1_4**	**MT2_1**	**MT2_2**	**MT2_3**	**MT2_4**	**MT3**	**MT4**	**MT5**
Na_2O		0.020	0.010	0.010	0.010	0.090	0.010	0.010	0.010	0.010	0.020	0.010
MgO		0.080	0.040	0.080	0.050	0.290	0.010	0.070	0.150	0.070	0.140	0.110
Al_2O_3		1.70	1.19	2.34	1.86	5.43	1.39	2.82	4.41	1.61	2.63	3.59
SiO_2		94.3	95.6	91.5	91.7	88.2	94.1	89.6	83.9	97.4	94.9	86.1
P_2O_5		0.100	0.120	0.280	1.060	0.200	0.230	0.760	0.510	0.020	0.040	0.370
K_2O	%	0.460	0.300	0.520	0.400	1.28	0.320	0.620	1.00	0.490	0.690	0.860
CaO		0.070	0.060	0.080	1.07	0.230	0.180	0.340	0.110	0.010	0.030	0.110
TiO_2		0.060	0.040	0.090	0.060	0.340	0.050	0.100	0.120	0.050	0.120	0.120
V_2O_5		0.081	0.088	0.097	0.022	0.027	0.036	0.115	0.058	0.003	0.008	0.068
MnO		0.003	0.002	0.002	0.363	0.066	0.003	0.003	nd	0.002	0.002	0.002
$Fe_2O_{3(Total)}$		2.23	1.01	2.99	1.24	1.59	0.730	3.03	5.95	0.390	0.940	5.76
CuO		0.183	0.197	0.679	0.792	0.115	1.32	0.675	0.393	0.028	0.022	0.329
Sc		2.60	1.80	3.50	3.30	7.30	1.90	3.80	8.90	2.40	3.10	4.90
Cr		90.0	85.0	50.0	18.0	37.0	29.0	109	115	12.0	15.0	62.0
Co		7.00	5.00	7.00	733	39.0	5.00	12.0	23.0	7.00	4.00	19.0
As		111	76.1	216	332	196	127	756	942	49.1	106	112
Br		1.10	1.20	0.600	nd	1.30	0.900	nd	4.60	nd	1.00	nd
Rb		Nd	18.0	32.0	nd	55.0	nd	30.0	22.0	23.0	18.0	51.0
Mo		31.0	17.0	42.0	32.0	8.00	14.0	54.0	218	nd	1.00	60.0
Sb		3.20	1.90	8.90	3.80	4.30	4.00	24.9	55.0	1.00	1.90	3.90
Cs		1.00	Nd	Nd	1.00	3.00	nd	nd	nd	2.00	2.00	3.00
Ba	**mg/kg**	160	170	140	150	380	nd	550	130	210	260	200
La		4.20	4.50	15.0	12.0	32.0	9.90	30.6	51.0	8.10	10.8	18.9
Ce		9.00	9.00	28.0	28.0	59.0	18.0	44.0	57.0	19.0	28.0	34.0
Nd		6.00	7.00	28.0	16.0	21.0	12.0	35.0	28.0	9.00	10.0	31.0
Sm		0.900	0.900	4.00	2.70	4.00	1.60	6.60	4.20	1.10	1.50	6.10
Eu		0.400	0.400	1.30	1.50	1.20	0.600	2.30	1.60	0.300	0.400	2.40
Tb		0.050	0.050	1.40	0.050	0.600	0.050	1.50	0.050	0.050	0.050	1.80
Yb		0.900	0.900	2.00	1.30	1.90	0.900	4.30	2.20	0.400	0.900	2.50
Lu		0.240	0.230	0.480	0.410	0.430	0.220	0.840	0.600	0.070	0.130	0.540
Th		1.10	0.800	1.80	2.30	5.20	1.30	2.50	4.40	1.30	2.80	2.60
U		9.40	9.70	20.5	19.0	6.00	8.10	26.7	30.4	1.30	0.900	22.0
Quartz		87	94	90	92	76	96	94	85	94	91	87
Phyllosilicates		9 *	Traces	8 *	5 *	21 *	Traces*	6 *	12 *	6	6 *	9 *
Hematite	**%**	Traces	Traces	Nd	Traces	Traces	Traces	Traces	Traces	nd	nd	Traces
Cuprite		Traces	Traces	Traces	Traces	Traces	nd	nd	Traces	nd	Traces	Traces
Azurite		nd	Nd	Nd	nd	Traces	Traces	nd	nd	nd	nd	Traces

Luminescence studies

The first luminescence measurements performed in La Turquesa mine [22] were used to identify eventual heating of coarse quartz grains extracted from rock fragments and sediment. The results previously obtained pointed out that in shaft L2, the TLn signals of the enriched quartz coarse grains fraction have a higher intensity than those of the TLr. The same behaviour was found for the shaft L3, indicating that the analysed quartz retains most of the unchanged geological signal. The detailed description of these luminescence measurements were reported in the previous work[22], and the Semi-quantitative luminescence protocol applied demonstrates the heating of some analysed samples, corroborating the results obtained by TL protocol [22]. In addition, this semi-quantitative protocol was used to plan further luminescence approaches, by evaluating the behaviour of quartz grains to regenerative protocols for the determination of the absorbed dose. In general, quartz grains have slightly sensitivity changes when natural signals are compared with regenerative signals (after irradiation with 5 Gy). In this work, the most evident sensitivity changes were observed for samples MT2_1 and MT3, indicating that the quartz of these samples is not the most suitable one for the application of the luminescence regenerative protocols to determine the absorbed dose. The ratio between the absorbed doses obtained by IRSL and OSL signals, using the INIT protocol, was less than 1 for most of the samples allowing to infer about the purity of the analysed quartz: IRSL/OSL <1 point to low feldspars contamination. The OSL signals obtained using the semi-quantitative protocol, were also useful to detect the eventual heating of coarse quartz grains extracted from analysed samples, as well as to estimate the average of the apparent absorbed dose (Fig. 3).

Regarding the quartz extracted from the sediment used as reference for the luminescence signal boundary of last mining activity (MT2_1), it has the lowest apparent absorbed dose (about 1 Gy). This means that in this sample, the geological signal was bleached by light and/or heat exposure. After the bleach of the geological signal, the absorbed dose obtained reflects the time since the MT2_1 sediment was deposited in shaft L3, probably corresponding to the end of last mining activities. Regarding the quartz grains extracted from the rock fragments used as reference for the luminescence signal boundary of geological signal (MT3 and MT4), they have low apparent absorbed doses, especially the sample MT4 with 3 Gy. These low doses are probably a consequence of the loss of geological signal during recently mining activities. The sample collected in the non-exploited copper vein (MT5) and used as reference for the luminescence signal boundary of geological signal has the highest apparent absorbed dose preserving the geological signal. For the rock fragments MT1_4 (shaft L2), MT2_2, MT2_3 and MT2_4 (shaft L3) high values of apparent absorbed dose were obtained, 15 - 29 Gy, pointing to the absence of heating and indicating that the analysed quartz retains most of the unbleached geological signal. For the rock fragments MT1_1, MT1_2 and MT1_3, collected in shaft L2, lower apparent absorbed doses were obtained, ranging from 4 Gy to 8 Gy, suggesting that the quartz grains extracted from these samples were probably bleached by the "fire-setting" procedure. Despite the lower values obtained for these three samples, an incomplete bleaching (partial removal of the natural geological signal) was observed, due to the heterogeneous heating conditions associated to this mining procedure. Thus, an overestimation and a spread of results of the apparent absorbed dose occur. The lower apparent absorbed dose (about 4 Gy) obtained for sample MT1_1 indicates that quartz from this sample must have had more homogeneous heating conditions. In this case, the sample MT1_1 seems to have better bleaching conditions, and can be considered as a representative sample of the heating event related with "fire-setting" in the pre-historic period.

Comparing the two approaches, TL and semi-quantitative protocols, the use of "fire-setting" techniques to copper ore extraction in the prehistoric seems to be confirmed, being the semi-quantitative protocol a better option since it enables to evaluate diverse luminescence signals (IRSL, OSL, TL) using low amount of material, and in a faster way.

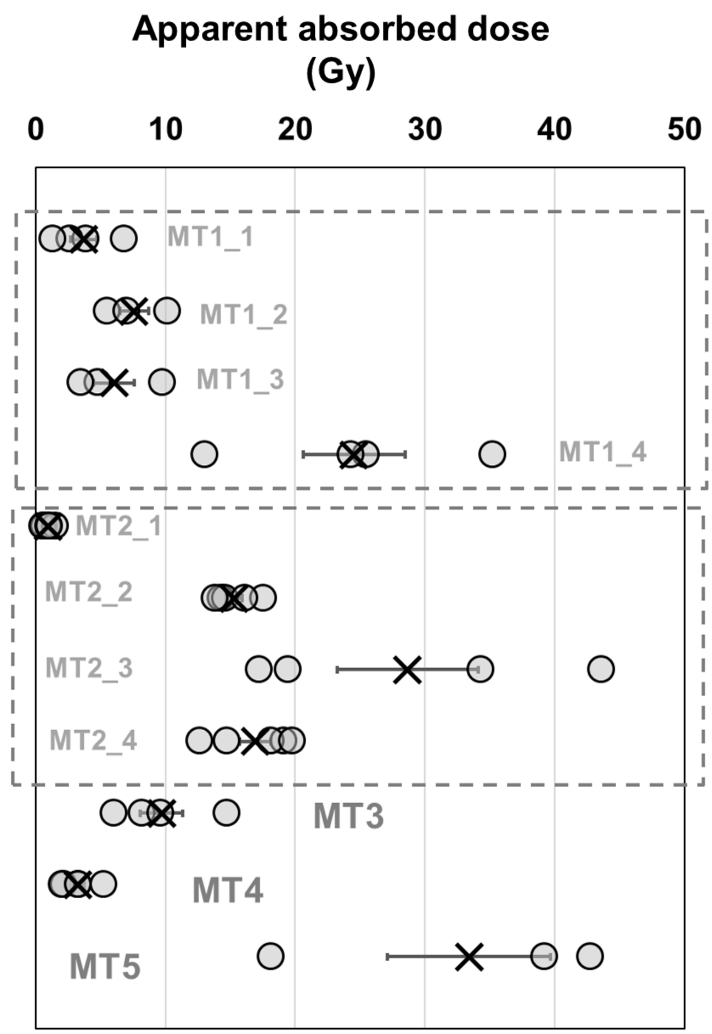

Fig. 3 Apparent absorbed dose, obtained by applying the INIT luminescence protocol to enriched quartz coarse grains fraction extracted from samples collected at La Turquesa mine (Cornudella de Montsant, Catalonia, Spain). The absorbed dose was obtained considering the OSL signals of five aliquots for each sample. The average and the respective uncertainty are highlighted (X)

Considering that sample MT1_1 had better bleaching conditions, this sample was the only one selected to further luminescence protocols, performing the quartz purity and the dose recovery tests. The quartz purity test shows that OSL IR depletion ratio of the quartz grains from MT1_1 was smaller than 10 % and the dose-recovery test shows that the mean of dose recovery ratio (measured/given dose) for three aliquots was 1.06 ± 0.02, pointing to the applicability of SAR-OSL protocol to determine absorbed dose in this sample.

The quantitative analyses performed by SAR-OSL protocol on sample MT1_1, only 15 of the 24 aliquots have acceptable results. The measured material shows a recycling ratio ~1, as expected based on quartz purity test. The OSL signal is dominated by the fast component, which is usually considered better for quartz OSL dating (Fig. 4a). No consistent effect of preheat temperature in the De was observed, and there is a wide dispersion of values for each temperature tested (Fig. 4b). For each aliquot, the De obtained shows high uncertainties (an example in Fig. 4c) and the obtained robust mean using the 15 accepted values was 8 ± 1 Gy (Fig. 4d). The over dispersion of values and the uncertainties observed in each aliquot might be a consequence of the heterogeneous heating processes that produces an incomplete bleach. Some grains may have been exposed to sufficiently high temperatures to completely empty the latent OSL signals, whereas other grains still carry a residual OSL geological signal. The existing residual remains of the copper mining activities may explain the observed heterogeneity of the bleaching processes of MT1_1 material. Thus, the determination of the equivalent dose in incompletely bleached samples using multi-grain aliquots can lead to significant dose overestimation.

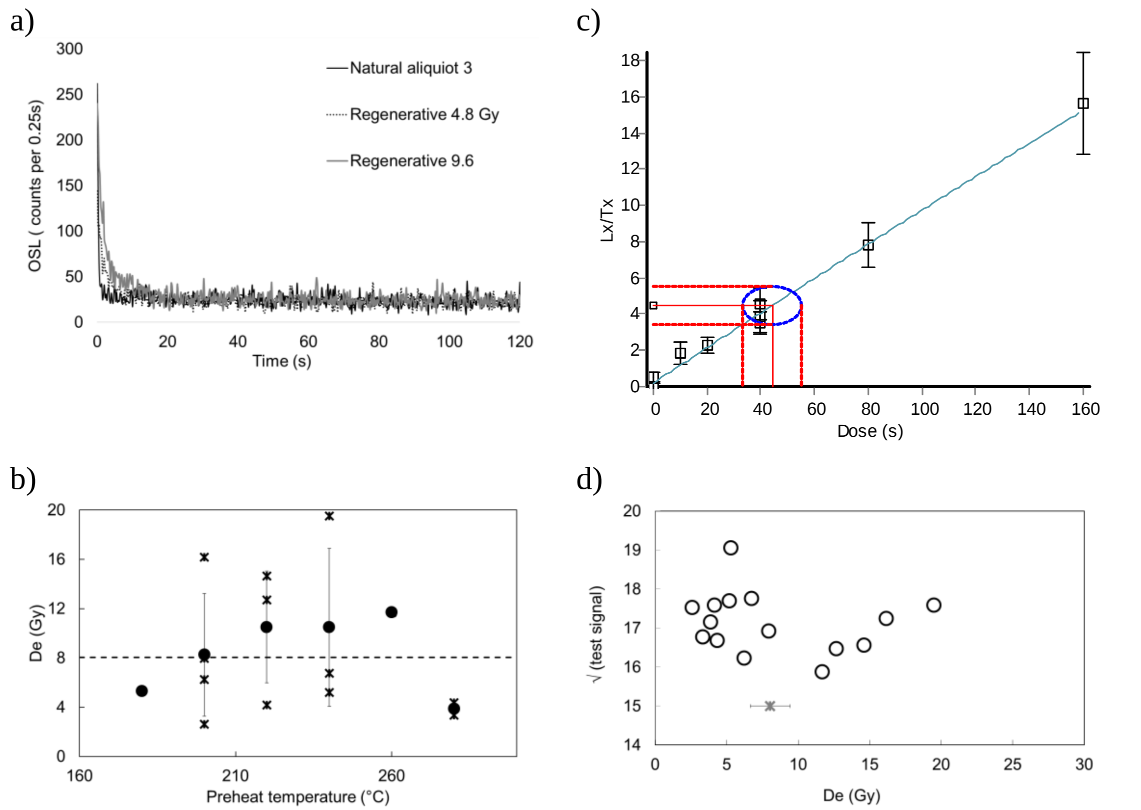

Fig. 4 SAR-OSL results for quartz from sample MT1_1 collected at La Turquesa mine (Cornudella de Montsant, Catalonia, Spain): a) OSL natural and regenerative curves for aliquot 3; b) De values as a function of preheat temperature (mean values of each temperature - full marks); c) example of sensitive corrected OSL (Lx/Tx) as a function of regenerative doses for aliquot 13 at preheat 240 °C; and d) Square root of tests signal as a function of De (robust mean - cross mark)

Considering the K, Rb, Th and U contents obtained by INAA and FGS (Table 4), as well as the estimated dose rate of sample MT1_1 (2.8 ± 0.1 Gy/ka), and the absorbed dose obtained by SAR-OSL (8 ± 1 Gy), the luminescence age obtained for this sample is 2.8 ± 0.4 ka. This date indicates a chronological framework between 1400 and 600 BC, that is, a span of 800 years.

Table 4 Chemical elements content obtained by INAA and FGS for sample MT1_1 collected at shaft L2 from La Turquesa prehistoric mine (Cornudella de Montsant, Catalonia, Spain).

		INAA	FGS
K	(%)	0.46	0.402
	±	0.02	0.008
Rb	(mg/kg)	14.0	nd
	±	0.7	nd
U	(mg/kg)	9.4	8.3
	±	0.5	0.8
Th	(mg/kg)	1.10	2.3
	±	0.06	0.2

(nd – not determined)

The historical-archaeological interpretation of the luminescence age here obtained confirms the prehistoric character of the mining work documented during the archaeological excavations. This fact is supported by the unequivocally prehistoric attribution of the assemblage of macrolithic mining tools recovered [58]. As previously mentioned, the lead isotope analysis also showed that probably the mine was exploited in the Late Chalcolithic (2800-2300 cal BC), due to the coincidence of the isotopic signature of the mine with a copper awl of Coveta de l'Heura (Ulldemolins). The set of mining tools more elaborated and with hafting devices to be handled, as well as the isotopic coincidence with the smelting vessel of the Balma del Duc (Montblanc), point to an exploitation in the Early-Middle Bronze Age (2300-1350/1300 cal BC) [24]. Regarding the radiocarbon dating [21] of the shaft L1, it is not possible to know if there was mining exploitation in medieval times, although there is no doubt that during this period there was a filling phase. The luminescence ages obtained for shaft L2 may indicate an exploitation phase at the end of the Middle Bronze Age, or in the Late Bronze Age (3.0 ± 0.4 ka, 1.0 ± 0.4 ka), or already in the Iron Age. Considering the archaeological evidence, this late age may be a consequence of the uncompleted bleach of the quartz grains observed, resulting in a higher range of the luminescence age. This fact is also supported by the archaeological investigations carried out on settlements, and on circulation of metals in Priorat County, from the year 2000 until now. This revealed that during the Iron Age, copper was mainly imported from the south of the Iberian Peninsula (the mining basin of Linares, Jaén), and to a lesser extent, from the southeast [59, 60], and that local copper comes from the Molar-Bellmunt-Falset basin (south of the country).

Finally, it is important to highlight that the luminescence age of the sample MT1_1 collected at shaft L2 is subsequent to the shaft L1. From a stratigraphic point of view and taking into account the way of operating in ancient mining, most probably the mining shafts L2 and L3 were opened after the shaft L1. As a result, the new luminescence ages provide an *ante quem* date for it.

Conclusions

The compositional studies enabled a more detailed compositional characterization of the mined Cu-vein materials and geological background at La Turquesa mine. Despite the heterogeneity in samples composition, a relation between bedrock samples and the sediment was found.

The luminescence protocols approach used in this work, particularly the semi-quantitative protocol, has more advantages than the TL protocol, as it needs lower amount of material and measurement time, it enables the estimation of the absorbed dose, as well as the study of multiple luminescence signals (TL, IRSL and OSL). This prior comprehensive luminescence study of samples enables to design dating protocols in a more suitable way.

The selection of samples as luminescence boundaries for both geological and last mining activity signals reveals to be a good strategy for the interpretation of the luminescence results, and better understand the luminescence proprieties of the analysed materials, enabling a better establishment of the chronological framework of the studied contexts.

This work demonstrates the suitability of luminescence for identifying “fire-setting” techniques in mining contexts and evaluate the absolute dating properties of the samples. The results obtained from luminescence measurements allowed inferring that sample MT1_1 collected at shaft L2 was exposed to “fire-setting” conditions, as shown by the lower apparent absorbed dose obtained. The luminescence age of this sample points to mining exploitation at La Turquesa mine during the Middle/Late Bronze Age.

Considering that the character of mining often leads to destruction of the archaeological record making difficult to date the contexts and lithic tools, the used methodology in this work, by dating through luminescence, is a valuable contribution to more accurate absolute dating of ancient mining activities with "fire-setting" evidence.

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