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The Pulpí gigantic geode (Almería, Spain): geology, metal pollution, microclimatology, and conservation

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J. García-Guinea National Museum of Natural Sciences (CSIC), José Gutiérrez Abascal, 2, 28006 Madrid, Spain **Abstract** The discovery of the giant Geode of Pulpí (Almería, Spain) was considered as an important highlight in the geological heritage of Spain. Projects developed for their conservation were immediately initiated with legal figures of protection and tourist projects. The Geode has a tourist interest, which must be tempered by environmental restrictions limiting the public visits. First results demonstrate that a continuous visit of two or three people for more than 10 min provokes the appearance of condensation and risks corrosion of the gypsum crystals. In addition, the electron microprobe analyses confirms (1) the hydrothermal phases of iron-manganese in carbonated host

rock; (2) the presence of sulphides with Fe–Zn–Pb–Ag–Sb–Cu–Hg–As–Te–Se; and (3) Ba, Ca, and Sr sulphates with mercury traces. The present proposal to label the geode and the mining environment as geological-natural heritage is feasible, although any tourist adaptation must not permit visits to the geode indoor and Hg levels must be controlled.

Keywords Geo-mining heritage · Geode · Gypsum · Environmental management · Microclimatic monitoring

Introduction

Geo-mining heritage in Spain

The mining areas became potential tourist attractions when the extractive activity ends. This is due to the high natural value of its physical environment and the ethnographic importance of the systems and infrastructures of exploitation. The Iberian Peninsula has been an area of mining tradition since ancient times, and it shows numerous traces of extractive activity through different cultures. In the later decades of last century the mining economic activity decreased in Spain, causing the closure of many mines and associated industries. The action in recent years has been the socioeconomic revaluation of the mining areas abandoned, by means of the restoration

and adding value as tourist attraction of mines and diverse installations of extraction (Calaforra and Fernández-Cortés 2005). One of the most noticeable examples in the Spanish territory is the mining area of Río Tinto (Huelva, southwest of Spain), which contains the largest concentrations of metal and sulphur deposits known in Europe (Mitjavila et al. 1997; Leistel et al. 1998; Solomon et al. 2002). After the general mining crisis in the Iberian Pyrite Belt in Huelva province in 1987, all the social agencies of the region aimed at tapping the significant historic capital in mining to spark new tourist initiatives. Another example of conversion of mining activity into tourist resources is the mineralization of mercury in the region of Almadén (Ciudad Real). The market recession of the 1970s and 1980s, together with environmental problems associated with poorly planned mercury extraction (Martínez-Frías et al. 1998; Ferrara et al. 1998; Higueras et al. 2003; Nevado et al. 2003; Rytuba 2003), brought an end to the mining. Significant efforts have been done to diversify the economy of the region, to rehabilitate Almadén's historic and geological heritage and to promote historic and scientific understanding. In addition, the remains of the Roman mines in Las Médulas (León) are an important geotouristic site in Spain (Sánchez-Palencia et al. 1998). It was included in the UNESCO List of World Heritage Sites in 1997. The principal objectives of Las Médulas management include the protection, promotion, and diffusion of information about this mining area and the coordination of public and private tourist activities.

Big crystals in hypogeal and mining environments

Although isolated examples of big crystals of different minerals are preserved in hypogeal spaces (Palache 1932; Rickwood 1981), the most spectacular cases are the Cave of the Swords and the Cave of the Crystals, both in the mining district of Naica (Chihuahua, Mexico). The first one, discovered in 1910, is a single 80 m diameter cavern, situated 120 m below the ground surface, and there are large "prismatic" gypsum crystals of up to 2 m in length and 25 cm in diameter (Foshag 1927; Hill and Forti 1997). These crystal formations have been damaged over the years by the activities of mineral collectors, and only dusty and opaque crystals remain. In April 2000, the world's biggest and purest gypsum crystals were discovered in the same mining area, after the excavation of a 300 m long communication tunnel (Lazcano-Sahagún et al. 2001; Lazcano-Sahagún 2002; London 2003). The crystal formations reach 10 m in length and 2 m in diameter. The cave atmosphere registers air temperatures close to 50°C and humidity at saturation point and these environmental characteristics make it unfeasible to open the cave for tourism. There are other gigantic crystals without reliable references with respect to their characteristics, genesis, or state of conservation, e.g., the gigantic crystals of gypsum in Debar (Macedonia) or the large halite and sylvite crystals in the potassium mines of Carlsbad (New Mexico, USA) (Minette 1999). The mining activity has caused the destruction of large crystallizations and currently there are only examples of minerals collections. Examples include the large crystals of fluorite in the mine Rogerley (Weardale, UK) (Fisher and Greenbank 2000). In the case of the gigantic geode of gypsum of the mine Cozzo Disi (Sicily, Italy) there are only references and some graphic documents, which have not been contrasted scientifically (Forti 2004).

The mining activity or water pumping wells construction has permitted the discovery of large geodes whose end has been the tourism adaptation. In this

sense, tourism has assured in many cases conservation of the environmental heritage, because added economic and cultural values are factors that can be used to help develop their protection. This is the case of the gigantic geode of celestine crystals, which was discovered in 1897 in Put-in-Bay (Ohio, USA) or the Grotta Santa Barbara in the mining district San Giovanni (Sardinia, Italy) with numerous examples of barite crystals (Sarritzu 2005; Forti et al. 2005). Other declined mining districts, such as the Upper Silesia (Poland) case, employ many retired miners as tourist guides along 28 ancient mines preserved for tourist purposes, e.g., halite crystal formations in the Wielitzka mine near Krakow are being refurbished as an important geo-mining heritage and as a local wealth source by tourism.

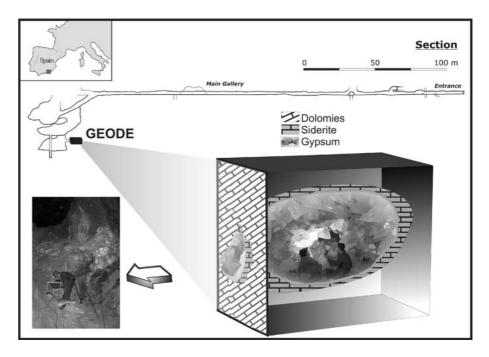
Along with the previous examples of mining environments that have been revalued as tourist-didactic attraction we emphasize in this article the contribution of the scientific world to the valorization and protection of the giant Geode of Pulpí (Almería, Spain) and its mining environment. In this case the singular geo-mining and ethnographic values converge with the discovery of a huge geode, which has become one of the most prominent worldwide geological phenomena. The giant Geode of Pulpí (Almería, Spain) was discovered in 1999 by mineral collectors inside an old iron and lead mine (Pilar de Jaravia mining district). It is found 3 km from the coast at a depth of 50 m (Palero et al. 2000). The volume of the void is 10.7 m³, with 8 m length, 1.8 m width, and 1.7 m height, with a funnel-shape entrance (Fig. 1). This cavity is completely covered with gypsum crystals of 0.5×0.4×0.3 m³ size, and some of them are 2 m long (García-Guinea et al. 2002). This work collects the lines of action directed to the conservation and evaluation of the tourist potential of this geological patrimony. The main efforts have been directed to the articulation of legal figures of protection and research studies for evaluating the visits viability inside the geode, the geological origin of geode minerals, and the potential danger of heavy metals for visitors.

Methodology

Pulpí mining district: geological setting

The Argar culture was characterized by a flourishing metallurgy of copper, silver, and gold that appeared at the beginning of the second millennium BC in the Almería region of southeastern Spain. This culture developed a dynamic trade with centers in the eastern Mediterranean reaching its peak between 1700 and 1000 BC and spread all over the Mediterranean. The discovery of silver and lead sulphide in Herrerías and Sierra Almagrera in 1838 AD brought about a brilliant mining period. The Aguilón mountain range was also a

Fig. 1 Old iron and lead mine section and scheme of the giant Geode of Pulpí (Almería, Spain)



subject of intensive lead—iron mineral exploration and mining, particularly the Pilar de Jaravia mine having the largest quarries and pits and the mineral processing plant. Nowadays, this extraction area includes archaeological remains of milling, smelting and lead—iron slag heaps, and a railway to Águilas harbor. Mining activities were definitively closed in 1970 AD.

The Fe-Pb-Ag-Ba-Sb-Hg Pilar de Jaravia mine is hosted in the Alpujárride complex (Betic Cordillera) between the Palaeozoic dolomite-marble bed and the

characteristic Triassic regional blue-grey metapelite, e.g., Sierra Almagrera (Morales-Ruano 1994; Martínez-Frías 1998; Martínez-Frías et al. 1998). The carbonate bed displays a remarkable mineralization of iron—manganese with siderite substitution in depth and oxy-hydroxide in the outer levels. The regional calc-alkaline volcanism, Neogene in age, was escorted with an intense hydrothermal Ba-Sb-Ag-Au-Fe-Zn-Hg-bearing activity in a wide metallogenetic belt from Cabo de Gata to Cartagena. In the local surroundings of Pilar de Jaravia, the

Fig. 2 Detail views of the crystals inside the giant Geode of Pulpí (Almería, Spain)



volcanism is shoshonitic, tracking regional NS faults and forms similar mineralization, as follows: (1) Fe-Mn-Pb-Ag-Ba-Sb (Sierra Almagrera-Herrerías), (2) Fe-Mn-Ba-Hg-Sb-Pb-Ag-Zn-As (Valle del Azogue, next to Pilar de Jaravia), (3) Fe-Mn-Pb-Ag-Sb-Cu-Hg-Ba-Sr-As (Pilar de Jaravia). In the Pilar de Jaravia case, three different mineralization phases under hydrothermal conditions are clearly observed: first, iron-manganese mineralization such as siderite and Fe-Mn oxy-hydroxides; second, sulphides and sulphosalts such as galena, pyrite, and bournonite; and third, sulphates and mercury such as baryte, celestine, and mercury. The mercury emissions are present in sulphates and host rocks analyzed during this study, in the Azogue Valley mercury ore deposit and in other small mine located 3 km to east of Pilar de Jaravia.

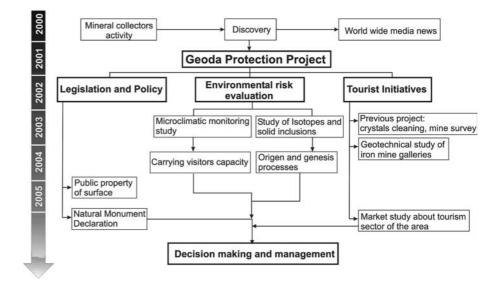
The large geode cavity with large crystal sizes, perfect shapes, high transparency, and minor solid inclusions (Fig. 2) must be formed in a unique geological environment along three main stages (García-Guinea et al. 2002): (1) karstification of Triassic dolomites under conditions of pronounced acidification, in the presence of hydrothermal fluids rich in hydrogen sulphide, (2) deposition of fine needles of Celestine (SrSO₄) in the walls of the void generated, (3) gradual cooling with slow growth of gypsum crystals sealing in the fine celestine needles. Combined stable isotope and fluid inclusion data indicate that this later fluid was a result of dissolution–recrystallization of earlier marine Tertiary evaporates.

Microclimatic monitoring and electron microprobe analysis (EMPA)

After the geode discovery, one of the first steps towards its conservation was to initiate an investigation to

describe its microclimate under natural conditions and its response to occasional visits by small groups of visitors. It is in short, to define to what extent visits to the geode could impact its natural environment. Using the results of the monitored visits, different situations were simulated with respect to the number and frequency of visitors, modeling and what could happen if the geode were opened to tourists (Fernández-Cortes 2005). The monitored visits were typified by a restricted number of people, a limited time within the geode, and direct contact between the air within the geode and the visitor. Thirty experimental visits were undertaken, with groups of between one and three people remaining in the interior of the geode for 5-30 min. A customized data logger, with special sensors designed for the narrow range of measurements expected, was installed to measure the physical characteristics of air temperature, temperature at the crystal surface, relative and absolute humidity, dew point, atmospheric pressure, and rate of airflow. Temperature and relative humidity of the air were measured by a Vaisala Humicap® humidity and temperature probes HMP45A (Humicap180[®] and Pt100 sensors), rate of air flow was measured by hot film anemometer model EE70 (E + E Elektronik Ges.m.b.H), air pressure by a silicon capacitive absolute pressure sensor model PTB101B (Vaisala Barocap®), temperature at the crystal surface by a self-adhesive patch Pt100 sensor (Labfacility Ltd), and the absolute humidity and dew point by the model EE30EX (E+E Elektronik Ges.m.b.H), which combine a humidity sensor HC1000-40 (measuring range 0–100% RH and accuracy $\pm 2\%$, between 0 and 90% RH, and $\pm 3\%$, between 90 and 100% RH) and a temperature sensor Pt1000 (measuring range -40 to 60° C and accuracy $\pm 0.2^{\circ}$ C). Continuous monitoring of variables that are relatively simple to measure, such as temperature, and in particular the

Fig. 3 The approaches and process of the protection project in the giant Geode of Pulpí (Almería, Spain)



calculation of recovery time following monitored visits, forms a very useful tool for determining the possibility of visits to an enclosed space like the geode.

The crystal-chemical characteristics of the Pilar de Jaravia samples, i.e., sulphates, sulphide-sulphosalts, carbonates, and silicates, were determined on the basis of a large series of electron microprobe analyses (EMPA) (Jeol Superprobe JXA-8900M), bulk and channel-selected (TAP, PETJ, LIF, PETH) X-ray spectra searches and identification routines. The standards used were natural and synthetic crystals from a collection stored at the 'Servicio de Microscopía Electrónica Lluis Bru' (Complutense University, Madrid).

Results

Conservation projects of the giant Geode of Pulpí

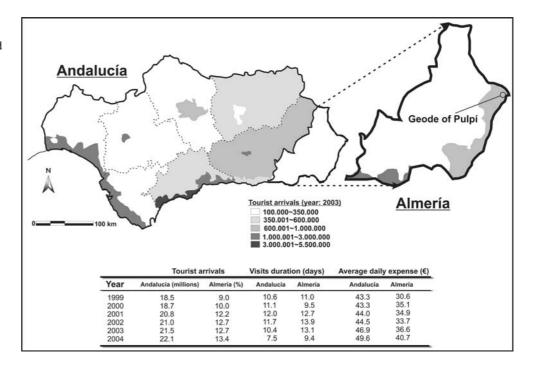
Following the discovery of the geode, two actions were taken related to its conservation. First, the urgent protective measures adopted for avoiding the danger of the gypsum crystals extraction, even more after the extensive media diffusion after the discovery (García-Guinea and Calaforra 2001). Second, the search of legal protection figures for the geode and its environment according to the Spanish legislative framework.

The first line of action for protection of the geode was closing and controlling access to the mine, along with the following main projects (Fig. 3): (1) cartography and geotechnical study on the security of the mine's galleries,

(2) environmental valorization of the geode by means of cleaning the crystals surfaces using nonaggressive solutions for the gypsum, and (3) isotopic study of the minor solid inclusions captured inside gypsum crystals during its growth, for determining the environmental conditions during its genesis (García-Guinea et al. 2002).

With respect to conservation of the geode as a geological heritage, Spain generally does not have a specific strategy for conservation of geodiversity, although the national legislature includes two laws that facilitate the protection of geological heritage: the Law of Historic Heritage (since 1985) and the Law of Conservation of Wild Flora and Fauna (since 1989). Most of the Spanish regions have performed laws that develop the Law of Conservation. A more specific way for protecting the geode is considering it as a locality of geological interest, including those of tourist interest (Gallego-Valcarce 1996), which permits some legal protection. In this sense the Spanish environmental legislation would be able to assure the protection of the geode by means of "minor" statements as natural monument, juridical concept applied to geological features, paleontological deposits, and other special interesting geo-elements with singular or important values from a cultural, scientific, or landscape standpoint (Consejería de Medio Ambiente de la Junta de Andalucía 1999). This concept implies that any natural monument has a sustainable tourist use. Sustainable tourism must be economically viable, ecologically sensitive, and culturally appropriate (Wall 1997). Management of these protected geological features is the responsibility of the environmental authorities, but in

Fig. 4 Spatial distribution and temporal evolution of tourism activity in Andalucía region and Almería [data collected from Instituto de Estadística de Andalucía (2004) and Consejería de Turismo, Comercio y Deporte (2005)]



contrast, there is also a state legislation about mining activities, and so its management falls to the competent authorities for industry. This legal overlap in the management of geological heritage can reinforce its conservation, though on occasions the diversification of responsibility can lead to a failure in coordination of conservation strategies.

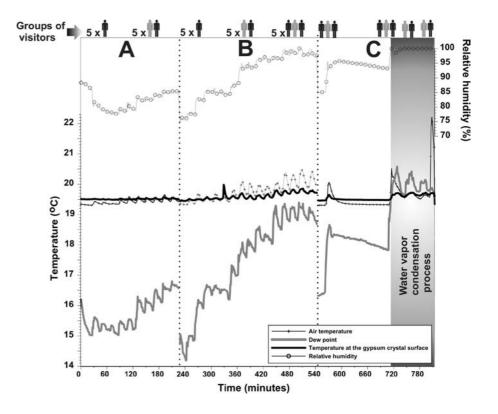
Andalusia is the tourist region by excellence of the Spanish territory, with an increasing evolution in the number of tourists during recent years (Fig. 4). The region is visited yearly by an average of 21 million tourists. In this context, the east coast of Almería province where the mine of the geode is located, reached to a million tourists in 2003. The characteristics of the visits (time of stay and average daily expense) (Fig. 4), along with the inertia of the intense Andalusia tourist offering, favor new tourism development, as visits to natural parks. mining sites, or show caves. For example, around 8 lakhs tourists visit the different tourist caves, 25% of the demand of subterranean tourism in Spain (Fernández-Cortes 2005). From this point of view, a more ambitious alternative could be to contemplate the geode and the mining environment as geological-natural patrimony, in the framework of the protection of the old mining industry vestiges of the Iberian Peninsula southeast (Calaforra et al. 2001). With this perspective the mining environment and the geode would be able to integrate in a global geo-heritage protection project in a wide geographical context. In this sense, there are prior proposals referring to the nearby mining region of 'Cuevas de Almanzora' as an area with a great variety of mining and geological resources, which also needs to be protected (Martínez-Frías 1999). The initiatives of Andalusia Government are focused to protect the exterior zone by avoiding any license of mining activity and the design of tourist project of the mine. Nevertheless, any geo-tourist regulation of the geode has to resolve first the essential question about if it is possible to visit the inside of the geode without generating an irreversible impact on the environmental conditions and gypsum crystals characteristics.

Microclimatic study

Under natural conditions the air temperature inside the geode and the temperature of the surface of the crystals are around 19.5°C, markedly higher (by around +3.1°C) than the mean dew point. The highest level of relative humidity in the air of the geode is 85%. These psychometric characteristics of the air and the crystal surface within the geode reflect a stable microclimate in which conditions do not favor the condensation of water vapor on the crystal surface.

One of the most sensitive variables for detecting the impact of human presence is the measurement of condensation on the gypsum crystals as a result of an increase in temperature, and water vapor in the air caused

Fig. 5 Temporal evolution of environmental variables inside geode during the controlled visits (each *vertical line of dots* separates different experiments in the time: *a* time remaining of 5 min, *b* time remaining of 10 min, *c* time remaining more than 10 min)



by respiration. The condensation processes have been measured and interpreted in cave environments at different scales (Dragovich and Grose 1990; Dublyansky and Dublyansky 1998, 2000; De Freitas and Schmekal 2003). A study of condensation is extremely important in the case of the geode, since condensation on the crystals' surface would literally dissolve them. This phenomenon can be controlled by monitoring both dew point and air temperature in the interior of the geode, together with the temperature of the crystals surface and air relative humidity, during any controlled visit. Condensation of water vapor on a surface occurs when the dew point temperature of the air is higher than the temperature of the rock surface.

Figure 5 shows the evolution of environmental variables inside the geode during the controlled visits. Recovery to ambient temperature was complete after the visits of one person during 5 min. However, during the second series of visits by two people for 5 min there was a progressive accumulation of heat of 0.1°C. After these visits, the air temperature at some points exceeded that of the crystal surface, although the latter remained above the dew point. Entry by one person into the geode hardly affects relative humidity of the air. In contrast, when the number of people was raised to two, relative humidity in the geode showed mean increases per visits of 1.9%.

As the residence time of visitors inside the geode was increased from 5 to 10 min the destabilization of its microclimate became more significant, so the dew point of the air increased to 19°C, very close to the temperature of the crystal surface of 19.5°C. During the series of visits by three people for 10 min, a total thermal increase of 0.2°C was recorded and the relative humidity fluctuated between 96 and 100%. Saturation of the air inside the geode was reached during the third visit of three people for 10 min. The phenomenon of condensation on the gypsum crystals occurred during visits of two or three people for more than 10 min. After such a visit, the

difference between the dew point of the air and the temperature of the rock was positive and saturation of the air was reached (Fig. 5). The subsequent visits meant that the conditions favorable to potential condensation were maintained. The total recovery time value of the initial natural conditions was 27 h.

Electron microprobe analyses (EMPA), geological origin and metal pollution

Several features suggested us performing chemical analyses, by electron microprobe analysis (EMPA), of carbonates, sulphates, silicates, sulphides, and sulphosalts, to elucidate both, the geological origin of geode minerals and the potential danger of heavy metals for visitors. Analysis was conducted on (1) mining waste and iron-lead slag heaps among the archaeological mining architectural heritage, (2) neighboring mercury valley (the Valle del Azogue), and (3) mercury in the former chemical analyses of the gypsum macro-crystals. Table 1 shows that all carbonate and sulphate samples contain mercury ranging from 0.10% in oxy-hydroxides up to 2.07% in baryte samples and antimony ranging from 0.04 to 0.1% in the same way. These chemical results are in good agreement with Martínez-Frías et al. (1997) who described the Valle del Azogue mineral deposit as an interesting example of Upper Miocene, Hg-Sb-(base metal sulphides) hydrothermal mineralization with kaolinite, quartz, baryte, calcite, sericite, gypsum and minor base-metal sulphides (sphalerite, pyrite). exhibiting significant anomalies of Ba (>4,000 ppm), Hg (>3,000 ppm), Sb (>10,000 ppm), Zn (>2,000 ppm), Ag (>100 ppm), As (>800 ppm), and Pb (>1,200 ppm). Note the remarkable similarities with the Pilar de Jaravias case, which, in addition, also exhibits Bi (>6,000 ppm) and Sr. Table 2 shows high amounts of Sb, Pb, and Cu in bournonite, Pb in galena, and Fe in pyrite. Furthermore, it is interesting to note

Table 1 Percentage of chemical elements in host rock of Pilar de Jaravias mine (Almería, Spain) analyzed by electron microprobe analysis (EMPA)

	S (%)	As (%)	Ca (%)	Ba (%)	Sb (%)	Sr (%)	Mg (%)	Zn (%)	Mn (%)	Fe (%)	Hg (%)	Bi (%)	Pb (%)
Goethite 1			1.49		0.02		1.30		3.45	55.98	0.01		
Celestine Fib.1	17.16		0.24	5.45	0.08	42.40					0.53		
Celestine Fib.2	16.43		0.07	18.77	0.04	34.71					0.10	0.40	
Barite Fib.1	13.07		0.07	57.99	0.04	2.90					2.07	0.94	
Barite Fib.2	13.37			55.98	0.05	4.53				0.12	0.75	0.96	
Dolomite 1			21.23		0.10		9.29			0.13	0.6		
Dolomite 2		0.10	19.99		0.08		5.79			0.15	1.5		
Dolomite 3		0.08	23.72		0.06		13.2			1.33	0.28		
Siderite 1			22.37				3.38		3.05	0.15	0.82		0.01
Siderite 2			2.09				1.22		3.33	35.08	1.77		
Siderite 3	0.09							0.43	0.12	52.85	1.12		0.06
Vein Quartz 1						0.45							
Vein Quartz 2					0.03	0.45							0.05

the 0.06% of Te and 0.30% of Ag in galena, the 0.02% of Se in Bournonite, and the 0.09–2.24% of Hg in the sulphidic phases. The new data confirm the narrow relationships between the Valle-del-Azogue and Pilar-de-Jaravia deposits; the existence of three different mineralization phases under hydrothermal conditions, as namely: (1) iron–manganese in carbonated host rock; (2) sulphide, sulphosalts, and sulphates with Fe–Zn–Pb–Ag–Sb–Cu–Hg–As–Te–Se–Ba; (3) supergenic celestine and gypsum phases with hydrothermal vapors of mercury.

Mineral extraction activities are excluded from the scope of major environmental European Union directives or receive certain freedoms for interpretation (Hámor 2004). Heavy metals, especially copper, must be considered as important factors in the aquatic and riparian ecosystems (Ciszewski 1997; Apodaca et al. 2000; Benito et al. 2001; Ashley et al. 2004; Morillo et al. 2005). From the health point of view, the Pilar de Jaravia slag heaps and ground masses with Fe-Zn-Pb-Ag-Sb-Cu-Hg-As-Te-Se-Ba must be kept out of the reach of human beings. Examples of surface and groundwater pollution have been identified in other abandoned mine sites (Rosner 1998; Iribar et al. 2000; Lee 2003; Harrison et al. 2003). In accordance with the World Health Organization (http://www.WHO.int), the intake of arsenic in drinking water has been associated with disorders. However, there is no evidence of any specific illness caused by drinking water containing arsenic at the maximum acceptable concentration of 0.01 mg/L. Barium element can cause serious toxic effects to the heart, blood vessels, and nerves. The maximum acceptable concentration of barium in drinking water has been set at 0.7 mg/L. Copper is an essential and beneficial element in human metabolism and is generally considered to be nontoxic except at high doses, i.e., 2 mg/L. Lead has long been recognized as a general metabolic poison which causes a variety of human disorders, particularly of the nervous system. The maximum acceptable concentration of lead in drinking water is 0.01 mg/L. Zinc is an essential element and is considered to be nontoxic. Furthermore, water containing zinc levels above 5.0 mg/ L has an undesirable astringent taste. Mercury is a toxic element, with particularly damaging effects on the brain and central nervous system. It serves no beneficial physiological function in man. The maximum acceptable concentration for mercury is set at 0.001 mg/L. Many of these elements are phyto-toxic, which are in good agreement with the vegetation shortage observed in the Pilar de Jaravia surrounding area. Dealing with tourist purposes for the Pilar de Jaravia area, it will be desirable to wash the compact rocks and cover the poly-metallic ground with soil, vegetation, and clean water to avoid possible powder intakes. Assuming concentrations of vapor mercury in mine up to 375 $\mu g/m^3$ such as in the next Valle-del-Azogue case (Navarro-Flores et al. 2000) there will not be hydrargyrism damages for the unusual visitor.

Conclusions

From the geological point of view, the electron microprobe analyses confirm the hydrothermal stages of ironmanganese in carbonated host rock, sulphide, sulphosalts, and sulphates with Fe–Zn–Pb–Ag–Sb–Cu–Hg–As–Te–Se–Ba and Ca and Sr sulphates with mercury vapors. From the point of view of the environmental management of the Pulpí Geode surrounding area, these elements must be kept out from the human living in both potable waters and breathing powders. The presence of large concentrations of vapor mercury in mine, which can reach up to 300 $\mu g/m^3$ will not be a cause for hydrargyrism damages for the unusual visitor.

The micro-environmental analyses demonstrate that the condensation of water vapor on the gypsum crystals of the geode is the critical parameter that limits human presence inside it. Continuous visits of two or three people for more than 10 min would provoke the appearance of condensation/evaporation phenomena, bringing with them the risk of corrosion of the magnificent gypsum crystals. The recovery time of the geode environment would exceed 1 day. The results obtained in the environmental monitoring of the geode suggest that it is impossible to allow visitors inside it, not only because of the mechanical impact of the visitor on the

Table 2 Percentage of chemical elements in metallic sulphides of Pilar de Jaravias mine (Almería, Spain) analyzed by electron microprobe analysis (EMPA)

	S (%)	Se (%)	Te (%)	Ba (%)	Sb (%)	Sr (%)	Fe (%)	Hg (%)	Bi (%)	Pb (%)	Cu (%)	Ag (%)
Pyrite-1	51.02						44.84	1.89	0.24	1.34		
Galena-1	12.99		0.05		0.11	0.18	0.02	0.60	0.22	86.87		
Galena-2	11.78				0.70	0.16		0.09	0.33	80.20		0.07
Galena-3	13.38				1.27	0.23		1.75	0.13	84.92		0.31
Galena-4	13.26			0.02	0.49	0.20			0.15	86.14		
Galena Rim (PbCO ₃) -5			0.07			0.20		1.70		72.82		
Bournonite-1	19.39			0.08	24.23	0.22			0.18	42.07	13.64	
Bournonite-1	19.25	0.02		0.09	24.51	0.14		2.24	0.18	43.12	13.39	

crystals but also due to the risk of condensation of water vapor. For these reasons, the conclusion directed to the competent environmental authorities is to recommend that the mine be equipped with tourism only if there is to be no physical contact between the visitors and the interior of the geode.

Nevertheless, there are many other initiatives with a potential for geo-tourism that are currently starting up and which may provide a salutary socio-economic skill for this particular rural area of Spain. The main project could be the re-evaluation of the geo-mining heritage, currently undergoing a phase of abandonment and deterioration. It includes tourist initiatives such as the utilization of certain mines and their mining-industrial surroundings. In this context the giant Geode of Pulpí is an emblematic example of how the evident tourist interest of the surrounding area must be tempered by

environmental restrictions that clearly limit visits by the public. It is evident that the needs to develop geo-tourism in order to better understand our natural surroundings must occur within the ambit of the divulgation of geo-diversity, but always within the margins of sustainability that would permit the conservation of our geological heritage.

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References

- Apodaca LE, Driver NE, Bails JB (2000)
 Occurrence, transport, and fate of trace elements, Blue River Basin, Summit County, Colorado: an integrated approach. Environ Geol 39(8):901–913. DOI 10.1007/s002549900066
- Ashley PM, Lottermoser BG, Collins AJ, Grant CD (2004) Environmental geochemistry of the derelict Webbs Consols mine, New South Wales, Australia. Environ Geol 46(5):591–604. DOI 10.1007/s00254-004-1063-7
- Benito G, Benito-Calvo A, Gallart F, Martin-Vide JP, Regues D, Blade E (2001) Hydrological and geomorphological criteria to evaluate the dispersion risk of waste sludge generated by the Aznalcollar mine spill (SW Spain). Environ Geol 40(4–5):417–428. DOI 10.1007/s002540000230
- Calaforra JM, Fernández-Cortés A (2005) Geotourism in spain: resources, environmental management. In: Dowling R, Newsome D (eds) Geotourism. Elsevier, Oxford, pp 199–220
- Calaforra JM, Moreno R, García-Guinea J, Guerrero M, Romero A (2001). La geoda gigante de Pulpí (The giant Geode of Pulpí): Patrimonio geológico y minero. Medio Ambiente 37:42–43
- Ciszewski D (1997) Source of pollution as a factor controlling distribution of heavy metals in bottom sediments of Chechlo River (South Poland). Environ Geol 29(1–2):50–57. DOI 10.1007/s002540050103

- Consejería de Medio Ambiente de la Junta de Andalucía (1999) Decreto 225/1999 de 9 de noviembre, de regulación y desarrollo de la figura de Monumento Natural de Andalucía (Law 225/1999 of 9th November, about Natural Monument regulation and development). Boletín Oficial de la Junta de Andalucía 146:16177–16181
- Consejería de Turismo, Comercio y Deporte (2005) Boletín de indicadores turísticos de Andalucía (Bulletin of tourist index in Andalusia). No. 36. Junta de Andalucía, Seville (Spain)
- De Freitas CR, Schmekal A (2003) Condensation as a microclimate process: Measurement, numerical simulation and prediction in the Glowworm Cave, New Zealand. Int J Climatol 23(5):557–575. DOI 10.1002/joc.898
- Dragovich D, Grose J (1990) Impact of tourist on carbon dioxide levels at Jenolan Caves, Australia: an examination of microclimatic constraints on tourist cave management. Geoforum 21(1):111–120. DOI 10.1016/0016-7185(90)90009-U
- Dublyansky VN, Dublyansky YV (1998) The problem of condensation in karst studies. J Caves Karst Stud 60(1):3–17
- Dublyansky VN, Dublyansky YV (2000)
 The role of condensation in karst hydrogeology and speleogenesis. In: Klimchouck AB, Ford DC, Palmer AN,
 Dreybrodt W (eds) Speleogenesis, evolution of karst aquifers. National Speleological Society, Huntsville, pp 100–112.

- Fernández-Cortes A (2005) Caracterización microclimática de cavidades y análisis de la influencia antrópica de su uso turístico (Caves microclimatic characterization and human impact analysis due to tourist use). Servicio de Publicaciones de la Universidad de Almería. PhD, University of Almería, Spain
- Ferrara R, Maserti BE, Andersson M, Edner H, Ragnarson P, Svanberg S, Hernandez A (1998) Atmospheric mercury concentrations and fluxes in the Almaden District (Spain). Atmos Environ 32(22):3897–3904. DOI 10.1016/S1352-2310(98)00102-2
- Fisher JE, Greenbank L (2000) The Rogerley mine, Weardale, County Durham, England. Rocks Miner 75(1):54–61
- Forti P (2004) I giganti di grotta (The giant of cave). Speleologia 50:54–57
- Forti P, Pagliara A, Galli E, Rossi A, De Waele J, Naseddu A, Papinuto S (2005) Studio morfologico e mineralogico di dettaglio del concrezionamento del sistema carsico di Santa Barbara (Miniera di San Giovanni, Iglesias) (detailed morphological and mineralogical study of Santa Barbara karst system). Memorie dell'Istituto Italiano di Speleologia (Le Grotte di Miniera: Tra economia mineraria ed economia turistica) Series II, vol XVII, pp 57–68
- Foshag WS (1927) Selenite caves of Naica, Mexico. Am Mineral 12:252–256

- Gallego-Valcarce E (1996) Patrimonio Geológico: Aspectos legales, protección y conservación (Geological Heritage: Legal aspects, protection and conservation). In: Dirección General de Información y Evaluación Ambiental del Ministerio de Obras Públicas, Transportes y Medio Ambiente (eds) El Patrimonio Geológico. Bases para su valoración, protección, conservación y Utilización. Ministerio de Obras Públicas, Transportes y Medio Ambiente, Madrid (Spain), pp 79–85
- García-Guinea J, Calaforra JM (2001) Mineral collectors and the geological heritage. Eur Geol Mag 1:4–7
- García-Guinea J, Morales S, Delgado A, Recio C, Calaforra JM (2002) Formation of gigantic gypsum crystals. J Geol Soc Lond 159:347–350
- Hámor T (2004) Sustainable mining in the European Union: the legislative aspect. Environ Manage 33(2):252–261. DOI 10.1007/s00267-003-0081-7
- Harrison J, Heijnis H, Caprarelli G (2003) Historical pollution variability from abandoned mine sites, Greater Blue Mountains World Heritage Area, New South Wales, Australia. Environ Geol 43(6):680–687. DOI 10.1007/s00254-002-0687-8
- Higueras P, Oyarzun R, Biester H, Lillo J, Lorenzo S (2003) A first insight into mercury distribution and speciation in soils from the Almadén mining district, Spain. J Geochem Explor 80(1):95–104. DOI 10.1016/S0375-6742(03)00185-7
- Hill C, Forti P (1997) Cave minerals of the world. National Speleological Society, Huntsville
- Instituto de Estadística de Andalucía (2004) El turismo en Andalucía: Año 2003 (The tourism sector in Andalusia: year 2003). Consejería de Economía y Hacienda de la Junta de Andalucía, Seville (Spain)
- Iribar V, Izco F, Tames P, Antiguedad I, da Silva A (2000) Water contamination and remedial measures at the Troya abandoned Pb–Zn mine (The Basque Country, Northern Spain). Environ Geol 39(7):800–806. DOI 10.1007/ s002540050496
- Lazcano-Sahagún C (2002) Cueva de los cristales (Cave of the Crystals). AMCS Activ Newslett 25:72–77

- Lazcano-Sahagún C, Fisher R, Shackleford M (2001) Naicás subterranean marvels. NSS News June:166–169
- Lee CH (2003) Assessment of contamination load on water, soil and sediment affected by the Kongjujeil mine drainage, Republic of Korea. Environ Geol 44(5):501–515. DOI 10.1007/s00254-003-0786-1
- Leistel J, Marcoux E, Thiéblemont D, Quesada C, Sánchez A, Almodóvar G, Pascual E, Sáez R (1998) The volcanichosted massive sulphide deposits of the Iberian Pyrite Belt. Miner Depos 33(1– 2):2–30
- London D (2003) New "Cave of the Crystals" at Naica, Chihuahua, Mexico. Earth Sci Mag 2003:24–27
- Martínez-Frías J (1998) An ancient Ba–Sb– Ag–Fe–Hg-bearing hydrothermal system in SE Spain. Episodes 21(4):248– 251
- Martínez-Frías J (1999) Mining vs. geological heritage: the Cuevas del Almanzora natural area (SE Spain). Ambio 28(2):204–206
- Martínez-Frías J, Flores AN, Hernández RL (1997) First reference of pyrite framboids in a Hg–Sb mineralization: The Valle del Azogue mineral deposit (SE Spain). Neues Jb Miner Monat 4:175–184
- Martínez-Frías J, Navarro A, Lunar R, García-Guinea J (1998) Mercury pollution in a large marine basin: a natural venting system in the south-west Mediterranean margin. Nature Resour 34(3):9–15
- Minette JW (1999) The Carlsbad halite caves. Mineral Rec 30:369–372
- Mitjavila J, Martí J, Soriano C (1997) Magmatic evolution and tectonic setting of the Iberian Pyrite Belt volcanism. J Petrol 38(6):727–755
- Morales-Ruano S (1994) Mineralogía, geoquímica y metalogenia de los yacimientos hidrotermales del SE de España (Águilas-Sierra Almagrera) (Mineralogy, geo-chemistry and metal genesis of hydrothermal outcrops in SE Spain, Águilas-Sierra Almagrera). Consejo Superior de Investigaciones Científicas and Universidad de Granada, Granada (Spain)
- Morillo J, Usero J, Gracia I (2005) Study of fractionation and potential mobility of metal from the Guadalquivir Estuary: changes in mobility with time and influence of the Aznalcóllar Mining Spill. Environ Manage 36(1):162–173

- Navarro-Flores A, Martínez-Frias J, Font X, Viladevall M (2000) Modelling of modern mercury vapour transport in an ancient hydrothermal system: environmental and geochemical implications. Appl Geochem 15:281–294. DOI 10.1016/S0883-2927(99)00046-3
- Nevado JJB, Bermejo LFG, Martin-Dolmeadios RCR (2003) Distribution of mercury in the aquatic environment at Almaden, Spain. Environ Pollut 122(2):261–271. DOI 10.1016/S0269-7491(02)00290-7
- Palache C (1932) The largest crystal. Am Mineral 17:362–363
- Palero F, Gómez F, Cuesta JM (2000) Pilar de Jaravía: La Geoda Gigante de la Mina Rica (The Giant Geode of Rica Mine). Bocamina, Revista de minerales y yacimientos de España 6:54–67
- Rickwood PC (1981) The largest crystals. Am Mineral 66:885–908
- Rosner U (1998) Effects of historical mining activities on surface water and groundwater—an example from northwest Arizona. Environ Geol 33(4):224–230. DOI 10.1007/s002540050241
- Rytuba JJ (2003) Mercury from mineral deposits and potential environmental impact. Environ Geol 43(3):326–338. DOI 10.1007/s00254-002-0629-5
- Sánchez-Palencia FJ, Fernández-Posse MD, Fernández-Manzano J, Orejas A, Pérez-García LC (1998) Las Médulas (León), la formación de un paisaje cultural minero (Las Médulas, León, the formation of a mining-cultural landscape). El Oro en España. Boletín Geológico y Minero 109(5–6):157–168
- Sarritzu R (2005) La Grotta di S. Barabara da gioiello minerario a risorsa del territorio. Memorie dell'Istituto Italiano di Speleologia (Le Grotte di Miniera: Tra economia mineraria ed economia turistica) Series II, vol XVII, pp 155–160
- Solomon M, Tornos F, Gaspar OC (2002) Explanation for many of the unusual features of the massive sulfide deposits of the Iberian pyrite belt. Geology 30(1):87–90
- Wall G (1997) Is ecotourism sustainable? Environ Manage 21(4):483–491