DEGRADATION OF PALEONTOLOGICAL SAMPLES WHICH CONTAIN PYRITE AND/OR MARCASITE – CONSIDERATIONS ON THEIR CONSERVATION

MACOVEI Monica, GRIGORE Dan, SEBE-RĂDOI Oana Gabriela, DUMITRAȘ Delia Georgeta, CRUȘOVEANU-RUSU Simona

Abstract. The natural form under which iron disulphide is ordered is isometric (pyrite) or orthorhombic (marcasite). The most common case is where the form of crystallization is represented by pyrite (cubes or radial and framboidal arrangements). The degree of alteration of the samples is variable, mainly related to the actual amount of pyrite, as well as relative humidity of the storage medium. The current situation needs to be carefully analyzed and optimal conservation methods and restoration solutions have to be provided – in the case of already affected material. Various ways of preserving the degradable material can be proposed: insulation, coating, immersion, storage in a controlled environment.

Keywords: pyrite, fossil, microfossil, degradation, conservation.

Rezumat. Degradarea materialului paleontologic ce conține pirită sau/și marcasită – observații asupra conservării. Forma naturală sub care se dispune disulfura de fier este cea izometrică (pirită) sau ortorombică (marcasită). Cazul cel mai frecvent este cel în care forma de cristalizare este reprezentată de pirită (cuburi sau dispuneri radiare și framboidale). Gradul de alterare al probelor variză în principal legat de cantitatea existentă de pirită, precum și de umiditatea relativă a mediului de păstrare. Situația prezentă trebuie atent analizată și oferite soluții optime de conservare și de restaurare – în cazul materialului deja afectat. Se pot propune diverse metode de conservare a materialului degradabil: izolare, acoperire, imersie, depozitare în mediu controlat.

Cuvinte cheie: pirită, fosilă, microfosilă, degradare, conservare.

INTRODUCTION

The National Geology Museum (NGM) is located in the building originally destined in 1906 to the headquarters of the National Institute of Geology; nowadays, the museum is just a department of the institute. The exhibitions were set up in 1990, based on the researchers' collections and donations. Several samples from the collections of the National Museum of Geology (Bucharest) contain pyrite or marcasite (FeS_2) or they are totally represented by the latter. This paper refers to samples from paleontological collections (from the museum collections or from researchers' study collections). We intend to estimate the degree of alteration and the mechanisms involved in it and to underline the importance of good preservation, or, in some cases, a restauration of the older paleontological material that has already been damaged. Samples containing pyrite and marcasite require increased attention; simple control of humidity and aeration is not enough, the alteration still has place, though at a lower rate.

It is known that the pyrite makes pseudo-morphoses from various plants or plants, replacing totally or partially organic residues. Sedimentary pyrite or marcasite can also be deposited after the fossilization process, in the remaining voids or can be later created by various dissolutions. Similarly, various pseudo-morphoses (e.g. limonite on pyrite) are made on the charge of the pyrite. If the alteration did not affect the form of the fossil, from a paleontological point of view, the sample is still viable, as shown in the case of Goniatite specimen from Alton marine band of Westphalian Coal Measures, ammonite from HODGKINSON & MARTIN (2004). The problems occur when a paleo-environment reconstruction is intended; environmental conditions are approximated by making a parallel to the present situation of the conditions that generate some of the minerals.

There are numerous studies on the alterations made on the pyrite and marcasite in nature, and also in the collections of the museums all over the world, but no final decision on the best way of preservation. There are two principal methods of conservation: one of them refers to different coatings (usually acrylic substances) and one is focused on a controlled environment (exhibits are kept under anaerobic conditions, with strict humidity control). Some studies even suggest that bacterial activity may be involved in these processes of alteration (TEMPLE & COLMER, 1951; BEIJERINCK, 1904). These are very rare cases (very high humidity is involved, 95%), therefore it is not the case in a museum environment. Also, the light may be an aggravating agent, especially in the case of permanently displayed samples.

Sometimes, paleontological samples may lose all their integrity following mineralogical transformations that occur through the oxidation of the pyrite or marcasite. It is important to preserve the original mineral that may give indications of the fossilization environment and contribute to the reconstruction of the paleoenvironments.

In paleontology, it is also extremely important to keep the heliotypes, so their preservation is essential. A first way to prevent pyrite oxidation is to limit the humidity of the storage space to lower than 60%, or in the case of organic carbon-rich samples less than 30% and a treatment with ammonia vapours to inhibit the reactions that have been already started (HODGKINSON & MARTIN, 2004), or with ethanolamine thioglycolate treatment (CORNISH & DOYLE, 1984; CORNISH, 1987).

Another way of preventing pyrite degradation is to cover the samples with different resins (COSTAGLIOLA et al., 1997), but in this case is recommended to use those resins that are long lasting in time without changing their aspect (colour, integrity, transparency, elasticity, etc.). Usually the compounds don't interfere with possible future geochemical analyses due to their composition that is very different from the paleontological material. The process of coverage though has to be very thorough, and requires a special laboratory with proper ventilation.

In the case of small samples (micropaleontological samples) their preservation in silicone fluid (HOWIE, 1979) is recommended, which can be suitable even for a display show, under a magnifier in a transparent box. Also, for such exhibited specimens (Fig. 3e), grains of silica gel can be placed nearby to absorb humidity and to give a water-like look to the display case. This material is nontoxic and non-flammable and no chemical reaction is involved. Silica gel is known to be suitable for the control of humidity, especially when dealing with the alternation of humid periods and dry periods because after having absorbed the humidity the grains have to lose it (this can be obtained with an alternation of an arid period or by heating). It is advisable to put sachets with silica gel in the drawers with pyrite samples from the deposit area, being careful in choosing its type (DINIZ, 2006).

The collections in a museum are usually arranged by sampling location (geographical region) so many fossils from the same formations are stored together and exposed to the same environment conditions, which makes them decay approximately in the same time. The current norms regarding the storage conditions of geological collections do not reflect the current knowledge and sometimes are contradictory (BAARS & HORAK, 2018). There should be a dynamic standard that can be applied in all the repositories.

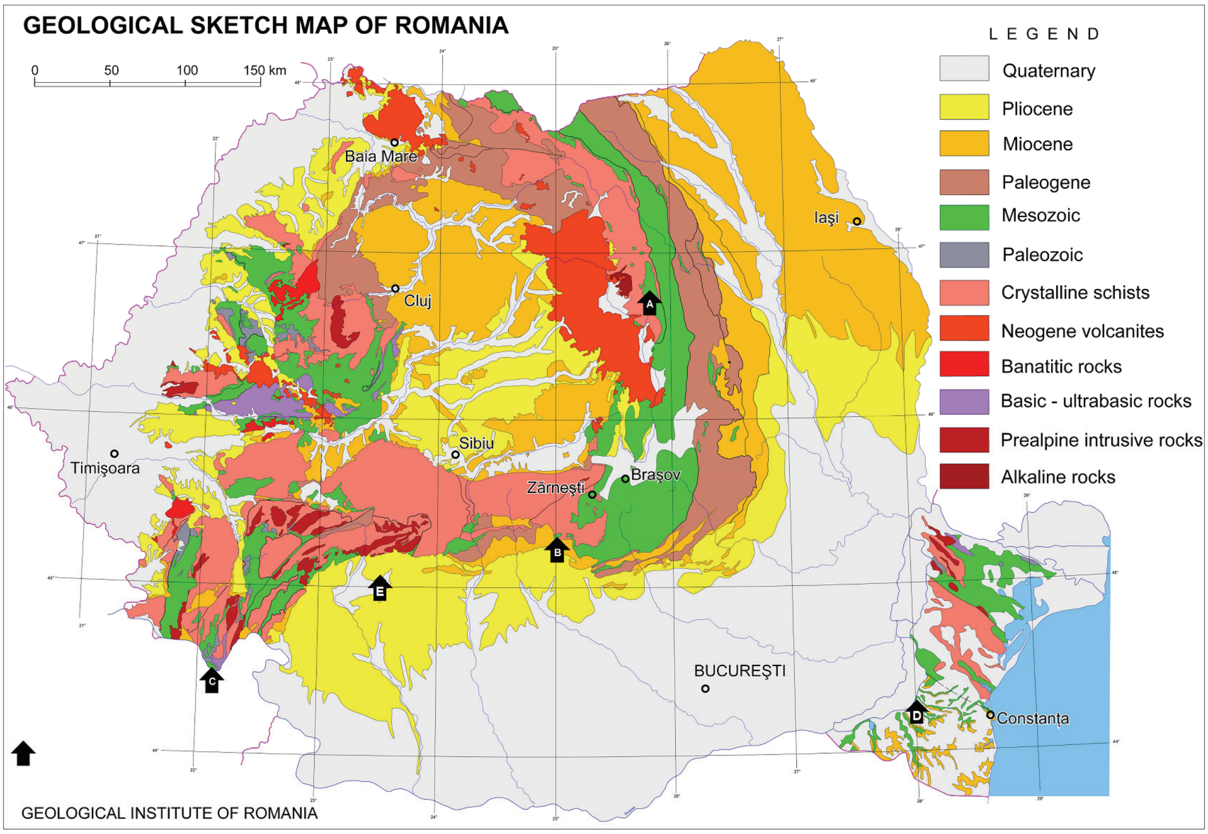

Figure 1. The map location of the paleontological sites of origin: A – Lacu Roșu, B – Rucar-Bran, C – Svinița, D – Cernavodă, E - Morilor Valley – Gorj County (simplified by Gheuca Ion after SĂNDULESCU et al., 1978, with annotations).

SITES OF ORIGIN

Regarding the geological setting, the samples originate from the Romanian orogenic areas – East and South Carpathians (Fig. 1 A, B, C, E) and one from the platform area - Dobrogea (Fig. 1, D). The samples were selected from various formation type and ages as examples in this study.

The first set of samples (Fig. 1A) are provided from Haghimas Mts – Ghilcoş (Transylvanides, SĂNDULESCU, 1984); the oldest – of the Kimmeridgian -Tithonian age, from the Acanthicum Beds (GRIGORE, 2002; 2011) / Ghilcoş Formation (DRAGASTAN, 1997); this kind of strata contains fine fractions in the terrigene sedimentary series. Lithology is mainly represented by nodular limestones, sandstones, siltstone and marls. The pyrite is dispersed in the lumachelle beds that consist of ammonites especially, but is found also in the small ammonites from marls, some of them entirely pyritized and with an oxidation crown. In most of these cases the pyrite takes a framboidal form, while in some more compact limestones from the basal Kimmeridgian, of dark blue or green color (Platynota Zone; GRIGORE, 2002), the pyrite is cubic, found as isolated crystals.

The second and third set of samples belong to the Dambovicioara and Svinita sedimentary basins (Figs. 1B and 1C) that are Lower Cretaceous deposits, more carbonaceous than the first one described above, and belong to Danubian Autochthon (SĂNDULESCU, 1984) respectively, to the Getic Nappe (PATRULIUS, 1969; SĂNDULESCU, 1984).

In Dambovicioara the deposits of marls overlay recifal limestones of Tithonian and are filling a graben structure. The Dambovicioara Formation (PATRULIUS, 1963; PATRULIUS & AVRAM, 1976) of Hauterivian-Lower Aptian age is 350 m thick and consists of a carbonatitic series; the following lithotypes are comprised: various limestones - glauconitic, sublithographic, detritique-oncolithiques or bioclastiques, with cherts, and marls, all in centimetric and decimetric beds.

In the Svinita area, we find the same carbonaceous (marly) deposits – Murguceva and Svinița formations (Avram, 1976; 2001), the Upper Tithonian-Lower Aptian age – covering an entire structure of a turbiditic series of Greben Formation (POP, 1998), of Middle Kimmeridgian-Middle Tithonian age (GRIGORE, 1996). In the lower part (Murguceva Formation – Upper Tithonian to Middle Hauterivian) limestones with cherts prevail, while in the Svinița Formation marlous deposits are dominant (marls and clays). In this last Formation, they are described by AVRAM (1976) two levels with pyritized ammonites (pp. 61 and 62).

The other two examples are of pyritized microfossils from the marl deposits from South Dobrogea and Getic Depression. The Cernavoda Formation of Lower Cretaceous (Upper Berriasian – Lower Aptian) developed some detritic and carbonatitic series of deposits, white marl levels and containing foraminifera and ostracods, some pyritized (CRUȘOVEANU-RUSU, 2015). The last example, from the Getic area, is represented by pyritized foraminifera from the Morilor Valley Formation, of the Badenian age and developed as marls with thin interbedded sands levels.

MATERIAL AND METHODS

In the present paper samples from the National Geological Museum (ammonites from Patrulius and Avram collections, see Figs. 2 and 3) - which appear as registered in the museum in the year 1976, have been analysed. Also, the ammonites from the Grigore Collection (Fig. 4) were still under research at the time of the analysis. To complete our present research some information about pyritization of microfossils (Fig. 5) were taken into account, as examples.

Figure 2. Pyritized Lower Cretaceous ammonites from Avram Collection (NGM)
a) *Melchiorites melchioris*, b) *Phyllopachyceras eichwaldi occidentale*, c) *Protetragonites crebrisulcatus*, d) *Phyllopachyceras eichwaldi occidentale*; all from Upper Barremian – Șvinița.

The samples have been analysed both macroscopically and under the Carl Zeiss Jena binocular (especially for the micropaleontological samples) to assess their degree of alteration. The alteration depended largely on the quantity of pyrite contained initially. For further study and analysis the samples with a higher degree of alteration have been chosen and, in particular, those who suffered loss of cohesion. The museum entry register stipulates that some of them were already affected by depreciation by the enter date. The pictures have been taken with a Sony Camera α68, equipped with a Sony Lens DT 3.5-5.6/18-55 SAM II.

RESULTS

From the analysed material, three groups of degradation have been identified: for the micro-samples the pyrite quantity didn't interfere with the specimen integrity, but raised some problems regarding the ornamentation of the tests

Figure 3. Pyritized Lower Cretaceous ammonites from Avram Collection (NGM)
a) *Melchiorites melchioris*, b) *Costidiscus* aff. *olcostephanoides*, c) *Phyllopachyceras eichwaldi occidentale*, d) *Eulytoceras* cf. *platyformis*, e) *Phyllopachyceras eichwaldi occidentale;* all from Upper Barremian – Svinița.

(that sometimes is very important in a specific identification of the genus), the other group was obviously altered by structural disintegration (that is the case of the ammonites, that are entirely or have a big percent of pyrite) and the last group is represented by the pieces with small nested pyrite (probably due to a second generation of deposition, after the fossil is formed, GOLD, 2011). The last group is not as affected regarding integrity, but the esthetical value.

The pyritization is known to be a paleo-environmental indicator that shows an anoxic environment, usually where there is enough organic matter (linear correlation between the pyritization degree and the concentration in organic carbon – PETRUS, 1976).

The first observation was on the smell in the storage room that was sulphur-like (LARKIN, 2011 indicates that the observations made on altered fossils should start with this and that the rest of the observations are very easy to make).

The pyrite alteration affects the labels and the storage boxes (if they are from paper) (LARKIN, 2011). In the exposed samples textile materials a dark pigmentation has also been observed, like a burned sport.

We found some examples of pyritized fossils of different species (Figs. 2; 3; 4; 5), from different environments, of different sizes and from different storage locations. The samples from the collections of micropaleontology have been stored in an office environment, the rest of them in the National Museum of Geology repository storage (exception: fig. 3e, which represents a museum piece from the permanent exhibition). From those characteristics, the most deteriorative is the content amount of H2S, followed by their size.

From the Grigore Collection, pyrite / marcasite areas could be easily identified - they had a shining appearance at the time of sampling, but now they have only dark-grey material in those spots. In this case, the integrity of the parts is not jeopardized, especially due to the small quantities of the affected material, but this process should be mentioned and it should be taken into account when referring to the ammonites conque decoration. The situation is similar for microfossils showing partial pyritisations. The Patrulius Collection had a lower degree of pyritisation while the Avram Collection presented the most altered specimens (former entirely pyritized ammonites).

Figure 2 shows examples of the most altered samples, whose integrity has been lost, some of them are very fragmented (Figs. 2a and 2b, partially 2c – the highly fragmented material is stored into the plastic box). In some cases (Fig. 2d, partially 2c) the alteration caused cracks into the samples, exposing more surface for further degradation. As it can be seen, the simple isolation in plastic boxes didn't stop the degradation.

Figure 3 only shows cracked pyritized ammonites conques, at position 3a we see a specimen of *Melchiorites melchioris* (Tietze) that has been previously covered in lacquer and that slowed the process of alteration (the cracks that can be seen on the specimen are probably prior to the covering (the entry registry mentions that some samples of this collection are in a poor state prior to the reception). 3b and 3d are examples of pyritized ammonites that hadn't been taken entirely out from their substrata. That maintained their integrity to some extent (the negative form is also available for further study).

Some pyritized ammonites are displayed in the permanent exhibition of the museum. For exemplification there is a specimen of *Phyllopachyceras eichwaldi occidentale* Weidmann (Fig. 3e) that suffered three deep cracks and a few superficial ones along time. This fossil has been exposed to neon light, but it does not a higher alteration than the one stored in closed drawers (with no exposure to light except in rare cases).

The big difference between the Grigore Collection (Fig. 4) and the Avram Collection (Figs. 2 and 3) is that in the first case fossils are calcified and secondary pyrite deposits are formed in voids, while in the second one the ammonites are entirely pyritized, both kind of fossils are hosted in marlstone. Size is also a big difference between the two of them, the ammonite specimens from the Grigore collection present large calcified conques (some of them over 10 cm in diameter), while the ammonites from the Avram collection don't rise above 5 cm.

Figure 5 depicts a specimen of *Siphonaperta* cf. *S. agglutinans* (in SEBE, 2009). This is a foraminiferous agglutinant with a qvincveloculin test, consisting of five chambers fitted with sharpened needles. The specimen is entirely pyritized. The microfossils presented in CRUŞOVEANU-RUSU (2016) were selected, the pyritized ones being excluded from that study especially for the reason that their ornamentation wasn't visible enough.

The oxidation of pyrite (FeS2) under oxygen and water vapours results in sulphuric acid (H2SO4) and various hydrated iron sulphates (WALLER, 1987):

$$FeS_2+3O+H_2O \Rightarrow FeSO_4 + H_2S$$

Therefore, the reaction results into iron(II) sulphate (light green crystals, which, if dehydrated, become colourless) and sulphurated hydrogen that evaporates into the air, with a stronger contribution to the physical decay of the samples (H2S vapours have a high degree of corrosion).

Iron(II) sulphate can be found in various states of hydration, and several of these forms exist in nature (JAMBOR et. al., 2000):

- FeSO4·7H2O (mineral: selanterite, colourless to white or green, also greenish-blue to blue with increased Cu content; colourless to pale green in transmitted light)
- FeSO4·6H2O (mineral: ferrohexahydrite, bluish green, colourless, white, light brownish)
- FeSO4·5H2O (mineral: siderotile, yellowish, white, light green)
- FeSO4·4H2O (mineral: rozenite, colourless to white, pale green, may be the dehydration product of melanterite)
- FeSO4·H2O (mineral: szomolnokite, pale yellow or reddish-brown, may also be light blue, very pale greenish white to white, rarely pink due to cobalt. Szomolnokite forms as a final member of a series of gradual dehydration products derived from melanterite and rozenite. The reaction of rozenite to szomolnokite is reversible, though at a slower rate compared to the alteration of melanterite to rozenite. The presence of szomolnokite indicates that the original melanterite was free of copper, since siderotile would form from a Cu-bearing melanterite (ONDRUS et. al., 1997)

The resulting compound may vary in colour from white-pale yellow to yellow and orange (see examples in Figs. 3b, 3c, 4 a-d). The most intense case can be observed on the ammonites that are still preserved in their substrata. (Figs. 3b, 4d), the newly formed minerals generate a dusty-like aggregate, that easily loses cohesion with the parent structure. The degree of coloration depends on the humidity and chemical content (the newly formed compounds range between white – grey – yellow – orange). Studies have identified that they are comprised of rozenite Fe+2S04-4H20, gypsum CaS04-2H20 and iron hydroxide (goethite α-Fe3+O(OH)) in BECHERINI et al. (2018), beside this BLOUNT (1993) found kornelite Fe+32(S04)3-7H20, coquimbite Fe+3 2(S04)3-9H20, quenstedtite Fe+32(S04)3 • 10H2O, szomolnokite Fe+2S04H20, melanterite Fe+2S04-7H20, rhomboclase HFe+3(S04)2-4H20, roemerite Fe+2Fe+3, 2(S04)4-14H20, alunogen Al2(SO4)3•17H2O, halotrichite Fe+2A12(S04)4-22H20, hydronium jarosite (H30)Fe+33(S04)2(OH)6.

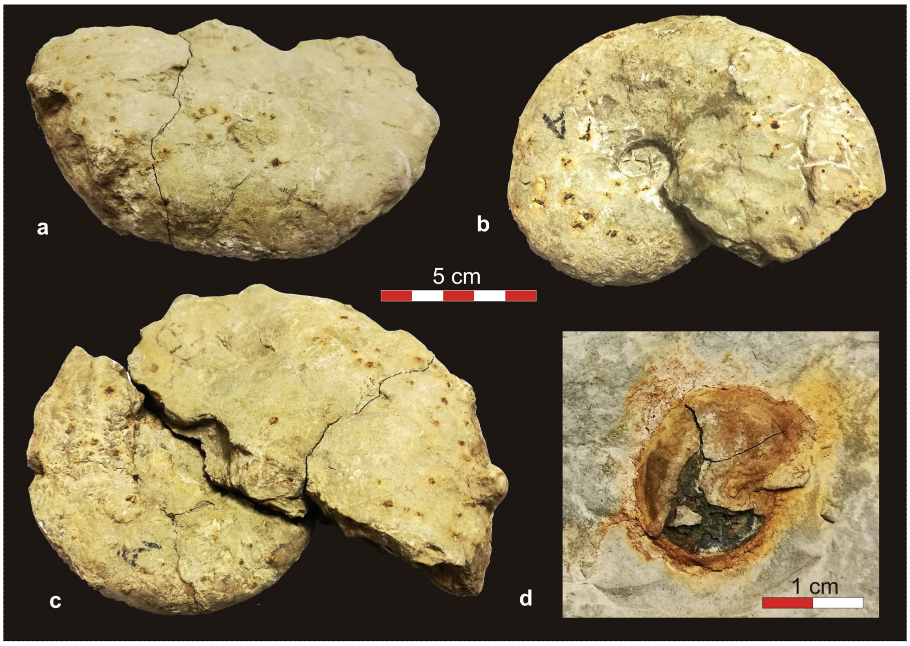

Figure 4. Pyritized Kimmeridgian – Lower Tithonian ammonites from the Grigore Collection (NGM) – a, b and c) spots of framboidal pyrite oxidized on large specimens of *Taramelliceras* from Upper Kimmeridgian, d) entirely pyritized and oxidized to a small conque of a small *Glochiceras* specimen from the Lower Tithonian marls.

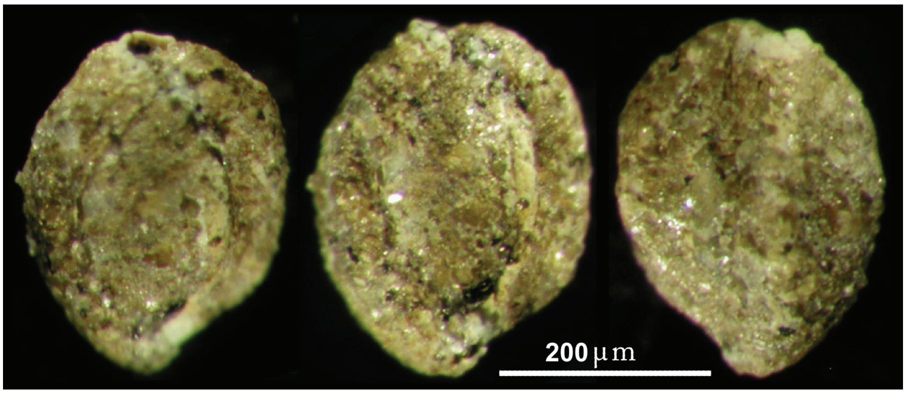

Figure 5. Picture under the magnifier that exemplifies the partially content of pyrite in a micropalontological fossil (the same specimen with three posing positions, from left to the right – aperture view, front view and back view): *Siphonaperta agglutinans* (SEBE, 2009).

The conservation conditions of the paleontological material of the National Geological Museum are generally satisfactory. The samples are kept in metal inserts, in cardboard boxes or, in the case of those known to have a higher degradation potential, in closed plastic boxes. The surface of the drawers is covered with plastic foil to reduce dust deposition. A horse pelvis bone was also stored for 15 years in the room and it did not suffer any visible degradation other than a loss of consistency (collagen lost and maybe some fungus intervention), proving that the humidity does not exceed an average of 45-50% (HOWIE, 1979; LANDER, 2014). However, there are periods in which there is an area exposed to flooding near the respective room (the groundwater being at a shallow depth), which can increase the humidity of the deposited air for short periods of time. Regarding the temperature, it can be correlated with the indoor temperature (the display cases and drawers don't preserve temperature, or the percent is very low (BECHERINI et al, 2018).

CONCLUSIONS

The present study started to build an inventory of pyrite-containing samples and their assessment of the current degradation stage. From the direct observations made on the samples we drew the conclusion that none of the applied covering is suitable for the protection after the degradation process has started (the Avram collection). The samples were covered with protective lacquer but the researcher mentioned that the fossils had already started to deteriorate. We concluded that the covering didn't stop the alteration process; it has only slowed it down.

The samples that we found without covering and that hadn't been stored in sealed plastic boxes were the most affected by the environmental conditions.

As the environmental conditions are not optimal for preserving samples sensitive to humidity and temperature variations in open air, it is advisable to keep all the samples in plastic boxes, but only after they have been treated with ammonia vapours.

For the exposed items we propose to ensure a drier environment and a lower temperature variation. This involves using silica gel and special machineries designed for exhibit show cases. For the already affected samples we intend to try a restoration and gas treatments to stop the process.

It is advisable to make 3D copies of the fossils, as today's technology provides a non-destructive and accessible way: 3D scanning and printing. These solutions (especially the digitization of the samples) also makes easier to exchange knowledge. At the same time, the samples will no longer be exposed to free air during their assessment.

The best-preserved samples were those that were stored in technical oil, as the substance prevented the oxygen from reaching the minerals, so they didn't alter. We mention that this treatment was applied as soon as possible after their collection. The study observations could still be carried out on these samples, especially since they were stored in transparent recipients. If needed, they can be emerged and dried but this is not advisable, any contact with the oxygen can lead to their degradation.

ACKNOWLEDGEMENTS

This paper was financially supported by the „Programul de finanțare a Instalațiilor și Obiectivelor Speciale de Interes Național/ The Program for the Financing of Installations and Special Objectives of National Interest – IIN2019", „Geologia resurselor naturale ca instrument de bază pentru dezvoltarea durabilă în concordanță cu standardele europene/Geology of natural resources as a basic tool for sustainable development in accordance with European standards" - PN-III-P1-1.2-PCCDI-2017-0346 and National Program „Elaborarea hărților naționale hidrogeologice și de vulnerabilitate a acviferelor, un suport necesar pentru autorități în stabilirea de măsuri adecvate de protejare a apelor subterane/ Elaboration of national hydrogeological and vulnerability maps of aquifers, a necessary support for authorities in establishing appropriate measures to protect groundwater – PN19-45-01-02", both of the Romanian Government. We would like also to thank Dr. Gheorghe Popescu and Dr. Marius Stoica from the University of Bucharest (Faculty of Geology and Geophysics) for granting access to the micropaleontological sample.

REFERENCES

AVRAM E. 1976. La succession des depots tithoniques superieurs et cretaces inferieurs de la region de Svinița (Banat). *Dări de seamă ale Ședințelor.* Institutul de geologie și geofizică. Bucharest. **62** (4): 53-71.

AVRAM E. 2001. The Murguceva and Svinița Formations (Late Tithonian – Aptian) outcrops North of the Svinița Village area (SW Romania). *GeoEcoMarina*. Institutul Național de Cercetare-Dezvoltare pentru Geologie și Geoecologie Marină. Bucharest. **5-6**: 65-71.

BEIJERINCK M. W. 1904. Ueber die Bakterien, welche sich im Dunkeln mit Kohlensäure als Kohlenstoffquelle ernähren können. *Centralbl Bakteriol Parasitenkd Infektionskr Hyg Abt.* II. Gustav Fischer Verlag. Jena. **11**: 593-599.

BAARS C. & HORAK JANA. 2018. Storage and conservation of geological collections—a research agenda. *Journal of the Institute of Conservation*. Publisher: Taylor & Francis (Routledge). London. **41**(2): 154-168.

BECHERINI FRANCESCA, DEL FAVERO LETIZIA, FORNASIERO MARIAGABRIELLA, GUASTONI A., BERNARDI ADRIANA. 2018. Pyrite Decay of Large Fossils: The Case Study of the Hall of Palms in Padova, Italy. *Minerals*. MDPI AG. Basel. **8**(40): 1-14.

BLOUNT ALICE M. 1993. Nature of the alterations which form on pyrite and marcasite during collection storage. *Collection Forum.* SPNHC. Washington, DC. **9**(1): 1-16.

COSTAGLIOLA PILAR, CIPRIANI CURZIO, MANGANELLI DEL FA CARLO 1997. Pyrite oxidation: protection using synthetic resins. *European Journal of Mineralogy*. Schweizerbart'sche Verlagsbuchhandlung Science Publishers. Stuttgart. **9**: 167-174.

CORNISH LORRAINE. 1987. The treatment of decaying pyritiferous fossil material using ethanolamine thioglycolate. *Geological Curator*. The Geological Curators' Group. London. **4**(7): 451-454.

CORNISH LORRAINE & DOYLE A. 1984. Use of ethanolamine thioglycolate in the conservation of pyritized fossils. *Paleontology*. Palaeontological Association. London **27** (2): 421-424.

CRUȘOVEANU-RUSU SIMONA 2016. *Biostratigrafia depozitelor cretacice interceptate în forajele geotehnice din zona Centralei Nucleare Cernavodă*. Licence these (Unpublished data). Universitatea București. 112 pp.

DINIZ PINTO PATRICIA WIVIAN. 2006. *Preservacao e acesso – vitrine com controle de umidade para material fossil: um estudo de caso em clima quente e umido*. Dissertation. Federal University of Minas Gerais. 127 pp.

DRAGASTAN O. 1997. Transylvanides – a Jurassic-Cretaceous paleoenvironmental and depositional model. *Acta Paleontologica Romaniae*. Societatea Paleontologilor din România. Editura Eficient. București. **1**: 37-44.

HODGKINSON S. & MARTIN S. 2004. *History and mineralisation of highly degraded pyrite fossil collection*. Available online at http://nora.nerc.ac.uk/id/eprint/509280/1/ir04037.pdf (accessed 25.02.2019).

HOWIE F. M. P. 1979. Museum climatology and the conservation of palaeontological material. *Special Papers in Palaeontology*. Palaeontological Association. London. **22**: 103-125.

GOLD D. 2011. *Taphonomy and Diagenesis of Ammonites from the Whitby Mudstone Formation of the Yorkshire Lias*. BSc (Honours) Degree in Palaeobiology and Evolution. University of Portsmouth. 147 pp.

GRIGORE D. 1998. Upper Kimmeridgian and Lower Tithonian sequence of the Greben Formation in the Svinița – SW of the Southern Carpathians. *Anuarul Institutului Geologic al României.* Institutul Geologic al României. Bucureşti. **70**: 81-86.

GRIGORE D. 2002. *Formațiunea cu Acanthicum din regiunea Lacu Roșu (Msv. Hăghimaș-Carpații Orientali) – posibil hipostratotip al limitei Kimmeridgian – Tithonic. Stratigrafie. Paleontologie*. Dissertation these submitted to "Alexandru Ioan Cuza" University. Iași. 347 pp.

GRIGORE D. 2011. Kimmeridgian – Lower Tithonian Ammonite Assemblages from Ghilcoș – Hăghimaș Massif (Eastern Carpathians – Romania). *Acta Palaeontologica Romaniae*. Edit. Presa Universitară Clujeană. Cluj Napoca. **7**: 177-189.

JAMBOR J. L., NORDSTROM D. K., ALPERS C. N. 2000. Metal-sulfate Salts from Sulfide Mineral Oxidation. In: Alpers C. N., Jambor J. L., Nordstrom D. K. (Eds.) Sulfate Minerals. Crystallography, Geochemistry, and Environmental Significance. *Reviews in Mineralogy and Geochemistry*. Mineralogical Society of America. Washington. **40**: 303-350.

LANDER STACEY LEE 2014. *A study of the diagenetic alteration of bone from the Crown Mines in Johannesburg, South Africa*. Available online at http://wiredspace.wits.ac.za/bitstream/handle/10539/15229/MSc%20S. %20 Lander.pdf?sequence=1&isAllowed=y (accessed February 20, 2019).

ONDRUS P., VESELOVSKÝ F., HLOUSEK J., SKALA R., VAVRIN I., FRÝDA J., ČEJKA J., GABASOVA A. 1997. Secondary minerals of the Jáchymov (Joachimsthal) ore district. *Journal of the Czech Geological Society*. Prague. **42**(4): 3-76.

PATRULIUS D. 1963. Schița stratigrafică a seriei neocomiene de Dâmbovicioara: Hauterivian, Barremian şi Bedoulian de facies pelagic şi recifal. *Asociația Geologică Carpato-Balcanică, Congresul al v-lea, 4-19 Septembrie 1961 - Comunicări științifice. Secția II, Stratigrafie –v*. Publisher: Asociația Geologică Carpato-Balcanică, București. **III** (2 fascicule): 117-128.

PATRULIUS D. 1969. *Geologia Masivului Bucegi și a Culoarului Dîmbovicioara*. Edit. Academiei Republicii Socialiste România. București. 321 pp.

PATRULIUS D. & AVRAM E. 1976. Stratigraphie et corrélation des terrains néocomiens et barrémo-bédouliens du Couloir de Dâmbovicioara (Carpathes Orientales). *Dări de seamă ale Ședințelor.* Institutul de geologie și geofizică. Bucharest. **62**(4): 135-160.

PETRUS I. 1976. *Pirita sedimentară.* Edit. Academiei Republicii Socialiste România. București. 134 pp.

POP G. 1998. Stratigraphic distribution and biozonation of Tithonian praecalpionellids and calpionellids from the South Carpathians. *Romanian Journal of Stratigraphy - Dări de seamă ale Ședințelor.* Institutul de geologie și geofizică. Bucharest. **77**(4): 3-25.

SĂNDULESCU M., KRÄUTNER H., BORCOŞ M., NASTASEANU S., PATRULIUS D., ŞTEFĂNESCU M., GHENEA C., LUPU M., SAVU H., BERCIA I., MARINESCU F. 1978. *Geological map of Romania, 1:1,000,000*. Institute of Geology and Geophysics. Bucharest.

SEBE OANA GABRIELA. 2009. *Microfauna Badeniana si Sarmatiana de pe profilul Valea Morilor (Vestul Bazinului Dacic)*. Licence these (Unpublished data). Universitatea București. 230 pp

TEMPLE K. L. & COLMER A. R. 1951. The autotrophic oxidation of iron by a new bacterium: Thiobacillus ferrooxidans. *Journal of Bacteriology*. American Society for Microbiology. Washington DC. **62**(5): 605–611.

WALLER R. 1987. *An experimental ammonia gas treatment method for oxidised pyritic mineral specimens*. Triennial report. ICOM Committee for Conservation. Sydney. 623-630.

Macovei Monica
Geological Institute of Romania
1st Caransebeş Street, 012271 - Bucharest
E-mail: macovei.monica@yahoo.com

Grigore Dan
Geological Institute of Romania
1st Caransebeş Street, 012271 - Bucharest
E-mail: dan1_grigore@yahoo.com

Sebe - Rădoi Oana Gabriela
Geological Institute of Romania
1st Caransebeş Street, 012271 - Bucharest
E-mail: oana_sebe@yahoo.com

Dumitraş Delia Georgeta
Geological Institute of Romania
1st Caransebeş Street, 012271 - Bucharest
E-mail: d_deliaro@yahoo.com

Crușoveanu-Rusu Simona
Geological Institute of Romania
1st Caransebeş Street, 012271 - Bucharest
E-mail: rusu.mona82@gmail.com

Received: March 20, 2019
Accepted: August 09, 2019