

PYRITE GENERATIONS FROM THE PERMIAN/TRIASSIC BOUNDARY SECTION, BÁLVÁNY, BÜKK MTS., HUNGARY

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ABSTRACT

Three pyrite generations were described in the Bálvány Composite Section based on morphology, WDX and $\delta^{34}\text{S}$ data. Among them the 0.1–0.2 mm size, isotopically light euhedral pyrite is early diagenetic. This generation was found in the whole section. The “boundary shale” is characterised by microbial pyrite framboids, which formed on the surface, or close to the surface of the sediment around the redox boundary with the presence of dysoxic bottom-water. This, and the laminated structure of the sediment prove anoxic conditions in the whole sediment. Most probably there was dysoxic bottom water. The third generation is also euhedral, but has a larger grain size (1–2 mm). Based on $\delta^{34}\text{S}$ data and sphalerite inclusions, this generation is of late diagenetic or hydrothermal origin. This type occurs only in the shale and the top of the underlying limestone. The sulphides of the section are almost totally oxidised.

Key words: $\delta^{34}\text{S}$, pyrite, Bálvány-hill, Permian – Triassic boundary.

INTRODUCTION

Related to a multidisciplinary research project (Haas et al. 2004, Haas et al. 2007), we studied the pyrite content and its sulphur isotope composition of the Bálvány Composite Section. This carbonate-dominated section contains the continuous Permian – Triassic boundary.

The sulphur isotope composition of authigenic sulphides (predominantly pyrite) can provide useful data about the environment of the sulphide formation (connection of the pore- and the sea-water, oxygen content of the bottom water). There are three general sources of sulphur in a carbonatic sediment. The sulphides, the sulfates and the so called carbonate associated sulfates (CAS). In the same rock usually the sulphides contain isotopically light sulphur and the sulphates contain isotopically heavy sulphur because of the fractionation. Kaiho et al., (2006) studied the sulphur isotopes at the Bálvány and Meishan (S-China). They made selective sulphur extraction in the Bálvány-section. They separated the CAS and the sulphide sulphur. The CAS was varied between +10.2 – +26.6 ‰ $\delta^{34}\text{S}$. They observe fluctuations from which the biggest is in the boundary shale. They conclude this signal profile is simultaneous in both sections and also in Siusi (Italy). This shift to lighter isotope values can be the result of increased sulphide formation. They give four different hypotheses for the extra sulphur: 1: release of H_2S from the euxinic ocean water due to abrupt warming by volcanic CO_2 or impact shock wave; 2: volcanism penetrated huge sulphide ore deposit; 3: extraterrestrial impact into sulphide rich sediment or ore; 4: release of mantle origin sulphur by impact of huge asteroid (>70 km).

Gorjan et al. (2007) investigate sulphate and sulphide $\delta^{34}\text{S}$ and pyrite morphology (this only at Bulla) in the Bulla section (Italy) and the Bálvány section. They use the same samples from Bálvány as Kaiho et al. (2006). Their sulphide $\delta^{34}\text{S}$ values in the Bálvány section are 10–15 ‰ more negative than the sulphate $\delta^{34}\text{S}$ (Kaiho et al. 2006). They do

not distinguish among the different pyrite fractions and not separated them, thus their result could be questionable (see this study), but their observation about dysoxic/euxinic condition in the seawater at the P/Tr boundary is likely correct. Shen et al. (2007) report pyrite framboids from the Meishan section (S-China) with narrow size distribution and average diameter of 4.6–8.7 μm . It coincides with the mass extinction event. They think this is the sign of dysoxia, which was a global scale marine event during the Permian–Triassic transition. Jiang et al. (2006) publishes two different pyrite generations (none of them is framboidal) from the same section. One of them has a bacterial origin which formed in the shallow burial zone. Its $\delta^{34}\text{S}$ value varies between -15 – -40 ‰. The second appears at the top of the upper Permian Changxing Formation, and has volcanic origin with much higher $\delta^{34}\text{S}$ value. The highest is +2.2 ‰ $\delta^{34}\text{S}$. This pyrite forms distorted and elongated cubes and interlocking crystal forms of pentagon-dodecahedron.

LOCATION, GEOLOGICAL SETTING

The section is located close to the top of the Bálvány Hill in the Bükk Mountains (about 120 km NE of Budapest). This composite section is exposed in two outcrops within a distance of a few hundred meters from each other. The outcrop containing the lower part of the section is situated on the northern slope of the hill and is called “Bálvány North”. The upper part of the section is cropping out at the eastern side of the hill and is referred to as “Bálvány East”. The section contains the top of the black, thick bedded Nagyvisnyó Limestone Formation and the lower part of the Gerennavár Limestone Formation.

The upper Permian, thick bedded, inner ramp facies Nagyvisnyó Limestone Formation is rich in fossils. It is followed by a thin bedded, fossil-poor limestone, belonging to the lowermost part of the Gerennavár Limestone Formation. Between the two limestones there is an about one

meter thick shale, which forms the uppermost part of the Nagyvisnyó Formation. This layer can be interpreted as boundary shale between the Permian and Triassic layers. It contains numerous relics of upper Permian bivalve and brachiopod fauna (Csontos Kis and Pelikán 1990, Hips and Pelikán 2002, Haas et al. 2004, Posenato et al. 2004, 2005). Conodont data (Haas et al. 2004, 2007) also support the upper Permian age for the shale. The next 8.5 m thick limestone contains only a few ostracods and primitive arlandias. After 17 m of mudstone limestone, a brownish grey, thick bedded limestone starts which is a typical rock type for the Gerennavár Formation. This limestone is more than 100 m thick, dominantly ooidic, sometimes bioclastic with grainstone texture. These facies indicate continuation of sediment deposition in shallow marine environment after the ecological crisis.

MATERIALS AND METHODS

We collected 34 samples from the Bálvány sections for mineralogical studies (9 samples from the limestone part, 13 from the shale of the Nagyvisnyó Formation, and 12 samples from the Gerennavár Formation).

500 g of crushed samples was weighted for micro-mineralogical studies. First the carbonate component was dissolved, with 10 v/v% hydrochloric acid, then the residue was disintegrated with ultrasound and washed out in a 0.25 mm sieve. The coarser fraction was ground in agate mortar (except large single pyrite crystals). This carbonate-free residue was washed until neutral pH. Using a 0.063 mm sieve the 0.25–0.063 mm fraction was separated from the finer material. Heavy mineral separation was done by settling in bromoform (density 2.78 g/cm³). From the heavy-fraction, the pyrite grains were separated under a stereomicroscope.

Sulphur isotope measurements

Three samples contained unaltered pyrite of which we tried to measure the sulphur isotope composition. These samples are from the eastern section: the “boundary shale” (BK 3) and just below (BK 2) and above the “boundary shale” (BK 4). The BK 2 pyrite sample composed of small euhedral crystals. The sulphur content of the BK 3

“pyrite” sample was too low to perform isotope measurement, because of oxidation. The BK 4 sample contained both euhedral pyrite types, which could be separated under stereomicroscope, thus we were able to determine the sulphur isotope composition separately.

The digestion of the samples and the precipitation of sulphur as BaSO₄ were done in a laboratory of the Geological Institute of Hungary. The digestion was done by a mixture of Na₂CO₃ and KNO₃. After filtering the solution, all the sulphur content was precipitated as BaSO₄ by BaCl₂. This process extracts all the sulphur (sulphide, sulphate) content of the sample.

The sulphur isotope ratio was determined in the barium-sulphate using the method of Halas et al. (1982), at the Nuclear Research Institute of the Hungarian Academy of Science, Debrecen. NBS-127 barite standard was used as reference material. The measurements were done in a high-precision McKinney-Nier type stable isotope mass-spectrometer. For further technical details see Hertelendi et al. (1986). The δ³⁴S data are reported as ‰ relative to the Vienna Canyon Diablo Troilite (V-CDT) standard.

RESULTS

Description of the heavy fraction

The >63 µm heavy mineral fraction dominantly build up by limonitised

rock fragments and limonitised, hematitised pyrite and marcasite crystals. The >63 µm heavy mineral residue is generally 0.25 g (between 0.006–2.009 g). More than 99 % of the sulphides is oxidized. Only two samples (BK 2 and BK 4), both from the Nagyvisnyó Formation of the “Bálvány East” section contained enough unaltered pyrite for δ³⁴S measurements. These samples are from the eastern section just below and above the “boundary shale”. The BK 4 sample contained two pyrite types, which could be separated under stereomicroscope.

Detrital pyrite and sphalerite are also found in the section. Detrital pyrite occurs as inclusions in almandine, dravite and ferrotschermakite and as accessory mineral in amphibolite. Sphalerite is found in individual, 200 µm size grains in the shale and above the shale.

Morphology

All the samples contained subordinate singenetic and/or postgenetic pyrite or Fe-oxihydroxides after pyrite. The phases were divided into three main morphology groups: euhedral pyrite, framboidal pyrite (Fig. 1), and subordinate amount of infilling of fossils (Fig. 2). The euhedral pyrite was subdivided to two groups according to their size.

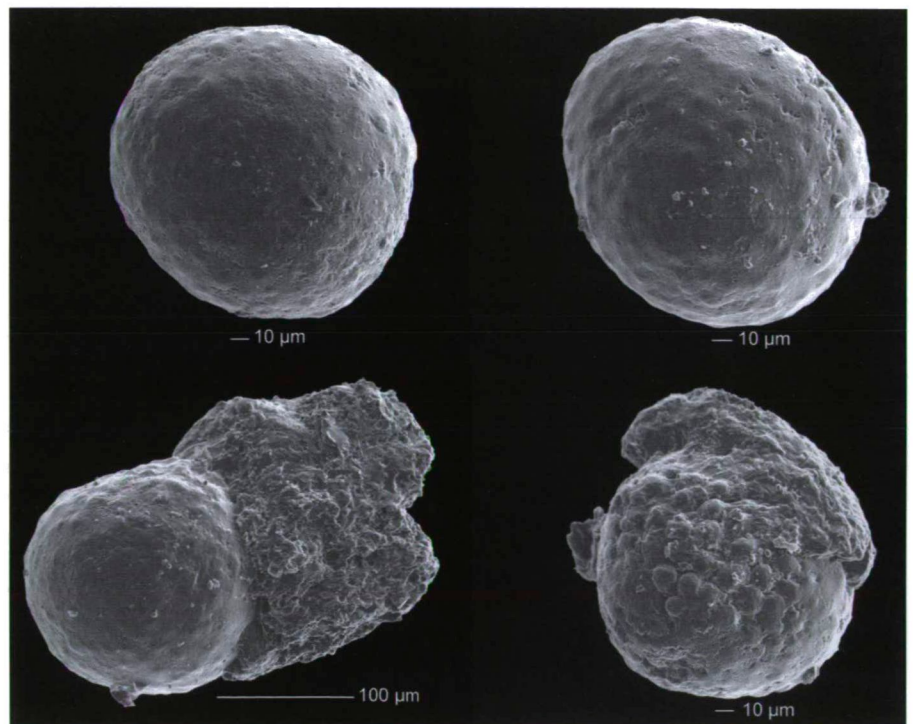


Fig. 1. Framboidal pyrites from the “boundary shale”.

The euhedral pyrite with relatively small crystals (0.1–0.2 mm) (Fig. 3) are typical for the section. The euhedral pyrite with relatively large crystals (1–2 mm) (Fig. 4) occurs only in few samples around the „boundary shale”. Framboidal pyrite is characteristic only for samples from the „boundary shale” and nearby samples below and above that. In these samples the framboids are abundant.

Euhedral pyrite with large crystals:

Many combinations appear from simple hexaeder to more complex forms. Characteristic growth-lines are also visible. The corners and the edges are sharp, unrounded. The surfaces of the crystals are usually oxidized. According to WDX measurements the Zn and Cu content are under the detection limit. In polished surfaces small sphalerite inclusions were visible in the crystals.

Framboidal pyrite:

The sizes of the framboids are between 100–150 μm . The morphological properties allowed us to easily separate the framboids from other spherule-looking grains under stereomicroscope. Also the polished, condrum-like inner structure was significant (Fig. 5). All the spheres are oxidizing without any sulphur content remaining. The composition of the framboids was measured by WDX on polished surfaces. The chemical compositions are listed in Table 1.

Sulphur isotope data

The sulphur content and isotope data are listed in Table 2. The BK 2 and the BK 4 (small euhedral crystals) samples have similar $\delta^{34}\text{S}$ values: -15.8‰ and -17.7‰ . The large crystals of sample BK 4 have a significantly different value: $+7.8\text{‰}$.

DISCUSSION

Based on the -16 and -18‰ values, the small euhedral pyrite was formed in the sediment. If there would be anoxic environment in the water column, the $\delta^{34}\text{S}$ value has to be more negative for the pyrite which could be formed on the sediment surface. It can not be formed in the water column because of their size. Based on this assumption the sea-water was not anoxic. The formation of pyrite framboids is around the redox

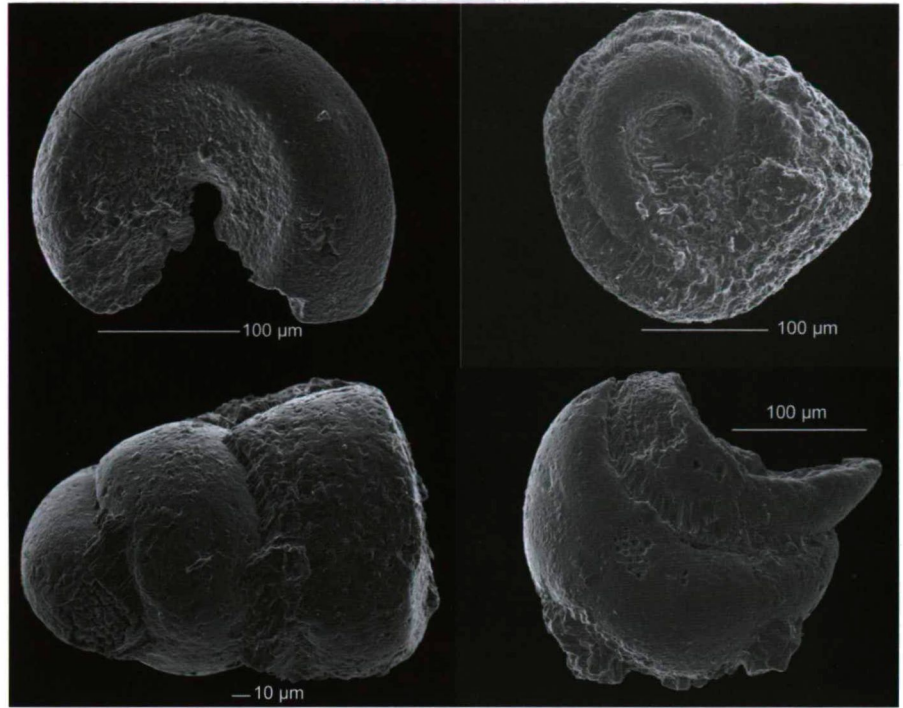


Fig. 2. Pyrite infilling of fossils from the Nagyvisnyó Formation.

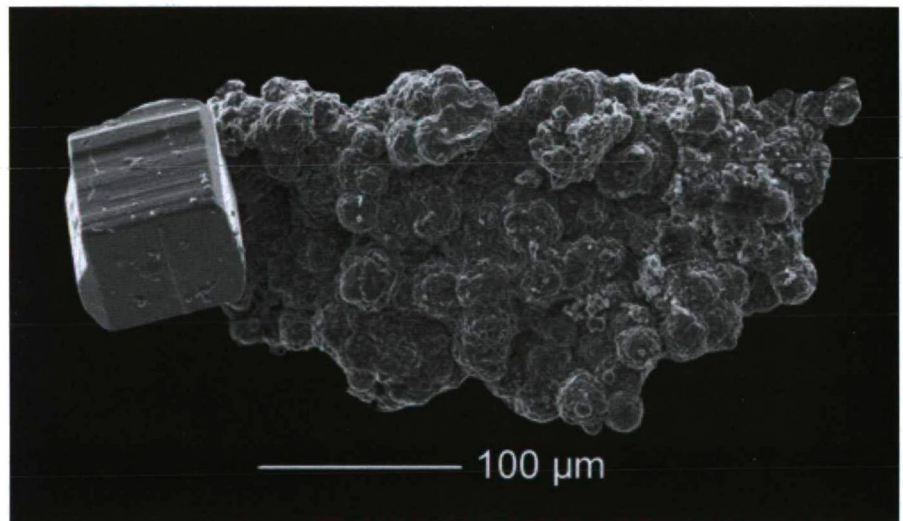


Fig. 3. Euhedral pyrite crystal with growth lines from the “boundary shale”.

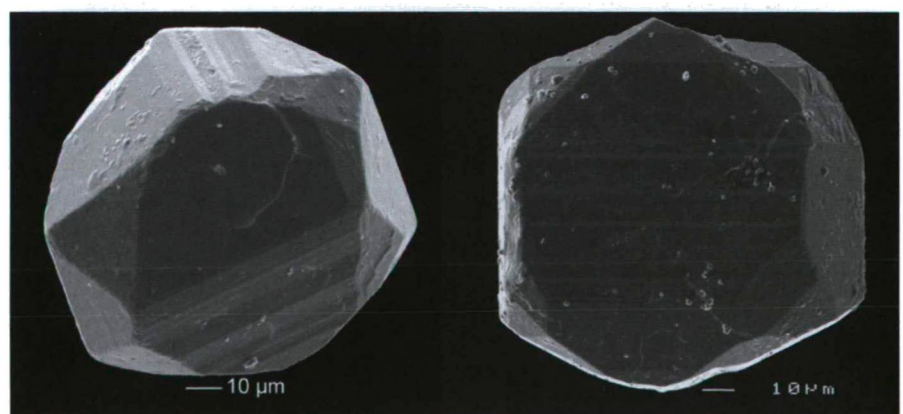


Fig. 4. Euhedral pyrite crystals with growth lines from the Nagyvisnyó Formation.

boundary, because it needs partly oxidised sulphur (Wilkin and Barnes

1997). This formation happens in the topmost layers of the sediment with the

presence of dysoxic bottom-water. Framboids can syngenetically form in the water column, if the redox boundary is in the water, or they can form diagenetically in the sediment. They can be easily distinguished from each other, because the syngenetic framboids are smaller (<6 μm) and have narrow size distribution. The size of them is limited, because the dense particles rapidly sink out of the water column. The diagenetic framboids are much bigger than them (Wilkin et al. 1997, Wignall et al. 2005). This size difference is important especially in weathered samples, as we have at the Bálvány-section, because the oxidation can change the geochemical composition of the sample, but the pseudomorphs after the framboids can easily be examined (Wignall et al. 2005). Thus the bottom water most probably was dysoxic. The not anoxic sea-water is also supported by the presence of megafauna. In contrast to this, the "boundary shale" and the overlying beds are laminated. The presence of fossils together with the lamination is controversial. The fossils could have suffered short transportation. The lack of bioturbation could be the result of the mass-extinction or the boundary of the anoxia was at the sediment surface or very close to that. These questions require more work to understand them.

The $\delta^{34}\text{S}$ of the large euhedral pyrite is +7.8 ‰, which is 26 ‰ higher than the small crystals. It means this type of pyrite generation can not be early diagenetic. It has to be formed in a system which was closed from the seawater. Most probably this generation was formed by a later hydrothermal event, but based on the $\delta^{34}\text{S}$ value, late diagenetic origin can not be excluded. Presence of sphalerite inclusions agrees with both interpretations.

At the Ursula Creek (British-Columbia, Canada) a continuous Permian – Triassic deep water section is known. Here a continuous decrease can be seen in the oxygen fugacity of the bottom-water during the Changshingian, marked by the lack of bioturbation, concentration of authigenic uranium minerals and formation of framboidal pyrite. This resulted anoxia at the end-Changshingian – early-Triassic (Wignall and Newton 2003).

In the Gartnerkofel (S-Caravancas) section and the Gartnerkofel-1 drill core around the Permian – Triassic boundary large amount of pyrite was formed. The pyrite is partly framboidal and partly euhedral (small hexaeders). The oxidation of the pyrite was done in two steps: during the Cretaceous and the Holocene. The sizes of the framboids are between 20–100 μm . The -18 – -27 ‰ $\delta^{34}\text{S}$ values of the framboidal pyrite support its bacterial origin. The pyrite is syngenetic–diagenetic, and was formed in reductive environment (Attrep et al. 1991, Holser et al. 1991). This "two step oxidation" could be the case in the Bálvány section also, because a Cretaceous metamorphism is proved there. More data has to be collected to prove this comparison.

Many similarities can be found among the Bálvány section and the other sections around the world: significant mass-extinction below the biostratigraphical boundary, followed by low oxygen fugacity and pyrite formation, the presence of the "boundary shale" and the similar facies of the limestones. Based on these data some peculiarities can be found in the whole Paleothetys, but local processes strongly influenced or overprinted them.

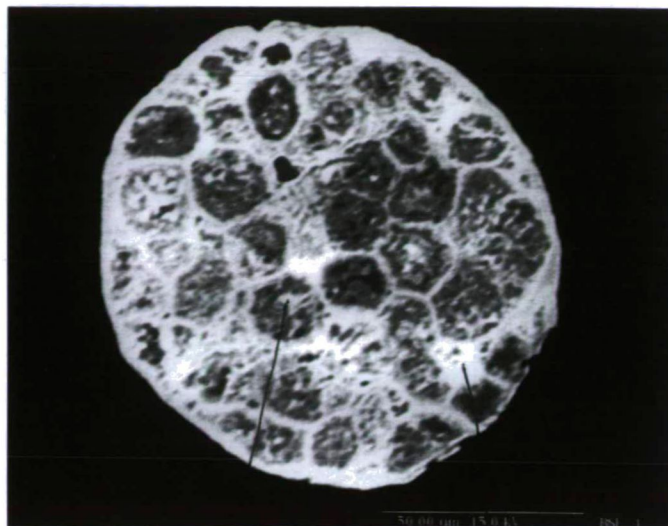


Fig. 5. Condrum like inner structure of a pyrite framboid from the "boundary shale" (backscattered electron image).

Table 1. WDX data of the framboidal pyrite. Elements under detection limit: Na, K, Mn, Ti, Cr, Ni (and S by EDX).

Analysis	Grain	SiO ₂	Fe ₂ O ₃	MgO	Al ₂ O ₃	CaO	Summ.
123	79	2.81	75.41	0.54	0.82	0.32	79.91
124	79	3.06	79.61	0.47	0.98	0.47	84.59
125	80	1.96	77.96	0.31	0.13	0.24	80.59
126	80	4.27	75.31	0.67	2.24	0.50	82.99
127	81	4.92	73.22	0.36	1.57	0.54	80.61

Table 2. Sulphur content and $\delta^{34}\text{S}$ ‰ of the pyrite separates from the Bálvány section.

Sample	S %	$\delta^{34}\text{S}$ ‰
BK 2 (small crystals)	5.82	-15.8
BK 4 (small crystals)	9.60	-17.7
BK 4 (large crystals)	53.30	+7.8
BK 3 (small crystals)	0.08	non measurable

CONCLUSIONS

The small euhedral pyrite was formed in the sediment, with -16 and -18 ‰ $\delta^{34}\text{S}$ values.

The formation of pyrite framboids happened in the topmost layers of the sediment is around the redox boundary with the presence of dysoxic bottom-water. This, and the laminated structure of the sediment prove anoxic conditions in the whole sediment. Most probably there was dysoxic bottom water. The not anoxic sea-water is also supported by the presence of megafauna.

The large euhedral pyrite has 26 ‰ $\delta^{34}\text{S}$, thus this type of pyrite generation can not be early diagenetic. Most probably this generation was formed by a later hydrothermal event, or has late diagenetic origin. Presence of sphalerite inclusions agrees with both interpretations.

"Two step oxidation" (Cretaceous and Holocene) of the pyrite could be the case in the Bálvány section as it mentioned in the Gartnerkofel sections.

ACKNOWLEDGEMENTS

We acknowledge the financial support of the Hungarian Scientific Research Fund (OTKA) grant 7966. The authors are also grateful István Futó for sulphur isotope measurement.

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Received: May 12, 2008; accepted: July 30, 2008

