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Review

Epithermal Bicolor Black and White Calcite Spheres from Herja Ore Deposit, Baia Mare Neogene Ore District, Romania-Genetic Considerations

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Abstract: White, black, or white and black calcite spheres were discovered during the 20th century within geodes from several Pb-Zn ± Au-Ag epithermal vein deposits from the Baia Mare ore district, Eastern Carpathians, Romania, with the Herja ore deposit being the maiden occurrence. The black or black and white calcite spheres are systematically accompanied by needle-like sulfosalts which are known by the local miners as "plumosite". The genesis of epithermal spheres composed partly or entirely of black calcite is considered to be related to the deposition of calcite within voids filled by hydrothermal fluids that contain acicular crystals of sulfosalts, mostly jamesonite in suspension. The proposed genetic model involves gravitational concentration of sulfosalt acicular crystals towards the base of open spaces within paleochannels of epithermal fluid flow and the subsequent formation of calcite spheres by geochemical self organization of amorphous calcium carbonate that crystallized to calcite via vaterite.

Keywords: calcite spheres; jamesonite; berthierite; gravitational concentration; Herja; Baia Mare; Romania

1. Introduction

The Herja epithermal ore deposit, located in the Neogene Baia Mare ore district, Eastern Carpathians, Romania is known for the presence of fizélyite [1], but it is also renowned among mineral collectors for several mineralogy peculiarities, e.g., black calcite associated to jamesonite or siderite, marcasite pseudomorphs after pyrrhotite, tabular pyrrhotite, rosette-like semseyite crystal aggregates, ring-shaped jamesonite crystals, short prismatic stibnite crystals, loose siderite spheres with central hollow space, as well as white, black or bicolor white and black calcite spheres (Figure 1a–c). The exquisite bicolor—approximately half black and half white—calcite sphere from Herja (Figure 1c) hosted by the County Museum of Mineralogy "Victor Gorduza", Baia Mare is indexed as a Romanian national patrimony mineral specimen. The specimen was stolen from its secure place during the night of January 25/26, 2014 and is still missing.

Figure 1. Epithermal calcite spheres from the Herja ore deposit hosted by County Museum of Mineralogy, Victor Gorduza", Baia Mare; (**a**) White dominated calcite sphere (4.5 × 4.5 × 5 cm) with a minor black calcite section (not visible), sample 177099; the sphere has apparently an inner void hosting solid inclusions as indicated by the noise that occurs when the sample is joggled; (**b**) Black calcite sphere (6 × 6 × 6 cm), formed of rhombohedra of up to 10 mm long edges; A3 axis of each rhombohedron seems to be parallel to the radius of the sphere; the black calcite is covered by small-sized siderite spheres and apparently marcasite "dust"; sample 12990; (**c**) Bicolor calcite sphere composed of uneven volumes of white and black calcite. The sample is classified as a Romanian national patrimony specimen and was hosted by the County Museum of Mineralogy, Victor Gorduza", Baia Mare until January, 2014 when it was stolen; (**a**) and (**b**) photos by Ioan Bereș, (**c**) photo by Valentin Ganța.

The research focuses on the occurrence of calcite/carbonate spheres from the Baia Mare ore district, with emphasis on such samples from Herja epithermal ore deposit. It updates the available mineralogical data and offers information acquired from former geologists, miners and other staff of the Herja mine. Valuable data were provided by Victor Gorduza (1942–2014), founder of the Mineralogical Collection Baia Mare (1976–1992), and afterwards, head of the County Museum of Mineralogy in Baia Mare (1992–2010). This information is important for at least two reasons: (i) the mine has been closed since 2006, and (ii) the former staff of the mine are rapidly disappearing without leaving written documents for future generations. The paper proposes a genetic model for the formation of carbonate bicolor spheres from Herja and from other ore deposits in the Baia Mare ore district, and, by extrapolation, for similar epithermal samples possibly known elsewhere in the world.

2. Geological Setting

The Herja Pb-Zn-Ag-Sb and subordinately Au ore deposit is located in the Baia Mare ore district from Gutâi Mountains, Eastern Carpathians, NW Romania (Figure 2). The deposit consists of a conjugated veins system striking generally ENE-WSW counting over 250 vein structures [2]. At the ore deposit scale 67 veins were considered "principal" [3], some of them being mined almost 1000 m on strike and more than 500 m on dip. Prior to the mid 1990s Herja was unanimously considered an excellent example of a Pb-Zn mesothermal deposit according to Lindgren's classification of ore deposits. Afterwards, the deposit was described as low sulfidation [2].

The ore deposit is related to the Neogene post-collisional volcanism that occurred due to the complex interaction among Alcapa and Tisia-Getia terranes with the south-western edge of the European plate during Neogene [5–7]. It was structurally controlled by Dragoș Vodă transform fault [8,9], etc., which contributed to the channeling of the hydrothermal fluids. Detailed geological and mineralogical data on the Herja ore deposit are given by [2], and a geological overview of the Herja ore deposit and its mineralogy was recently made by [10]. Additional information on mineralogy and geology of Herja area may be found in [11–32].

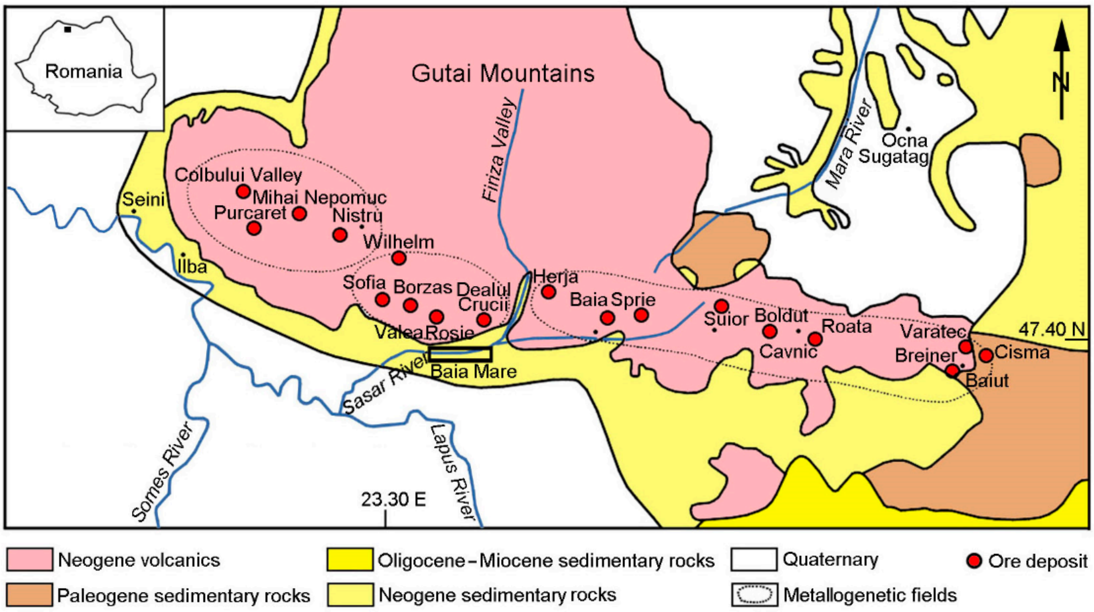

Figure 2. Simplified geology of the Baia Mare ore district, NW Romania with location of main ore deposits including Herja (modified after [4]).

Zn, Pb, Ag, Sb, S and minor Au were produced from the Herja ore deposit [2,3,33,34], etc. The deposit was reputed for its massive galena ore (e.g., Șălan vein), sphalerite rich-ore (e.g., Zincos vein), and high grade silver ore with up to 4 kg/t Ag in the upper part of almost all the veins [33]. An exception was the Clementina vein with high Ag grades from surface (approximately 600 m ASL) down to +425 mining level [33]. According to the same author, gold was scarce at Herja, with hieratic grades of up to 5 g/t in the upper part of Șălan vein.

3. Previous Data

The first black and white hydrothermal calcite spheres from Herja were found in 1958. They were laying in the lower part of geodes from several veins, e.g., Şălan (numbered as vein #10), Clementina (numbered as vein #60), and Ignaţiu (numbered as vein #40). At the time of their discovery, the miners used to call them "the mineral balls from Herja". These black and white calcite spheres were considered by the geologists of the Herja mine only as mineralogical curiosities, without any further interest. Until 2005, such bicolor carbonate spheres were noticed at different mineral shows in Romania, but afterwards, they totally disappeared from the public market. However, based on XRD data, [35] it was revealed that fake cm-sized black/grey calcite spheres composed of synthetic aluminum oxide (Al_2O_3) with subordinately spinel balls covered by jamesonite debris and needles glued on their surface are still exhibited at mineral shows in Romania (Figure 3).

Several testimonies from the time of the discovery of hydrothermal calcite spheres in the underground mining works are still preserved, like that transmitted verbally by Alexandru Dunca, who was working as a standardizer at Herja mine at the time: "In some geodes, balls of various sizes could be noticed. Some were black, some were black and white, and nevertheless not all of them had the colors equally distributed. The miners were surprised by such a find, and they used to play with them". Another eye witness, geologist Victor Gorduza, stated that "the white and black balls were laying in a mass of plumosite filling geodes located in the veins, and one needed to clean the balls in order to collect them. The black part of the calcite bicolor balls was always below".

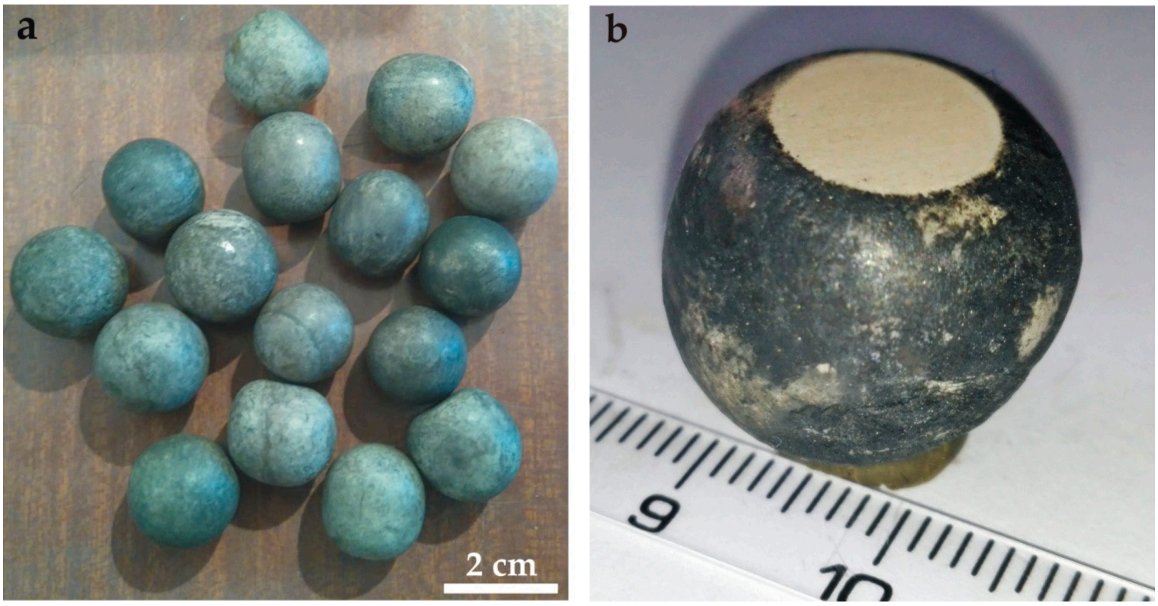

Figure 3. (**a**) Group of fake calcite spheres exhibited at a mineral show in Cluj-Napoca (Romania) in 2016; (**b**) Jamesonite detritus and needles are glued onto the surface of synthetic aluminum oxide (Al_2O_3) + spinel balls, as identified by [35] based on XRD data.

The first mention of carbonate spheres from Herja in the Romanian geological literature is credited to [36], who stated that at Herja occur as white, black, and white and black calcite spheres. Later, [37] mentioned the existence at Herja of almost perfect white and black, black, or white calcite spheres formed of small-sized flattened calcite rhombohedra arranged "en échelon". These authors also stated that this crystal morphology was formed at relatively low temperatures and that the black calcite from the spheres contains jamesonite needle-like crystals. According to [37], similar calcite sphere occurrences are known in Romania, i.e., Hărțăgani, South Apuseni Mountains and Stânceni, Eastern Carpathians.

Floating spheres from the hydrothermal environment, i.e., the loose hydrothermal carbonate ones from Herja, were mentioned for the first time by [32] as a mineralogical novelty for Romania. These authors analyzed smooth, hollow siderite spheres, 20 to 30 mm in diameter (Figure 4), and concluded that they were formed in geodes from hydrothermal fluids by coating gas bubbles while floating. A similar interpretation was further proposed by [20], who examined spheroidal crystal aggregates associated to jamesonite hair-like masses from several ore deposits in Baia Mare region. According to this author, carbonate loose spheres occur in Herja and Baia Sprie, but they were also sometimes mentioned in the Săsar and Cavnic ore deposits.

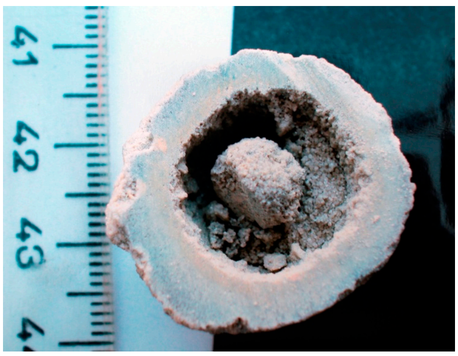

Figure 4. Cross-section through a hollow siderite sphere from the Herja ore deposit which contains inside free siderite rhombohedron crystals and a smaller siderite sphere partially cut during the sawing of the sample (from [32] (p. 134) with written permission from the editor).

4. New Observations on Carbonate Spheres from the Herja Ore Deposit/Baia Mare Ore District

The examined material was collected during the period of underground mining activity at Herja; some of the views expressed here were gathered in the field on the basis of on-site observations. These samples belong to County Museum of Mineralogy "Victor Gorduza", Baia Mare (MusMin) or Mineralogy Museum of Babeș-Bolyai University, Cluj-Napoca (MMBBU).

The available oral communications, the field evidence and the existing samples indicate that two morphologic types of hydrothermal carbonate spheres occur in the Herja ore deposit, (i) attached to substrate, and (ii) loose/free. With regards to the mineralogy of the carbonate spheres from Herja, two mineral compositions have been already mentioned, i.e., calcite and siderite [2,20,32].

4.1. The Attached Carbonate Spheres

This type of sphere occurs as single, double or groups of globular items usually displaying an almost smooth surface composed of minute euhedral rhombohedra (Figure 5a). They were formed by deposition upon a pre-existing mineral substrate, and thus represent a late mineral sequence. Generally, these spheres are up to 4 cm in diameter, larger ones being rare. Their color reflects their mineralogy, i.e., white for calcite (Figure 5), brownish for siderite, and black for calcite with jamesonite impurities.

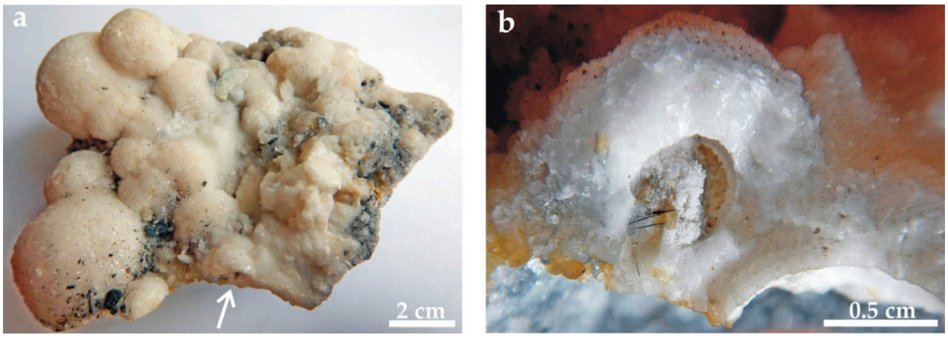

Figure 5. Attached spheres from Herja (private collection Ioan Mârza). (**a**) Group of calcite spheres that represent relatively late mineral sequence deposited on glassy microcrystalline hydrothermal quartz sequence bearing sulfides and sulfosalts; note that some late sulfosalt crystals occur on the calcite spheres; (**b**) Detail of (**a**), viewed as indicated by the arrow in (**a**), which shows the inner void of a white calcite sphere hosting several jamesonite needle-like crystals covered by sandy white calcite grains.

The available cross sections of such spheres reveal, in some cases, the even deposition of subsequent carbonate sequences that creates a concentric development of the spheres deposited from hydrothermal fluids, or fibroradial morphology. White calcite attached spheres sometimes show an inner empty space partly filled with other crystals/minerals, e.g., jamesonite, formed previously and partially covered by cemented sandy calcite (Figure 5b).

The sample 273/27 from Herja hosted by MMBBU (Figure 6) is composed of black calcite attached spheres up to 2.5 cm in diameter covered by continuous sequence of about 1 mm width siderite. Apart from the compact layer covering black calcite spheres, siderite also occurs as late millimeter to sub-millimeter sized individual euhedral crystals (flatten rhombohedra) and as fillings of fissures that cut black calcite (Figure 6d,e). Late smaller-sized siderite spheres occur locally, but they are incomplete, being apparently broken. They seem to be empty, but some contain minute crystals or crystal remnants (Figure 6b,c). The imprints of similar spheres, which were almost completely removed, are preserved on the surface of some bigger ones, and are highlighted by traces of external "walls" and by the contrast of their imprint and the rest of the supporting spheres (Figure 6b). The available cross-sections through these spheres reveal their black calcite composition and the late siderite deposition (Figure 6d–f). They also show the internal structure of the spheres, i.e., (i) the existence of an inner quartz crystal that apparently supported the formation of the sphere; (ii) the fibroradial pattern, and (iii) the concentric layering formed of different crystal growth sequences (Figure 6d–f).

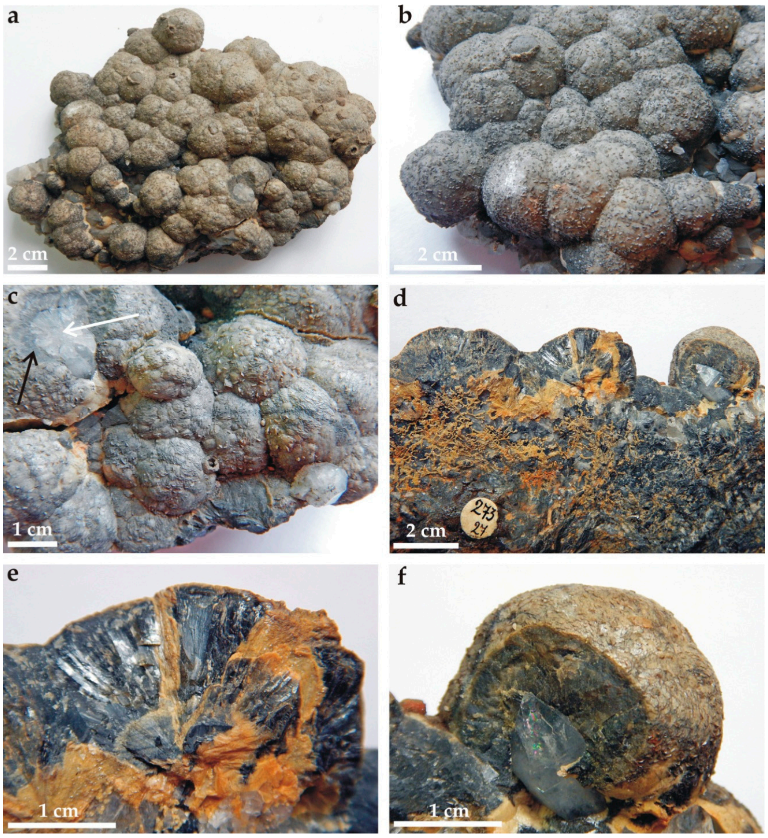

Figure 6. Attached black calcite spheres from Herja covered by siderite as continuous deposition layer, small hollow broken attached spheres, and minute euhedral crystals (sample 273/27, MMBBU). (**a**) General view of attached black calcite spheres covered by siderite; the black calcite is not visible; (**b**) Detail that highlights the shape of carbonate spheres and the presence of siderite wall remnants of a partly removed sphere; note the contrast between the imprint of the hollow broken sphere, and the rest of the specimen's surface, which is covered by minute siderite crystals; a small sphere seems to be developed on a quartz crystal, which is not completely covered by carbonates; (**c**) Detail view focused on surface morphology that also shows a small broken sphere with crystal remnants in the inner space (lower part of the image); the arrows indicate the inner structure of a broken sphere with a central quartz crystal, covered by black calcite and thin siderite external sequence; (**d**) Cross-section through a series of three black calcite spheres, a dominant massive one (left), a fibroradial one (center), and one developed on a quartz crystal (right); (**e**) Detail of (**d**) that shows the fibroradial inner structure of the black calcite sphere with at least two concentric layers and the late siderite deposition at the surface and along fissures; (**f**) Detail of (**d**) that reveals the quartz crystal on which the massive black calcite sphere covered by siderite apparently formed.

The cross-section through the "root" of a single attached black calcite sphere (sample RCol/2/F, MMBBU) shows that it is massive, while the surface of the spheroidal shape is composed of numerous individual black calcite rhombohedra of less than 1mm in size (Figure 7).

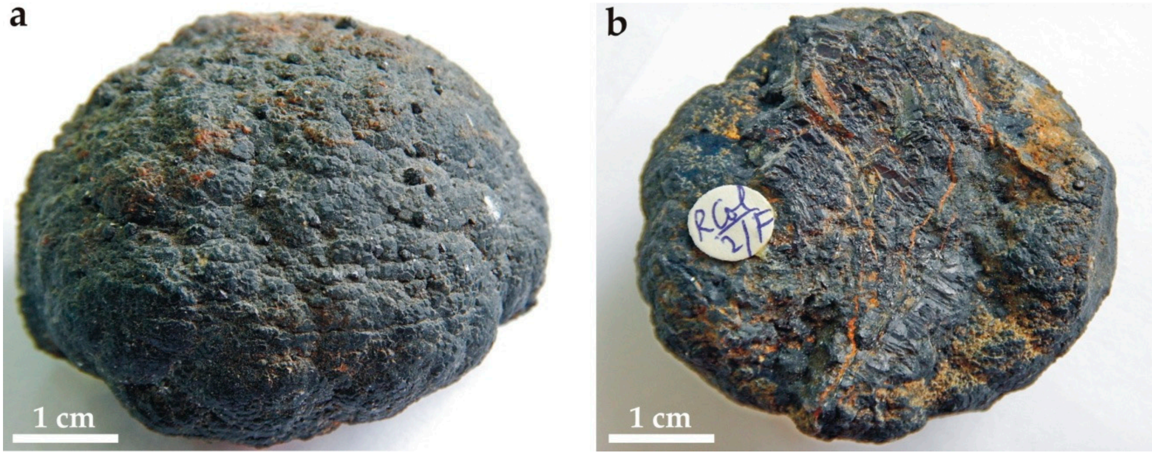

Figure 7. (**a**) Attached single black calcite sphere from Herja (sample RCol/2/F, MMBBU); (**b**) Cross-section through the base of the sphere that corresponds to the connection to the substratum, with no clear, well-developed inner crystal like that in Figure 6f; however, the black calcite contains abundant needle-like jamesonite crystals. Note the late siderite deposition along the fissures.

4.2. The Loose Carbonate Hydrothermal Spheres

The absence of a supporting zone or contact to the substratum suggests that the loose spheres might be interpreted as floating spheres or floats. Mineral floats are known from various geological environments, i.e., marine (oolites and pisolites), karst (cave pearls) and hydrothermal ore deposits [32].

A hollow incomplete siderite sphere (sample RCol/2/C; MMBBU) of 3.1 cm diameter has massive walls with the width ranging from 3 to 6 mm and an inner void of approximately 2 cm in diameter (Figure 8). Euhedral rhombohedra siderite crystals of 1 to 2.5 mm in length occur attached on the inner wall of the sphere (Figure 8). According to the sample description file, it was collected from a jamesonite-rich environment in the Herja mine. Unfortunately, there are no available data about the presumed infilling of the sphere. This specimen likely belongs to the loose hydrothermal spheres described previously by [32] and presented in Figure 4.

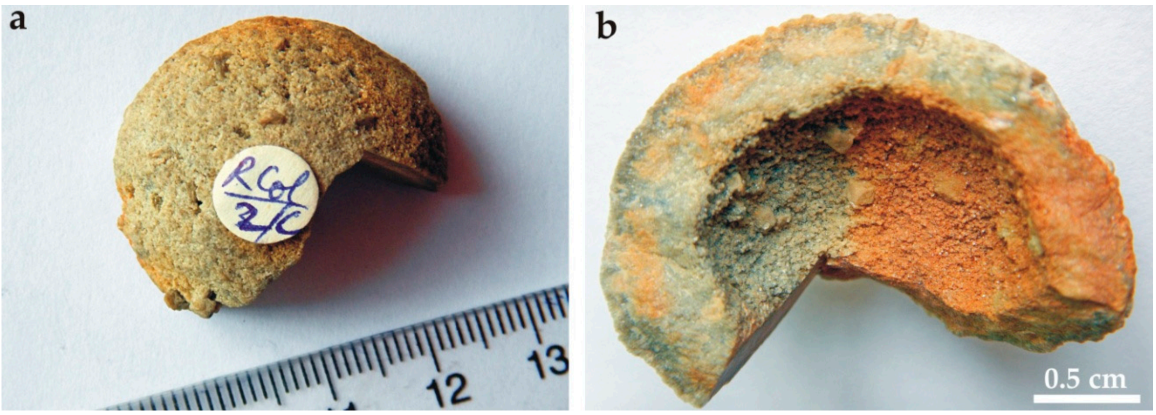

Figure 8. Siderite hollow sphere from Herja (sample RCol 2/C; MMBBU). (**a**) External view of broken siderite sphere; (**b**) Inner view of the sphere with euhedral rhombohedra siderite crystals deposited on the interior wall of the sphere; note the variation of the width of the sphere's wall.

A 6 cm long loose siderite spheroid-like sample from Herja shows a different distribution pattern of individual flattened siderite rhombohedra (Figure 9), which are arranged in an ordered style in the rounded part (Figure 9a,b) and are randomly distributed in the elongated part respectively (Figure 9a,c).

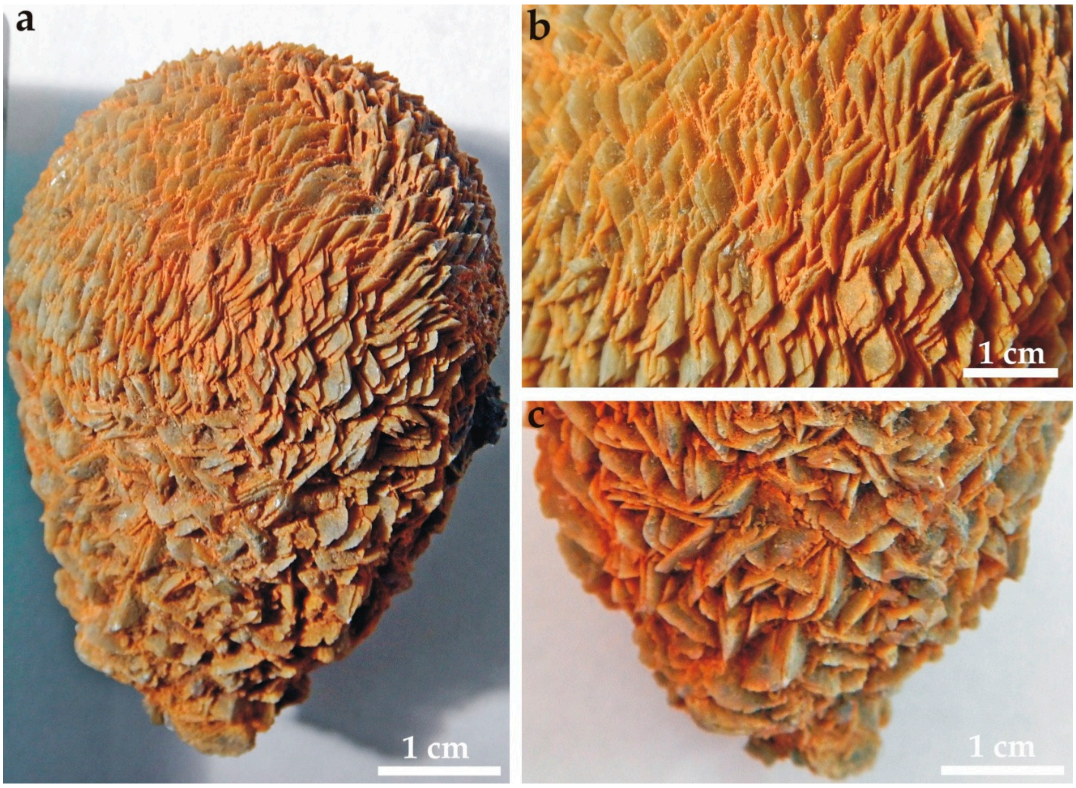

Figure 9. Loose spheroid-like/egg-shaped siderite specimen from Herja (sample RCol2/B; MMBBU). (**a**) The rounded and elongated shape of the sample reflects the ordered and disordered arrangement respectively of the individual flat rhombohedra siderite crystals; (**b**) Detail of (**a**) focused on the rounded section of the sample; (**c**) Detail of (**a**) showing the elongated section of the sample with randomly distributed flat rhombohedra siderite crystals.

The loose calcite spheres from the Baia Mare ore district might be white, black or bicolor, white and black (Figures 1 and 10), and display on their surface white or black flattened rhombohedra calcite crystals. They generally are of 1.5 to 5 cm in diameter, with the largest ones being up to 7 cm and the smallest less than 1 cm. The volume proportion of white and black parts is variable, being generally dominated by one color, usually black. Some samples are considered to be half white and half black, but rigorous observation reveals that they are unequal. The limit between the two contrasting color sections of the bicolor spheres is usually planar and is always sharp. The coexistence of black and white calcite was also noticed for individual crystals or crystal aggregates that possess a more or less euhedral shape [10]. However, a gradual transition from one color to another was noticed for some calcite specimens as well. Several broken black calcite crystals or crystal groups of various morphologies including spheroidal ones revealed that they are also black inside, not only at the surface. This fact indicates that the color of calcite is not a superficial one given by an outward sulfide-rich black shell.

Twinned loose spheres composed of black calcite also exist (Figure 11). Each individual black calcite sphere does not exceed 25 mm diameter and is composed of flattened calcite rhombohedra intimately associated to jamesonite (Figure 11a).

Similar to the single spheres or to the attached ones (Figure 6), the loose black calcite twin spheres associated with jamesonite are sometimes covered by siderite, as shown in Figure 11b. The late siderite deposition that occurs after jamesonite and black calcite deposition was reported by [10] in the paragenetic sequence of the late stage mineralization from the Herja ore deposit. According to the same author, only minor quartz was formed after the final siderite. It is worth mentioning that the last deposited siderite on black calcite spheres occurs as minute individual crystals, as well as attached spheres (Figure 11b).

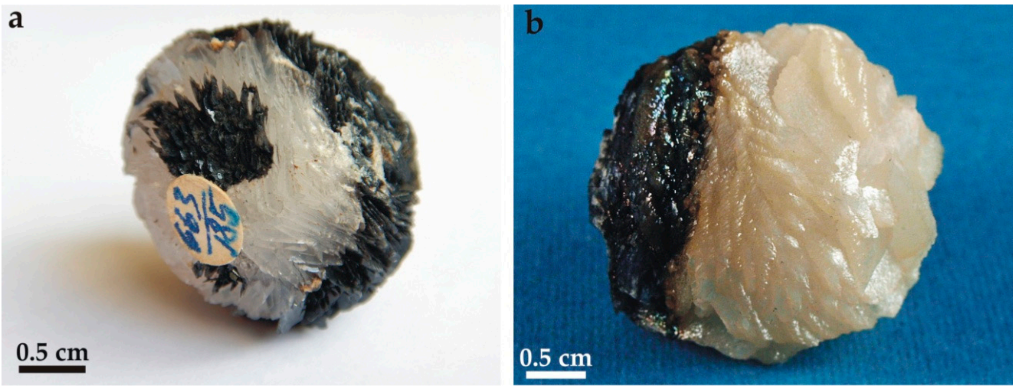

Figure 10. Bicolor calcite spheres from the Baia Mare ore district. (**a**) Black calcite dominated bicolor calcite sphere (28 mm diameter) from Dealul Crucii ore deposit with sharp limit between white and black sections; note two spots of black calcite on the top of the white calcite zone; sample 663/185 (MMBBU); (**b**) White calcite dominated bicolor calcite sphere (30 mm diameter) from the Herja ore deposit (width of white and black sections is 22 and 8 mm respectively). The white section of the sphere is built up of flattened rhombohedra crystals with the length of edges ranging from 4 to 7 mm. The black side of the sphere is flattened suggesting that it was once fixed on more or less planar substratum or on another sphere; sample 15778 (MusMin); (**b**) photo by Ioan Bereș.

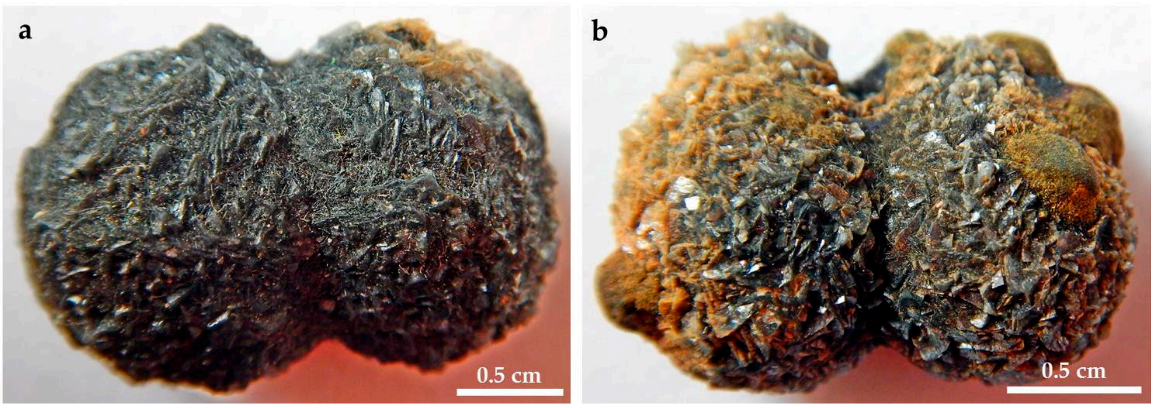

Figure 11. Twin black calcite spheres and related jamesonite "wool" from Herja. (**a**) Twin black calcite spheres with more abundant jamesonite preserved in the junction zone; sample RCol/2/Q, MMBBU. (**b**) Twin black calcite spheres formed of flattened calcite rhombohedra associated to jamesonite and covered by siderite minute crystals and attached spheres; sample RCol/2/S; MMBBU.

4.3. Mineral Assemblage of Carbonate Spheres

The mineralogical studies carried out for the Herja ore deposit [2,10,11] indicated that the black color of calcite is due to the presence of jamesonite or/and berthierite needle-like crystals inclusions. However, the available published data certified that jamesonite is the most frequent metallic mineral inclusion in black calcite. According to [10], the different colors of the calcite from Herja are due to impurities, i.e., the milky-white calcite contains ankerite impurities, the creamy-white calcite contains both ankerite and siderite mineral inclusions, the translucent calcite is depleted of any mineral inclusions, while the black calcite contains altogether ankerite, siderite, jamesonite and in minor amounts other sulfides (e.g., galena).

The so-called mineral "plumosite" was described during the 20th century in several ore deposits from the Baia Mare ore district by many authors as a distinct mineral species. The Herja ore deposit was known for its abundance of "plumosite" according to many authors [12,13,17,19–22,24–26] etc. A study of jamesonite deposited within geodes at Herja by [24] suggests that the feathery-acicular mineral frequently found in open spaces is an intermediate member of the jamesonite-benavidesite series with traces of Ag, Mn, and Tl. According to [25] "plumosite" is in fact jamesonite, but sometimes it could be boulangerite, and in the case of Săsar ore deposit it is robinsonite. The most recent overview of the "plumosite" from Herja by [29] confirmed that this supposed mineral species is in fact jamesonite. These authors also suggest that the most appropriate use of the term "plumosite" is to denominate any Pb-sulfosalt or Pb-sulfosalts mixture occurring with plumose texture or as fibrous aggregate. As such, berthierite was also recently identified by [10] as fibrous aggregates related to the black calcite from Herja.

According to the authors cited above, "plumosite" occurs in various shapes, i.e., (i) free needle-like crystals in voids; (ii) black fibrous-acicular or massive mineral masses in open spaces; (iii) monomineral sequence intermingled among other ore mineral sequences; and (iv) inclusions in other minerals, most frequently calcite and quartz. As shown above, the mineralogical composition of the so-called "plumosite" is, in most cases, jamesonite; consequently, from now on, we refer to "plumosite" as jamesonite.

Other less common minerals were identified in the black calcite mineral assemblage from Herja by [10], i.e., sphalerite, boulangerite, fülöppite, apparently fizélyite and plagionite, as well as poorly-identified uchucchacuaite.

5. Discussion

The experimental work carried out by [38] led to the growth of calcite crystals in agarose and Na-metasilicate gels from supersaturated solutions. Among the various morphologies of calcite crystals obtained experimentally by [38], we mention simple and twinned spherulites, rough and curved crystals, flattened rhombohedra, simple spherulites formed of single crystals terminated by rhombohedra. According to [38], rhombohedra with flat faces are growing by lateral spreading of macrosteps generated by hollow core dislocations. Another experimental result of [38] is the growth of calcite spherulites and/or single crystals on glass capillaries conditioned by the composition of the gels and the solution passing through the gel, and the presence of impurities that triggered the nucleation and the growth of calcite.

The attached and loose carbonate spheres from Herja, irrespective of their color, were found in open spaces along vein structures. The euhedral crystals on their rounded surface indicate that their shape is not the result of a mechanical processing/abrasion, but the result of deposition from hydrothermal fluids. The available samples from the Herja ore deposit confirm that the attached carbonate spheres are deposited on a firm mineral base, while the loose spheres are not attached to the substratum, or likely their connection is less clear or hidden by subsequent mineral deposition. The available evidence indicates that the loose spheres were always discovered dispersed within hair-like jamesonite nests located in open spaces. The existence of loose spheres with an internal void also suggests that these particular carbonate spheres could also float within hydrothermal fluid. Moreover, the presence of black calcite hosting always needle-like jamesonite crystals suggests that the carbonate deposition and the jamesonite occurrence always coexisted during the genesis of black calcite spheres.

The carbonate gangue (mostly calcite, subordinately siderite) from Herja was deposited from (super)saturated hydrothermal fluids, while the occurrence of the spheroidal shape was catalyzed by the presence of impurities that acted as support for the subsequent geochemical self-organization of carbonates resembling to the concretion formation in sedimentary environment [39]. Indeed, jamesonite/berthierite which is millimeters to centimeters and occurs as length needle-like crystals could act as favorable support for carbonate spherulites growth (Figure 5b), as suggested by black calcite spheres with coarse quartz crystal "spine" as well (Figure 6b,d,f). The carbonate spheres from Herja do not show any evidence of inherited textures, thus suggesting that their formation was the result of geochemical self-organization; see [39,40]. The growth of attached carbonate spheres over a substratum consisting of previously formed spheres also indicates a decreasing intensity repetitive pattern, as the size of the spheres is gradually decreasing (e.g., Figures 6 and 11b). The occurrence of cm-sized calcite/carbonate spheres correlated to the lack of abundant small-sized spheres reflects the competitive particle growth that supported the formation of larger spherical items by dissolution of the smaller ones due to their higher solubility [40,41]. The subsequent regularly disposed calcite rhombohedra forming the outer section of the spheres as they are visible on the spheres' surface (e.g., Figures 1 and 6) is the result of geometrical selection of the crystals growing perpendicularly on the substratum [42].

5.1. Environment of Formation

A black and white calcite fragment from Herja, including its connection zone to its base, revealed a greater abundance of jamesonite crystals towards its rooted zone with an almost pure jamesonite basal thin depositional layer [10]. Gradually, away from the base on which it is grown towards its limit to the white calcite sequence the black calcite contains fewer and fewer jamesonite needle-like crystals, with the last jamesonite crystals being aligned along the contact black-white calcite. This observation suggests a segregation of already deposited jamesonite crystals within the fluid from which black and white calcite precipitated. We could thus infer the gravitational concentration of jamesonite crystals within the fluid from the open space where euhedral calcite crystals, and that crystal groups have grown, as well as the separation within the hydrothermal fluid of two layers, one with jamesonite crystals in suspension and another one without/depleted of jamesonite solid impurities. This assumption is also confirmed by field evidence, i.e., the bicolor calcite spheres found in situ generally had their black side down and their white part up. The same relationship is illustrated by the sample shown in Figure 12, which is composed of a series of white calcite spheres developed on one side and another series of black calcite spheres developed on the other side, with both series being attached to the same separation area and grown in opposite directions. The late siderite deposition masked the contact between the white and black calcite of the specimen (Figure 12a). There is no information concerning the spatial position of the sample in the field, but it is likely that the white part was originally situated above the black one. Two dense fibroradial berthierite crystal aggregates similar to a trunk, a longer central one and a right-lateral shorter one, both apparently broken, occur on the black side of the same sample (Figure 12b) among black calcite spheres. These trunks could act as a veritable catalyst for the growing spheres; individual needle-like berthierite crystals certainly played a role in the calcite spheres deposition. Additionally, on the black side of the specimen shown in Figure 12, berthierite is frequent, and occurs as crystal bundles among black calcite rhombohedra.

Similarly, the gravitational concentration of crystals within fluids, or gravitational banding is considered to be the mechanism for the genesis of the so-called Uruguay-type agates [42,43]. This particular type of agates consists of horizontal bands composed of euhedral quartz crystals (0.5–4 μm) and spherulites (up to 200 μm) which were gravitationally concentrated from the fluid filling the open spaces during the growth of the agates [42].

The carbonate gangue from Herja precipitated from late hydrothermal bicarbonate fluids flowing through structurally controlled veins/hydrothermal breccia dykes with open spaces. The field evidence confirmed that the open spaces in Herja, as well as those in other ore deposits from the Baia Mare ore district, may sometimes exceed several meters in length, tens of centimeters in width and meters in vertical development. The late/final mineralization pulse from Herja postdated the main sulfide deposition and contains abundant carbonate gangue as well as scarce sulfides, and several Sb, Pb, Fe sulfosalts, of which jamesonite is the most abundant [10]. These authors also indicate that the carbonate deposition occurs after significant jamesonite formation, continued during the deposition of the last sulfides and sulfosalts (e.g., galena, pyrite, sphalerite, stibnite, boulangerite, fülöppite, etc.), and ended the epithermal deposition in association to minor hydrothermal quartz.

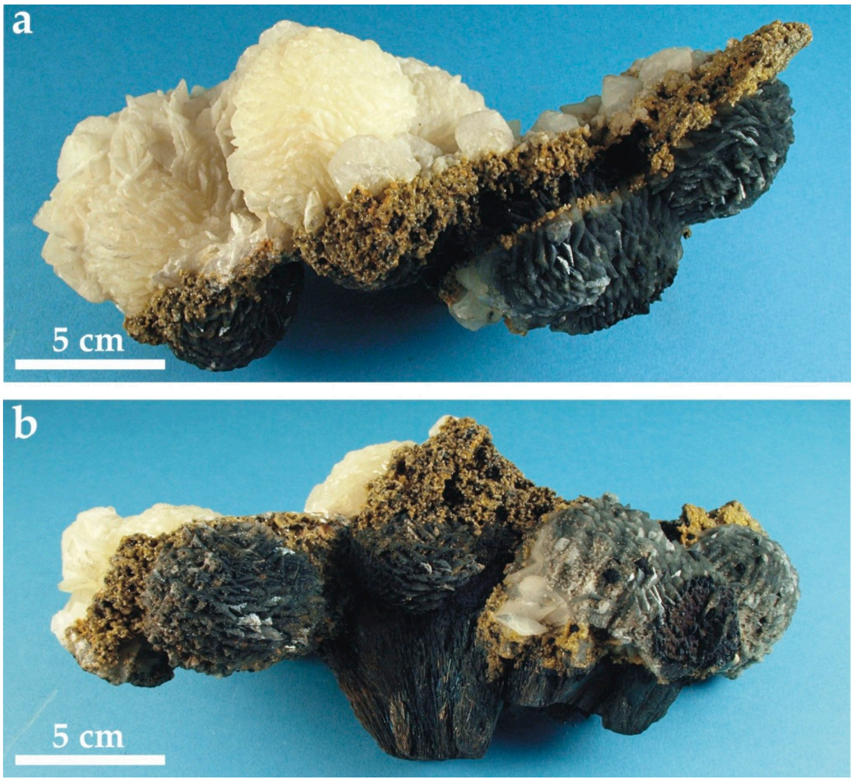

Figure 12. White and black calcite spheres from Herja, sample 9096; MusMin. (**a**) White and black calcite spheres with the diameter ranging from approximately 4 to 6 cm, formed of individual flatten rhombohedra; note the clear distinction between the white and black parts, which are separated by a planar surface partly masked by late siderite deposition; (**b**) Tilted view of the black section of the sample that reveals the presence of trunk-like berthierite fibroradial massive aggregates; late white calcite rhombohedra occur on the siderite from the black side of the sample.

We envisaged that due to their needle-like morphology and their friable character, a large amount of the already deposited plumosite-like minerals, i.e., mostly jamesonite and subordinately berthierite, was enclosed as solid impurities by the later bicarbonate-rich hydrothermal fluids moving through the evolving ore bodies and responsible for the deposition of calcite gangue. The behavior of the plumosite-like already crystallized mineral impurities within the moving hydrothermal fluid throughout an open space, in which these minerals were already deposited but not covered by an overlying mineral sequence, was controlled by the fluid dynamics (speed, flow type), i.e., (i) gravitational settlement within a low velocity steady flow, or (ii) random/homogeneous distribution/dispersion within a turbulent fluid flow. In the first case scenario, at least two hydrothermal fluid layers might appear in a given open space, a lower one with abundant solid impurities, e.g., jamesonite needle-like crystals concentrated gravitationally, and an upper one depleted of or without jamesonite mineral impurities. Optionally, a gas bubble could also appear, triggered by the degassing of the hydrothermal fluids (temperature and pressure decrease/drop). The morphology of the open spaces may also provide favorable conditions for local jamesonite crystals enrichment in suspension within the hydrothermal fluid.

As mentioned previously, the deposition of carbonate spheres from Herja, whether loose or attached, took place within open spaces where jamesonite acicular crystals were gravitationally concentrated within the lower part of open spaces filled by carbonate-rich hydrothermal fluids. The black or white color of calcite is controlled by the existence and respectively the absence of plumosite-like sulfosalts dispersed within the hydrothermal fluids responsible for calcite deposition; thus, we can conclude that the black calcite, irrespective of its morphology—i.e., isolated rhombohedra crystals, crystal crusts or spheres—formed from hydrothermal fluids that contain solid sulfosalts impurities (Figure 13), while the white calcite crystals and spheres deposited from hydrothermal fluids that did not contain such solid acicular impurities.

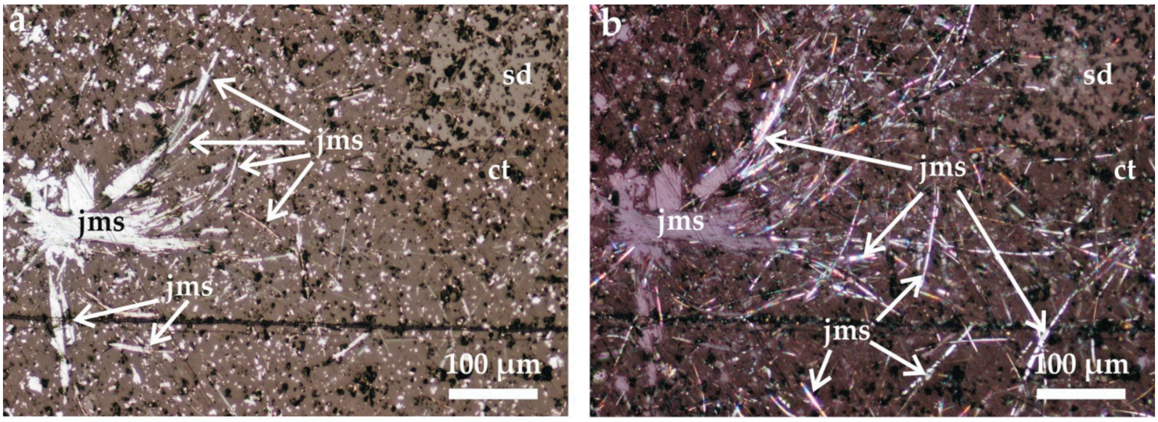

Figure 13. Reflected light microphotographs in plane polarized light (**a**) and in crossed polarizers (**b**) of black calcite from Herja. The real size of needle-like jamesonite crystals hosted by calcite and not entirely exposed at the surface of the polished section is better seen in (**b**) due to transparency of calcite and reflection of light upon jamesonite crystals "sunk" within calcite. Abbreviations: jms, jamesonite; ct, calcite; sd, siderite.

The eventual decrease of the (hydrothermal) fluid volume within an open space where loose calcite spheres grew caused their settlement together, with the remaining "plumosite" microcrystals previously gravitationally concentrated within the fluids at the bottom of the open space. These sulfosalts formed a feathery mineral fabric that was generically called "plumosite", or more suggestively, as in the slang of the miners from Herja, "mineral wool", that potentially enclosed carbonate loose spheres.

5.2. Genetic Mechanism of Bicolor Spheres Formation

Hydrothermal ore bodies represent former pathways of the hydrothermal fluid flow and occur due to fluid flow channeling. The estimated hydrothermal fluid flow focused within about 200 m wide fractured zone that subsequently become the Betze-Post ore deposit (1150 metric tons Au) from the Carlin trend, Nevada is 20 to 500 kg/s, which is the equivalent of a Darcy flux of approximately 8×10^{-8} to 2×10^{-6} m^3/m^2s [44]. Geothermal fluid velocities estimation by [45] based on tracer tests and on stimulation tests in a geothermal site from Rhine graben, north of Strasbourg, France are in the order of 0.25–0.36 m/h and 0.02–0.17 m/h, respectively. Based on well temperature profiles, [46] inferred that groundwater fluid flow velocity in fracture zones may reach up to 1.1×10^{-6} m/s, which is three orders of magnitude greater than the velocity of the fluid flow in the country rocks. Steady state circulation is inferred for fluid flows in fracture zones within the convection cell of the geothermal systems [44]. However, as observed by [46], fluid flow velocity is different in the center and near the boundary of the fracture. Moreover, hydrothermal brecciation event(s) may significantly change the fluid flow regime through severe changes (e.g., hydrothermal eruptions), but the time span of such an event is significantly shorter than the steady state flow of the hydrothermal fluids.

Two different types of open spaces within an evolving vein structure could be inferred from the perspective of the hydrothermal fluid flow dynamics, i.e., (i) "open" geodes, with high velocity hydrothermal fluid flow passing through due to hydrothermal eruption(s), and (ii) "closed" geodes with steady-state fluid flow.

The calculated density of calcite is 2.711 g/cm^3 and a void within a calcite sphere is a prerequisite condition for the floating of the sphere within a lower density aqueous fluid; otherwise it would sink. The void ensuring the floatability of a calcite sphere could be central, as noticed in some of the specimens (e.g., Figures 4 and 8), or/and the empty spaces could be randomly distributed within the mass of the sphere—for example, as pores—or as core dislocation, as reported by [38]. As suggested previously, the bicolor calcite from Herja was formed close to the interface of two fluid layers: one denser, due to the presence of jamesonite impurities. and the other less dense, depleted of mineral impurities. In this case, several forces are exerted on a floating sphere (Figure 14), e.g., its own weight F, the buoyant forces according to Archimedes' principle F_A, distinctive for each of the white and black volumes.

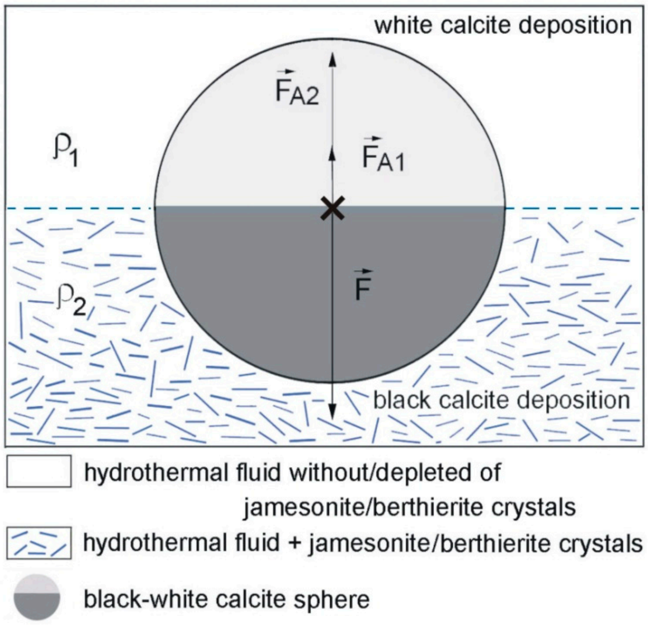

Figure 14. The floatability of ideal half black-half white bicolor calcite sphere at the interface between two hydrothermal fluid layers, the lower one containing gravitationally-concentrated jamesonite needle-like crystals, and the upper one without jamesonite impurities. The physical parameters involved are ρ_1 and ρ_2—the densities of the upper and the lower hydrothermal fluid layers, respectively; V_1 and V_2—the volumes of the white (upper), and the black (lower) calcite sections of the sphere; F_{A1} and F_{A2}—the buoyant forces exerted on the sphere by the two hydrothermal fluid layers; and F—the gravitational force of the entire sphere. Note the increasing abundance of jamesonite crystals gravitationally concentrated towards the lower part.

The force vector acting on the sphere F is:

$$F = mG, \tag{1}$$

where F is the force vector, m is the mass of sphere, and G is the gravitational acceleration.

According to Archimedes' principle, upon a sphere located at the limit between two fluid layers like in Figure 14, two distinctive upward forces, F_{A1} and F_{A2}, corresponding to the weight of the volumes of the two fluid layers displaced by the sphere, exert. For the floating of the calcite sphere at the interface between the two fluid layers, the following condition should be fulfilled:

$$F = F_{A1} + F_{A2}, \tag{2}$$

or,

$$mG = \rho_1 V_1 G + \rho_2 V_2 G, \tag{3}$$

where ρ_1 and ρ_2 are the densities of the two fluid layers, and V_1 and V_2 are the immersed volumes of the sphere within the fluid layers having the densities ρ_1 and ρ_2 respectively. One can replace

$$V_1 + V_2 = V, \tag{4}$$

where V represents the total volume of the sphere. This leads to the relationship:

$$V_1 = V - V_2, \quad (5)$$

By replacing Equation (5) in Equation (3) and dividing by G, results the following:

$$V_2 = (m - \rho_1 V)/(\rho_2 - \rho_1),$$

The density of the upper fluid layer could be considered constant, being the density of the hydrothermal fluid saturated in calcite and depleted of any other metallic compound, while the density of the lower fluid layer varies with the amount of solid jamesonite impurities floating within the same hydrothermal fluid. It is obvious that if the density of the lower fluid layer, ρ_2, decreases, the volume of the black calcite from the lower part of the sphere increases. Accordingly, if the density of the lower fluid layer increases, less black calcite will form. In other words, a relatively lower density of the basal fluid layer will allow more volume of the sphere to be immersed in the fluid hosting mineral impurities, thereby leading to an increase of the volume of black calcite deposited on the lower portion of the floating sphere and vice-versa. Obviously, the volume of white calcite is correspondingly varying, increasing or decreasing in connection to the density of the basal fluid layer. Spheres with equal white and black volumes will form when the following condition is fulfilled during the growing process:

$$\rho_2 = 2m/V - \rho_1, \quad (6)$$

This mechanism explains the fluctuation of the black and white volume ratio of the floating bicolor hydrothermal calcite spheres.

Below, we illustrate by a simple example the theoretical considerations listed previously. One can consider the case of a black calcite hollow sphere with the volume of 2 cm^3 and an inner void of 0.75 cm^3. It is possible to make the assumption that quarter of the volume of both the black calcite and the hydrothermal fluid consists in fact of jamesonite solid impurities. For the sake of simplicity, we consider that the density of hydrothermal fluid is equal to that of pure water, 1 g/cm^3, the density of calcite is 2.7 g/cm^3, and that of jamesonite is 5.5 g/cm^3. Consequently, the density of the black calcite is 0.75×2.7 g/cm^3 + 0.25×5.5 g/cm^3 = 3.4 g/cm^3, and that of the hydrothermal fluid is 0.75×1 g/cm^3 + 0.25×5.5 g/cm^3 = 2.125 g/cm^3. The value of the gravitational force of the black calcite sphere is 1.25 $cm^3 \times 3.4$ $g/cm^3 \times G$ = 4.25 $g \times G$, and the value of the buoyant force exerted on the sphere is 2 $cm^3 \times 2.125$ $g/cm^3 \times G$ = 4.25 $g \times G$, where G is the gravitational acceleration. According to these values, the black calcite sphere floats within the fluid. The densities of the samples shown in Figures 10a and 11a were measured by hydrostatic weighting in distilled water at 23 °C using a Partner digital scale with three significant digits, and the reproducible acquired results are 2.695 and 2.825 g/cm^3 (±0.005), respectively. These values confirm the presence of heavier than calcite mineral impurities (e.g., jamesonite/berthierite) within the black calcite twin spheres from Figure 11a, and the possible existence of a void within the bicolor sphere from Figure 10a needed to counterbalance the heavier density of the black calcite section of the sphere. However, according to the density measurements, the volume of jamesonite included in black calcite twin spheres is smaller as compared to the value considered in the above calculation, e.g., 4.46:95.54 versus 25:75, respectively.

Amorphous calcium carbonate (ACC) is a gel-like precipitate with up to 18 wt% water [47]. ACC, or $CaCO_3 \cdot H_2O$ has a porous structure formed of Ca-rich nanoscale framework filled with water and carbonate ions, with the Ca packing density of the framework similar to that of calcite, aragonite, and vaterite, suggesting the way the amorphous matter passes into crystallized material [48]. Based on experimental approach, [47] revealed the kinetics and the mechanism of ACC crystallization to calcite, via vaterite at environmental conditions (7.5–40 °C). This process takes 4 to 16 h and occurs in two stages [47], (i) ACC particles dehydrate and crystallize as individual vaterite particles; (ii) vaterite transforms to calcite by dissolution of vaterite and calcite reprecipitation with the reaction rate being controlled by the surface area of calcite.

The spherulitic growth of vaterite is mostly controlled by calcium carbonate supersaturation and occurs by central multidirectional growth and by unidirectional growth followed by low-angle branching [49].

The presence of sulfosalt crystals as impurities dispersed within the lower hydrothermal fluid layer or as fibroradial massive aggregates, as shown in Figure 12, could also mechanically contribute to enhancing the apparently loose carbonate spheres to float by temporary supporting. The dense network of acicular crystals might act as a propping system for the spheres. The orientation of these thin acicular crystals is, in principle, horizontal, due to the fact that the vertical (or oblique) orientations are very instable and the crystals will rotate to the equilibrium (horizontal) position. The ephemeral physical support could also be embedded by the crystallizing calcite of the spheres and finally captured within the loose spheres. Such sulfosalt needle-like remnants may be observed macroscopically (Figures 11 and 12), as well as at the microscopic scale (Figure 13).

According to the available mineralogical data [10], a massive deposition of jamesonite predated the crystallization of black calcite from Herja. Jamesonite/berthierite crystals, and perhaps coarse quartz crystals already deposited within open spaces, acted as initial "noise" in the sense of [40] that triggered the geochemical self-organization of carbonates. Vaterite crystallized from gel-like ACC, and typically formed spheres and spherulitic aggregates upon supersaturation with calcium carbonate. Subsequently, vaterite was replaced by calcite, either due to its metastable character below approximately 400 °C, or by the mechanism described by [47], with dissolution of vaterite and calcite reprecipitation. The growth of vaterite and then calcite engulfed jamesonite/berthierite solid impurities gravitationally concentrated within the hydrothermal fluid at the bottom of the geodes, and thus, the black calcite part of the spheres formed. The white part of the spheres formed from hydrothermal fluids/ACC free of jamesonite/berthierite crystals. The temporary support of sulfosalts trunks like those in Figures 12 and 15 allowed the apparently loose carbonate sphere genesis to occur. The sharp limit between the two parts of bicolor calcite spheres indicates that the top of the sphere crystallized form a fluid without jamesonite crystals; otherwise, the calcite would have embedded some jamesonite inclusions, becoming black, and the black portion of the sphere crystallized from a fluid containing jamesonite crystals (Figure 15). According to [10], the limit white-black calcite in the case of centimeters-sized crystals is underlined by co-parallel jamesonite crystals. This observation is confirmed by the sharp limit between the white and black sections of the bicolor calcite spheres.

According to [10], siderite deposition was partly synchronous with calcite, and also occurred after calcite, as proved by numerous specimens (e.g., Figure 1b, Figure 6, Figure 11b, Figure 12). Two possible mechanisms could be envisaged for the genesis of hollow siderite spheres, i.e., (i) continuous siderite cover deposited on calcite spheres, as in Figure 6, with subsequent dissolution of calcite which is more soluble than siderite and escape of the inner solution that dissolved calcite through micropores of the already deposited siderite shell; and (ii) gel-like precipitate of readily soluble salts formed in a low concentration carbonate environment, followed by siderite deposition and subsequent removal of the salts by dilute fluids passing through the micropores of the outer siderite wall. The complete escape of the fluid/water from the inner void of the spheres occurred later, in a fluid/water free environment.

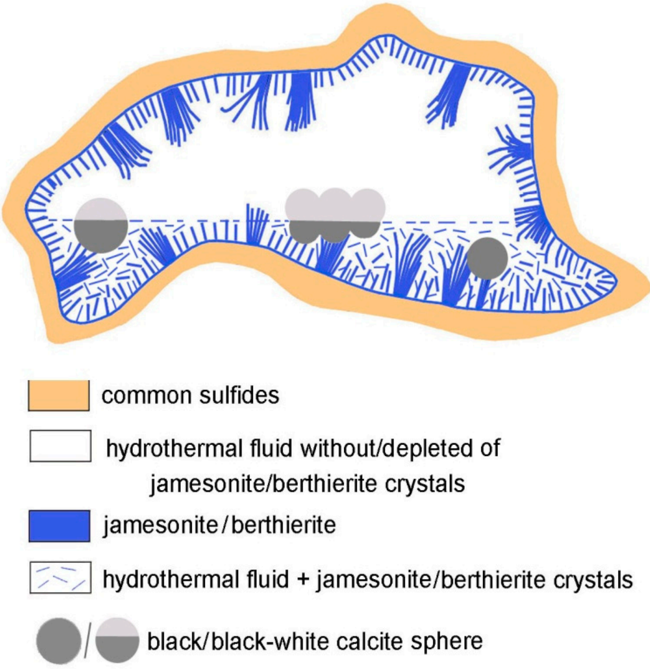

Figure 15. Schematic representation (not to scale) of a geode during late and final stage hydrothermal deposition from the Herja ore deposit where black and bicolor white and black calcite spheres formed. The walls of the geode are covered by late common sulfides sequence (sphalerite, galena, and chalcopyrite) followed by jamesonite/berthierite continuous sequence, needle-like crystals and fibroradial crystal groups. Loose sulfosalt crystals gravitationally concentrated at the bottom of the geode due to steady state hydrothermal fluid flow. Calcite spheres formed at the interface between the fluid layers with and without sulfosalt impurities would be bicolor, white in the upper part and black in the lower part, while those formed within the lower fluid layers would be black. Apparently loose calcite spheres were in fact temporary supported by dense jamesonite fibers network and/or fibroradial crystal groups.

6. Conclusions

The carbonate spheres from Herja and from other ore deposits in the Baia Mare ore district were formed in open spaces along veins or breccia dyke structures. The apparently loose bicolor calcite spheres were always found at the bottom of geodes that contained "plumosite"-like mineral infillings, e.g., jamesonite and berthierite. Statistically, they were found more frequently with the white section upwards and the black one downwards toward the basement, where they landed after the leakage of the hydrothermal fluids from the open space in which they were formed.

The formation of calcite spheres seems to be the result of the geochemical self organization of carbonates controlled by the existence of jamesonite/berthierite needle-like crystals that allowed the initiation of ACC concentration and subsequent crystallization to calcite, via vaterite. The apparent loose spheres were temporary partly supported by jamesonite/berthierite needle-like crystals forming a dense network or fibroradial groups. The hypothesis of the floating of carbonate spheres seems less plausible. The evolving black calcite spheres or black calcite sphere sections of bicolor spheres precipitated from hydrothermal fluids that contained gravitationally-concentrated jamesonite/berthierite solid impurities, while white calcite precipitated from hydrothermal fluids depleted of or without such solid impurities. The limit between the white and the black sections of the calcite spheres corresponds to the limit between the hydrothermal fluid without or with jamesonite/berthierite solid impurities.

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