

Microminerals in Gallstones



Ekaterina V. Mashina and Vasily N. Filippov

Abstract Microminerals and inclusions were studied in cholesterol and pigment gallstones by electron microscopy. It has been established that the micromineral diversity in gallstones is due to the presence of a class of oxides, chlorides, sulfates, sulfides, silicates, carbonates, and native-metal phases of iron and copper. It has been noted that pigment gallstones, in contrast to cholesterol gallstones, are characterized by the accumulation of heavy metals such as bismuth, lead, niobium and gold.

Keywords Gallstones · Biominerals · Inclusions · Metals

Introduction

The scientific direction of biomineralogy is at the junction of a number of sciences, primarily medicine, zoology, botany, biochemistry, mineralogy, organic mineralogy, paleontology, geology of mineral deposits, etc. One of the topical issues of biomineralogy is the problem of pathogenic mineral formation in the human body. Along with kidney stones, dental calculi and others, gallstones are often formed in the human body. The process of gallstone formation has not been studied in detail because of the latent course of the initial stage of cholelithiasis. At present, a lot of studies have been undertaken to find out why and how gallstones are formed, but so far there is no generally accepted theory. In general, cholelithiasis is a multifactorial and multistage disease characterized by impaired cholesterol, bilirubin and mineral metabolism. The general factors of cholelithiasis development include: ecology, various metabolic disorders, food, unhealthy life style (alcoholism, smoking, etc.), and age (aging is associated with increased formation of gallstones) (Dadvani et al. 2009). According to a common classification, gallstones are divided into two main

E. V. Mashina (✉) · V. N. Filippov
IG Komi Scientific Center, Ural Branch of the Russian Academy
of Sciences, Syktyvkar, Russia
e-mail: borovkova@geo.komisc.ru

groups: pigment and cholesterol. Pigment gallstones occur in less than 20% of cases (Korago 1992). The main organic component of cholesterol stones is cholesterol, pigment is the salt of bilirubin (calcium bilirubinate, copper bilirubinate) (Li et al. 1995). The mineral component in the gallstone has not been studied enough. It is known that the main mineral phases in the gallstones are calcium carbonate (vaterite, aragonite and calcite) and calcium phosphate (carbonate-apatite and hydroxylapatite) (Efimova et al. 2005; Mashina 2014; Mashina et al. 2015). However, in addition to calcium and phosphorus, other chemical elements, which may be included in various minerals, are also present in gallstones. Based on this, the purpose of this study was to study microminerals and inclusions in cholesterol and pigment gallstones by electron microscopy.

Materials and Methods

The gallstones of the inhabitants of the Republic of Komi were investigated. Based on the structural studies (X-ray diffraction and IR spectroscopic analysis), the gallstones were divided into six groups: group 1—cholesterol (10 samples); group 2—cholesterol + calcium phosphate (4 samples); group 3—cholesterol + calcium carbonate (7 samples); group 4—pigmented (3 samples); group 5—pigment + calcium phosphate (2 samples); group 6—pigment + calcium carbonate (4 samples). The samples were studied by JSM 6400 analytical scanning electron microscope equipped with an energy-dispersive spectrometer “Link”.

Results and Discussion

The results of our study showed that only halite and iron oxide, as well as various polymetallic compounds of titanium, iron, calcium, aluminum, magnesium, manganese and zinc, could be found in the cholesterol stones of group 1, apparently being organometallic compounds (mass. %): (a) Ti 21.38, Si 15.20, Mg 14.13, Ca 3.24, Pb 1.89, Cr 0.33; Ti 30.46, Pb 15.33, Si 6.72, Mg 5.38, Cr 3.72, Ca 1.89, Al 0.67; (b) Fe 56.74, Ca 6.49, Si 2.42, Al 1.03, Zn 0.82, Ti 0.60; Pb 41.01, Ti 11.13, Cr 10.28, Ca 4.75, Mg 3.39, Si 3.14; Ti 47.67, Si 3.60, Ca 3.52, Mg 2.79, Al 1.43; Si 23.43, Mg 20.77, Ti 5.86, Ca 2.51, Al 0.76; Si 18.77, Ti 10.63, Ca 9.01, Mg 7.85, Zn 2.72, Al 1.15; (c) Ca 28.48, Si 15.14, Al 7.18, Fe 6.07, Sr 1.33, Mg 1.21; Ca 22.93, Fe 17.07, Al 9.48, Si 9.34, Mg 1.42, Mn 0.42; Fe 55.13, Zn 20.84, Si 7.61, Mn 4.23, Ti 1.64, Cu 1.01; Fe 39.67, Mn 0.34 (Fig. 1a–c). Halite formed elongated dendritic crystals (Fig. 1d), and iron oxide had a spherical appearance. In the cholesterol samples of group 2, micromineralites were found: albite, barite, hematite and gypsum. Barite was traced in the form of joint clusters having a crystal-like appearance (Fig. 1e), and single grains of irregular shape. Albite had a

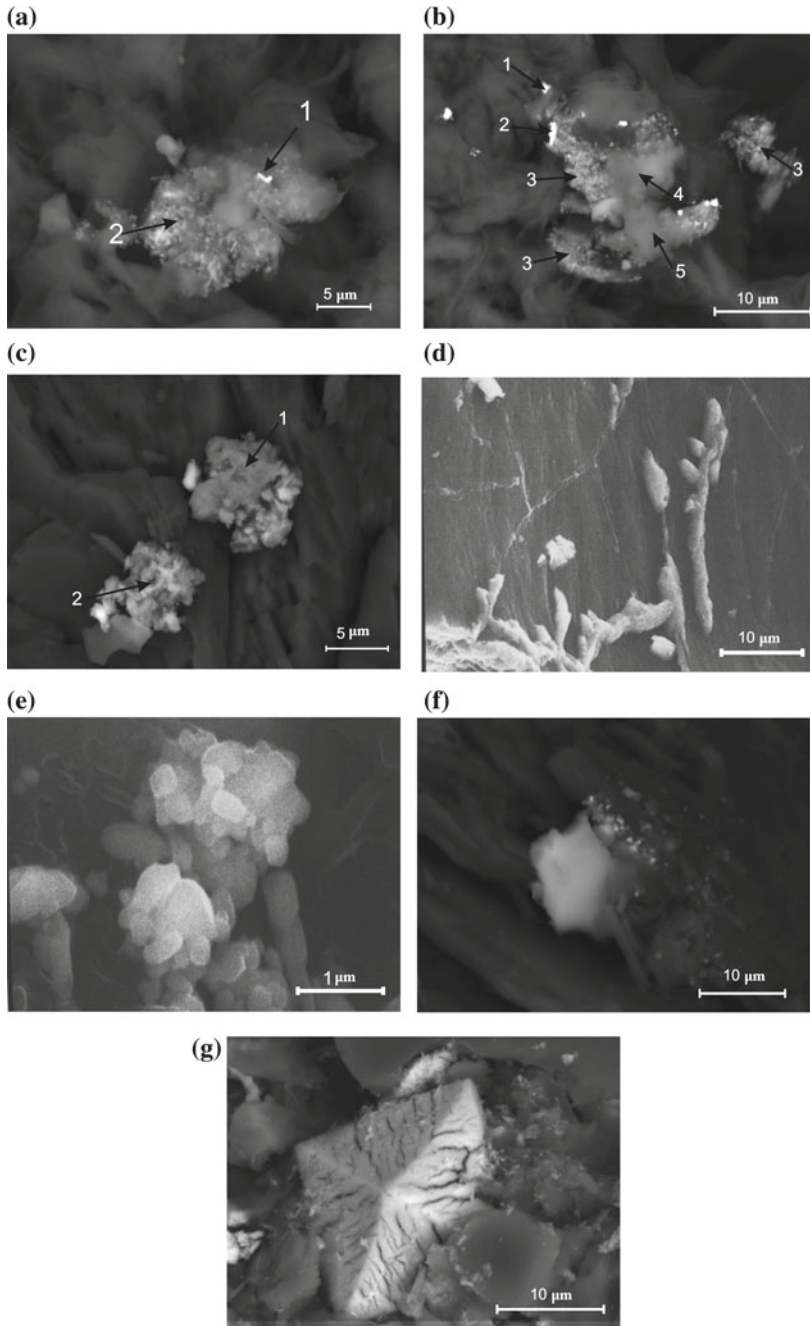


Fig. 1 Microminerals and inclusions in cholesterol gallstones: **a** (point 1)—Ti-Si-Mg-Ca-Pb-Cr; **a** (point 2)—Ti-Pb-Si-Mg-Cr-Ca-Al; **b** (point 1)—Fe-Ca-Si-Al-Zn-Ti; **b** (point 2)—Pb-Ti-Cr-Ca-Mg-Si; **b** (point 3)—Ti-Si-Ca-Mg-Al; **b** (point 4)—Si-Mg-Ti-Ca-Al; **b** (point 5)—Si-Ti-Ca-Mg-Zn-Al; **c** (point 1)—Ca-Si-Al-Fe-Sr-Mg; **c** (point 2)—Ca-Fe-Al-Si-Mg-Mn; **d**—halite; **e**—barite; **f**—albite; **g**—weddellite

plate-like shape (Fig. 1f). In the gallstones of the 3rd group, barite, dolomite and weddellite were found, and various inclusions of zinc, copper, iron and chromium were recorded. Weddellite formed enveloped crystals of about 20 μm (Fig. 1g); as a rule, this mineral was found in the composition of urinary stones.

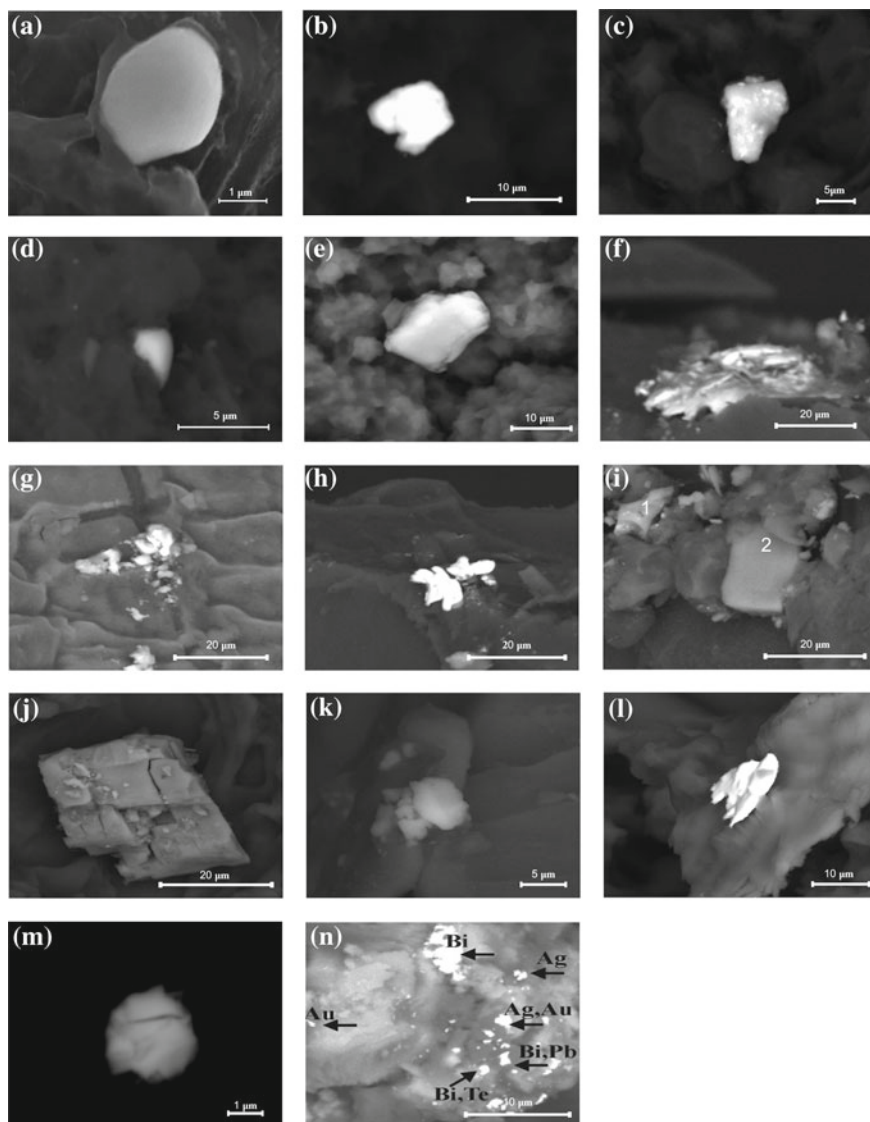


Fig. 2 Microminerals and inclusions in pigment gallstones: **a**—Fe-Ni; **b**—Fe-Ni-Mn; **c**—Fe-Ni-Si; **d**—Fe-Cu-Al-Zn; **e**—silicon oxide; **f**—Cu-Ni-Cr; **g**—Cu-Ni-Fe; **h**—Cu; **i**—1—albite, 2—microcline; **j**—dolomite; **k**—sylvite; **l**—zinc; **m**—Bi-Nb; **n**—Au, Ag

The electron microscopic study of the pigment gallstones showed that the following microminerals and inclusions were recorded in the samples of group 4: pyrite, silicon oxide, various native-metal compounds of iron (Fig. 2a–d). Silicon oxide was shown to be represented by prismatic grains (Fig. 2e). In the pigment gallstone of group 5, albite, microcline, as well as the inclusion of native copper and the native metal compounds of copper and nickel were found (Fig. 2f–i). Albite was found in the form of elongated angular grains up to 10 μm in size, microcline formed tabular crystals up to 15 μm (Fig. 2i). The samples of group 6 included: sylvite, dolomite, copper sulfate, copper oxide, weddellite, native-metal phases of iron (>70 mass. %) and copper (>60 mass. %): Fe–Ni–Si; Fe–Ni–Mn; Fe–Al; Fe–Ni; Cu–Zn–Pb. The dolomite had a rhombohedral appearance; the sylvite was represented by accumulations of individual grains (Fig. 2j,k). Crystalline grains were also found to be almost entirely (up to 98 wt%) composed of zinc (Fig. 2l) and microinclusions of bismuth (71 mass. %) and niobium (Fig. 2m), silver and gold (mass. %): Au 56; Ag 13; Au 12; Ag 16, Au 6 (Fig. 2n).

Macro- and microelements are not synthesized in the body, they are transferred primarily with food, water and air. Mineral substances entering the body form various compounds with high-molecular proteins. The authors (Lamanova et al. 2010) studying such pathogenic formations as the calcification of the blood system, believe that the disintegration of metal-binding proteins under the influence of various factors inevitably leads to the accumulation of free metal ions in the medium, which means that the formation of certain new minerals is possible according to specific oxidation-reduction and acid-base conditions in the source of mineralization. It should be noted that among the elements discovered by us there are toxic: aluminum, lead, barium, bismuth and potentially toxic: silver and gold.

Conclusion

Thus, the electron microscopy study of gallstones complements the information on the composition of the studied objects. It has been found that the micromineral diversity in gallstone is due to the presence of a class of oxides, chlorides, sulfates, sulfides, silicates, carbonates and iron-copper compounds that predominate among the native-metallic phases. It has been noted that pigment gallstones, in contrast to cholesterol gallstones, have a richer spectrum of microinclusions, and are also characterized by the accumulation of heavy metals, of which bismuth, lead, niobium and gold can be distinguished.

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