Hydrous sulphates formed during oxidation of colloform pyrite from Chiprovtsi Ag-Pb deposit, NW Bulgaria

D.A. DIMITROVA[1], V.G. MLADENOVA[2] AND L. HECHT[3]

[1]Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria (didi@geology.bas.bg)
[2]Sofia University "St. Kliment Ohridski", 1504 Sofia, Bulgaria (vassilka@gea.uni-sofia.bg)
[3]Natural History Museum, 10115 Berlin, Germany (lutz.hecht@museum.hu-berlin.de)

The Chiprovtsi Ag-Pb hydrothermal deposit, located in NW Bulgaria, comprises several metallic mineralizations, among which in the eastern part of the area occurs the low-temperature cinnabar-pyrite-fluorite mineralization. Pyrite is presented as grains, cubic and colloform habit. The latter one usually accompanies cinnabar formation followed by barite-calcite deposition. The colloform pyrite more easily reacts when exposed to air/aqueous oxidation because of its fine porous aggregate structure.

The studied samples also include metacinnabar, ankerite, fluorite and quartz. The colloform pyrite contains As up to 4.77 wt%, which is included during the oxidation-crystallization process in the newly formed sulphates, remaining in almost the same content (0.50-4.50 wt%). The oxidation process took place in room conditions (relatively low air humidity and 20-25°C). Mostly, the pyrite colloform aggregates during oxidation usually split along the elongation of the needle-like individuals (*c*-axis), which formed the spherulites. The pyrite sample disintegration to grainy powder is accomplished within 2-3 years.

The resulting efflorescent minerals were difficult to distinguish because of their complex occurrence and minute aggregate size. The following hydrous sulphates were identified using XRD and SEM-EDS with very good reliability: szomolnokite ($Fe^{2+}SO_4.H_2O$), aluminocopiapite ($Al_{2/3}Fe^{3+}{}_4(SO_4)_6O(OH)_2.20H_2O$), coquimbite ($Fe^{3+}{}_2(SO_4)_3.9H_2O$), halotrichite ($Fe^{2+}Al_2(SO_4)_4.22H_2O$) and voltaite ($K_2Fe^{2+}{}_5Fe^{3+}{}_3Al(SO_4)_{12}.18H_2O$). All of them occur as well formed micro- to nano-sized crystal habits: fibers (halotrichite), cubic and more complex combinative forms (voltaite), prismatic (szomolnokite), platy and platy-sheet hexagonal (aluminocopiapite and coquimbite, respectively), rounded (effect of partial dissolution).

The chemical reactions occurred release Fe^{2+} and H_2SO_4, followed by dissolution of the existing calcite and ankerite and further oxidation of Fe^{2+} to Fe^{3+}.

Silicon isotope variation of chert beds from later Archean to Proterozoic as a tracer of paleo-environmental variation in ocean

T. DING, D. WAN AND S. TIAN[1,2]

[1]Institute of Mineral Resources, CAGS, Beijing, China
[2]Key Laboratory of Isotope Geology, CAGS, Beijing, China

The silicon isotope compositions of chert beds from later Archean to Proterozoic have been investigated. The results are shown in Figure 1.

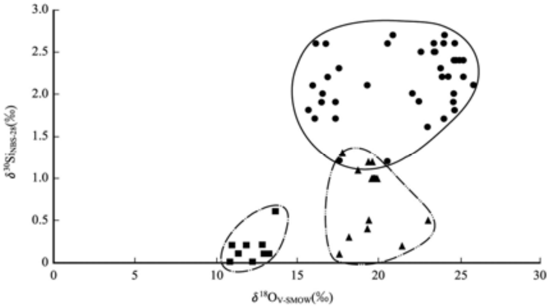

Figure 1: The relation between δ^{30}Si and δ^{18}O for some chert beds from later Archean to Proterozoic. ■ Later Archean Wutai Group; ▲Early Proterozoic Futuo Group; ● Middle Proterozoic Shisanling Group.

The δ^{30}Si values of quartz belts in banded quartz-sulfide formation of later Archean Wutai group vary from 0.0‰ to 0.6‰., with an average of 0.19‰. The δ^{30}Si values of chert belts in carbonate formation of early Proterozoic Futuo Group vary from 0.1‰ to 1.3‰, with an average of 0.76‰. The δ^{30}Si values of chert belts in carbonate formation of middle Proterozoic Shisanling Group vary from 1.2‰ to 2.6‰, with an average of 2.04‰. We know that the δ^{30}Si values of quartz in BIF formation of later Archean vary from -0.8 to -2.2, with an average of -1.28‰ [1]. There is a trend of increase of δ^{30}Si value from cherts of later Archean to early and middle Proterozoic, which is in consistent with the changes of paleo-environmental conditions in ocean, such as decrease of temperature and silicon content and increase of biological activity from Archean to Proterozoic.

[1] Ding *et al.* (1996) *Silicon Isotope Geochemistry*, Geological Publishing House, Beijing, China.