

Editorial

Editorial for Special Issue “Pyrite Varieties and LA-ICP-MS Geochemistry in Ore Genesis and Exploration”

Valeriy V. Maslennikov ^{1,*} and Ross R. Large ²

¹ South Urals Federal Research Center of Mineralogy and Geocology UB RAS, Institute of Mineralogy, Chelyabinsk District, 456317 Miass, Russia

² Australian Research Council Hub for Transforming the Mining Value Chain, Centre for Ore Deposits and Earth Science, University of Tasmania, Hobart, TAS 7005, Australia; ross.large@utas.edu.au

* Correspondence: maslennikov@mineralogy.ru

The chemistry of pyrite represents a potentially promising new frontier for the research and exploration of different types of ore deposits. Tl is extremely toxic, and Te (and increasingly Sb and even As) is in demand for high-tech applications or can provide a vector for ore deposit exploration and targeting. The application of pyrite in the characterization of ore deposits, fertility studies and exploration vectoring requires the use of progressive modern methods such as LA-ICP-MS and other principally new analytical technology in the field of ore geology. The development of LA-ICP-MS trace element mapping of pyrite aggregates has revolutionized our understanding of metal-sulfide paragenesis and is becoming a key technique in ore deposit genesis and geometallurgy studies. Contributions of genetic/evolutionary models of ore deposits based on pyrite compositions are also presented in this Special Issue. Special attention is dedicated to the comparison between trace elements and their associations in the different genetic origins of pyrite, including hydrothermal, hydrothermal sedimentary, biogenic, diagenetic and metamorphic varieties. This Special Issue contains a wide collection of papers on pyrite varieties in orogenic gold, sediment hosted gold deposits and massive sulfide ore deposits. The pyrite varieties from oil shale are also compared with pyrite from ore deposits. Other recently developed innovative technologies also included for further discussions.

In our review paper [1], we attempted to determine the timing and chemical association of Au relative to the growth of pyrite aggregates from successive orogenic fluid events through a combination of textural studies of pyrite, with LA-ICPMS mapping and spot analyses of eleven orogenic deposits. A spectrum of invisible gold relationships in pyrite has been observed, which suggests that relative to orogenic pyrite growth, gold introduction in some deposits is early at the start of pyrite growth; in other deposits, it is late toward the end of pyrite growth, and in a third case, it may be introduced at the intermediate stage of orogenic pyrite growth. In addition, we report a distinct chemical association of invisible gold in pyrite in the deposits studied. For example, in the Gold Quarry (Carlin type), Mt Olympus, Macraes and Konkera deposits, the invisible gold is principally related to the arsenic content of pyrite. In contrast, in Kumtor and Geita Hill, the invisible gold is principally related to the tellurium content of pyrite. Other deposits (Golden Mile, Bendigo, Spanish Mountain, Witwatersrand Carbon Leader Reef (CLR) exhibit both the Au-As and Au-Te association in pyrite. Some deposits of the Au-As association have late orogenic Au-As-rich rims on pyrite, which substantially increase the value of the ore. In contrast, deposits of the Au-Te association are not known to have Au-rich rims on pyrite but contain nano- to microinclusions of Au-Ag-(Pb-Bi) tellurides. Generally, pyrites with Ni/Co > 0.1 carry the highest levels of invisible Au and As. This may relate to the surface charge on pyrite being dependent on As content and Ni/Co ratio, with the more Ni-As-rich pyrites being favorable for gold capture from the hydrothermal fluid compared with the As-poor, Co-rich pyrite variety.



Citation: Maslennikov, V.V.; Large, R.R. Editorial for Special Issue “Pyrite Varieties and LA-ICP-MS Geochemistry in Ore Genesis and Exploration”. *Minerals* **2021**, *11*, 131. <https://doi.org/10.3390/min11020131>

Received: 14 January 2021

Accepted: 27 January 2021

Published: 28 January 2021

Publisher’s Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

A similar approach is used in the paper on the study of pyrite nodules in ore diagenites of the Urals massive sulfide deposits associated with various background sedimentary rocks [2]. The nodules are found not only in sulfide-rich black shale but also in sulfide–carbonate–hyaloclastite, and sulfide–serpentinite diagenites of the non-metamorphosed Saf'yanovskoe, Talgan, and Dergamysh deposits, respectively. The nodules consist of a core made up of early diagenetic fine-grained pyrite and a rim composed of late diagenetic coarse-crystalline pyrite. The cores of nodules are enriched in trace elements in contrast to the rim. Each type of nodule displays specific trace element features. The nodules from sulfide–black shale diagenites are commonly enriched in most trace elements, which is typical of the sulfides in organic-rich sediments. The nodules from sulfide–carbonate–hyaloclastite diagenites are rich in elements sourced from seawater, hyaloclastites and dissolved ore clasts. The nodules from sulfide–serpentinite diagenites are rich in Co and Ni, which are typical trace elements of ultramafic rocks and primary ores from the deposit. Each type of nodule exhibits its own specific accessory mineral assemblages with dominant galena and fahlores, various tellurides and Co–Ni sulfoarsenides in sulfide–black shale, sulfide–hyaloclastite–carbonate and sulfide–serpentinite diagenites, respectively. The general outcome of this paper emphasizes the important role of mineral composition of ore clasts and background sediments in the formation of specific authigenic mineral and trace element features of the nodules studied. This result helps us to understand mineral and trace element diversity of massive sulfide deposits.

Mid-ocean ridges containing areas with hydrothermal activity and black smokers are included in this issue as the most important sites for the recent formation of numerous varieties of hydrothermal pyrite. The Pobeda hydrothermal field was recently discovered in a mafic-ultramafic complex in the MAR. In Reference [3], the massive sulfide ores of the Pobeda hydrothermal fields are grouped into five mineral microfacies reflecting the transition from feeder zone facies to seafloor diffuser and diagenetic microfacies. The evolution of monosulfides and numerous pyrite varieties is carefully illustrated in the plentiful photomicrographs. It is shown that spongy, framboidal and fine-grained pyrite varieties replaced pyrrotite, greigite and mackinawite “precursors”. The later coarse and fine banding oscillatory-zoned pyrite and marcasite crystals are overgrown or replaced by unzoned subhedral and euhedral pyrite. In the spectrum of microfacies, the amount of isocubanite, wurtzite and unzoned euhedral pyrite decreases versus an increasing portion of framboidal, fine-grained and spongy pyrite and also marcasite and its colloform and radial varieties. This change is interpreted to be the result of decreasing temperature during mineral microfacies formation. The trace element characteristics of massive sulfides of the Pobeda seafloor massive sulfide (SMS) deposit are subdivided into four associations: (1) high temperature—Cu, Se, Te, Bi, Co and Ni; (2) mid temperature—Zn, As, Sb and Sn; (3) low temperature—Pb, Sb, Ag, Bi, Au, Tl and Mn; (4) seawater sourced—U, V, Mo and Ni. The high contents of Cu, Co, Se, Bi, Te and values of Co/Ni ratios decrease in the spectrum from unzoned euhedral pyrite to oscillatory-zoned and framboidal pyrite, as well as to colloform and crystalline marcasite. In the paper, it is suggested that the temperatures of mineralization decreased and seawater influence increased in the same direction, resulting in the general zonal character of the SMS deposit.

The fourth paper in the Special Issue explains sedimentary pyrite textures, their trace element and sulfur isotope ratios in pyrite varieties to understand paleo-redox conditions during the deposition of the Mesoproterozoic Bijaigarh Shale [4]. The combination of reflected light microscopy, LA-ICP-MS and SHRIMP-SI is involved in this study. Key redox sensitive or sensitive to oxidative weathering trace elements (Co, Ni, Zn, Mo and Se) and ratios of (Se/Co, Mo/Co and Zn/Co) measured in sedimentary pyrites from the Bijaigarh Shale are used to infer atmospheric redox conditions during its deposition. Low concentrations of the trace elements, particularly Se and Mo and their ratios (i.e., below the global mean values for the Proterozoic), suggest relatively low oxygen conditions during deposition in the basin. It is suggested that decreasing oxygenation and closure of open ocean connection during deposition of the unit potentially caused a lower input

of sulfate in the ocean, resulting in ^{34}S -rich seawater and subsequently an increase in $\delta^{34}\text{S}$ pyrite upstratigraphy values. This significant outcome indicates that owing to partial ocean connectivity of the Vindhyan Basin during the deposition of the lower part of the Bijaigarh Shale (1210 + 52 Ma), there remains a possibility of extrapolating these paleoredox conditions in a more global context in the Mesoproterozoic. The data of this paper could be useful in defining the non-ore pyrite composition background to elaborate new geochemical element criteria for SEDEX deposits for exploration.

Recognition of the geochemical features of the metalliferous black shale varieties associated with oil–gas deposits is an important step in developing exploration criteria for related ore deposits. This is among the tasks of the paper dedicated to the extensive Bazhenov oil-bearing Formation (Western Siberia) [5]. Some nodule-like pyritized bituminous layers and pyrite nodules are similar to pyritized microbial mat fragments, showing a typical fine laminated structure as depicted in the paper for the first time. The laminated “nodular” pyrite has high concentrations of As and Sb relative to other pyrite types. This pyrite could be an indicator of primary organic matter concentration on the base of bacterial chemosynthesis from CH_4 -seepage activity in the Jurassic. Framboidal pyrite, formed due to interaction with organic matter, is enriched in redox-sensitive elements such as Mo, V, Au, Cu, Pb, Ag, Ni, Se and Zn in comparison with the host shales and nodular pyrite.

Some papers in the issue are dedicated to new technologies in the study of pyrite. Crystal habits, thermoelectricity and trace element composition of pyrites from the main ore-forming stage of the huge Shuangwang gold deposit were studied by a microbinocular, a BHTE-06 thermoelectric coefficient measuring instrument, and HR-ICP-MS [6]. Spatial distribution of crystal habit, thermoelectricity and trace element composition of pyrites were delineated by contour maps of morphology index, P-type frequency and primary halo elements (e.g., supra-ore halo elements Ba, Sb; near-ore halo elements Pb, Zn and Cu; and sub-ore halo elements Co, Mo and Bi). Based on the above results, four target areas were proposed for deep gold exploration in the future. These targets are consistent with the deep extending trend of the proven gold ore bodies, indicating the effectiveness of typomorphic characteristics of pyrites to vector deep (concealed) gold ore bodies.

In the final paper of the Special Issue [7], the application of the U-Th-He method for the direct dating of pyrite provides an original methodological approach for measurement of U, Th and He in single grains without loss of parent nuclides during the thermal extraction of He. It is important that the age of Uzelga VMS deposit (the Urals) formation is consistent with independent (biostratigraphic) estimations of the age of ore formation (ca, 389–380 Ma) and is remarkably older than the probable age of the regional prehnite-pumpellyite facies metamorphism (~340–345 Ma). These results indicate that the U-Th-He dating of ~1 mg weight pyrite samples is possible and opens new perspectives for the dating of ore deposits. The relative simplicity of U-Th-He dating in comparison with other geochronological methods makes this approach interesting for further applications. The relative ease of U-Th-He dating in comparison with other geochronological methods and the small amount of the material (~0.5–1 mg) required for this dating technique make this approach interesting for further development. The problem of the behavior and preservation of U in pyrite remains open and could be resolved with further research.

The idea that pyrite varieties are a very useful record of geochemical, geological and ore-forming processes is certainly not new. However, the capabilities of the present-day LA-ICP-MS method in terms of high sensitivity and using mapping of trace elements continues to provide new insights into how these ore-forming processes take place, and in what order, during formation of gold [1], massive sulfide [2,3] and other deposits. This method yields plentiful trace element data on pyrite varieties in oil shales, which could be useful to develop inorganic–organic models of oil formation and predict the metal potential of adjacent pyrite mineralization [4]. Research on trace elements in pyrite of black shales in different basins should be considered as a new step useful for the recognition of sedimentation conditions and in the reconstruction of the geochemical evolution of oceans [5]. Any comparison of pyrite varieties related to fertile ore-bearing

and barren black shale horizons is a key approach to improving predictive criteria in mineral exploration. New complex technologies applied to hydrothermal pyrite allow new recommendations for the discovery of deeply located gold deposits [6]. This Special Issue finally investigates the provocative topic of employing an innovative U-Th-He method for the direct dating of pyrite [7]. This and other innovative methods to study pyrite are awaiting further development.

Author Contributions: V.V.M. and R.R.L. wrote this paper. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by State Contract of the IMin no. AAAA-A19-119061790049-3.

Acknowledgments: The Guest Editors express their appreciation to Francis Wu and the *Minerals* editorial team for their encouragement and logistical assistance throughout this project. We also thank all reviewers for their time and comments.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Large, R.R.; Maslennikov, V.V. Invisible Gold Paragenesis and Geochemistry in Pyrite from Orogenic and Sediment-Hosted Gold Deposits. *Minerals* **2020**, *10*, 339. [[CrossRef](#)]
2. Safina, N.P.; Melekestseva, I.Y.; Ayupova, N.R.; Maslennikov, V.V.; Maslennikova, S.P.; Artemyev, D.A.; Blinov, I.A. Authigenesis at the Urals Massive Sulfide Deposits: Insight from Pyrite Nodules Hosted in Ore Diagenites. *Minerals* **2020**, *10*, 193. [[CrossRef](#)]
3. Maslennikov, V.V.; Georgy Cherkashov, G.; Artemyev, D.A.; Firstova, A.; Large, R.R.; Tseluiko, A.S.; Kotlyarov, V.A. Pyrite Varieties at Pobeda Hydrothermal Fields, Mid-Atlantic Ridge 17°07′–17°08′ N: LA-ICP-MS Data Deciphering. *Minerals* **2020**, *10*, 622. [[CrossRef](#)]
4. Mukherjee, I.; Deb, M.; Large, R.R.; Halpin, J.; Meffre, S.; Ávila, J.; Ivan Belousov, I. Pyrite Textures, Trace Elements and Sulfur Isotope Chemistry of Bijaigarh Shales, Vindhyan Basin, India and Their Implications. *Minerals* **2020**, *10*, 588. [[CrossRef](#)]
5. Ivanov, K.S.; Maslennikov, V.V.; Artemyev, D.A.; Tseluiko, A.S. Highly Metalliferous Potential of Framboidal and Nodular Pyrite Varieties from the Oil-Bearing Jurassic Bazhenov Formation, Western Siberia. *Minerals* **2020**, *10*, 449. [[CrossRef](#)]
6. Wang, J.; Liu, Z.; Wang, K.; Zeng, X.; Liu, J.; Zhang, F. Typomorphic Characteristics of Pyrites from the Shuangwang Gold Deposit, Shaanxi, China: Index to Deep Ore Exploration. *Minerals* **2019**, *9*, 383. [[CrossRef](#)]
7. Yakubovich, O.; Mary Podolskaya, M.; Vikentyev, I.; Fokina, E.; Kotov, A. U-Th-He Geochronology of Pyrite from the Uzelga VMS Deposit (South Urals)—New Perspectives for Direct Dating of the Ore-Forming Processes. *Minerals* **2020**, *10*, 629. [[CrossRef](#)]