



## **Contrasting trace element composition of diagenetic and syngenetic pyrites: implications for the depositional environment**

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Trace element contents in pyrite grains from sections of different setting and age (including modern sediments) were analysed and evaluated in their litho-geochemical context in order to detect possible connections between depositional environment and pyrite composition. Conventional chemical separation techniques, as usually applied in studies dedicated to pyrite chemistry (e.g., Huerta-Diaz and Morse, 1990) are generally inadequate to detect such kind of differences, because they often yield a mixed environmental signal from pyrites formed at different times and different parts of the water-sediment boundary region. In old, consolidated sedimentary rocks, late, epigenetic remobilization further complicate the decipherment of the original environmental signal. In such situations, additional to observation of geochemical and morphologic criteria which allow to discriminate between different genetic types, the use of in situ analytical techniques with high spatial resolution and low detection limits are crucial to achieve success. The spatial resolution of laser-ablation ICP-MS proved to be insufficient to investigate the composition of minuscule framboids, while the EMP yield unsatisfactory detection limits for most of the genetically relevant elements. The best option in terms of both resolution and sensitivity was given by synchrotron  $\mu$ -XRF, though digestion of carefully cleaned grains followed by analysis with conventional ICP-MS may also yield satisfactory results, provided that the analyzed pyrite grains are genetically homogenous.

Our results indicate that trace element contents in pyrite depend primarily on the site and mechanism of pyrite formation with distinct features for diagenetic and syngenetic pyrites. Diagenetic pyrite formed within the anoxic sediments reflect the composition of pore water or that of the pyritized precursor phase (e.g., Fe-minerals, organic rests, etc) and generally has high contents of heavy metals. In such kind of pyrites the degree of trace metal pyritization (DTMP) increases with increasing oxygen deficiency, similar to  $DOP_R$  (degree of pyritization of reactive Fe). The highest gradient in the increase of DTMP with bottom water oxygenation (as indicated by DOP) was found for the elements  $Ni < Cu < Mo = As < Tl$ . In contrast, syngenetic pyrite formed within the euxinic water column is typically enriched in oxyanionic elements like As, Mo and Sb, but is low in heavy metals and variations in element concentrations reflect changes in seawater composition. High resolution element distribution maps (Cu, Zn, Pb, As, Se, Mo) on recrystallized pyrite grains by means of synchrotron  $\mu$ -XRF, suggests that some resulted from agglomeration and welding of framboids and that - on a whole - this process does not substantially alters the average trace element content of the initial framboids.

Huerta-Diaz, M.A. and Morse, J.W. (1990): A quantitative method for determination of trace metal concentration in sedimentary pyrite. *Marine Chemistry* 29: 119-144.