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Ge distribution in supergene willemite (Zn_2SiO_4): new insights from the Bou Arhous deposit (Morocco)

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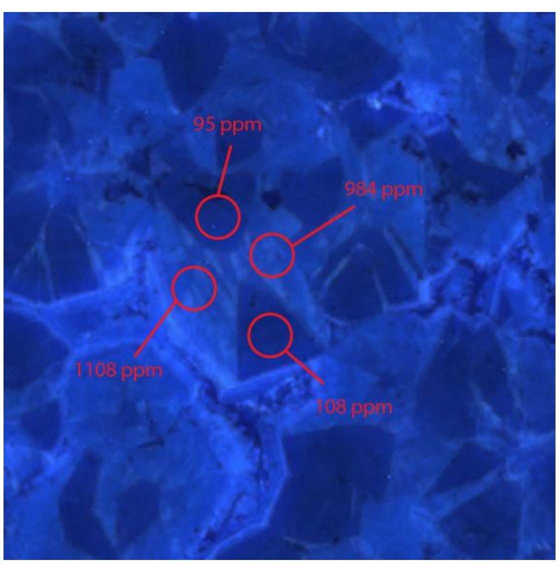
Willemite, (Zn_2SiO_4) usually reported in hypogene non-sulfide deposist is described as the main ore mineral in the carbonate-hosted supergene Bou Arhous zinc deposit. This deposit is located in the intracontinental High Atlas range that formed during the Tertiary. Hence, the Bou Arhous deposit largely differs from other deposits of the district, which rather expose carbonate ores [1].

Based on a set of microscopic observations, it was possible to establish that willemite replaced primary sphalerite. CL imaging allowed three successive generations of willemite to be distinguished, with evidence of dissolution-reprecipitation under surface conditions. Early willemite is characterized by sector zoning, revealed by CL imaging (Figure 1). Bright blue sectors display high Ge content (up to 1100 ppm by EPMA and LA-ICPMS) compare to dark blue-indigo sectors (less than 200 ppm). The Ge content is related to the Si-Ge substitution, which is negatively correlated to the Zn-Pb substitution (with up to 2 wt% of PbO, in dark sectors). In other words, it means, that significant amounts of Ge can be incorporated only in Pb-free domains of willemite. Willemite with sector zoning is coated by a well-developed stage of oscillatory-zoned willemite, showing Ge contents that range between 22 and 858 ppm. The Ge content is positively correlated to the PbO content ranging between 0.06 and 0.84 wt%. In this case, there is a positive correlation between Ge-Si and Zn-Pb substitutions, similar to that observed in the Ge-rich willemite from the Tres Maria Deposit in Mexico [2]. Following this stage, a major dissolution episode is observed; releasing zinc and silica in the supergene solutions, allowing the precipitation of 1) late Ge- willemite occurring as small crystals, and 2) newly formed zinc clays [3]. Hence, according to the nature of zoning (sector versus oscillatory), the incorporation of Ge was either controlled by crystallographic factors or by the nature of the meteoric solutions.



Furthermore, willemite is coeval with other oxidation-related species, like cerussite ($PbCO_3$). Stable isotope (O and C) measurements on cerussite and willemite suggest low temperature formation (around 20°C) in equilibrium with a fluid of meteoric origin. The formation of the High Atlas Belt during the Tertiary has contributed to the exhumation of the sulfide orebodies and the development of vertical conduits for percolation of meteoric waters. A supergene origin for low temperature zinc silicate is proposed. Although the origin of silica in such a carbonate environment is not well established, local sources exemplified by diagenetic quartz within the host limestone have probably contributed to the genesis of willemite.

Figure 1: Willemite with sector zoning. The Ge content was obtained by LA-ICPMS.

References:

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