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Distribution of trace elements in the supergene oxidation zone of Zn-Pb deposits : new insights from Belgium MVT deposits

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New observations and elementary analyses of willemite (Zn_2SiO_4) mineralisations from historical non-sulphides Zn-Pb deposits of La Calamine (Eastern Belgium) have been carried out in samples from collections of the Geological Survey of Belgium. This study aims at evaluating the critical element distribution and deportment. Willemite occurs as a variety of types that continuously formed between the protore stage (sulphides) and the late supergene stage (carbonates and hydrated phases). Different types of willemite may be distinguished by their shapes and zoning characteristics, supporting a polyphase non-sulphide mineralisation, after the protore stage. This is also marked by a significant change of major elements composition in the late generation of willemite. LA-ICP-MS measurements of minor and trace elements also reveal a strong variability between the different willemite types, although no direct link with willemite shape or zoning patterns can be pointed out. Among trace elements, we can notice abnormal contents in P, Cd, As, Pb, Ag and Sb, the three latter ones being related to tiny galena inclusions. While Ga and In contents are very low (less than 4 ppm) or below detection limits, respectively, significant Ge contents up to 250 ppm were measured; such contents are consistent with other values reported from willemite mineralizations throughout the world. The concentrations measured in willemite are very similar to those in sphalerite (averaging 250 ppm), supporting a role as precursor for sphalerite. However the supergene origin of willemite in Belgian deposits is controversial and the implication of low temperature hydrothermal fluids for willemite precipitation cannot be ruled out. This also questions the origin of Ge further incorporated in zinc silicates.