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A Mineralogical and Geochemical Study of Energy Critical Metals in the Carbonate-Hosted Zn-Pb Mine Tailings, Ireland

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Large volumes of mining tailings have been generated as a consequence of extracting metals and minerals. Repurposing mine tailings thus becomes an essential part of sustainable mining initiatives. This work investigates the mineralogy and geochemistry of mine tailings from the historic Tynagh carbonate-hosted Zn-Pb-Ag-Cu deposit in Ireland, with a focus on understanding the deportment of energy critical metals such as Ge, Ga and In for recovery purpose. Bulk geochemical data of tailing samples have revealed areas in the tailing ponds enriched in Zn and Pb. *In-situ* SEM-EDS analysis indicates the tails contain a variety of major Zn-containing mineral phases, including a biogenic Zn mineral (>90 wt.% Zn), Zn silicate (i.e. hemimorphite), Zn sulfide (i.e. sphalerite), Zn (hydro)carbonate (i.e. hydrozincite and smithsonite), and Zn (hydro)oxide. *In-situ* LA-ICPMS analysis suggests that there is a selective mineralogical deportment of trace metals, including Ge, Ga and In. The primary sphalerite in the Tynagh deposit is relatively barren in Ge and Ga and extremely depleted in In. Germanium resides almost equally in the Zn- silicate and sulfide mineral phases which have low Fe contents (<1 wt.%). This may suggest a comparable chalcophile and lithophile affinities of Ge when Fe is not a major constituent of host mineral. In the secondary mineral phases containing higher amounts of Fe, preferred uptake of Ge is observed to be associated with enrichment of As. Gallium shows occasionally high content in couple with Cu and Ag enrichments in the Zn silicate relative to other mineral phases, reflecting a favored incorporation of Ga^{3+} through coupled substitution with monovalent cations (e.g. Cu^{+}, Ag^{+}) for Zn^{2+} in the hemimorphite in the tailings. Indium remains depleted in almost all the secondary mineral phases, which may be due to a primary depleted source and/or an oxidic and low-temperature environment unfavorable for the precipitation of In.