

# Multistage Hydrothermal Silicification and Fe-Tl-As-Sb-Ge-REE Enrichment in the Red Dog Zn-Pb-Ag District, Northern Alaska: Geochemistry, Origin, and Exploration Applications

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## Abstract

Geochemical analyses of major, trace, and rare earth elements (REE) in more than 200 samples of variably silicified and altered wall rocks, massive and banded sulfide, silica rock, and sulfide-rich and unmineralized barite were obtained from the Main, Aqqaluk, and Anarraaq deposits in the Red Dog Zn-Pb-Ag district of northern Alaska. Detailed lithogeochemical profiles for two drill cores at Aqqaluk display an antithetic relationship between  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and  $\text{TiO}_2/\text{Zr}$  which, together with textural information, suggest preferential silicification of carbonate-bearing sediments. Data for both drill cores also show generally high Tl, Sb, As, and Ge and uniformly positive Eu anomalies ( $\text{Eu}/\text{Eu}^* > 1.0$ ). Similar high Tl, Sb, As, Ge, and  $\text{Eu}/\text{Eu}^*$  values are present in the footwall and shallow hanging wall of Zn-Pb-Ag sulfide intervals at Anarraaq but are not as widely dispersed. Net chemical changes for altered wall rocks in the district, on the basis of average Al-normalized data relative to unaltered black shales of the host Kuna Formation, include large enrichments (>50%) of Fe, Ba, Eu, V, S, Co, Zn, Pb, Tl, As, Sb, and Ge at both Red Dog and Anarraaq, Si at Red Dog, and Sr, U, and Se at Anarraaq. Large depletions (>50%) are evident for Ca at both Red Dog and Anarraaq, for Mg, P, and Y at Red Dog, and for Na at Anarraaq. At both Red Dog and Anarraaq, wall-rock alteration removed calcite and minor dolomite during hydrothermal decarbonation reactions and introduced Si, Eu, and Ge during silicification. Sulfidation reactions deposited Fe, S, Co, Zn, Pb, Tl, As, and Sb; barite mineralization introduced Ba, S, and Sr. Light REE and U were mobilized locally.

This alteration and mineralization occurred during Mississippian hydrothermal events that predated the Middle Jurassic-Cretaceous Brookian orogeny. Early hydrothermal silicification at Red Dog took place prior to or during massive sulfide mineralization, on the basis of the dominantly planar nature of Zn-Pb veins, which suggests filling of fractures that developed in previously lithified rock. Uniformly low Ca and Mg and uniformly negative Ce anomalies in highly siliceous Red Dog wall rocks reflect hydrothermal decarbonation reactions and pervasive silicification owing to conductive cooling of oxidized metalliferous fluids. Similar Ca and Mg depletions are evident at Anarraaq but generally lack associated silicification, possibly because temperatures of the hydrothermal fluids were too low (<180°C) or because the thermal contrast between the fluids and wall rocks was smaller owing to the greater depth of alteration and mineralization there, compared with Red Dog. Chalcophile element anomalies (Fe, Zn, Pb, Tl, As, Sb) in wall rocks at both Red Dog and Anarraaq are attributed to sulfidation reactions, coeval with subsurface Zn-Pb-Ag mineralization, during the mixing of oxidized metalliferous fluids with  $\text{H}_2\text{S}$ -rich fluids derived locally within the Kuna Formation.

Sedimentary wall rocks in the Red Dog district are characterized by a distinctive suite of geochemical anomalies, especially for Zn, Pb, Tl, As, Sb, Ge, and  $\text{Eu}/\text{Eu}^*$ . At the Aqqaluk deposit, wall rocks without visible sphalerite or galena (<300 ppm Zn + Pb) have anomalous  $\text{Eu}/\text{Eu}^*$ , Tl, Sb, and As for up to ~100 m stratigraphically below Zn-rich silica rock. At Anarraaq, the Tl anomaly is most extensively developed, and enrichment relative to unaltered black shale of the Kuna Formation is present up to 62 m above the highest Zn-Pb sulfide zones. The magnitude of the enrichment and systematic behavior of Tl in the district make Tl a promising geochemical exploration guide for Red Dog-type Zn-Pb-Ag deposits elsewhere.

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