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Revisiting redox-driven pathways of tin cycle from source to deposit

DR. JULIE ANNE-SOPHIE MICHAUD[1], CHRISTIAN SCHMIDT[2] AND MARIA ANNA NAUMOVA[3]

[1]Leibniz University Hannover
[2]GFZ Helmholtz Centre for Geosciences
[3]Deutsches Elektronen-Synchrotron DESY

Recent years have seen tin largely overlooked as a pivotal critical metal driving the technological revolution and the green energy transition. Its demand is soaring as it powers a diverse array of modern applications, arousing renewed interest in the scientific community. Tin ore deposits are the result of a complex interplay of crustal processes and intensive parameters to enrich tin by a factor of more than 1000 compared to the average crustal ppm level. The model for magmatic-hydrothermal tin ore formation, established for more than three decades, dictates that reducing conditions and redox reactions play a crucial role for tin transport and concentration because of the greater solubility of Sn^{II} in reduced granitic magmas and fluids. Yet, no study has systematically documented the tin oxidation state in crustal rocks involved in tin-ore formation, which was mainly due to analytical challenges. This study shows that X-ray Absorption Near Edge Structure (XANES) spectroscopy allow direct assessment of the tin oxidation state at concentrations as low as 30 ppm. Here, we report the oxidation state of tin for a wide range of reference materials and natural rock samples, often for the first time. Our findings that Sn^{IV} is dominant in crustal metamorphic, magmatic and hydrothermal rocks suggest that redox conditions play a smaller role in economic tin-ore formation than previously postulated, with redox reactions being significant, but not essential, during granitic magma generation and crystallization. Moreover, tin can serve as a new redox indicator to help solving major questions such as redox conditions in the continental crust or Earth's redox evolution.