

Growth of nanostructured calcite under hydrothermal conditions in presence of organic and inorganic selenium

G. MONTES-HERNANDEZ^{1*}, G. SARRET¹, R. HELLMANN¹, L. CHARLET¹, F. RENARD¹

¹Institut des Sciences de la Terre (ISTerre), OSUG/CNRS, UJF, BP 53X, 38041 Grenoble, France

Abstract

Selenium is an important trace metalloid, whose global cycle is controlled by fluid-rock interactions in the Earth's upper crust, interactions with bio-molecules in soils and living systems, and atmospheric transport in ashes. The cycling of selenium is often intimately associated with carbonate phases, with Se being generally incorporated as an impurity in calcite crystals or adsorbed on carbonate nanoparticles. In order to better understand the interaction of aqueous selenium species with carbonates, we studied the precipitation of calcite under hydrothermal conditions (30-90°C, 25-90 bar) in a CO₂-H₂O-Ca(OH)₂ medium in the presence of aqueous inorganic and organic selenium compounds. Aqueous carbonation reactions in the presence of selenium at elevated temperatures and pressures, relevant for long-term CO₂ sequestration in reservoirs and other natural geological systems, have until now not been investigated to the best of our knowledge. Macroscopic measurements, Electron microscopy (FESEM and TEM) and synchrotron X-ray absorption spectroscopy (XAS) were used in a complementary manner to investigate kinetic effect of Se, crystal size, structural order (crystallinity), morphology of crystal faces, crystal organization, and selenium speciation in the calcite samples. XAS data analysis showed clear evidence for the incorporation of selenite oxyanion (SeO₃²⁻) into the calcite crystal structure. At low Se content (1.3 mg/g calcite), a single site was observed with Se surrounded by six Ca atoms, whereas additional sites, probably corresponding to surface sorption sites, were found with increasing Se content. XAS also showed that seleno-L-cystine (Secys) was chemically fragmented during carbonation, and the solid phase contained elemental and oxidized Se, in hexagonal or amorphous form depending on the experimental conditions, with a minor proportion of Se(IV). Moreover, FESEM and TEM measurements revealed a very complex effect of Secys on the particle size and aggregation/agglomeration process, leading to the following calcite morphologies: rhombohedra, elongated rhombohedra (*c*-axis elongation), scalenohedra, star-like and shell-like crystal aggregates, and irregular calcite polycrystals. The aggregates and irregular polycrystals, which we designate as nanostructured calcite material, were constituted of nanometer-sized calcite crystallites (<100nm). The star and shell-like crystal aggregates, which were observed only in the presence of Secys, may be due to crystal growth in the presence of associated secondary organic compounds due to a simultaneous chemical fragmentation of Secys. Overall, the results from this study show that selenium (of biotic or abiotic origin) can be integrated into the crystallographic structure of calcite under hydrothermal conditions. This has relevance for geological processes in diverse environments, such as hydrothermal systems along mid-ocean ridges, or underground reservoirs associated with massive injection of CO₂ for long-term geological sequestration. For more details refer to Montes-Hernandez et al. [1-3].

[1] Montes-Hernandez et al. (2011) *Chem. Geol.* **290**, 109-120. [2] Montes-Hernandez et al. (2009) *J. Hazardous Mater.* **166**, 788-795. [3] Montes-Hernandez et al. (2008) *Crystal Growth & Design.* **8**, 2497-2504.

Compositional data analysis to constrain the geochemical footprint of iron oxide copper-gold deposits

JEAN-FRANÇOIS MONTREUIL^{1*}, LOUISE CORRIVEAU², AND ERIC GRUNSKY³

¹Institut de la Recherche Scientifique –Eau-Terre-Environnement, jean-francois.montreuil@ete.inrs.ca (* presenting author)

²Geological survey of Canada, Québec, louise.corriveau@nrncan.gc.ca

³Geological Survey of Canada, Ottawa, eric.grunsky@nrncan.gc.ca

Introduction

Lithogeochemical analysis of alteration haloes is an important exploration vector towards hydrothermal ore deposits. Iron oxide copper-gold (IOCG) systems display a systemic development of hydrothermal alteration types from sodic, to calcic-iron, and high to low temperature potassic-iron and potassic alteration paragenesis that indiscriminately replace host rocks at local and regional scales. Where intense and pervasive, alteration leads to complete and systemic mineralogical, chemical and textural transformation of precursor rocks, resulting geochemical composition for each alteration type is reproducible irrespective of the nature of the original host. However the zoning in the alteration haloes and the types of deposits formed vary as a function of unidirectional, cyclical or non unidirectional evolution of the hydrothermal system [1]. To further the development of geochemical vectors to IOCG and affiliated deposits and orient exploration campaign in under-explored settings, we document the geochemical signature of hydrothermal alteration from the Great Bear magmatic zone (GBMz) IOCG systems through the application of compositional data analysis based on the log-ratio approach and principal component analysis (PCA).

Results and Conclusions

PCA has enabled the characterisation of the geochemical signature of the diagnostic alteration types. When compared to the other IOCG alteration types defined in the preceding section, potassic and potassic-iron alteration show relative enrichment in K, Al, Ba, Si, Rb, Zr, Ta, Nb, Th and U. In contrast, when compared with the other alteration types, calcic-iron alteration exhibit relative enrichment in Ca, Fe, Mn, Mg, Zn, Ni and Co. Sodic alteration is relatively enriched in Na, Sr and Zr compared to the other alteration signatures.

The observed compositional variations established for each alteration type were thereafter portrayed in IOCG alteration indexes. Combined with the IOCG alteration vector to mineralization model, the resulting IOCG alteration indexes led to the development of an IOCG alteration discrimination diagram that provides a useful tool to quickly evaluate if a geochemical composition is related to IOCG-associated hydrothermal alteration. Plotting the alteration indexes on the GBMz regional geology map further demonstrates that the IOCG alteration indexes can provide a framework for field evaluation of the potential fertility and maturity of the GBMz IOCG systems and ultimately vector to ore during exploration.

[1] Corriveau, Williams & Mumin (2010) GAC, Short Course Notes, **20**, 89-110