

Fluid inclusions, REE and sulfur isotope geochemistry of the Lavrion carbonate hosted ore deposit, SE Attica, Greece

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The Pb-Ag-Zn sulfide mineralization of the ca. 3000 year old mining district of Lavrion, comprises mainly mantos and skarn-type massive sulfides. The area is a part of the Attico-Cycladic Belt (ACB). Late Miocene granitoid dykes and a granodiorite stock intruded the footwall of the detachment fault that separates the Basal Unit from the overlying Cycladic Blueschist Unit. Late Miocene porphyritic S-type granitoid rocks occur as sills along or within the hangingwall close to the detachment fault. The manto-type ores are spatially associated with the detachment fault, shear bands within marbles, and the shear contacts between marbles and the intercalated metaclastics of the Basal Unit, indicating that the most important structural control of the Lavrion mineralization is related to the large-scale back-arc Miocene extension in the Aegean. The mineralizing event postdated the mylonitic deformation stage of the marbles, as proved by the alignment of ore bodies with the mylonitic foliation planes or by their crosscut relationship. Wall-rock alteration is characterized by carbonatization and minor silicification. Ore deposition involved mainly marble dissolution and replacement, and open space filling.

Fluid inclusion studies provide evidence for deposition of sulfides of the manto-type mineralization at temperatures of about 280°C from fluids having salinities between 14 and 17wt% NaCl eq. Quartz and fluorite deposition occurred at lower temperatures (250 to 125 °C) from fluids having highly variable salinities (1-19 wt% NaCl eq.). The $\delta^{34}\text{S}_{\text{CDT}}$ values of galena, sphalerite and pyrite range between -4.8 to +3.99 per mil. Most paired samples of sphalerite-galena, sphalerite-pyrite and galena-pyrite show either reversed fractionations or unreasonably high temperature values, indicating either sulfur isotope disequilibrium or noncontemporaneous precipitation of sulfides. Chondrite-normalized REE patterns in fluorites show slightly increasing LREE and decreasing HREE contents. All fluorite samples possess weak negative Ce and pronounced positive Eu anomalies. A meteoric water influx late into the granodiorite stock is documented by the fluid inclusions in quartz of widespread extensional quartz veins. There is no clear evidence whether a direct genetic link exists between the manto-type massive sulfides and the Late Miocene igneous activity in the footwall of the detachment or along the detachment fault. Ag-rich sulfide mineralization forming tension gashes within hydrothermally altered hornfels postdates contact metamorphic phenomena.

Adsorption energy trends on UO₂ and ThO₂ surfaces

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Determining the interaction of adsorbates such as water and oxygen with surfaces of uranium and thorium dioxide is important for the long-term storage of these isostructural nuclear fuel materials. The semi-conducting versus insulating nature of UO₂ and ThO₂, respectively, makes comparison of surface-adsorbate interactions with these materials possible as a function of electronic structure in addition to surface structure. Previously, the quantum mechanical code CASTEP was used to calculate surface energies for UO₂ and ThO₂, and the (111) surface was found to be the most stable relative to the (110) and (100) surfaces in both cases (Skomurski *et al.*, 2006). In this study, CASTEP was used to investigate the interaction of water and oxygen with UO₂ and ThO₂ slabs of finite thickness representing each crystallographic orientation. The effect of model set-up on adsorption energy trends is discussed for single versus double-sided models in a periodic setting.

On a defect-free (111) surface, the adsorption of molecular water is found to be more favorable than dissociated water for both UO₂ and ThO₂. On the more reactive (110) surface, however, the opposite trend is favored. The adsorption of molecular and atomic oxygen is investigated as a function of spin configuration to determine the very first steps of oxidation on UO₂ surfaces. On both the (111) and (110) surfaces, the adsorption of atomic oxygen leads to oxidation of near-surface uranium atoms. Investigations into possible transition state spin configurations for oxygen interacting with the substrate are discussed. A co-adsorption case for water and oxygen is tested on both UO₂ and ThO₂ surfaces. On the UO₂ (111) surface, the presence of water is found to enhance the oxidation of near-surface uranium atoms, a phenomenon attributed to the semi-conducting nature of UO₂ as this trend is not observed on the insulating ThO₂ surface. Finally, the distance dependence of this "surface proximity effect" (Rosso and Becker, 2002) is tested as a function of distance between adsorbates on the (110) surface. By using quantum mechanical methods to investigate the very first interactions of oxygen and water with actinide oxide surfaces, we start to develop a mechanistic understanding of processes that ultimately affect oxidation and dissolution rates on the macroscopic scale.

References

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