The influence of muscovite and orthoclase on the precipitation of $CaCO_3$ polymorphs

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Carbonate mineralization and polymorphic formation are key issues in underground CO_2 storage and biomineralization processes. Previous research has focused on understanding the growth mechanisms of carbonate polymorphs in the presence of organic templates. However, few attention has been paid to inorganic substrates which may play a significant role in controlling carbonate mineralization. The aim of this study is to gain insight into the growth process and the polymorphism of $CaCO_3$ on muscovite and orthoclase, using both experimental and computational techniques.

$CaCO_3$ crystals were produced by mixing 0.07 M $CaCl_2$ and 0.07 M $NaHCO_3$, which results in a growth solution that is supersaturated with respect to all three polymorphs of $CaCO_3$, calcite, aragonite, and vaterite. If applying amorphous glass as a substrate, pure rhombohedral calcite is formed within ten minutes, which keeps stable for at least three days. However, if using a freshly-peeled (001) muscovite surface as a substrate, more than half of the precipitation is aragonite with a dumbbell-like shape. If applying freshly-cleaved orthoclase (001) and (010) surfaces as substrates, both vaterite and calcite precipitate. We hypothesize that muscovite and orthoclase stabilize less stable polymorphs through the strong interfacial interactions and lattice geometric matching between the charged mineral surface and overgrown carbonate. TEM analysis reveals special interfacial characteristics between the mineral surfaces and $CaCO_3$ crystals. Molecular modeling confirms that the strong electronic interactions of muscovite with aragonite surfaces make aragonite the most stable polymorph on muscovite. Likewise, orthoclase is conducive to vaterite.

Speciation and transport behavior of ^{99}Tc and ^{129}I

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Fission products ^{99}Tc (technetium) and ^{129}I (iodine) are important dose contributors in risk assessment, because of their high abundances, long half-lives (>10^5 yrs), and presumably high mobility in the environmental media. Both ^{99}Tc and ^{129}I are redox-sensitive and exhibit complex geochemical behavior, with their fate and transport in the environment dictated by chemical speciation [1]. This work provides an overview of ^{99}Tc and ^{129}I with regard to their basic chemistry, occurrence, speciation, separation, analysis, fate and transport. Redox-sensitive Tc primarily exists in two (+7 and +4) stable oxidation states in the environment, with TcO_4^- as the mobile species under oxidizing conditions. Laboratory experiments with controlled redox conditions indicate that the occurrence of reducing conditions could potentially lead to Tc reduction and retardation of redox-sensitive ^{99}Tc. Iodine occurs in multiple oxidation states (ranging from –1 to +7), and inorganic and organic species may be hydrophilic, atmophilic, or biophilic. Organically-bound iodine can be a significant fraction of total iodine in the atmosphere, biosphere, hydrosphere, and lithosphere [2]. Speciation, input concentration, and residence time effects will influence the biogeochemical cycling of anthropogenic ^{129}I deposited on surface soils.

[1] Hu *et al*. (2008) *Geochemical Transactions*, 9:12. doi:10.1186/1467-4866-9-12. [2]. Hu *et al* (2009) Chapter 10. Geochemical cycling of iodine species in soils. *Comprehensive Handbook of Iodine: Nutritional, Biochemical, Pathological and Therapeutic Aspects*. V.R. Preedy, G.N. Burrow and R.R. Watson (editors), pp. 93–105, Academic Press, Oxford.