

New halogen incorporation mechanism in serpentine group minerals: Crystal chemical consideration

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Introduction: Recent geochemical studies revealed that serpentinites contain a significant amount of halogens. However, how halogen ions are incorporated into serpentinites is not well understood. Commonly assumed mechanism is "OH⁻ substitution" in serpentine group minerals (chrysotile, lizardite and antigorite). Although this mechanism will be fine for F, but may not be adequate for larger halogens (Cl, Br, I). Here, I propose new halogen incorporation mechanism in lizardite and antigorite from crystal chemical point of view.

Calculation methods: In order to assess present new incorporation model, first-principles calculation was conducted. Quantum-Espresso package was used to optimize the halogen incorporated model structures. In the present study, lizardite and antigorite ($m=17$ polysome) are considered. For our proposed mechanism, charge balance should be observed; so $Mg^{2+} = X^- + Al^{3+}$ substitution (X^- = halogen) is assumed to introduce halogen to a vacant site. For lizardite, enthalpy difference between two models (OH⁻ substitution and our model) was calculated for following equation: $Mg_2AlSi_2O_8XH_2 + H_2O = Mg_2AlSi_2O_9XH_4$. Former corresponds to the OH substituted model (with Al introduced), and latter corresponds to our new model. Although this comparison is crude (as free H₂O is included in the equation), it could provide systematic trend with kinds of halogen atoms. Since antigorite has a very large unit cell and many vacant sites, only $Mg^{2+} = Cl^- + Al^{3+}$ substitute in five vacant sites are considered so far.

Results and Discussion: From close inspection of crystal structures of lizardite and antigorite, vacant sites ideal for halogens are identified. The vacant sites are surrounded by four protons (of OH⁻) forming elongated tetrahedron (i.e., XH_4^{3+}) if halogen is located. Such vacant sites provide local structure similar to halogen ions in aqueous solution.

In order to further assess present incorporation mechanism, first-principles calculations of lizardite and antigorite containing halogens in those sites were conducted. The structural optimizations confirmed that halogens could be well accommodated into the tetrahedral vacant sites in lizardite. The calculated enthalpy difference between OH substitution and present models in lizardite revealed that larger halogens prefer our model over the OH substitution model. There is single vacant site in lizardite, but antigorite ($m=17$) has 17 crystallographically different vacant sites. Most sites have local structures more or less similar to that of lizardite (locating in 6-membered SiO₄ ring). But there is another kind of vacant site which is locating in 8-membered SiO₄ ring. This local structure is surrounded by six protons, but it can be regarded as two tetrahedral proton sites with edge sharing. Substitution of Cl⁻ to this site (one of tetrahedral sites) showed lower enthalpy compared to those of other lizardite-like sites, and can accept more larger ions. Therefore, Cl⁻ (and other larger halogens) will prefer this site in antigorite ($m=17$). Not all antigorite polysomes have this site.

Present study suggests that our new proposed incorporation mechanism is promising, and it should be further studied experimentally. Present new incorporation mechanism would be important to understand elemental partition behavior of halogens in subduction zones.

Keywords: halogen site, serpentine, crystal chemistry, incorporation mechanism, elemental partition