

## Possible redox state control on the cycle of volatiles in the Earth's interior

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Based on noble gas isotope signatures such as  $^3\text{He}/^4\text{He}$  and Ne isotope systematics for MORBs and OIBs, the occurrence of degassed and less degassed mantle has been inferred. Since He (and possibly Ne) is quite easily movable and chemically inert, it is expected to be easily degassed from the magma reservoir during magmatic processes at a shallow depth. To explain the occurrence of primordial components such as  $^3\text{He}$  in the Earth's interior, among various proposals the existence of non-recycled mantle has been conjectured to be most likely by many noble gas researchers. Since noble gases are not related to any chemical reaction, they shall not be controlled by the redox state of the Earth's interior.

On the other hand, volatiles composed of active elements such as H, C, N, S and so on are more or less change their properties according to the redox state of the environments. For example,  $\text{CO}_2$  is a typical form in the oxidized state and if it is saturated in a magma at a depth, it is easily degassed at a shallow depth as  $\text{CO}_2$  bubbles due to the decrease of solubility of  $\text{CO}_2$  in a magma with the decreasing pressure. While in the reduced state,  $\text{CO}_2$  is difficult to remain as stable and C exists as diamonds (or graphites) and/or hydrocarbons. C and hydrocarbons are not easy to work as volatiles at a depth and would remain there unless they might be carried to a shallow place associated with mantle plumes.

In the same manner, the behavior of S is much variable depending on its chemical form controlled by the redox state. In the oxidized state,  $\text{SO}_2$  is degassed easily at a shallow depth from a magma. In the reduced state, S reacts easily with metal elements such as Fe or Cu and forms sulfide minerals like FeS, FeS<sub>2</sub> or CuS. When sulfide minerals are formed, they remain at a depth without forming volatiles.  $\text{H}_2\text{S}$  also works as volatiles, but its chemical behavior in volcanic gas would be different from that of  $\text{SO}_2$ .

N exists generally as  $\text{N}_2$  at the surface of the Earth and soluted in a magma to some extent. However, it has been inferred that the solubility of N in a magma might be increased in a much reduced state compared to that in an oxidized state. Furthermore, in a much reduced state, N would exist as  $\text{NH}_3$  and it might be not easy to be degassed from a deep mantle.

In the case of H,  $\text{H}_2\text{O}$  is most common form at a shallow depth in the oxidized state. When recycled  $\text{H}_2\text{O}$  goes into the deep mantle and the deep mantle is in the reduced state, however,  $\text{H}_2\text{O}$  might be not stable and would be decomposed.

Thus, some active elements would change their chemical form depending on the redox state, which would surely control the cycle of volatiles in the Earth's interior. Although the deep mantle is inferred to be less oxidized than the upper mantle, we have no good knowledges about their state. Based on such information from noble gas isotopes, kimberlites and E-chondrites, I have suggested a possibility that the deep mantle might be more reduced than what has been conjectured so far based on C-chondrites (1). Further, significant depletion of H, C, N, S related to Si in the earth compared to chondrite values might be related to the cycle behavior of these elements controlled by the redox state. However, we have no sufficient data on the chemical properties of such elements at high pressures under the reduced state. To promote our proper understanding of the cycle of volatiles in the Earth's interior, we should pay more attention to the issues mentioned here.

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