

D" layer as a result of the Earth protocore disintegration and as a source of primordial noble gases?

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The aim this work is to demonstrate the way of D" layer formation which is alternative to that in the model proposed to resolve the conflict between geophysical and geochemical data [1]. According to the new concept, D" layer is a result of the protocore disintegration due to its interaction with the liquid core. The protocore is now completely or partly destroyed. Moreover, it could be covered by products of outer core crystallization or entirely substituted by them.

It is supposed that the Earth accretion began on the solid protocore, which consisted of a mixture of metal iron and a small amount of material similar to chondrites. Then, the liquid outer core was formed due to partial melting of material, which was accreted on the protocore. Liquid core activated the protocore disintegration from outside. As a result of such disintegration the silicate component of the protocore floated to the core-mantle boundary and formed D" layer. By that time the overlying mantle had been degassed during liquid core formation. But the protocore was not degassed because it did not participate in this process. Due to this, its silicate component and D" layer have to contain volatiles including primordial noble gases. Besides cumulate-like silicate component, D" layer has to contain some quantity of dense intercumulus liquid of the external core. Because of volatiles presence, partial melting of silicate material in D" layer begins, and blocks of less dense and more plastic material appear. These blocks form diapirs and can trigger «plum» streams. Entrainment by convective mantle flow of D" material with some quantity of external core intercumulus liquid could be a reason of PGE patterns in the mantle.

Thus, it is possible to meet the constraints formulated by I.Tolstikhin and A.W.Hofmann [1]. The existence of two reservoirs of the mantle material with noble gases of a different isotope composition, the solution of xenon paradox and the explanation of D" layer origin don't necessarily require assuming subduction of the most ancient crust (together with regolith on it) down to the core-mantle boundary and the crust preserving there during ~4.4 Ga, as these authors suppose.

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[1] Tolstikhin & Hofman (2005) *Phys.Earth Planet. Interiors*, **148**, 109-130.

The mechanism of phosphate immobilization by the replacement of carbonates by apatite

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Whenever phosphate bearing fluids come into contact with carbonates, reequilibration may be achieved by the dissolution of the carbonate, generating a Ca-rich fluid which, combined with the phosphate, results in supersaturation with respect to apatite at the mineral-fluid interface. We have investigated the mechanism of this replacement reaction experimentally, using both biogenic aragonite, and inorganic aragonite and calcite as starting materials, reacted in a batch reactor with phosphate solutions over a range of temperatures. In all experiments the reaction product is hydroxyapatite (HAP). The replacement reaction is pseudomorphic and even in a morphological structure as complex as the cuttlebone of *Sepia officinalis*, the delicate morphology is preserved after complete replacement of the aragonite by HAP. The activation energy of the reaction in the cuttlebone is 38.6kJ mol⁻¹. In the experiments with inorganic aragonite and calcite, the sharp replacement interface moves from the original crystal surface into the parent, with a polycrystalline product made up of hexagonal needles of HAP. The replacement of aragonite by apatite involves a molar volume decrease which promotes the generation of porosity in the reacted rim, thereby allowing mass transport between the internal reaction interface and the fluid reservoir. These textural features are typical of an *interface-coupled dissolution-precipitation mechanism* [1,2]. This mechanism is a very efficient method of reequilibration and operates at diagenetic temperatures, controlling the distribution of elements in aquatic sediments.

[1] Putnis C.V., Tsukamoto K. & Nishimura Y. (2005) *American Mineralogist*, **90** 1909-1912. [2] Putnis A. & Putnis C.V. (2007) *Journ. Solid State Chem.* **180**, 1783-1786.