Pb isotope fractionation during photodissociation of tetraethyllead in aqueous solution

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Laboratory experiments, modeling photodissociation of tetraethyllead under irradiation with ultrviolet light in aqueous solution have been performed. The dissociation of $PbEt_4$ includes breaking the lead-carbon bond and removing the ethyl groups one by one according to the following scheme:

$Pb(C_2H_5)_4 \rightarrow Pb(C_2H_5)^{3+} \rightarrow Pb(C_2H_5)_2^{2+} \rightarrow Pb^{2+}$

$PbEt_4$ is immiscible with water and has very low solubility in water saturated with air, whereas inorganic Pb^{2+} is insoluble in organic phase. Thus, two operationally defined fractions of Pb have been obtained in the experiments using C_{18} filled extraction cartridges: (i) alkylated Pb species, including parent $PbEt_4$ and its neutral dissociation products, dissolved in the organic phase, and (ii) inorganic Pb^{2+} and ionic tri- and diethyllead dissolved in the aqueous phase. Photodissociation of tetraethyllead under irradiation with ultraviolet light was observed to be accompanied by both the classical mass fractionation and mass-independent fractionation of Pb isotopes. The extent of the mass-dependent isotope fractionation between the two operationally defined fractions of Pb is described by kinetic isotope fractionation factors of $0.99984 \pm 3.7\times10^{-5}$ and $0.99968 \pm 3.6\times10^{-5}$ for $^{206/204}$Pb and $^{208/204}$Pb isotope ratios, respectively. Mass-independence of Pb isotope fractionation is displayed by pronounced enrichment of ^{207}Pb isotope relative to the even isotopes in the fraction of unreacted tetraethyllead molecules during the photolysis and attributed to the magnetic isotope effect. The magnitude of this effect was dependent on the solution matrix, being the highest in the solution of low ionic strength with absence of radical scavengers. In contrast, no measurable Pb isotope fractionation has been observed in control experiments on dissociation of tetraethyllead due to attack by oxidative radicals in the dark. These experiments were based on the efficient conversion of hydrogen peroxide to hydroxyl radical according to the Fenton type reaction scheme.

Thickness of diamond-bearing metasomatic aureoles in the cratonic SCLM

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The distribution of subcalcic garnets in the SCLM of the Siberian craton suggests that: a) subcalcic garnets and diamonds are metasomatic phases in deep cratonic SCLM, b) the distribution of both phases in the lithosphere is laterally heterogeneous on relatively small scales and related to ancient structural controls [1]. Thus, the grade of a kimberlite will depend on its intersecting these previously active fluid conduits. However, the most obvious question is – what is the thickness of the metasomatic aureoles related to such ancient mantle conduits/veins? This information has an important application to diamond exploration.

Here we assume that the diamond-bearing metasomatic aureole probably consists of harzburgites and dunites and a central part represented by pyroxenites or eclogites, and lherzolites refertilized from dunite/harzburgite by melt-related metasomatism [1; Fig. 5D].

Garnet and chromite xenocrysts from kimberlites have been used to map the vertical distribution of rock types and processes in the Yakutian SCLM [2]. Knowing the depth distribution of different types of peridotite beneath the kimberlite pipes and using our original method we calculated the thickness of the metasomatic aureoles related to ancient mantle conduits/veins in the Yakutian SCLM. Using set with several parameters we obtain a thickness of diamond-bearing metasomatic aureoles varying from ~3 cm to 1.4 meters.

Calculated values of the thickness of the diamond-bearing metasomatic aureoles in the deep cratonic SCLM are similar to the thickness of the pyroxenite dikes and adjacent metasomatic aureoles in orogenic peridotitic massifs [3; references therein]. The small calculated thickness of the metasomatic aureoles also is consistent with the close association (often <1km) of both diamond-bearing and barren kimberlite pipes, indicating how easy it is for a kimberlite to miss intersecting the diamond bearing aureoles.

[1] Malkovets *et al*. (2007) *Geology* **35**, 339–342. [2] Griffin *et al*. (1999) *Tectonophysics* **310**, 1–35. [3] Beyer *et al*. (2006) *Jour. of Petrol*. **47**, 1611–1636.