The sorption of ferrous iron onto clay minerals: could aqueous Fe(II) outcompete with radionuclides for immobilization?

CHRISTOPHE TOURNASSAT, LAURENT CHARLET

LGIT - CNRS/UJF Université Joseph Fourier 38000 GRENOBLE FRANCE
Christophe.Tournassat@obs.ujf-grenoble.fr
Laurent.Charlet@ obs.ujf-grenoble.fr

Radioactive waste management frequently rely on the properties of clay minerals present in engineered or natural barriers to insure repository performance. One of these properties is the ability to fix radionuclides by sorption processes. Although this capacity has been well established for a wide range of potential pollutants in Na^+ and Ca^{2+} salt backgrounds, the influence of other salt backgrounds is poorly documented. In case of nuclear waste disposal, the dissolution of containers and reinforced concrete in anoxic conditions could lead to the launch of a large amount of ferrous iron in solution.

In the present study, we show that Fe^{2+} can strongly sorb onto the smectite particles. This adsorption can be explained and modeled by cation exchange on the basal planes of the particles and by specific adsorption on the edges, as previously described for other cations (Zn^{2+}, Co^{2+}, Ni^{2+}). Calculation of the thermodynamic exchange constants shows that Fe^{2+} behaves like Ca^{2+} for cation exchange whereas, for sorption on the clay edges sites, specific complexation constants are much higher than those published for Zn^{2+} and Ni^{2+}. Thus, based on thermodynamic models, sorption of Fe(II) on clay particles may potentially have a strong impact on clay immobilization capacity towards radionuclides. Competition between Fe^{2+} and cations of interest (Eu^{3+}, Ni^{2+}…) is currently being explored experimentally.

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Laser and stepwise-heating $^{40}Ar/^{39}Ar$ dating of kimberlite-like rocks from Sayan Foothills and peripheral part of the Siberian platform

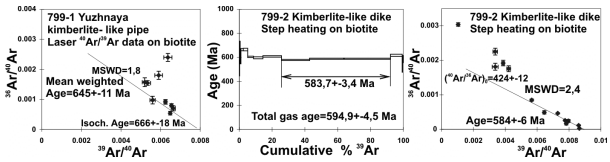
TRAVIN A.V.[1], ASCHEPKOV I.V[1], UDIN D.[1], PROSTYAKOV K.[1]

[1]United Institute of Geology, Geophysics and Mineralogy, SB RAS, Novosibirsk, Russia, travin@uiggm.nsc.ru

Introduction and geological background

The determination of time span of alkaline-ultramafic- and carbonatite magmatism on the margins of Siberian craton has significance for deciphering the history of Rodinia break-up. As a rule, dating with isochron methods (Rb/Sr, Sm/Nd) yields too high age error due to isotope disequilibrium. Simple K/Ar dating can overstate age due to the excess ^{40}Ar. We performed combined laser (ruby, pulsed) and step heating $^{40}Ar/^{39}Ar$ dating on mica from carbonatites and kimberlite- like rocks closely related and tracing the same rifting structure in East Sayan Foothills. Yuzhnaya pipe contains serpentinized cumulative dunites, rare mantle harzburgite, glimmerite xenoliths, shallow Cr-diopside, mica and K-feldspar intergrowths. The melilitite basalt (kimberlite) dikes include only glimmerites, mica and magnetites, coarse alkaline gabbro, close in mineralogical features to rocks in Belo-Ziminsky carbonatite massifs.

Figure.1 *$^{40}Ar/^{39}Ar$ data of the Sayan kimberlite-like dike.*



Results.

Average from 6 laser shots (Fig. 1) on mica from kimberlite pipe Yuzhnaja gives 645±11 Ma, concurring with isochrone age of 666±18 Ma. It fit within the error with K/Ar and Rb/Sr data (Alkaline rocks of the World, 1995). At the same time laser dating on biotite from a closely located kimberlite dyke yielded younger age of 608±8 Ma while stepwise heating on the same biotite (Fig. 1) yielded total gas age of 595±5 Ma with isochrone age of 584±6 Ma. High initial $(^{40}Ar/^{36}Ar)_0$=424±12 evidences for ^{40}Ar excess, overestimating laser and step heating total gas ages. Kimberlite-like dikes cut carbonatites massifs dated by Rb/Sr (620 Ma) and K/Ar (610 Ma) (Legend to East Sayan Geological map). Kimberlite-like dike 799-2 is younger than kimberlite pipe and carbonatites massifs.

Discussion

Ages of K-alkaline ultramafic magmatism in margins of Siberia craton reflect the final stage of break-up of Rodinia. On the base of our and previous data its time span in Sayan Foothills is about 70 Ma (from 666 to 584 Ma).

Thus for confident and precise dating of ultramafic-alkaline- carbonatite magmatism combined laser and stepwise heating $^{40}Ar/^{39}Ar$ dating on matrix micas should be used.

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