Kinetic aspects of the transformation of nanoparticles in the environment

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Much of the interest in environmental nanoparticles (NPs) is motivated by the expectation that they are more reactive than larger particles of similar composition. Nano-size effects on reactivity can take a variety of forms, however, and it can be challenging to resolve and quantify them. Most of the kinetic data that can be used for this purpose are for transformation of probe compounds in well-mixed NP suspensions. Representation of these data as both mass- and surface-area-normalized rate constants (k_M and k_{SA}) facilitates systematic evaluation of many aspects of the data, including whether there is an 'intrinsic' nano-size effect on probe reaction kinetics.

This approach has been applied to evaluating nano-size effects on data from controlled experiments on several specific systems, and the overall implication of these analyses is that these effects are more elusive and subtle than generally supposed. Expanding the scope of this analysis into a meta-analysis across data for different probe reactions, NP types, and test conditions provides additional perspective on several of the larger questions regarding NP reactivity in solution.

Perhaps the most central of these questions concerns the definition, interpretation, quantification, and normalization of rates for 'reactive surface area'. We will use meta-analysis of kinetic data that we have compiled to show that, where the effective 'order of reaction' with respect to surface area appears to differ from one, the source and scale of this effect are no more significant than any of a number of other approximations that are made in quantifying the kinetics of reactions of NPs.

Another outcome of our analysis is to suggest that the more reactive probe reactions are less sensitive to nano-size effects than the less facile probe reactions. This suggests that the most compelling evidence for significant nano-size effects is likely to come with probe reactions where significant rates are only observed with NPs, such as with dechlorination of dioxins or 1, 2, 3-trichloropropane by nano zero-valent iron (and not, say, carbon tetrachloride).

Even where quantitative kinetic data are scarce, insights can still be gained by predictive applications of the approach taken here. Examples of this may include the effect of particle size on transformation of the NPs (i.e. their aging).

The Siberian traps: What's new?

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Within a large trog in northern part of the Siberian platform magnitude of volcanic sequence sections reach a value of 3.5 km. From West to East along the trog next provinces are situated in order: Norilsk province of basitic igneous rocks; Kamenskaya province of alkaline-basitic rocks and Maimecha-Kotuiskaya province of alkaline-ultrabasic rocks.

Formation age interval of volcanic sequence is restricted within 251.7 ± 0.4 and 251.1 ± 0.3 Ma [1], at the same time the age of Norilsk-Talnakh Cu–Ni–PGE orebearing intrusion is equal to 251.2 ± 0.3 Ma and the age of Gulinsky volcano-plutonic complex is equal to 250.2 ± 0.3 Ma [1]. Noticeably difference is the age of Bolgokhtokhsky granodiorite intrusion (with Cu-porphyry mineralisation) situated in Norilsk province - 229.0 ± 0.4 Ma.

The geochronological investigations of author's dikes collection from Kamenskaya and Norilsk provinces revealed the new characteristic feature of the evolution trapp magmatism within time range of 251.7 ± 0.4 ÷ 229.0 ± 0.4 Ma.

Within Kamenskaya province a few hundred of dikes of different thickness (0.5—30 m) and lengths (from 3—5 m till 140 km) [2] have been revealed. All dikes cut volcanic sequence. $^{40}Ar/^{39}Ar$ step heating investigation yielded: age formation of sienitic dike - 249.4 ± 3.3 Ma; picritic dike – 248.5 ± 1.4 Ma; trachidoleritic dike - 247.4 ± 3.2 Ma; alkaline-basitic dike - 246.2 ± 3.3 Ma; bostonitic dike - 238.7 ± 3.1 Ma; vogesitic dike - 238.2 ± 3.0 Ma. Within Norilsk province doleritic dike yielded age value of 238 ± 1.6 Ma.

Hence taking into account Bolgokhtokhsky granodiorite intrusion age equal to 229.0 ± 0.4 Ma duration of discrete-continuous manifestations of tectono-magmatic processes on the North-West part of the Siberian platform count about 21 Ma.

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