# Review of issues associated with evaluation of Pitzer interaction parameters

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Aqueous geochemical models that predict solid and gas equilibria over a broad range of water compositions and temperatures are powerful tools for studying the geochemistry of natural waters, solving environmental problems and optimizing industrial processes. The Pitzer ion interaction model has been widely accepted as the most effective approach to predict chemical behaviour in concentrated solutions; however, the description of natural waters requires a large compilation of interaction parameters. These parameters are derived from experimental data such as isopiestic, electrochemical, and solubility measurements on simpler systems.

In this study, a large number of binary systems have been evaluated to understand issues which could potentially compromise the representation of more complex solutions. The results revealed that the concentration range within which Pitzer parameters are derived, together with the aqueous species that are included in the model, and the accuracy of temperature coefficients are of most importance.

For a system that is parameterized over a limited concentration range, model predictions may deviate substantially from the experimental data outside this range, as shown in many binary salt systems of interest in environmental studies such as $CaI_2$, CsF, $NiCl_2$, $CuCl_2$, $ZnCl_2$, and $Th(NO_3)_2$. Further evaluations of parameters within a chemical system will be hampered if any of the data points used in evaluating new parameters fall outside this concentration range. In particular, the new introduced parameters may be biased to compensate for inaccuracies in the original model rather than real chemical effects. It is possible to reduce the potential for introducing such systematic errors into an analysis by ensuring that the parameterization is valid up to the saturation limit of binary solids, and even to supersaturated conditions, if possible.

The standard Pitzer approach treats electrolytes as being completely dissociated. In some instances ionic species can be incorporated into the model; however, the addition of ion pairs and complexes into the solution model requires the determination of interaction parameters between these new species and each of the other species in solution. In addition, inclusion of ion pairs and complexes may compromise the model when moving away from the concentration range at which the model was derived. The ideal approach is to rely on the additional parameter $\beta^{(2)}$ to account for the effect of ion pairing or complexing in solution but this may not always be possible. However, it has been successfully demonstrated for the $NdCl_3$-$H_2O$ system, where the new model was able to eliminate $NdCl^{2+}$ and $NdCl_2^+$ species used in early development.

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# Os-Hf-Nd-Sr isotopic constraints on the origin of highly potassic basalts in northeast China

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The very young (about 0.6Ma-1721AD) Wudalianchi (WDLC) and Erkeshan (EKS) basalts in northeast (NE) China are characterized by high $K_2O$ contents ($K_2O/Na_2O>1$) and strong enrichment in incompatible elements, especially the large ion lithophile elements (LILEs) and light rare earth elements (LREE) and are isotopically similar to EM-I, which differ from the basalts in eastern China elsewhere. The origin of these WDLC and EKS potassic lavas is still under debate. Here, we present new Re-Os isotopic data, together with Sr-Nd-Hf isotopic and traditional elemental data to further constrain the origin of the WDLC and EKS potassic lavas. The $^{187}Os/^{188}Os$ ratios of the WDLC and EKS basalts range from 0.1187 to ~0.17. In general, samples with low Os concentrations have high $^{187}Os/^{188}Os$ ratios while samples with high Os concentrations have relatively low $^{187}Os/^{188}Os$ ratios. Since minor amounts of crustal contamination will alter significantly the Os isotopic composition of a basaltic magma with low Os concentrations, it is possible that the WDLC and EKS basalts were contaminated by minor crustal materials during magma ascent. The suprachondritic Os of some WDLC and EKS basalts may also possibly result from preferential melting of a metasomatized mantle peridotites which contain interstitial sulfides that are characterized by low Os concentrations and suprachondritic $^{187}Os/^{188}Os$. Nonetheless, since the WDLC and EKS basalts generally have relatively low $^{187}Os/^{188}Os$ ratios compared to the Cenozoic continental basalts in other localities such as Hannuoba, Columbia River, SE Australia and Central European, we think that the crustal contamination did not play an important role for formation of the WDLC and EKS basalts.

The WDLC and EKS basalts have unradiogenic Hf-Nd and radiogenic Sr isotopic compositions, with εHf range of -3.9 to -9.2, εNd values between -5.8 and -3.2 and $^{87}Sr/^{86}Sr$ ratios between 0.7051 and 0.7057, indicating the contribution of a metasomatized sub-continental lithospheric mantle (SCLM). In term of Os isotopes, the most unradiogenic sample has Os isotopic compositions as low as 0.1187, also confirming the contribution of an ancient SCLM for generation of the WDLC and EKS magmas. This sample gives a $T_{RD}$ model age as old as 1.2Ga, indicating that the SCLM underlying the WDLC and EKS area could be at least as old as Proterozoic.

Consistent with previous reports, these lines of evidences together suggest the WDLC and EKS mainly originated from an anicent metasomatized SCLM.

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