Prediction of elemental partition between fluid and melt by bond valence method

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Matsui, Onuma and others (Bull. Soc. fr. Mineral. Crystallogr., 1977) revealed that elemental partition between minerals and magma is mostly governed by local structure of ion sites in crystalline phases, and accordingly elemental partition has been predicted by Nagasawa model or similar models. However, these models can not be applied to partition between fluid and melt, as these models do not explicitly treat these phases. Recently, the author found that "bond valence" method can be applied to predict partition behavior. Initial tests to crystalline phases are promising. So, I'm currently trying to extend this method to fluid and melt.

Bond valence method is an extension of Pauling's original idea, that valence of central cation can be divided into each bond in ionic crystals. I.D. Brown extended this by including bond distance dependence to bond valence; longer bond has lower bond valence. In ionic crystals, bond valence sum on central atom coincides with its valence or very close to it. If deviation is large, something wrong with the structure. To date, several authors compiled bond valence parameters using databases of crystal structures for almost all elements except rare gases. Therefore, if crystal structure (or at least local structure) is known, bond valence sum (bvsum) can be calculated. For example, if we put Sr in M2 site of forsterite, we will have bvsum larger than 2, as Sr ion is too large for M2 site. This difference is related to "strain" energy, as bond valence equation ($\exp((R_0-r_{ij})/B)$) is identical to repulsive term of two-body inter-ionic potentials. So, I defined misfit parameter; misfit = abs(bvsum - Q) where Q is valence of central cation. If we take difference of misfits between two distinct crystallographic sites (e.g., M1 and M2 sites of forsterite), it can be related to partition coefficient. In this way, "partition coefficient" of intra- and inter-crystalline phases are calculated, and they can compare well with experimental data. This calculation is very simple, and only bond distances and bond valence parameters are necessary. Prediction of partition behavior such as perovskite/postperovskite is now possible. It was found that bond valence method can be used to quantitatively predict elemental partition, however, there are several unsolved issues, such as how to quantitatively relate difference of misfits to partition coefficients, and how to treat different valences consistently etc.

If we know the local structures of fluid and melt, partition behavior can be qualitatively predicted using present method. However, this is not the case at moment. Therefore, single virtual site for each fluid and melt was assumed, then partition behavior between two sites was evaluated by changing size of the sites. Based on Pearce et al. (doi:10.1029/2004GC000895), Ba, Cs, K, Pb and Sr prefer fluid, whereas REE, Nb, Ta, Zr, Hf etc. prefer melt. Such behavior was reproduced when the size of the site for fluid is about 3.2 A, and that of melt is 2.5 A. Using this local structure model, partition behaviors of other elements can be predicted. Alternatively, local structures of fluid and melt could be estimated by comparing precisely determined partition data with present model.

Keywords: bond valence method, elemental partition, fluid, melt, local structure