Solubility and species of Zn and Pb in water-chloride fluids at T-P conditions of granite magmas degassing

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Results of thermodynamic modeling of equilibrium relationship of complexes of Zn and Pb in water-chloride solutions as a function of T (600 - 900ºC), P (0.7-5 kbar), the composition and acidity of the fluid (NaCl, KCl, NaCl+HCl), as well as the initial concentration of Zn and Pb in the system in the form of $ZnO_{(c)}$, $PbO_{(c)}$ or $ZnCl_2$, $PbCl_2$ are presented. At 'magmatic' T-P parameters Cl-complexes fraction and total solubility of ore metals in solutions equilibrated with their solid oxides essentially increase with the increase of chloride ion concentration (C_{Cl}) and decrease of pH. The form of prevailing Cl-complexes varies with growth of C_{Cl} towards the increase of quantity of their Cl atoms as follows: $ZnCl^+$, $ZnCl_2^o$ - $ZnCl_4^{2-}$; $PbCl_2^o$ - $PbCl^{3-}$ - $PbCl_4^{2-}$. The increase of pressure and temperature decrease contributes to stability of Zn and Pb Cl-complexes. Zn/Pb (at.) > 1 in solutions equilibrated with $ZnO_{(c)}$ and $PbO_{(c)}$ within wide range of T-P-X parameters. It increases with the increase of C_{Cl} and acidity of the solution.

Results of thermodynamic simulation confirm the assumption about the leading role of Cl-complexes in the distribution of Zn and Pb between water-chloride fluids and granite melts during their degassing and agree with experimental data obtained at 800ºC and 1-5 kbar (Urabe, 1987; etc.) that show: (1) the increase of Zn and Pb distribution coefficients between fluid and granite melt ($D(Zn)^{f/m}$, $D(Pb)^{f/m}$) with the increase of Na and K chloride concentration in a water fluid, (2) the particularly sharp increase of $D(Zn)^{f/m}$ and $D(Pb)^{f/m}$ with addition of HCl to fluid phase (at T, P, C_{Cl} = const), (3) the higher values of $D(Zn)^{f/m}$ in comparison with that of $D(Pb)^{f/m}$ at given T-P-X conditions.

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Production of the Cordillera del Paine igneous complex by thermal migration zone refinining

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The Torres del Paine igneous complex consists of a silicic granitoid pluton overlying a contemporaneous mafic gabbro complex that are possibly cogenetic; recent dating studies indicate progressively decreasing age with stratigraphic depth [1, 2]. Descending through the ~1.5 km vertical stratigraphy, the upper 1 km consists of 70-72% SiO2 granite with abundant silicic aplites along the margins including the top. Beneath the granite is a zone of mixed diorite, which is underlain by a few hundred meters of hornblende gabbros. A recent model for graniotid formation by top down sill injection and reaction [3] predicts a similar overall vertical stratigraphy; isotopic measurements of a vertical Torres del Paine transect provides a first order test of this hypothesis.

We have undertaken Fe isotope analyses of previously characterized samples from the studies of Michael (1984, 1991)[4, 5]. We used high resolution MCICPMS techniques and a ^{57}Fe-^{58}Fe double spike method. Analytical precision is ~0.08 permil. Results indicate that 4 granite and evolved granite samples (SiO_2 >71%) have consistently heavy isotopic compositions relative to the IRMM standard (0.23 ± 0.08). Six monzogabbro/diorite samples average 0.09 ± 0.07. Notably, a mafic monzodiorite and two gabbros at the bottom of the Paine mafic complex average -0.80 ± 0.48, representing the lightest Fe isotopic compositions yet observed in igneous rocks. Finally, a dike porphyry sample also has a light isotopic composition of -0.39.

While further analyses are in progress, results thus far are consistent with the prediction that the isotopic variations reflect the role of thermal gradients and thermal diffusion in fractionating Fe isotopes. Specifically, heavier isotopic ratios for granites compared to diorites follows previoius observations of isotopic variations with silica content [6]. However, significantly light isotopic compositions in the bottom of the system provides evidence for a complimentary signature at the hotter part of an igneous body. Trace element modeling using IRIDIUM of top down differentiation will further assess the plausibility of this model.

[1] Michel *et al.* (2008) *Geology*. [2] Leuthold *et al.* (2009) *AGU*. [3] Lundstrom (2009) *GCA*. [4] Michael (1984) *Cont. Min Petrol*. [5] Michael (1991) *Cont. Min. Petrol.* [6] Poitrasson (2006) *Chem Geol.*