DISTRIBUTION OF ALKALIS (Na, Cs, Rb) BETWEEN SILICATE AND SULFIDE: IMPLICATIONS FOR PLANETARY VOLATILE DEPLETION.

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Introduction: The abundances of volatile elements in the Earth's mantle are correlated with their temperatures of condensation. This depletion can be due to either incomplete condensation of the elements during the nebula condensation or evaporation processes during planetary growth. Elements that have affinities with metals (siderophile) and sulfides (chalcophile) are additionally depleted due to their segregation into the core. Therefore, study of lithophile elements could be useful to isolate processes of volatilization and their effect on the abundance of the elements in the Earth's mantle. However, the correlation of these lithophile elements including alkali elements, with their temperatures of condensation shows a significant scatter, which is difficult to reconcile with a depletion by vaporization or incomplete condensation alone.

On the other hand, previous studies showed that alkali elements K and Na have affinities with sulfides with elevated O-contents (e.g. [1]). Several recent scenarios of core segregation suggested that sulfide phases might have played an important role on the distribution of the elements between core and mantle. For instance, the accretion of sulfur-rich embryos was invoked to explain the C/S ratio [2] and the isotopic Nd composition of the Earth's mantle [3]. Therefore, it is important to quantitatively constrain the effect of sulfide segregation during core-mantle differentiation on the budget of alkali elements in the Earth's mantle, and evaluate whether their depletion results uniquely from their volatilization.

Methods: We measured partition coefficients for Na, Cs and Rb between sulfide and silicate, by conducting experiments between 1 and 8 GPa and 1700 to 2000 °C using multi anvil press and piston cylinder apparatuses,. Starting material corresponded to mixtures of silicate powder (with variable Al and Mg content) and Fe metal powder with variable Si and FeS. We also added variable amounts of Fe_3O_4 to enhance O solubility in the sulfide phase. Alkalis were added to the starting material in the form of carbonates at levels of 3-5 wt% each in the silicate phase. Oxygen fugacity was estimated between IW-4 to IW+0.4. After characterizing samples textures, we analyzed each phase with a field-emmision electron microprobe. To determine concentrations of alkalis, we used standards of albite, pollucite and RTP for Na, Cs and Rb, respectively.

Results: Our experimental charges show two different types of texture: a silicate melt in equilibrium with either one FeS sulfide melt or with two immiscible liquid Fe-rich metal and FeS sulfide melt. Silicate and sulfide melts contain variable FeO (1 to 40 wt%) and O concentrations (up to 13 wt% O, corresponding to 30 mol% S), respectively. These two parameters correlate with each other, as previously found [4].
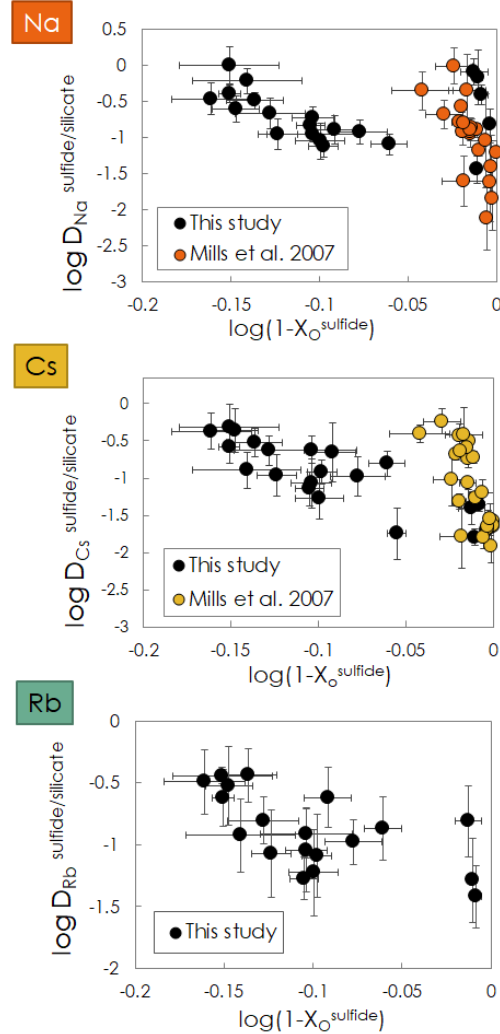

Figure 1: Molar partition coefficients between sulfide and silicate as a function of $log(1-X_O^{sulfide})$ with $X_O^{sulfide}$ being the molar concentration of O in the sulfide liquid.

We combined our experimental results with those of Mills et al. [5] and found that partition coefficients ($D_A^{sulf/sil}$) of alkalis between sulfide and silicate increase with the O content of the sulfide liquid (Fig. 1). However, we found that $D_A^{sulf/sil}$ increase faster for

sulfides having low O contents. It yields two different trends for sulfides having either lower or higher O concentration than 10-12 mol%.

Based on experimental data, we derived an expression predicting partitioning coefficients:

$$\log D_A^{sulf/sil} = \log \frac{X_{sulf}^A}{X_{sil}^A}$$
$$= a + \frac{b}{T} - 0.5 * \log X_{FeO}^{sil} + c * \frac{T_0}{T} * \log\left(1 - X_O^{sulf}\right) + d * \frac{T_0}{T} * \log\left(1 - X_S^{sulf}\right)$$

Where X_{sulf}^A, X_{sil}^A, X_{sil}^{FeO}, X_{sulf}^O, and X_{sulf}^S correspond to molar fractions of alkali A in the sulfide and silicate, FeO in the silicate, O and S in the sulfide and T represents temperature, respectively. We used two different regressions for the low and high-O sulfide liquids. We found a negligible effect of S on partition coefficients for the O-rich sulfides. Effects of pressure and silicate composition were also found unresolvable.

Model of core segregation: We used the expressions to model the distribution of alkalis between the Earth's core and mantle. We considered a model where the Earth was accreted from some S-rich embryos having a sulfide layer representing 10% the body's mass, between core and mantle, which is close to recent models of core segregation [2, 3]. We assumed that the sulfide and silicate fractions of accreted material fully equilibrate before reaching the solid mantle and falling down with no further equilibration until reaching the core. In addition, we considered that alkalis partitioned into the sulfide phases at the early stages of the Earth's accretion when the depth of the magma ocean was still relatively shallow. Indeed, at pressures higher than 20 GPa sulfides are not stable anymore, as the immiscibility gap closes around 20 GPa in the Fe-S-O system [6]. Finally, in order to calculate the distribution of alkalis between core and mantle, we assumed bulk planet alkali concentrations correlating with their temperatures of condensation following an exponential trend, as commonly observed in planetary and asteroidal materials (Fig. 2).
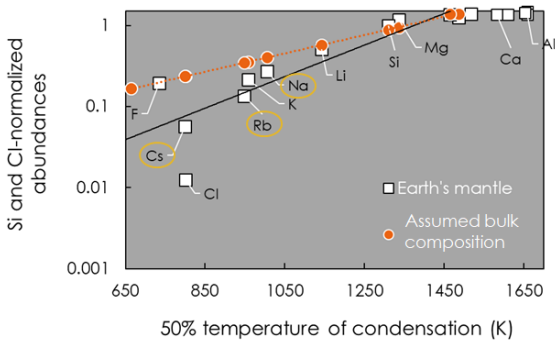

Figure 2 Assumed bulk Earth composition (orange circles) compared to the Earth's mantle composition (white squares) (normalized to Si and CI chondrite composition) [7].

Na/Al, Cs/Al, Rb/Al, Na/Cs, Rb/Cs and Na/Rb ratios for the Earth's mantle were calculated for different models with varying O contents in the segregated sulfide phases (Fig. 3). Resulting Na concentration is found close to the Earth's mantle whereas Cs and Rb are higher than the observed terrestrial values (Fig. 3**a**). On the other hand, while Rb/Cs falls within the range observed in the terrestrial mantle, Na/Cs and Na/Rb ratios are found lower (Fig. 3**b**). This suggests that sulfide segregation into the core cannot explain the observed fractionation of alkali elements in the Earth's mantle. The results imply that either (1) no sulfide phases were extracted to the Earth's core during its differentiation, (2) temperatures of condensation of alkalis may be inaccurate (e.g. [8]) (Na could be more refractory or Rb and Cs more volatile than commonly reported), or (3) additional fractionation processes such as atmospheric loss or impact erosion affected the abundances of alkali elements in the Earth's mantle.
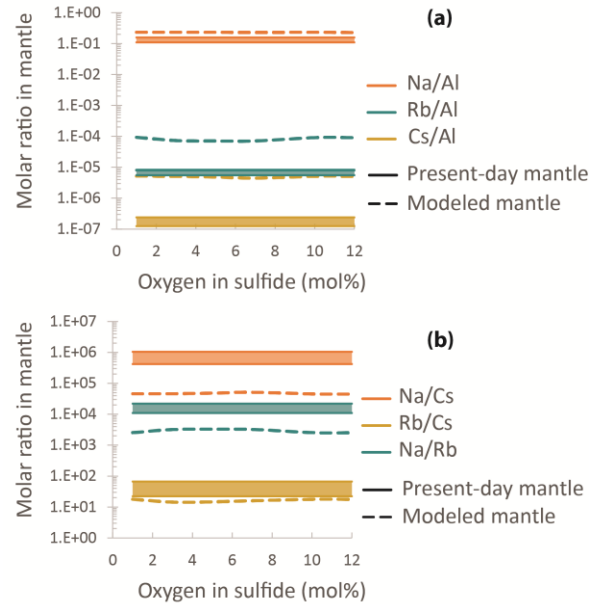

*Figure 3: Resulting alkali/Al (**a**) and alkali/alkali (**b**) ratios in the modeled Earth's mantle (solid lines) compared to the present day values (dashed lines) [7], as a function of the assumed O-contents in sulfides.*

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