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PARTITIONING OF Nb, Mo, Ba, Ce, Pb, Th and U BETWEEN IMMISCIBLE CARBONATE AND SILICATE LIQUIDS: EVALUATING THE EFFECTS OF P₂O₅, F, AND CARBONATE COMPOSITION. J.H. Jones* and D. Walker[†]. *SN4, NASA/JSC, Houston, TX 77058. [†]Lamont-Doherty Earth Observatory, Palisades, NY 10964.

Introduction. Previously we have reported carbonate liq./silicate liq. partition coefficients (D) for a standard suite of trace elements (Nb, Mo, Ba, Ce, Pb, Th, and U), and Ra and Pa as well [1]. In brief, we have found that immiscible liquid partitioning is a strong function of temperature. As the critical temperature of the carbonate-silicate solvus is approached, all partition coefficients approach unity. Additionally, for the overwhelming majority of the partitioning elements, lnD is a linear function of "ionic field strength," z/r , where z is the charge of the partitioned cation and r is its ionic radius.

The system in which our previous experiments were performed was a relatively simple one, CMAS + Na + Fe + CO₂. The silicate portion was initially a synthetic MORB and the carbonate was a 1:1 mixture of Na₂CO₃ and CaCO₃. The silicate:carbonate mixture was then prepared in proportions of either 1:1 or 1:2.

We considered it highly likely that additional components such as phosphorus or halogens might strongly influence partitioning behavior, especially for the actinides Th and U. Actinides are known to readily form complexes in aqueous solutions, and large changes in $D^{cpx/liq}$ which correlate with the addition of phosphate have been attributed to phosphate complexation of actinides in the silicate liquid [2]. Consequently, we have carried out a series of experiments to evaluate the effects of potential complexing agents on trace element partitioning between immiscible liquids.

In addition, the Soret effect in liquids provides an index of expected changes in trace element partitioning behavior deriving from changes in major element composition. This has been demonstrated in both silicate [3] and polymetallic sulfide liquids [4] which show strong Soret activity. We attempted to use the Soret effect in a predominantly carbonate liquid (with a small fraction of dissolved silicate) to anticipate the sensitivity of our partitioning results to such chemical parameters as the Na/Ca/Mg ratio of the carbonate liquid.

Experimental and analytical. Experimental procedures and preparation of starting materials have been described previously [1]. Briefly, starting materials consisted of reagent oxides, carbonates, phosphates and fluorides, which were mixed by grinding under acetone. Trace elements were spiked as reagent oxides or carbonates or as natural minerals. Three starting compositions of MORB+carbonate were prepared that also contained 2, 5 and 14.5 wt.% of Ca₃(PO₄)₂, and three other mixtures were prepared that contained 5, 10, and 14.5 wt.% CaF₂. Runs were performed in graphite capsules in a piston cylinder. Our standard run conditions were 4-24 hours at 1250°C and 10 kbar. Charges were analyzed by electron microprobe using standard techniques.

We note that our experimental charges have some tendency for the carbonate liquid to disperse onto the grain boundaries of the graphite capsule, presumably by a combination of reaction and capillary migration. Consequently, we have reduced our experimental run times to maximize our chances of finding two liquids. However, even in those cases where the carbonate liquid has been sequestered into the graphite, the remaining silicate liquid appears to have equilibrated with the carbonate. Thus, we infer that equilibrium is approached quickly [1] and that the chemical characteristics of our immiscible liquids are established early in the experiment. The difficulty that we have had in containing the carbonate is testimony to the mobility of carbonate liquids and may have implications for the extraction of carbonate-rich partial melts from planetary mantles.

To investigate possible Soret activity, Na/Ca and Mg/Na/Ca carbonate charges, with ~5% silicate and doped with our standard tracers, were placed in graphite capsules in a thermal gradient of ~200°C/4 mm according to our routine procedures [5]. The Na/Ca charge precipitated

CARBONATE LIQUID/SILICATE LIQUID PARTITIONING: Jones J.H. and Walker D.

immiscible silicate at the cold end ($\sim 1250^\circ\text{C}$) allowing an additional consistency check on partitioning information at a different Na/Ca/Mg ratio than previously investigated.

Results. The primary result of adding P or F to our MORB+carbonate system is to expand the carbonate liquid stability at the expense of the silicate. As more phosphate and fluoride were added, the silicate became less modally abundant. At least one reason for the expansion of the carbonate field is that P and F are both strongly partitioned into the carbonate phase. $D(\text{P})$ is about 4 and $D(\text{F})$ is 2-4, in favor of the carbonate. Consequently, as more phosphate and fluoride components are added to the system, the amount of carbonate should increase. In addition, however, the SiO_2 concentration of the carbonate liquid increases as the total amount of P or F increases, suggesting that the addition of these components promotes miscibility. For example, in the case of the 14.5 wt.% CaF_2 composition, there appeared to be complete miscibility, as only one phase was found.

The addition of P and F to our MORB+carbonate system apparently has only a minor effect on partitioning (Figures 1 and 2). While there does appear to be some modest change in D 's at low P and F contents, we cannot rule out that this is due to small differences in bulk chemical composition. In most cases the partition coefficients in the P- and F-bearing systems are within 30% of those in the P- and F-free system.

Surprisingly, the liquids of both our Soret experiments were quite homogeneous, showing no Soret effect. In addition, the immiscible liquid at the cold end of the Na/Ca carbonate Soret experiment showed carbonate/silicate partitioning entirely consistent with our previous results, although the linear trend of $\ln D$ with field strength may be marginally less steep. This result is consistent with our previous results being insensitive to the Mg/Na/Ca ratio in the carbonate system. This conclusion is reinforced by the surprising result that no measurable Soret activity was detected for any element.

Conclusions. On the basis of these new experiments, we conclude that our previous results are not strong functions of carbonate composition. We also conclude that our original partition coefficients are not strong functions of the abundances of minor, high-field strength components or of complexing agents. We therefore believe that our earlier results are likely to have greater application than would initially have been predicted.

References: [1] Jones J.H. et al. (1992) *Lunar and Planet. Sci. XXIII*, pp. 627-228. [2] Jones J.H. and Burnett D.S. (1987) *Geochim. Cosmochim. Acta* 51, 769-782. [3] Leshner C.E. (1986) *J. Geophys. Res.* 91, 6123-6141. [4] Jones J.H. and Walker D. (1991) *Proc. Lunar Planet. Sci. Conf. 21st.*, 367-373. [5] Leshner C.E. and Walker D. (1991) *Adv. Phys. Geochem.* 8, pp. 396-451.

