

THERMAL DIFFUSION IN Fe-Ni-S-P METALLIC LIQUIDS. John H. Jones[‡] and David Walker*. [‡]SN2, NASA Johnson Space Center, Houston, TX 77058. *Lamont-Doherty Geological Observatory, Palisades, NY 10964.

If a homogeneous solution is placed in a temperature gradient, compositional gradients within that solution may be established. In general, this process is referred to as thermal diffusion; in liquids it is called the Soret effect. The Soret effects that have been reported for metallic liquids have not been regarded as extremely important in the solidification and segregation of liquid alloys. For example, in the Sn-Pb system, compositional variations attributed to the Soret effect are ~10-15% [1]. Consequently, many metallurgical solidification processes are investigated by Czochralski growth ("crystal pulling"), with the solid-liquid interface in a steep thermal gradient (e.g., [2]).

Experimental. To explore the possibility that crystal pulling experiments could be affected by the imposed thermal gradient, we have carried out experiments to evaluate the Soret effect in liquid Fe-Ni-S-P alloys. Two different compositions have been investigated. The first (SS-1) contained 8 wt.% S, 1% P, and 10% Ni, with the remainder being Fe. The second composition (SS-3) contained 20 wt.% S, 0.3% P and 10% Ni. The starting materials were mechanical mixtures of natural pyrite, elemental P, and metallic Fe and Ni. Consequently, a given experiment may deviate somewhat from these nominal compositions.

The experimental charges were run in crushable MgO capsules, 3/16 inches in length. The experiments were carried out in a standard piston cylinder apparatus at 10-12 kbar, using BaCO₃ as a pressure medium. After the piston cylinder is loaded and pressurized, the sample is heated to ~800°C for 1-2 days to sinter the MgO and effectively seal the capsule. After sintering, the sample is raised to temperature, with the hot end of the charge at 1400-1450°C and the cold end at 1240-1280°C. The samples were typically held at temperature for 40-60 hours and quenched by cutting electrical power to the graphite resistance heater. The mounted and polished samples were then analyzed using the raster mode of a Cameca electron microprobe, either at Lamont-Doherty or JSC. The Lamont analyses were performed using a 800X raster, while the JSC analyses were made with a 2000X raster. Although analytical sums were sometimes low, this does not influence our primary conclusions.

To specifically evaluate our approach to steady state, two samples of the SS-3 composition were run for 18.5 hours (SS-3-4) and 115 hours (SS-3-3).

Results. All experiments except SS-3-1 contained two phases, (Fe,Ni) metal and a metallic liquid. The solid metal was homogeneous and confined to the cold end of the charge while the liquid exhibited a Soret effect, primarily in the concentrations of S and P. The Soret coefficient for P for the SS-1 experiment, calculated as in [3], was $\sim -1 \times 10^{-3}/^{\circ}\text{C}$. The (solid metal/liquid metal) partition coefficient for P at the cold end of the charge for SS-1-22 was 0.19, in general agreement with the one bar experiments of [4].

In the first experiment using the high-S composition, SS-3-1, the P concentration decreased by nearly a factor of two from the cold to the hot end, as the S concentration increased by about 20% (Table 1). The Soret coefficients for P in SS-3-1,3,4 were calculated to be $\sim -3 \times 10^{-3}/^{\circ}\text{C}$, approximately three times larger than that for SS-1. The magnitude of this Soret coefficient is comparable to those measured in silicate systems [3]. In one experiment, SS-3-5 (which was somewhat colder than the others and contained more solid metal), the Soret coefficient for P was $\sim -7 \times 10^{-3}$. This increase in the Soret coefficient appears to be directly related to the S concentration of the metallic liquid, which in turn is attributable to the greater modal abundance of solid metal, which excludes S. As will be seen below, this same explanation appears to account for the difference in the P Soret coefficients between the SS-1 and SS-3 compositions. The similarity between the P Soret coefficients of SS-3-4 (18.5 hours) and SS-3-3 (115 hours) lead us to believe that we have closely approached steady state.

One complication of our experiments is that some reaction with trace impurities in the MgO

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container has apparently occurred. Several of our experimental charges contained a few grains of calcium phosphate and forsterite at the cold end of the charge. Because phosphate is an additional sink for P, it is possible that our experiments only yield minimum Soret coefficients for P. However, the similarity of the P Soret coefficients between the short- and long-duration experiments leads us to believe that this is not a serious effect.

Discussion. We find that the liquid solution model of Jones and Malvin [5] serves to predict differences in the P Soret coefficient between experiments, as well as to predict differences in P concentration between the hot and cold ends of an individual experiment. For example, the melt model of [5] predicts that the effect of S on P should be $\sim 2.5 \times$ larger in the SS-3 experiment than in SS-1. The measured difference in the P Soret coefficients between these two experiments is $2.9 \times$. Similarly, the melt model predicts that the activity coefficient of P at the hot end of the SS-1 charge should be 19% higher than at the cold end and that the P concentration at the hot end should be proportionally lower. The measured P concentration at the hot end of SS-1 is about 17% lower than at the cold end -- in good agreement with the prediction. For SS-3-1 the model predicts that the cold end should have about twice the P content of the hot end, in agreement with the measured P concentrations. Therefore, the melt model, which was originally used to model (solid metal/liquid metal) partitioning, also serves to predict the effect of S on minor melt constituents when that melt is placed in a thermal gradient. The only experiment where the difference in P concentration is not predicted to within 30% is SS-3-4, which was of shorter duration than other experiments and may not have totally reached steady state.

Earlier we speculated that the steep thermal gradients involved in Czochralski growth might influence segregation [4]. In order to explain some of the unusual results of [2], we predicted that S and P would attempt to unmix in a thermal gradient and that P might migrate to the cold end and S to the hot end of the system. This is indeed the type of behavior that we observe in our Soret experiments. Even if the liquid is magnetically stirred, there will always be a stagnant boundary layer at the solid-liquid interface; and it is possible that, in a steep thermal gradient, the liquid from which a crystal is grown may not be representative of the composition of the bulk liquid.

Table 1
Representative Compositions Generated in Thermal Diffusion Experiments
(wt. %)

	SS-1-22 (Lamont)			SS-3-1 (JSC)	
	Hot <u>Liquid</u>	Cold <u>Liquid</u>	<u>Solid</u>	Hot <u>Liquid</u>	Cold <u>Liquid</u>
Fe	74.1	76.5	86.9	66.3	62.1
Ni	8.9	8.6	9.2	8.1	8.5
S	13.7	11.3	0.04	24.1	20.0
P	<u>0.8</u>	<u>1.0</u>	<u>0.2</u>	<u>0.14</u>	<u>0.26</u>
Σ	97.6	97.4	96.0	98.6	100.1

References. [1] Verhoeven J.D. et al. (1972) *Metall. Trans.* 3, 1437-1441. [2] Sellamuthu R. and Goldstein J.I. (1985) *Proc. Lunar Planet. Sci. Conf. 15th.*, C677-C688. [3] Walker D. et al. (1981) *Proc. Lunar Planet. Sci. Conf. 12th.*, 991-999. [4] Malvin et al. (1986) *Geochim. Cosmochim. Acta* 50, 1221-1231. [5] Jones J.H. and Malvin D.J. (1990) *Metall. Trans.*, Submitted.