**VAPOR PRESSURES AND EVAPORATION COEFFICIENTS OF FE, NA AND K OVER CHONDRULE COMPOSITION MELTS.** A. V. Fedkin[1], L. Grossman[1,2], and M. S. Ghiorso[1]. Dept. of the Geophysical Sciences, [2]Enrico Fermi Institute, University of Chicago, Chicago, IL 60637. avf@uchicago.edu.

**Introduction:** Although vapor pressures are expected to be very high at temperatures experienced by molten chondrules, chemical and isotopic evidence of significant evaporative losses from chondrules is rare. The free evaporation flux of species x in moles-cm$^{-2}$-sec$^{-1}$, $J_x$, from a molten droplet is given by the Hertz-Knudsen equation,

$$J_x = \alpha_x P_x^v \Big/ \sqrt{2\pi m_x RT},$$

in which $m_x, P_x^v$, and $\alpha_x$ are the molecular weight, equilibrium vapor pressure and evaporation coefficient of species x, resp., R is the gas constant and T is the temperature. Thus, computation of evaporative changes in chondrule composition during melting requires accurate thermodynamic models of gas-liquid-solid systems for determination of the dominant evaporating species and their vapor pressures, and measurements of evaporation rates in experiments at controlled and known T and oxygen fugacity, $f_{O2}$, to obtain evaporation coefficients. In this work, thermodynamic modelling of published results of evaporation experiments is used to obtain evaporation coefficients of Fe, Na and K from the silicate portion of chondrule melts.

**Technique:** For a given S-free, bulk chemical composition, T and $f_{O2}$, the MELTS computer code [1] calculates the activities of all components in all phases, the equilibrium amounts of all liquid and solid metallic, silicate and oxide phases, and their densities. Vapor pressures of all species were calculated from activities of the formal MELTS components by equilibrating published furnace gas compositions with starting compositions of charges used in evaporation rate studies in a manner analogous to that in [2]. For example, the vapor pressure of K is obtained from the equilibrium constant for the reaction,

$$2KAlSiO_{4(l)} \Leftrightarrow 2K_{(g)} + Al_2O_{3(l)} + 2SiO_{2(l)} + \frac{1}{2}O_{2(g)}$$

Depending on experimental conditions, the $f_{O2}$ governing such reactions may be controlled by the furnace gas or by the evaporating sample itself. In our modelling, we assume that escape of vaporized species is unimpeded by ambient gas, even in 1-bar gas-mixing experiments, that the $f_{O2}$ of residual furnace gas in vacuum experiments is that of air, and that diffusion rates in the samples are fast enough to support evaporation rates.

**FeO:** Evaporation rates of Na and Fe from a simulated chondrule composition melt (sample 1) were measured by [3] in 1-bar $H_2$-$CO_2$ gas mixtures that yielded log $f_{O2}$=-9.2 at 1729, 1778, 1828 and 1880 K, corresponding to 0.15, 0.58, 0.99 and 1.40 log units below iron-wustite (IW), resp., abbreviated IW-0.15, *etc*., hereafter. As $P_O^{drop}/P_O^{gas}$, in the notation of [2], is always $\leq 10^{-3}$ for these runs, the furnace gas controlled the $f_{O2}$. As in [2], the Hertz-Knudsen equation was used to calculate the amount of each element removed from the droplet in a small time interval, the composition was recalculated, the vapor pressures were calculated for the new composition, and the process repeated for a total time equal to the duration of the experiment. The same values of $\alpha_{Mg}$ and $\alpha_{SiO}$ were used as in [4], and the values for $\alpha_{FeO}$ and $\alpha_{Na}$ were obtained by fitting to the measured curves of FeO and $Na_2O$ concentration *vs* time, assuming that $\alpha_{FeO}$ arising from $Fe^{2+}$ is the same as from $Fe^{3+}$. No solid phases were observed to form in the experiments, so nucleation of the olivine±orthopyroxene otherwise predicted in the model at 1778 and 1729 K was suppressed. At 1828 K, for example, the vapor pressures of SiO and Mg were calculated to rise from $5.8\times10^{-6}$ to $6.3\times10^{-6}$ and from $5.5\times10^{-7}$ to $5.7\times10^{-7}$, resp., and those of Fe and Na to fall from $1.7\times10^{-5}$ to $1.1\times10^{-5}$ and from $2.1\times10^{-4}$ to $6.0\times10^{-5}$, resp., during the 32-minute experiment. The values obtained for $\alpha_{FeO}$ are 0.03, 0.035, 0.045 and 0.07 at 1880, 1828, 1778 and 1729 K, resp.

The same model was applied to the change in composition of a molten chondrule analog evaporated in vacuum ($P\leq1.3\times10^{-8}$ bar) at 1973, 2073, 2173 and 2273 K, reported in [5]. We calculated an initial atomic ferric/ferrous ratio of ~0.054 at each temperature, and that $P_O^{drop}/P_O^{gas}\sim10^4$. In this case, vapor pressures were calculated from the $f_{O2}$ governed by the activity ratio of $Fe^{3+}/Fe^{2+}$. Despite the constancy of the atomic $Fe^{3+}/Fe^{2+}$ ratio, which is dictated by the assumption of equal evaporation coefficients, their activity ratio differs at each time step due to the evaporative change in melt composition. At 2073 K, for example, log $f_{O2}$ varies from IW+1.86 to IW+0.7 over the 28 minute duration of the experiment. No solid phases were predicted in any of our model simulations, so the olivine and magnetite seen in the experiments are interpreted here as quench products. The best fits to the FeO loss curves imply $\alpha_{FeO}$ of 0.13, 0.14, 0.16 and 0.14 at 2273, 2173, 2073 and 1973 K, resp. The average of these, 0.14, is a factor of 3 higher than 0.045, the mean of our data obtained by interpretation

of the slightly lower temperature data in [3]. Both of these are significantly below the values of $\alpha_{FeO}$, 0.22-0.28, suggested in [6] by interpretation of vacuum experiments between 2000 and 2300 K.

**Alkalies:** The values obtained for $\alpha_{Na}$ by interpretation of the data from [3], discussed above, are all 8-9x10$^{-4}$ over the T interval 1729-1880 K. Our model was also applied to the Na and K loss rate data reported by [7] in 1-bar CO-$CO_2$ gas mixtures and in 9x10$^{-5}$ bar $H_2$ at 1723 K. In the CO-$CO_2$ experiment, $P_O^{drop} / P_O^{gas}$ is very small, and log $f_{O2}$ is determined by the furnace gas at IW-0.5. This treatment yields $\alpha_{Na}$ = 6x10$^{-4}$, in good agreement with the above value based on [3], and $\alpha_K$ =1x10$^{-4}$. In $H_2$, $P_O^{drop} / P_O^{gas}$ is very large, and log $f_{O2}$ is calculated to vary from IW+2.8 to IW-1.4 during the experiment, leading to $\alpha_{Na}$ = 0.03 and $\alpha_K$ = 0.01. The reason for the very poor agreement with the CO-$CO_2$ data is not known, but both determinations are much more satisfactory than the impossible values, $\alpha_{Na}$>1 and $\alpha_K$>1, from the PCR treatment [8].

**A Metallic Fe-Bearing System:** Cohen and Hewins [9] melted and partially evaporated a Ni-free, CI-like composition at 1838 K in a 1-bar $H_2$-$CO_2$ gas mixture, whose log $f_{O2}$ was measured to be IW-3. They showed the texture and mineralogy of the run products and reported the composition of the olivine and mesostasis after 1, 2, 4, 6, 12 and 18 h. In this experiment, metallic Fe spherules coalesced into a single central droplet which disappeared after 6 h, and the FeO content of the mesostasis fell gradually, but did not become zero, even after 18 h. Olivine is $Fo_{97-100}$. In the first 6h, the CaO and $Al_2O_3$ contents of the mesostasis increased greatly and the MgO and $SiO_2$ contents decreased. Modelling the droplet evolution is made difficult by the fact that no data were obtained within the first hour, during which all of the S, Na, K and C were lost, and no estimate of bulk chemical composition was made as a function of time. In this case, $P_O^{drop} / P_O^{gas}$ is very small, and vapor pressures are calculated for the $f_{O2}$ of the furnace gas. Liquid-crystal and redox equilibrium are assumed to be instantaneous. Solid silicates are assumed not to evaporate, and $\alpha_{Fe}$ is assumed to be 1.0 for liquid Fe, and to vary from 0.93 at 1720 K to 1.0 at 1810 K for solid Fe [10]. Using $\alpha_{FeO}$=0.02, close to that derived above from [3], the initial FeO content of the mesostasis is <1 wt % and falls with time at log $f_{O2}$=IW-3 (Fig. 1), whereas it is still ~4 wt % after 1 h in the experiment. Also at this $f_{O2}$, MgO and $SiO_2$ evaporate so quickly that the residual CaO and $Al_2O_3$ contents of the mesostasis rise much more rapidly than in the experiment. Further modelling was done at IW-2.3, which gave initial FeO of 4.7 wt % and lowered evaporation rates of MgO and $SiO_2$. At this $f_{O2}$, metal accounts for 92 % of the Fe atoms and 14 vol % of the sample initially. Mg-, Al-spinel appears at 1.5 h and is 2-3 wt % of the sample at 6 h. When the areal fractions of silicate and metallic phases on the droplet surface are set equal to their volume fractions, metallic Fe disappears very quickly. Petrography indicates, however, that the surface fraction of metallic iron is much lower than this. If it is lowered by 99 %, metal persists and FeO in mesostasis stays at ~1 wt % for more than 6 h, as found experimentally (Fig. 1). Most Fe evaporates directly from the silicate liquid, whose FeO content is restored by metal oxidation at each time step (Fig. 2), rather than from the metallic one. Like the experiment, model olivine (43 wt %) is $Fo_{97.2}$ at 1 h and $Fo_{98.3}$ just before total dissolution at ~11 h. At these conditions, calculated time variations of CaO, $Al_2O_3$, MgO and $SiO_2$ in mesostasis are poor fits to the experimental data. Identical calculation with silicate crystallization suppressed gives a much closer fit, suggesting crystal-liquid equilibrium may not have occurred in the experiment.

**References:** [1] Ghiorso M. S. & Sack R. O. (1995) *Contr. Miner. Petrol., 119,* 197. [2] Grossman L. & Fedkin A. V. (2003) *GCA, 67,* 4205. [3] Tsuchiyama A. *et al*. (1981) *GCA, 45,* 1357. [4] Grossman *et al*. (2002) *GCA, 66*, 145. [5] Hashimoto A. (1983) *Geochem. J., 17,* 111. [6] Alexander C. M. O'D. (2004) *GCA, 68*, 3943. [7] Yu Y. *et al*. (2003) *GCA, 67*, 773. [8] Alexander C. M. O'D. (2002) *MAPS, 37*, 245. [9] Cohen B. A. & Hewins R. H. (2004) *GCA, 68*, 1677. [10] Tachibana S. (2004) pers. comm.