**MODEL EVAPORATION OF CHONDRULE PRECURSORS IN NEBULAR SHOCKS.** A. V. Fedkin<sup>1</sup>, L. Grossman<sup>1,2</sup> and M. S. Ghiorso<sup>3</sup>, <sup>1</sup>Dept. of the Geophysical Sciences, Univ. of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637 avf@uchicago.edu, <sup>2</sup>Enrico Fermi Inst., Univ. of Chicago, <sup>3</sup>OFM Research-West, 7336 24<sup>th</sup> Ave NE, Seattle, WA 98115.

Introduction: It is widely accepted that evaporation of such elements as S, Na, K, Fe, Mg and Si would have resulted from the melting of ferromagnesian chondrules in a solar gas; yet, the measured isotopic mass-fractionations of volatile elements in chondrules are very small [1]. There are a number of possible explanations for this, including too little time at high temperature for significant evaporation [2]; re-introduction of nearly completely volatilized elements either by backreaction/recondensation [3] or by parent body processes [4]; and chondrule melting in systems with unusually high oxygen fugacity, fo2, and/or ambient pressures of volatile elements [1]. Which of these applies depends on the element of interest and on chondrule thermal history. In this work, we model evaporation-induced changes in bulk chemical composition for a chondrule melted by a shock wave.

Technique: The method employs the MELTS thermodynamic model for calculating the equilibrium weight and volume proportions of all phases, their compositions, and the activities of all components in the coexisting liquid at each evaporation step. We use a kinetic evaporation model that differs slightly from that described in [5] in that equilibrium vapor pressures are calculated from the equilibrium  $f_{\rm O2}$  of the condensed assemblage. The Hertz-Knudsen equation uses the equilibrium vapor pressures to calculate the fluxes of all species, from which the evolving chemical composition of the residue is computed. In the present work, a system of solar composition is assumed, and closed-system evaporation of a C-, S-, H<sub>2</sub>O-free but otherwise CI composition chondrule precursor in its complementary gas is studied. For evaporation into an ambient gas, evaporation rates are retarded by different amounts for different elements depending on the partial pressures in the ambient gas. The flux of oxygen from the species O2(g), for example, becomes  $2\alpha_0(f_{02}-P_{02})/(2\pi m_{02}kT)^{1/2}$ , where  $P_{02}$  is the partial pressure of  $O_{2(g)}$  in the ambient gas, and  $\alpha_0$  is an evaporation coefficient for oxygen. When the net outward flux of oxygen from all O-containing species is greater than that which is stoichiometrically equivalent to the net cation fluxes, the excess flux is supplied by reduction of iron oxide. When the opposite is true, the excess oxygen in the residue is used to oxidize iron and nickel. In this treatment, the residue naturally approaches redox equilibrium with its complementary gas, at a rate controlled by  $\alpha_0$ .

A model for shock wave production of chondrules from solid precursors has been developed which tracks the simultaneous evolution of the temperature and ambient pressure to which molten chondrules were subjected [6]. In this work, evaporation of chondrule precursors is modeled after they reach 1397 K. For a 7 km s<sup>-1</sup> canonical shock, chondrules are heated at ~4 K min<sup>-1</sup> from 1397 to 1742 K prior to arrival of the shock. When the shock arrives, the ambient gas pressure increases instantly by a factor of ~8 and remains there, while the temperature instantly rises to 1858 K, falls to 1730 K in ~2 min and then cools at ~50 K hr<sup>-1</sup>. According to Desch (pers. comm.), factors not yet taken into consideration could cause the pre-shock heating rate to be higher, the pre-shock temperature to be lower and the final cooling rate to be higher. Thus, cases were also investigated where these values were 20 K min<sup>-1</sup>, 1542 K and 200 K hr<sup>-1</sup>, resp., and these are referred to here as the "cool shock" cases. Evaporation of a 0.5 mm radius sphere was studied over a range of pre-shock pressures from 10<sup>-5</sup>-10<sup>-3</sup> bar and for a range of initial precursor oxidation states generated by equilibration at 1397 K over a range of log f<sub>02</sub> from IW-3 to IW. Evaporation coefficients,  $\alpha_i,$  used for Na\_{(g)}, K\_{(g)}, Fe\_{(g)}, Mg\_{(g)} and SiO\_{(g)} from silicate liquid are .064, .025, .056, .21, and .060, resp., at 1800 K. Their temperature dependences were assumed to be the same as that of Mg<sub>(g)</sub> in CMAS [7], except for that of Mg(g), which was obtained by modeling the data in [8]. A value close to 1 was used for  $\alpha_{Fe}$  and  $\alpha_{Ni}$  from both solid and liquid metallic NiFe, leading to higher intrinsic evaporation rates of these elements from metal than from silicate liquid. All other solid phases were assumed not to evaporate, and their surface areal proportions were assumed equal to their volume proportions. Cases were considered in which up to 95% of the metallic phase was isolated from the droplet surface.

**Results:** Fig. 1 shows the evolution of the equilibrium vapor pressure of oxygen as a function of time during exposure of various chondrule precursors to the passage of a cool shock, all for  $\alpha_0=10^{-4}$ . Three model runs are shown for the case of an initial  $P_{\rm H}^{\rm tot}=10^{-3}$  bar and no sequestration of metallic NiFe,

each for a different initial oxidation state of the precursor (solid lines). The initial proportion of the Fe in metallic form was 86, 93 and 96 % at IW-2, IW-2.5 and IW-3, resp. Everything else being equal, the more oxidized the precursor, the longer it takes for its  $f_{02}$  to fall to that of the ambient gas, and the more slowly evaporation takes place from the silicate liquid because vapor pressures of all species originating from that phase decrease with increasing equilibrium vapor pressure of oxygen. Two other model runs are shown at IW-3, one for  $P_{\rm H}^{\rm tot}=10^{-5}$  bar, and the other with 90% of the metallic NiFe sequestered. The rate of decline of the  $f_{O2}$  is more gradual at  $10^{-5}$  than at  $10^{-3}$  bar because it is driven by the difference between the vapor pressure and ambient pressure of  $H_2O_{(g)}$ , which is ~10<sup>2</sup> times lower at the lower P<sub>H</sub><sup>tot</sup>. Everything else being equal, the rate of decline of the  $f_{02}$  is greater when metal is sequestered because this decreases the rate of Fe evaporation from metal relative to that from the silicate, causing a more rapid increase in the ratio of reduced to oxidized Fe in the residue.

The fractions of Na, K, Fe, Ni, Mg and Si evaporated are plotted as a function of time for an assemblage initially equilibrated at a log  $f_{02}$  of IW-2 in Fig. 2a and IW-3 in Fig. 2b. In each, 90% of the metal is sequestered. In both cases, vapor pressures of Na and K are so high that they are virtually totally evaporated with the arrival of the shock, while the evaporated fraction of each of the other elements gradually increases and then levels off during postshock cooling. For the assemblage initially equilibrated at IW-2, ≤5 % of the Mg, Si and Ni, and <15 % of the Fe evaporate by the time the temperature falls back to 1470 K, where only 5% silicate liquid remains. Heavy isotope enrichment of these elements would be minimal. By this point, alkalis have begun to re-condense, with K reaching the 10 ppm level in the liquid and diluting the heavy isotope enrichment of the residual K. Much more Mg and Si evaporate from the IW-3 assemblage, despite the cutoff of the run at shorter evaporation time, where 23 % silicate liquid remains at 1590 K. This path would produce much larger isotopic massfractionations than are observed for these elements in chondrules.

In this work, evaporation of relatively oxidized precursors into a complementary solar gas has been investigated. In all cases, alkalis are nearly totally lost when the shock arrives. The degree of evaporation of the other elements from the silicate liquid increases with higher shock temperatures, lower post-shock cooling rates, decreasing  $f_{O2}$  of

equilibration of the starting material, increasing  $\alpha_0$ , increasing ambient pressure, and increasing sequestration of the metallic phase. Cases of relatively minor evaporative losses of Fe, Ni, Mg and Si have been found which do not require the ambient gas to be at high pressure or high  $f_{02}$ .

**References:** [1] Alexander C. M. O'D. (2005) *GCA*, 68, 3943-3969. [2] Tachibana S. and Huss G. R. (2005) *GCA*, 69, 3075-3097. [3] Grossman L. and Fedkin A. V. (2003) *GCA*, 67, 4205-4221. [4] Grossman J. N. and Brearley A. J. (2005) *MAPS*, 40, 87-122. [5] Fedkin A. V. et al. (2006) *GCA*, 70, 206-223. [6] Desch S. J. and Connolly H. C. Jr. (2002) *MAPS*, 37, 183-207. [7] Richter F. M. et al. (2002) *GCA*, 66, 521-540. [8] Hashimoto A. (1983) *Geochem. J.*, 17, 111-145.

