Cr DIFFUSION IN SPINEL: EXPERIMENTAL STUDIES AND APPLICATIONS TO COOLING RATE RECORDED BY CHEVRON ZONED Cr-SPINEL IN ALLENDE AND Mn-Cr COSMOCHRONOLOGY.

E. S. Posner[1], J. Ganguly[1] and R. Hervig[2], [1]Department of Geosciences, University of Arizona, Tucson, AZ 85721, USA, [2]School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA

Introduction: We have determined the Cr^{3+} diffusion kinetics in spinel as a function of temperature and $f(O_2)$ at 1 bar pressure from tracer diffusion experiments. The results have been applied to constrain the cooling rate recorded by a chevron shaped Cr zoning profile in spinel from Allende that has been argued to be a likely nebular condensate [1], and also to the problem of Mn-Cr thermo/Cosmo-chronology of the early solar system processes.

Experimental Studies: Two stocks of natural spinels from Sri Lanka were used to determine Cr diffusion kinetics in spinel. These stocks, which we refer to as "gem-gravels" and "cut-gems", have essentially the same compositions: Mg# = 0.977 for "gem-gravels" vs. Mg# = 0.984 for "cut-gems, with trace quantity of Cr in both. Cr_2O_3 was thermally evaporated under high vacuum condition and deposited on to highly polished surfaces of cut pieces of spinels. The latter were pre-annealed at or around the experimental T-$f(O_2)$ condition to equilibrate the point defects and heal the line defects or fractures. The samples were inserted into a vertical gas mixing furnace, in which $f(O_2)$ was controlled by a (computer controlled) flowing mixture of CO and CO_2, and monitored continuously by a zirconia sensor. After the diffusion anneals, the samples were quenched and analyzed for ^{52}Cr and also for the non-diffusing species ^{26}Mg, ^{27}Al, ^{56}Fe and ^{197}Au by depth profiling in a SIMS (Cameca 6f). The analyzed concentration profiles of ^{52}Cr were modeled according to the solution of diffusion equation for a semi-infinite medium and diffusion from a constant or thin-film source, as required by the data. Time series studies did not show any dependence of D on time.

The Arrhenius relations for the diffusion data are illustrated in Fig. 1. The data for each stock of spinel are internally consistent, but the D values between the two stocks differ by a factor of 7-10 at a fixed temperature. We do not have a completely satisfactory explanation for the observed difference in Cr diffusivity between the two stocks, but we speculate that this is very likely due to small but different degrees of departure from stoichiometry, as in wüstite (FeO_{1-x}), and the resultant difference in the "extrinsic" point defect concentrations between the two stocks. The experimental data at 1100 °C for the "cut-gems" show a positive dependence of D on $f(O_2)$ between $f(O_2)$ in the range of WM-2 – WM+2: D(Cr) ~ $\log(f(O_2))^{0.2}$ -18.3, which is indicative of diffusion mediated by point defects.

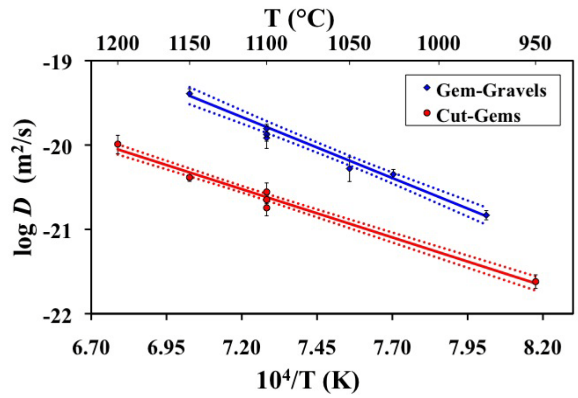

Fig. 1. Arrhenius relations of Cr diffusion kinetics in two stocks of nearly end-member Mg-spinels at $f(O_2)$ corresponding to WM buffer. The dashed lines represent ± 1σ error envelopes.

Cooling Rate of a Chevron-Zoned Spinel in the Allende Meteorite: Simon et al. [1] reported highly angular chevron shaped zoning in a large *in situ* spinel grain (ALSP1) within an olivine-rich object in the Allende meteorite (Fig. 2). They have argued against the possibility of an igneous origin of the spinel grain, and presented evidence that is suggestive of its formation by direct condensation from the solar nebula. We have constrained the cooling rate by finite difference modeling of the zoning profile starting with an initial condition given by the observed chevron zoning of the spinel crystal (in general, preservation of sharp corners in a zoning profile implies very rapid cooling). The idea was to determine the maximum ∫Ddt (referred to as <Dt> or DΔt) value, and thus the slowest permissible cooling rate, that would be required to preserve the chevron zoning (with the sharp corners) in the spinel. The results of simulation are shown in Fig. 2. Figure 3 shows another simulation of hypothetical initial profiles and the corresponding <Dt> values that could lead to the observed chevron zoned profile in the region of the spinel grain most sensitive to relaxation (indicated by a rectangular box in Fig. 3). From these simulations, we find a <Dt> value of ~$4(10^{-12})$ m^2 to be needed to preserve the chevron zoning in spinel. Using the Cr diffusion data in spinel, as determined in this study, this <Dt> value yields a cooling rate of the order of a degree to a fraction of a degree per hour. If the spinel grain had indeed formed by direct condensation from the solar nebula, then the inferred cooling rate implies the cooling rate of the nebular region from which the spinel grain had condensed.

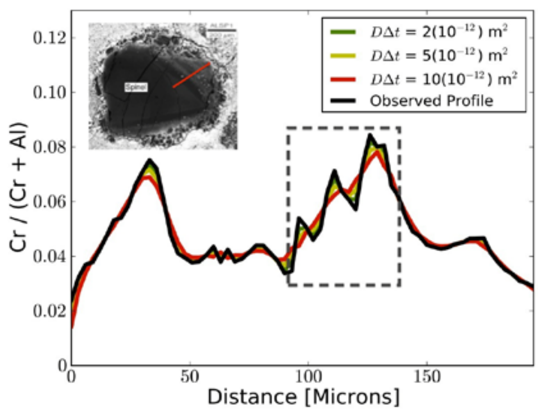

Fig. 2. Observed chevron-zoned Cr zoning in a spinel grain (inset) within an olivine-rich object in the Allende meteorite [1] and numerical simulation of the development of zoning profiles using different <Dt> values, if the observed profile is taken as the initial profile. The rectangular box shows the segment of zoning profile that is most sensitive to changes of <Dt> value.

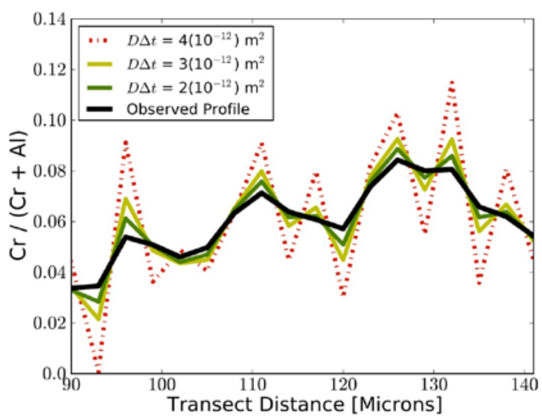

Fig. 3. Hypothetical initial profiles and the corresponding <Dt> values leading to the observed chevron shaped Cr zoning profile in spinel within the domain marked by a rectangular box in Fig. 2.

Closure temperature of Cr Diffusion in Spinel and Mn-Cr Cosmochronology: The Mn-Cr thermo/Cosmo-chronology, which is based on the decay of the short-lived ($t_{1/2}$ = 3.7 Ma) nuclide ^{53}Mn to ^{53}Cr, has been a widely used tool for the determination of the timing of early solar system processes. However, the interpretation of the Mn-Cr mineral ages requires an understanding of the diffusive closure temperature of this system in the host minerals such as olivine, orthopyroxene and spinel. Using the formulation of Ganguly and Tirone [2], we have determined the diffusive closure temperature (T_c) of Cr in spinel as function of initial temperature (T_o), cooling rate and grain size (Fig. 4). Figure 5 shows a comparison of T_c vs. cooling rate for spherical grains of spinel, olivine [3] and orthopyroxene [4] of 2 mm radius and T_o = 900 ^{o}C. The range of T_c for olivine and orthopyroxene reflects diffusion anisotropy, and were calculated using diffusion data along the fastest and slowest diffusion directions. The results summarized in Fig. 5 suggests that Mn-Cr chronology involving spinel could yield somewhat older age than that which excludes it, especially for slowly cooled samples.

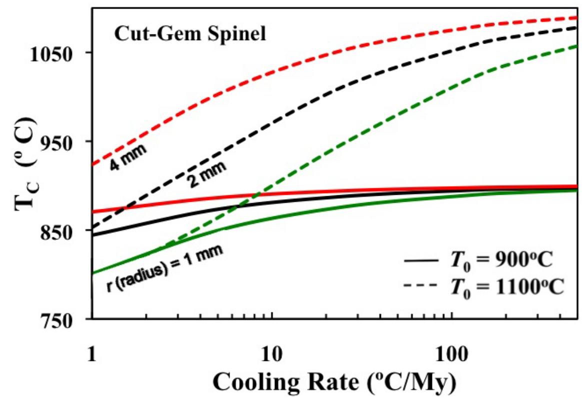

Fig. 4. Closure temperature (T_c) of Cr-diffusion in spherical grains of spinel as function of initial temperature (T_o), cooling rate and grain size, using the diffusion data for "cut-gem" spinels. Use of diffusion data for the "gem-gravel" could lower the T_c by ~10-50 ^{o}C depending on T_o and cooling rate

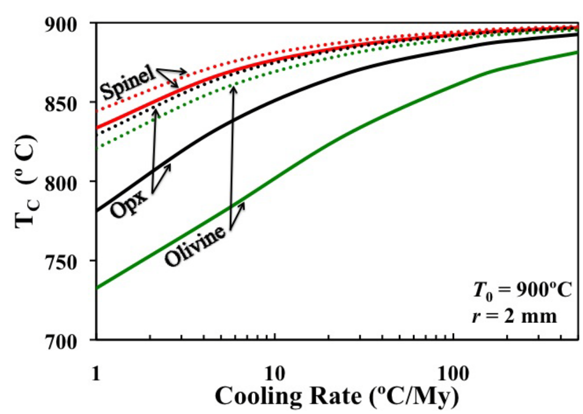

Fig. 5. Comparison of closure temperatures of Cr diffusion in spherical grains of spinel, orthopyroxene and olivine for T_o = 900 ^{o}C and radius of 2 mm.

References: [1] Simon S. B. et al. (2000) *Meteoritics & Planet. Sci., 35*,215-227. [2] Ganguly J. and Tirone M. (1999) *EPSL 170*, 131-140. [3] Ito M. and Ganguly J. (2006) *GCA 70*, 799-809. [4] Ganguly J. et al. (2007) *GCA 71*, 3915-3925.