OLIVINE AS A SOLAR SYSTEM RECORDER OF ^{53}Mn – ^{53}Cr CHRONOLOGY DURING THE EARLY CRYSTALLIZATION OF ANGRITES: IMPLICATIONS OF OLIVINE CRYSTAL CHEMISTRY AND SUBSOLIDUS REACTIONS FOR THE PARTITIONING OF Cr AND Mn AND THE RESETTING OF THE Mn-Cr CHRONOMETER.

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Introduction: Angrites are a diverse suite of silica-undersaturated mafic meteorites that represent some of the earliest stages of asteroidal differentiation and magmatism (~4.56 Ga) [1]. Their exotic compositions result in an interesting and important assemblage of minerals that includes Ca-rich olivine. At low temperatures, this exotic olivine exsolves into two olivine solid solutions, one between monticellite ($CaMgSiO_4$) and kirschsteinite ($CaFe^{2+}SiO_4$) and another between forsterite (Mg_2SiO_4) and fayalite ($Fe^{2+}_2SiO_4$). The ^{53}Mn-^{53}Cr chronometer has been used successfully to date the magmatic events of many of the volcanic angrites, but dating of angrites with a more extensive thermal history (e.g. plutonic angrites) yields younger ages. This abstract explores the crystal chemical rationale for how the redistribution of these elements causes the "resetting" of ^{53}Mn-^{53}Cr ages in olivine in angrites. The major objectives of this study are twofold: 1) to determine how Cr and Mn are initially distributed among the earliest angrite crystallization products, and 2) to understand how crystal chemistry influences the subsequent redistribution of elements during protracted sub-solidus thermal processing.

Analytical Approach: Thin sections of Sahara 99555, LEW 86010, and Angra dos Reis were examined and documented using backscattered electron imaging (BSE) on the JEOL JXA-8200 Superprobe electron microprobe (EMP) in the Institute of Meteoritics. Wavelength dispersive X-ray maps were collected for Cr, Ca, Mn, P and Ti, while energy dispersive (EDS) maps were collected for Mg and Fe. These maps were collected using a 15 kV accelerating voltage, a 500 nA beam current and a dwell time of 800 ms/pixel. Quantitative point analyses were conducted on various silicates and oxide phases using the EMP. Analyses were conducted at an accelerating voltage of 15 kV, a beam current of 20 nA, and a spot size from 1-3 μm. Combining the microprobe data, imaging of igneous zoning and exsolution lamellae, model mineralogy from the literature, and our knowledge of exchange and diffusion of Cr and Mn among/within phases, we examine the role of subsolidus processes on Cr-Mn chronometry.

Results: Microprobe data for the three angrites are presented in Figure 1. This figure compares CaO vs. MgO (Fig. 1a), MnO vs. MgO (Fig. 1b), and Cr_2O_3 vs. MgO (Fig. 1c) for igneous zoning of olivine in volcanic angrite Sahara 99555 with the subsolidus re-equilibrated olivine in LEW 86010 and Angra dos Reis.

Discussion: The angrites selected for this comparative study represent a sequence of increasing degrees of reequilibration. Saharra 99555 represents a very good estimate of the melt composition that cooled very rapidly, experiencing limited subsolidus re-equilibration [2], thus preserving igneous zoning. As shown in Figure 1 and illustrated by Mittlefehldt [2], Ca, Mn, Fe, and Ti increase and Cr decreases from core to rim. Therefore, the Mn/Cr ratio changes with crystallization and zoning so that the Mn/Cr ratio increases toward the rim. This zoning explains why reliable Mn-Cr isochrons could be obtained for single crystals in this sample [3]. There are several subsolidus processes that redistribute the Mn and Cr in olivine during subsolidus re-equilibration: diffusion of Cr, olivine exsolution resulting in Cr-Mn partitioning between Ca and Fe-Mg olivine, and homogenization and exchange of Mn.

Cr-Leakage from Olivine in Angrites and Disturbed Mn-Cr Ages: The redistribution of ^{53}Cr during a protracted thermal history has important implications for the interpretation of ^{53}Mn-^{53}Cr ages for the angrites. In particular, understanding how radiogenic ^{53}Cr is redistributed by diffusion in olivine is the key to interpreting ages that have been disturbed by thermal metamorphism. In order to disturb the ^{53}Mn-^{53}Cr isotopic systematics of an angrites olivine crystal, a net loss of Cr to an external host phase must occur. Migration and "leakage" out of olivine has been documented in both chondrites and lunar rocks that have experienced metamorphism in the deep lunar crust [4,5]. The extent to which Cr loss occurs is thus controlled by the suitability of other phases in the assemblage to host Cr. The corollary to this statement is that the eventual host phase for the excess radiogenic Cr depends on the valence state of Cr in the magmatic olivine. Recent work on Cr valence in angrites has revealed that both Cr^{2+} and Cr^{3+} are present in olivine [6]. Spinel and fassaite are potential host phases for the diffusive flux of trivalent ^{53}Cr from the olivine. This simple isotopic exchange reaction eliminates the need for complex exchange reactions involving the production of new phases as well as the coordinated movement of both divalent and trivalent cations between the two phases. This possibility could be easily tested with SIMS analyses
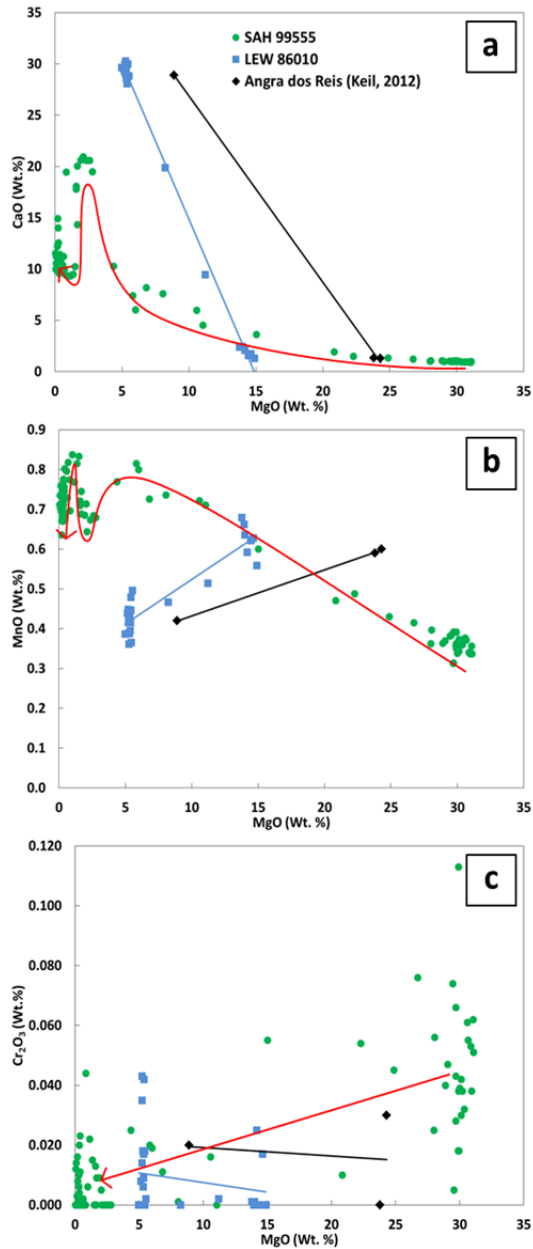
Figure 1. Core to rim olivine chemistry in angrites. The red arrow indicates crystallization sequence, from core to rim. a. CaO vs. MgO. b. MnO vs. MgO. c. Cr$_2$O$_3$ vs. MgO.

of the spinel and fassaite in annealed angrites. At the moment, it is unclear in what phase excess divalent ^{53}Cr may reside.

Redistribution during exsolution in olivine: Warner and Luth [7] determined the monticellite – forsterite solvus and Mukhopadhyay and Lindsley [8] determined the kirschsteinite – fayalite solvus. McKay et al. [9] estimated the cooling rate of LEW 86010 and determined that it equilibrated between 600°-700° degrees C. Fittipaldo et al. [10] studied the

thermal histories of Angra dos Reis and LEW 86010. These authors also estimated the dependence of the olivine solvus between high- and low-Ca olivines as a function of both composition and temperature. The preferred exsolution directions are (031) and ($\overline{0}$31) [11]. These are also the best twinning directions which can join up to three different crystals (trilling) [12]. These are the most appropriate planes for structural and lattice coherency between high- and low-Ca olivines (best fit plane) [12]. Both Mn and Cr are fractionated during exsolution. In LEW 86010, Mn is preferentially partitioned into the low-Ca olivine, whereas Cr is preferentially partitioned into the high-Ca olivine. This partitioning will be dependent on the proportions of Cr^{2+} and Cr^{3+}.

Diffusion of Mn: The original igneous zoning in olivine is illustrated in Figure 1b. Manganese increases along with Fe and Ca from core to rim. With metamorphism, Mn becomes increasingly homogenous and erases the original igneous zoning.

Sequence of reequilibration: The relationship among these processes are perhaps best illustrated in newly recognized angrite NWA 10463 [13]. This angrite preserves magmatic zoning of Fe-Mg-Ca, exhibits thin exsolution lamellae in the late-stage Fe-Ca-rich rims, and is both homogenous and depleted in Cr compared to many of the volcanic angrites.

Conclusions: The processes of exsolution and diffusion of Cr^{2+}, Cr^{3+}, and Mn^{2+} have a major effect on the application of the Mn-Cr chronometer on individual phases. The loss of Cr from olivine and the preferential fractionation of Cr and Mn into exsolution lamellae and host are important processes that are governed by cation size, charge, charge balance, and M1 and M2 sites. The olivine in volcanic angrites contain both Cr^{2+} and Cr^{3+} [6] and it has yet to be documented how valence state influences Cr diffusivities and solid state partitioning.

REFERENCES: [1] Keil, K. (2012) Chemie der Erde, 72, 191-218. [2] Mittlefehldt et al. (2002) Meteoritics & Planetary Science, 37, 345-369. [3] Sugiura et al. (2005) Earth Planets Space 57, e13-e16. [4] Grossman and Brearley (2005) Meteoritics and Planetary Science 40, 87-122. [5] Elardo et al. (2012) Geochimica et Cosmochimica Acta, 87, 154-177. [6] Shearer et al. (2016) Lunar and Planetary Science Conference, in press. [7] Warner and Luth (1973) American Mineralogist, 58, 998-1008. [8] Mukhopadhyay and Lindsley (1983) American Mineralogist, 68, 1089-1094. [9] McKay et al. (1998) Meteoritics & Planetary Science 33, 977-983. [10] Fittipaldo et al. (2005) Meteoritics & Planetary Science 40, 573-589. [11] Mikouchi et al. (1995) American Mineralogist, 80, 585-592. [12] Welsch et al. (2012) Journal of Petrology, 1-36. [13] Santos et al. (2016) Lunar and Planetary Science Conference, in press.