SPINELS IN THE D'ORBINGY ANGRITE M.E. Varela[1], S-L Hwang[2], P. Shen[3], F. Brandstätter[4], H-T Chu[5], T-F Yui[6] and Y. Iizuka[6]. 1-ICATE-CONICET, Avenida España 1512 sur, J5402DSP, San Juan, Argentina (evarela@icate-conicet.gob.ar) ; 2-Department of Materials Science and Engineering, National Dong Hwa University, Hualien, Taiwan, ROC; 3-Department of Materials and Optoelectronic Science, National Sun Yat-sen University, Kaohsiung, Taiwan, ROC; 4- Mineralogisch-Petrographische Abteilung, Naturhistorisches Museum, Burgring 7, 1010 Wien, Austria; 5-Central Geological Survey, PO Box 968, Taipei, Taiwan, ROC; 6=Institute of Earth Sciences, Academia Sinica,Taipei, Taiwan, ROC.

Introduction: One of the uncommon features in D'Orbigny, in addition to the olivinites and the Mg-rich olivine megacrysts, is the presence of large (~ 300-400 µm) spinel crystals [e.g., 1, 2, 3], similar to that described in Asuka 881371 [4]. The lack of equilibrium between spinel and a melt with the chemical composition of D'Orbigny, in addition to its texture indicating that spinels reacts-out in early stages of crystallization, led several authors [e.g., 1] to consider this phase as xenocrystic.

Here, we report detailed studies (EMPA, SEM, TEM and energy-dispersive X-ray (EDX)) on the different spinel types hosted by olivinites as well as by olivine, anorthite and augite in the groundmass of the angrite D'Orbigny. The results suggest that the compositional trend: Cr-Spinel-Al-Spinel-Hercynite drawn by the different types of spinels, may be the consequence of two physicochemical processes.

Sample and Results: The polished thick and thin-section samples used for this study are: Olivinite 1 and 3 (ICATE, Argentina) and D´Orbigny N1172 (NHM, Wien), respectively.

Analytical method: Samples were studied using a scanning electron microscope JEOL JSM-6610 (NHM, Vienna). Major element chemical compositions were obtained with an ARL-SEMQ (ICATE Argentina) and a JEOL JXA-8530F FE (NHM Vienna) electron microprobes. A JEOL 3010 analytical electron microscope (AEM) was used for imaging, TEM and EDX analyses (National Dong Hwa University, Taiwan).

Results: The petrography and chemical composition of spinels found in olivinites and in the D'Orbigny groundmass are as follow:

1-***Spinels in olivinites***: *1.1* ***S****pinel* ***F****ragments (SF):* Fragments have variable sizes (≈ 50 µm to 400 µm), irregular shapes with compact and/or porous textures. Both textures can be seen in a single fragment. They are chemically homogeneous with Al_2O_3 contents varying from 32.5 wt% to 38.4 wt% and Cr_2O_3 contents from 33.1 wt% to 36.5 wt% (Fig. 1). One fragment is chemically zoned (labeled as: 1.1 ZSF, Fig. 1) with high Al_2O_3 (54 wt% to 60 wt%) and low Cr_2O_3 (6.6 wt% to 7.8 wt%) contents. No chemical variation could be detected between the compact and porous part of these fragments. Only two **p**orous **d**ecomposition **r**ims (pdr) are chemically zoned with opposite trends. (pdr 1 and 2, Fig 1-2). *1.2 Euhedral Cr-Spinels (ECS):* crystals attached to primary glass inclusions hosted by olivine from olivinites. These spinels must have been coexisting crystals trapped during formation of the actual empty inclusions. *1.3 Tiny Cr-Spinels (TCS):* crystals present at olivine grain boundaries in olivinites.

The TEM-EDX data of the ECS attached to the Ca-Al-rich glass within olivine grains and the SEM EDX data of the TCS, show that spinels trapped by primary glass inclusions are richer in Cr_2O_3: 30wt% (~Al_2O_3: 42 wt%, MgO: 18 wt%, FeO: 10 wt%) as compared to those present at olivine grain boundaries (~Al_2O_3: 53 wt%, MgO: 19 wt%, Cr_2O_3: 19 wt%, FeO: 9 wt%). *1.4 Spinel in veins (SV):* subhedral to euhedral crystals (20 to 40 µm in length) were observed in pseudo-secondary/secondary veins in olivinites. Spinels ($Sp_{0.72}$ $Ch_{0.17}$ - $Sp_{0.74}$ $Ch_{0.16}$) show a constant increase in Al_2O_3 content coupled with a decrease in Cr_2O_3 content. The chemical compositions of these spinels cover the compositional gap between the Cr-rich spinel fragments in olivinites and the Cr-bearing Al-rich spinel present in D'Orbigny groundmass (Fig. 1).

2- Spinels in D'Orbigny groundmass: *2.1* ***E****uhedral (octahedra) to* ***S****ubhedral* ***S****pinels (ESS):* small hercynitic spinels enclosed in anorthite and olivine. *2.2* ***L****arge anhedral* ***S****pinels (LS).* Both types of spinels are Cr-bearing (about 7.5–11 wt.% Cr_2O_3) and show reaction borders. In the large spinel, these borders are much more extended with a highly porous texture. The small ESS (hercynitic spinels) can be chemically zoned over distances of few tenths of microns [1] with increasing Cr and Fe and decreasing Al towards the rims. The large spinel (LS) show a core homogeneous in composition. The extended reaction zone is compositionally inhomogeneous being richer in Cr, Fe and Ti and poorer in Mg and Al as compared to the core (Fig. 2).

Discussion: Olivinites as well as olivine megacrysts are the most magnesian phases encountered in angrites [e.g., 1, 2, 5, 6]. Since such a Mg-rich composition is far away from that of possible precipitates from angrite parent melts, Mg-rich olivine megacrysts (as well as olivinites) were considered as "xenocrysts"[e.g., 1, 6, 7]. However, the proposed "xenocrystic" olivines in the volcanic angrites Asuka 881371 and D'Orbigny overlap in composition with the Mg-rich olivines in the new angrite NWA 8535 [8, 9]. This indicates that Mg-rich olivines are not exotic to angrites but rather one of their early constituent phases (e.g., as proposed by [2]), forming either a small part of the rock (e.g., Asuka 881371 and D'Orbigny) or the majority of it (NWA 8535). Therefore, spinels hosted by Mg-rich olivinites and by D'Orbigny groundmass form a continuum trend that require a joint study. Spinels in NWA 8535 are dominated by chromite and are strongly zoned, with portions of grains containing substantial chromite grading into hercynite [9]. Unfortunately, no quantitative data have been reported for these spinels but we can expect they would overlap the trends defined by the chemical variation (Cr_2O_3: 36 wt% and Al_2O_3: 33 wt% to Cr_2O_3: 7 wt% and Al_2O_3: 57 wt%, Fig. 1) drawn by the different types of spinels hosted by olivinites. The zonation shown in one of the porous decompositional rims in spinel fragments (dpr1, arrow Fig. 1) matchs the previous chemical variation. This trend is in turn similar to that outlined by the estimated residual spinel compositions in the experimental studies (separate Allende runs at 1200 °C and increasing oxygen fugacities) of [10] (J-93, Fig. 1). This indicates that the compositional trend (e.g., increasing hercynite and decreasing Mg-Al spinel and chromite) shown by spinels hosted by Mg-rich olivines may be a consequence of the changing conditions ranging from extremely reducing to highly oxidizing. Giving additional evidences -to the many already found- indicating that D'Orbigny provides a record of increasing oxygen fugacities [2, 11, 12, 13].

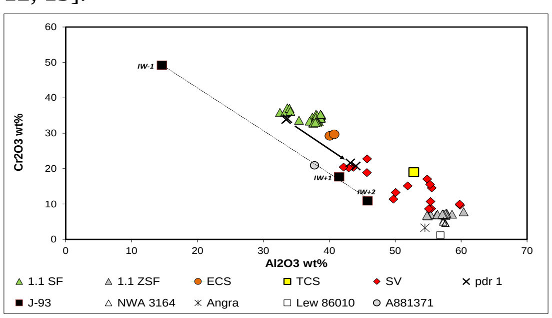

Figure 1: Binary diagram showing the trend in spinels hosted by olivintes compared with data from [10].

The second decomposition porous rim in spinel fragments is also chemically zoned (Fig. 2). This zonation linking rims that are richer in Fe and Cr and poorer in Al and Mg, as compared to the core, is akin to that outlined by spinels in D'Orbigny groundmass. But it is opposite to the main trend shown by spinels in olivinites and clearly indicates the presence of a second process (Fig. 2). The reaction zone shown by spinels in D'Orbigny groundmass has been previously described as "symplectic" [e.g., 1]. However, a look at Fig. 3 reveals that the reaction zone cannot be a symplectite because it consists at one side of spinel+anorthite and on the other side of spinel+olivine or spinel+augite. Thus, what this texture indicates is a reaction that took place before D'Orbigny spinels were included by these early phases. The textural relationship also suggests that spinel became unstable (due to increasing oxygen fugacity) and a spinel that is richer in Cr than the original one became stable. During such an early process oxygen fugacity must have been high enough to support Cr^{3+} and Fe^{2+} in spinel. Perhaps higher than the 0.5 log units above the iron-wüstite buffer (~IW + 0.5) estimated considering the V content of the Cr-bearing Al spinel and glasses in D'Orbigny [11]. The delicate structures of the highly porous envelope indicate that it was filled with olivine, anorthite and augite in a non-destructive way. We cannot precisely determine the exact process involved in such a reaction but the texture suggests massive mass loss of an unknown component and that this reaction remained incomplete, leaving a highly porous envelope of spinel enriched in $(Mg,Fe)Cr_2O_4$ over the original composition. SEM and TEM studies reveal that an Al-rich clinopyroxene (?) and FeS globules fill part of this highly porous envelope indicating that this reaction took place under high S activities. The joint study of all spinels reveals a Cr-Spinel-Al-Spinel-Hercynite trend. This, could define "The Angrite Spinel Continuum" from which, until now, only one trend has been considered.

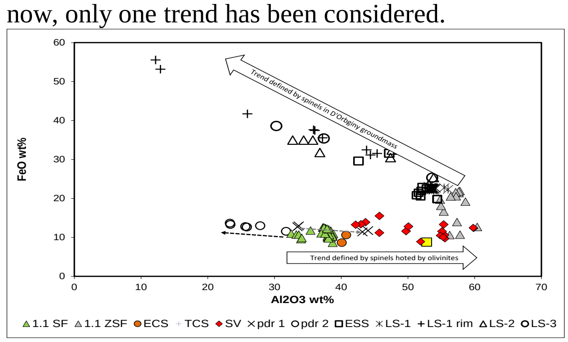

Figure 2: Binary diagram showing the proposed continuum trend.

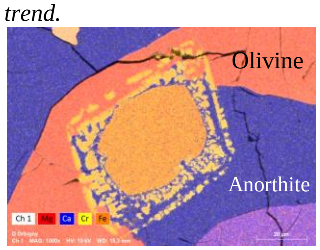

Figure 3: BSE compositional map of a LS hosted by olivine and anorthite.

References: [1] Mittlefehldt et al. (2002) MAPS **37,** 345-369; [2] Kurat et al. (2004) GCA **68,** 1901-1921; [3] Hwang et al. (2012) , [4] Yanai (1994) Proc. NIPR Symp. Antartic Meteorites **7**, 30-41; [5] Prinz and Weisberg (1995) Antartic Meteorites **20**, 204-206; [6] Mikouchi et al. (2001) MAPS A134-135 Suppl; [7] Prinz et al. (1990) XXX LPSC, 979–980; [8] Agee et al. (2015) 46th LPSC #2681; [9] Santos et al. (2016) 47th LPSC #2590; [10] Jurewicz et al. (1993) GCA **57,** 2123–2139; [11] Varela et al, (2005) MAPS 40, 409-430; [12] Varela et al. (2015) 46th LPSC# 1497; [13] Hwang et al. (2015) 46th LPSC, #1516.