HIGH NI-BEARING METAL AND SULFIDE PHASES IN THE D´ORBIGNY ANGRITE. Varela, M.E.[1], Hwang S-L.[2], Shen P.[3], Chu H-T.[4], Yui T.F.[5] and Iizuka Y.[5], [1]ICATE-CONICET Av. España 1512 Sur, 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]Central Geological Survey, MOEA Taipei, Taiwan, ROC;[5] Institute of Earth Sciences, Academia Sinica, Taipei, Taiwan, ROC.

Introduction: Angrites are a small enigmatic group of achondrites. They are ancient rocks (e.g, LEW Cliff 86010: 4,558.55 ± 0.15 Ma and D'Orbigny: 4,563.36 ± 0.34, [1-2]), that record an unusual primitive petrogenetic history. Their origin is not yet clearly understood. In part this is due to the few members of this group, a situation that is changing with the recent finds in cold and hot deserts (e.g., [3]). D´Orbigny is by far the largest (16.55 kg) angrite known and is peculiar in several aspects. Its unusual shape, the presence of plates of anorthite-olivine intergrowths, druse augite crystals in void spaces and the abundant presence of glass are some of the peculiarities. (e.g., [4-6]). Its mushroom-like shape is characterized by a front and back shields having compact lithologies. The space between these shields is filled by a highly porous lithology, with open voids and hollow spheres. The study of new material from the porous lithology reveals the presence of high content Ni-bearing metal with sulfides. This abstract reports these findings and their implications regarding the redox conditions prevailing during D'Orbigny formation.

Sample and Results: The polish thin sections (PTS) D´Orbigny P1-P2 and P3 (ICATE, Argentina) and D´Orbigny NDHU-1 (National Dong Hwa University, Taiwan) were studied by optical microscopy, analytical scanning electron microscopy (FE-SEM) coupled with phase analysis using a JEOL JXA 8230 and a ARL-SEMQ microprobes (LAMARX and ICATE, respectively). TEM samples were prepared from PTS by the FIB technique for selected area electron diffraction (SAED) using a JEOL 3010 AEM.

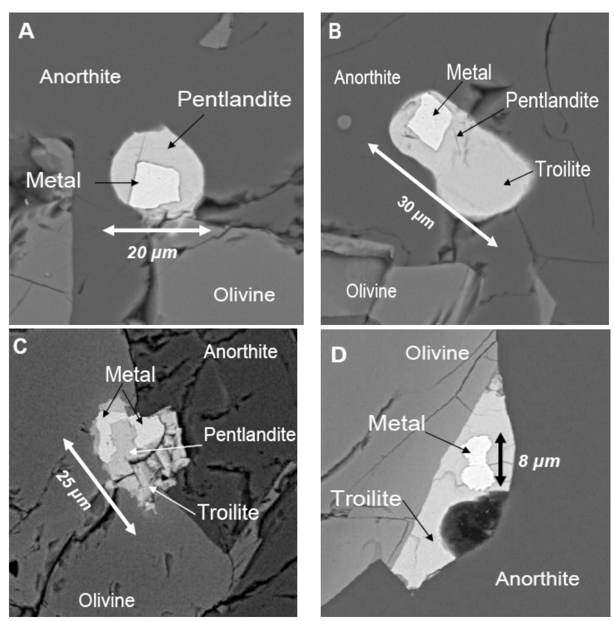
The presence of sulfides (troilite and/or pentlandite) including metal were observed in all studied PTS. These metal + sulfide associations (M-S) are more abundant in P1, small in size (20 to 30 µm) and with shapes varying form round, ellipsoidal to irregular. They are hosted by anorthite (Fig. 1 A-B) or by anorthite and olivine. The M-S (1) and M-S (2) consists respectively, of a perfectly rounded pentlandite globule and an ellipsoidal pentlandite + troilite globule. Both host euhedral high-Ni metal phases (Fig. 1 A- B, Table 1). In M-S (3) both metal (~ 54.5 wt% Ni) and sulfides have irregular shapes, the latter being mainly pentlandite and troilite as a very thin outer rim. Scan profiles performed in the M-S samples show inhomogeneous distribution of Ni in both pentlandite and metal.

The metal grains (e.g., M-S (4)) in the PTS D'Orbigny NDHU-1 differ from other M-S previously described. Metal have characteristic round shape, low Ni contents (15-17 wt%) with troilite as the associated sulfide phase (Fig. 1D).

Table 1: Representative analyses of the M-S (1-2) in P1 (in wt%).

	M-S (1)		M-S (2)		
	Metal	Pentl.	Metal	Pentl.	Troilite
Fe	46.4	45.7	48.3	44.6	62.4
Ni	53.4	20.7	51.5	21.1	
S		33.4		34.2	37.1
Total	99.8	99.8	99.8	99.9	99.5

Figure 1: BSE images of the high-Ni bearing (A-C) and Ni-bearing (C) metal and sulfides from PTS of D´Orbigny. A) M-S (1); B) M-S (2); C) M-S (3); D) NDHU-1 (4).



Discussion: Although widely believed to have been formed under oxidizing conditions (e.g., [3] and references therein), 10 out of 11 angrites contain metallic Fe-Ni alloys as minor components (< 2 %). An exception is NWA 2999 in which coarse Fe-Ni metal is up to about 10 % [7-8]. Unfortunately, in only few angrites, the Ni content of the metal grains have been reported. The metal grains in LEW 86010 have 4.5-6.8% Ni [9] and those in NWA 2999 varies from 4.9–10.7% Ni. The latter are characterized by chondritic relative abundances of the most highly siderophile elements (HSE: Ru, Pd, Re, Os, Ir, Pt and Au) [7]. The metal grains in NWA 2999 shares none of the refractory element, volatile element or redox characteristics of angrites and are therefore considered exogenous to the angrite silicate lithology possibly introduced by impact processes during brecciation of the angrite parent body surface [8]. Also, the presence of inclusions (~10 µm) of Fe-Ni metal and sulfides in olivine megacrysts in NWA 1670 are seen as unusual and their host Mg-rich olivine taken as xenocrysts [10]. The fact that all phases that indicate formation under reducing conditions are seen as exogenous to the angrite lithology is because melts chemically resembling those of bulk angrites have been successfully produced by partial melting of CM and CV chondrites under oxidizing (IW+2) conditions [11]. However, a silicate liquid created under such redox conditions should carry large amounts of Fe^{3+} and Ni^{2+}, but the former is present in very low amounts and the latter is almost completely missing in angrites, which were actually reported to contain Ni-bearing metal and sulfides. Previous studies from the angrite D'Orbigny showed that metal (39% Ni) is scarce, usually small and associated with sulfides [4]. M-S were also observed in olivinites, either forming ribbon-like trails of multi-phase [FeSx + Fe-Ni metal + bubbles] inclusions in round olivine fragments or co-existing with Si-Al-Ca glass + Cr-sp in primary inclusions of olivine groundmass of olivinites [12]. Recently, we have described the presence of sulfide blebs (Ni-bearing FeS) hosted by glass [13]. Glasses filling some of the abundant hollow shells (named glass sphere) contain small (1–50 µm) sulfide blebs (Ni-bearing FeS). Some sulfide globules have Fe-Ni metal grains forming a corona decorating the surface of the globule. A TEM study revealed that these inclusions are metallic bcc Fe (10% Ni) [13].

Our TEM results show that the high-Ni metal (Fe-50Ni) in D'Orbigny is a single crystal (fcc structure) with sharp edges (Fig. 2) showing no traces of bcc reflections in SAED patterns. Whereas the Fe (50% Ni) phase is a single crystal, the Fe (10% Ni) phase is always polycrystalline with "weir" domain boundaries (Fig.3).

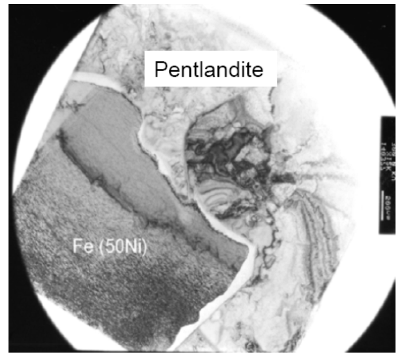


Figure 2, TEM bright field image of M-S (1) showing a single fcc Fe-50Ni metal in pentlandite.

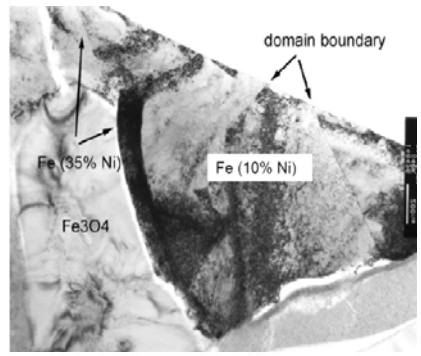


Figure 3,TEM bright field image showing a polycrystalline Fe (10% Ni) covered by Fe_3O_4

There is no specific COR between the polycrystalline Fe and the Fe_3O_4. A thin Fe (35% Ni) layer (fcc) is always present in between oxide and Fe (10% Ni), suggesting the preferential oxidation of Fe and the accumulation of residue Ni at the oxidation front.

According to [4-5], D'Orbigny provides us with a record of changing redox conditions, ranging from extremely reducing to highly oxidizing. The presence of high-Ni bearing metal and sulfide host by anorthite and anorthite + olivine give clear evidence that the early events during D´Orbginy formation were reducing, possibly with high S activity, as previously suggested [4].

References: [1] Amelin (2008) *GCA* **72**, 221-232; [2] Brennecka et al., (2010). *LPSC XLI,* Abstract #1402; [3] Keil (2012) Chemie der Erde **72,** 191-218; [4] Kurat et al., (2004) GCA **68,** 1901-1921; [5] Varela et al., (2003) GCA **67,** 5027–5046; [6] Varela et al., (2005) *MAPS* 40, Nr 3, 409–430 ; [7] Kuehner et al., (2006) *LPSC XXXVI,* Abstract # 1344 ; [8] Humayun et al., (2007) *LPSC XXXVII,* Abstract # 1221 ; [9] Prinz et al., (1988) *LPSC XIX*, 949-950 ; [10] Mikouchi et al., (2011). *Formation of the First Solids in the Solar System*. Abstract # 9142; [11] Jurewicz et al., (1993) GCA **57,** 2123–2139 ; [12] Hwang et al (2012) M&PSA 75, Abstract #5124; [13] Varela et al., (2014) *LPSC XLV*, Abstract # 1833.